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Health risk assessment of dissolved heavy metals in surface water in a subtropical rivers basin system of Giresun (north-eastern Turkey)

Fikret Ustaoğlu*, Handan Aydın

Biology Department, Faculty of Arts and Science Giresun University Gure Campus, 28200 Giresun, Turkey, emails: fikretustaoglu@hotmail.com (F. Ustaoğlu), mbatin28@hotmail.com (H. Aydın)

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ABSTRACT

Rivers have an extremely important role in providing drinking water to humans and animals. However, metal pollution in the water can endanger human health depending on the aquatic ecosystem. In this study, the status of 13 elements (Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Hg, Pb, U), which pollute waters in seven streams of north-eastern Turkey (Giresun) basin and the contamination level were investigated. Besides, waters were evaluated in terms of public health. In most cases, it was identified that the levels of Al element in the rivers exceeded the WHO acceptable limits. Furthermore, as Al elements' results of Nemerow index (P_n) and Contamination index (C_d) were examined, contamination was found according to both indexes. In terms of arsenic, risk of cancer (CR) for children and adults was low only in Aksu River. When water quality index (WQI), heavy metal pollution index (HPI), heavy metal evaluation index (HEI), hazard quotient, and hazard index were investigated. WQI, HPI, and HEI values were determined in the range of 14.26–21.57, 59.68–69.44, and 1.94–2.76, respectively. The water quality of the streams was determined as good quality and there was no potential hazard. However, due to the intensive anthropogenic activities in the river basins, it is considered that drinking water resources should be continuously evaluated and monitored.

Keywords: Environmental monitoring; Heavy metal; Water quality index; Health hazard index; Heavy metal evaluation index; Cancer risk

1. Introduction

Nowadays, the demand for freshwater and usage are increasing due to the rapid population growth. Therefore, it is foreseen that the gross water potential per capita is going to decrease by 2050 [1]. Water resources and water quality play a significant part in urban development and in the environment, especially in developing countries. There are more than 700 chemical contaminators in the waters. Among these pollutants, heavy metals are the most hazardous substances for the environment and humans due to their high toxicity and carcinogenicity [2,3]. Surface waters, which are part of the hydrosphere layer, are more exposed to metal contamination than other waters as well as more susceptible to it [4]. Metal contamination poses a great risk for river systems because, metals are permanent, not biodegradable and they cause a potential hazard to aquatic life and to the human population [5,6]. Heavy metals originated from anthropogenic as well as natural contribute to the deterioration of water quality in river systems. Natural originated ones are generally associated with the geological and lithological structure of the river basin such as bedrock erosion, soil leaching, and volcanic eruption [7–9]. Anthropogenic heavy metals stem from mostly sand and quarries, mining, metal smelting and refining, landfill leachates, agricultural runoff, industrial, and domestic wastewater [10].

The toxicity of any contaminator is largely dependent on the concentration of the contaminator; and the way humans and the environment are exposed to it [11]. Because heavy metals in aquatic environments are absorbed by organisms and passed to humans through the food chain, heavy metal accumulation in tissues can occur [12]. As a result, various

* Corresponding author.

diseases, including cancer, may arise which is a great threat and a source of concern for human beings [13]. Threats of human health and the environment also go up depending on the increase of concentrations of heavy metals in surface waters day by day. Therefore, it is essential to constantly assess water quality and sustainable management [14,15]. It could be insufficient to simply compare heavy metal concentrations in the water structure due to their high toxicity with acceptable limit values to properly assess their negative effects on humans. Even if concentrations of heavy metals in water meet international standards, they have potentially significant health risks [16]. Thus, in the last decade, pollution indexes have been used to assess the quality of surface water more effectively, sensitively, and comprehensively. These indexes are simple, useful, and easily understandable tools for water quality managers, environmental managers, decision-makers, and potential users to evaluate water quality [17].

In this study, in order to define the heavy metal contamination status of north-eastern Turkey (Giresun) rivers and possible contaminant sources, the water quality index (WQI), the Nemerow pollution index (P_n), the heavy metal pollution index (HPI), the heavy metal evaluation index (HEI), the degree of contamination (C_d) were used. In addition, hazard quotient (HQ), hazard index (HI), carcinogenic risk (CR) were calculated and the effects of heavy metals on human health were determined and also health risk was assessed. The present work is the first study in which heavy metal contents of rivers in the region are evaluated with indexes in terms of water quality and the effects of these heavy metals on human health are determined. Thus, it will be a reference for future studies.

In our studying area, Pazarsuyu Stream (PS), Batlama Stream (BS), Aksu Stream (AS), Yağlıdere Stream (YS), Gelevera Stream (GLS), Harşit River (HR), Görele Stream (GS) are large and important river basins, from which drinking water needs of the region is supplied. Although some of the physicochemical parameters of these streams have been investigated for their potential for contamination, no comprehensive index evaluation study has been encountered in which heavy metals in water are considered for public health [18–22]. So, it is thought that this study will fill a large gap in this field.

The aim of this study was to investigate the status of 13 metals, as potential contaminators of seven streams in Northeastern Turkey (Giresun) basin and to determine the contamination level. Specific objectives of the study are to assess the quality of surface water with the help of the WHO guidelines, as well as to assess the water samples in terms of public health. In this context, non-carcinogenic/carcinogenic risk of heavy metals in these streams is identified. As the data obtained will reveal the heavy metal amounts of the streams used as the major source of drinking water in the region, it is thought that the results of the study can be used as the fundamental data for future research. It will also, inform the public, policymakers, and managers about more effective sustainable management and protection of river basins.

2. Materials and methods

2.1. Study area and site description

Giresun, which is a city in north-eastern Turkey, has a population of approximately 450 thousand people and an area of 6,831 km^2. Ninety-four percent of its territory within the provincial borders are mountainous and these mountains are parallel to the coast. Therefore, plain areas with agricultural potential are limited. Hazelnut cultivation is carried out in the majority of the agricultural areas (73%), which make up approximately 23% of the province's land (Fig. 1). It receives more rain than the average rainfall in Turkey (623 mm) with 1,258 mm average rainfall. The average temperature is 17.8°C [23].

This study was conducted in seven streams of Giresun in the Black Sea sub-basins which are in north-eastern Turkey basins (Fig. 1). Features of the rivers such as coordinates of sampling points, length, flow, and annual water potential are shown in Table 1.

2.2. Sampling and analytical methods

Surface water samples were taken four times between May 2018 and April 2019 seasonally from discharge points representing all pollution load of river basins. The samples were taken 15–20 cm below the water and at this stage 2.5 L polyethylene bottles were used, which were previously washed with 4% HCl and rinsed with pure water. Water samples were transported to the laboratory using cold chain. After that they were filtered with 0.45 μm filter paper [25]. In order to prevent the samples from any contamination, concentrated HNO_3 was added until pH < 2 and it was stored at 4°C. In water samples, 13 elements (Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Hg, Pb, U) were measured with inductively coupled plasma-mass spectrometry (ICP-MS Agilent; Technologies/7700X). ICP Multi-element standard solution VI (Merck, Germany) were used to perform the method validation and quality control. All samples and standards were analyzed in three replicates in batches with a procedural blank. Analytical precision was within 10%, and the recoveries percentage ranged from 91% to 107%. The percent recovery for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Hg, Pb, and U were 107%, 93%, 99%, 98%, 105%, 94%, 93%, 95%, 106%, 97%, 105%, 99%, and 91%, respectively.

2.3. Water pollution assessment

2.3.1. Water quality index

Water quality index (WQI) is one of the best grading techniques calculated by considering the combined effect of individual water quality parameters on total water quality. It provides an effective and comprehensive perspective on the quality of the water used as drinking water and for domestic needs. Originally, WQI was developed by Horton [26] in the USA and is widely used in water quality studies [27]. WQI was calculated with the formula below:

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

where $W_i = w_i/\Sigma w_i$ is the relative weight. The W_i values (minimum 1, maximum 5) was assigned to each parameter by considering the relatively significant effects of heavy metals on human health and the significance in terms of portability

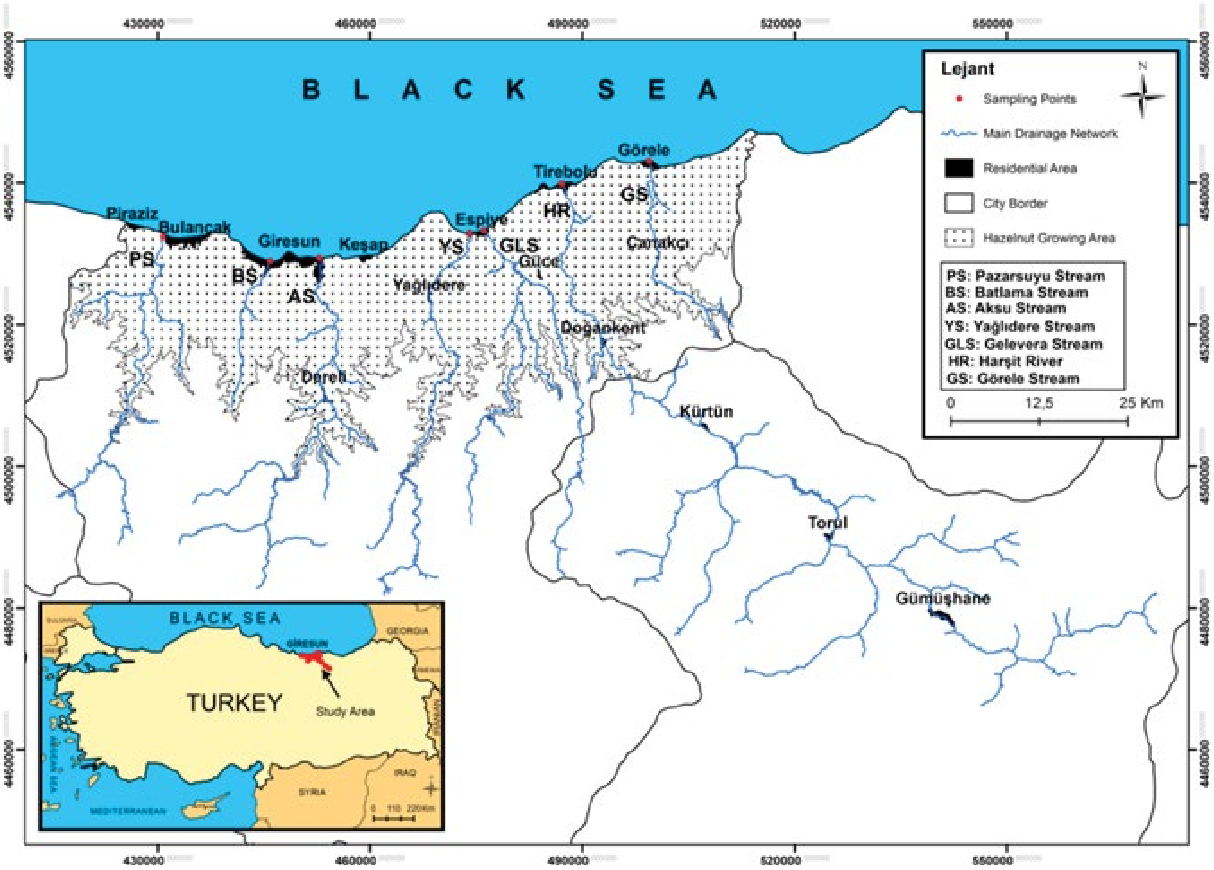

Fig. 1. Location of sampling stations in study area.

Table 1
General characteristics of rivers [20–22,24]

	Sampling point coordinates	Length (km)	Flow (m^3/s)	Water potential (hm^3/y)
Pazarsuyu Stream (PS)	40 56 37 N/38 10 30 E	80	21.4	542
Batlama Stream (BS)	40 54 32 N/38 21 20 E	40	4.4	139
Aksu Stream (AS)	40 54 45 N/38 26 25 E	75	17.8	562
Yağlıdere Stream (YS)	40 56 48 N/38 41 21 E	65	13.2	415
Gelevera Stream (GLS)	40 56 52 N/38 43 12 E	80	21.2	688
Harşit River (HR)	41 00 19 N/38 51 02 E	160	28	850
Görele Stream (GS)	41 01 59 N/38 59 46 E	49.2	10.1	319

[28]. Table 2 shows the highest weight (5) is Mn, Hg, As, Pb, Cr, and Cd, which have the most harmful effects on water quality [29]. C_i is the trace element concentration measured in water and S_i refers to the standard values determined by WHO [30] for drinking water. According to WQI, water quality is evaluated in five different classes: WQI < 50, excellent; 50 ≤ WQI < 100, good; 100 ≤ WQI < 200, poor; 200 ≤ WQI < 300, very poor; WQI ≥ 300, undrinkable [16].

2.3.2. Nemerow pollution index

The Nemerow index is frequently used to assess the contamination status of heavy metals in surface waters in a comprehensive and integrated way. This method is not only simple and flexible but also draws attention to the high concentration of contaminators [31]. Nemerow index value (P_n) is calculated with the formulas below [32]:

$$P_i = \frac{C_i}{S_i} \tag{2}$$

$$P_n = \sqrt{\frac{P_{i\,\mathrm{avr}}^2 + P_{i\,\mathrm{max}}^2}{2}} \tag{3}$$

Table 2
Relative weight of each heavy metal

Element	WHO, 2011	Weight (w_i)	Relative weight (W_i)
Al (μg/L)	200	4	0.07
Mn (μg/L)	400	5	0.09
Fe (μg/L)	300	4	0.07
Cu (μg/L)	2,000	2	0.04
Zn (μg/L)	3,000	3	0.06
Hg (μg/L)	6	5	0.09
Ni (μg/L)	70	4	0.07
As (μg/L)	10	5	0.09
Pb (μg/L)	10	5	0.09
Cr (μg/L)	50	5	0.09
Cd (μg/L)	3	5	0.09
Co (μg/L)	50	2	0.04
U (μg/L)	30	5	0.09
		$\Sigma w_i = 54$	$\Sigma w_i = 1.00$

In this formula; P_i is the single-factor index of individual metals, C_i is the concentration of heavy metals measured in waters, S_i is the standard values for drinking water determined by WHO [30], P_{iavr} is mean value of P_i, P_{imax} is maximum value of P_i. Consequently, P_n represents the interaction between the average pollution level and the maximum pollution factor. Nemerow index method divides water quality into two categories: $P_n \leq 1$ indicates, no contamination whereas; $P_n > 1$ indicates contamination [33].

2.3.3. Heavy metal pollution index

HPI is an evaluation method taking into account the combined effects of each heavy metal on overall water quality. Thus, many researchers have used HPI to comprehensively assess total water quality based on heavy metals [13,34]. HPI is calculated using the formulas below:

$$\text{HPI} = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \tag{4}$$

$$Q_i = \sum_{i=1}^{n} \frac{\left|M_i - I_i\right|}{S_i - I_i} \times 100 \tag{5}$$

where Q_i and W_i are the sub-index of the parameter and the unit weight of the *i*th parameter, respectively; n is the number of parameters considered; M_i, I_i, and S_i are the monitored values of heavy metals and ideal and standard values of the parameter, respectively; and sign (−) indicates the numerical differences between the two values, ignoring the algebraic sign. HPI < 100 means there is a low level of heavy metal contamination and does not adversely affect health. If HPI = 100, the risk is at limit and may adversely affect health, while HPI > 100 indicates that water cannot be used for drinking and is not suitable for consumption [35].

Table 3
Standard values (μg/L) for the indices (Pn, HPI, HEI, Cd) computation [30,36]

Metals	W_i	S_i	I_i	MAC
Mn	0.0025	400	100	400
Fe	0.0033	300	200	300
Ni	0.01428	70	20	70
Cu	0.0005	2,000	1,000	2,000
Zn	0.00033	5,000	3,000	3,000
As	0.1	50	10	10
Cd	0.33	5	3	3
Hg	0.167	6	1	6
Pb	0.1	100	10	10

2.3.4. Heavy metal evaluation index

HEI describes the overall tendency assessment of water quality within the scope of heavy metal contamination in the water like HPI. Therefore, it helps to interpret the water contamination level easily [37]. HEI is calculated using the following formula:

$$\text{HEI} = \sum_{i=1}^{n} \frac{H_C}{H_{MAC}} \tag{6}$$

Hereby H_c, is value observed for each parameter and H_{mac} indicates the value of maximum admissible concentration (MAC) for each parameter (Table 3). According to the MAC, the higher the concentration of metal, the worse the water quality [38]. HEI < 10 means low contamination, 10 < HEI < 20 means medium contamination, and 20 < HEI means high contamination [35].

2.3.5. Contamination index

Contamination index (C_d) is used to summarize the combined effects or degree of contamination of various parameters considered to be potentially harmful in domestic water and calculated with Eqs. (7) and (8) [39]:

$$C_d = \sum_{i=1}^{n} Cf_i \tag{7}$$

$$\text{Cf}_i = \frac{\text{CA}_i}{\text{CN}_i} - 1 \tag{8}$$

Hereby Cf_i, CA_i, and CN_i represent the contamination factor, analytical value and upper permissible concentration of the *i*th component. N denotes the "normative value," CN_i values were taken as MACs given in Table 3. C_d is examined in three levels: low (C_d < 1), medium (C_d = 1–3), and high (C_d > 3) [13,37].

2.4. Health risk assessment

2.4.1. Hazard quotient, hazard index, and cancer risk

Present health risk assessment methods and mathematical models differ from country to country and organizations, but they basically share the same principle. In this study, the health risk assessment method by USEPA [40] was used. While the risk of trace elements in water in terms of human health is assessed, it is usually taken into account the amount ingested and absorbed through dermal [41]. Therefore, average daily dose (ADD), obtained from direct digestion ($ADD_{ingestion}$) and dermal absorption (ADD_{dermal}), were calculated with modified Eqs. (9) and (10) suggested by USEPA [40]:

$$ADD_{ingestion} = \frac{C_{Water} \times IR \times ABS_g \times EF \times ED}{BW \times AT} \quad (9)$$

$$ADD_{dermal} = \frac{C_{Water} \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \quad (10)$$

where $ADD_{ingestion}$ shows average daily dose by ingestion and ADD_{dermal} shows average daily dose by dermal, μg/kg/d; C_{water} reveals concentration of the metals in surface water, μg/L; IR depicts ingestion rate (L/d), in this study 2 for adult and 0.64 for children; EF stands for exposure frequency, in this study, 365 d/y; ED shows exposure duration (years), in this study 70 for adults and 6 for children; BW indicates average body weight (kg), in this study 70 for adults and 20 for children; AT shows averaging time (d), in this study 25,550 for adults and 2,190 for children; SA reveals exposed skin area (cm^2), in this study, 18,000 for adults and 6,600 for children; ABS_g was the gastrointestinal absorption factor, which is dimensionless. K_p indicates dermal permeability coefficient in water (cm/h); ET is the exposure time during bathing and shower, in this study 0.6 h/d; CF is the unit conversion factor, 1 L/1,000 cm^3 [16,41]. Table 4 shows values of metals and toxicological parameters used for health risk evaluation.

The possible non-carcinogenic risks of heavy metals ingested and absorbed dermally were calculated and evaluated for children as well as adults. The non-carcinogenic risk was calculated with risk hazard quotient formula (HQ) through dividing average daily dose (ADD) by reference dose (RfD) [43]. HI represents total amount of HQs and potential non-carcinogenic formed by all heavy metals. HQ and HI were calculated with the equations below [40]:

$$HQ = \frac{ADD_{ingestion}/ADD_{dermal}}{RfD_{ingestion}/RfD_{dermal}} \quad (11)$$

$$HI = \sum\left(ADD_{ingestion} + ADD_{dermal}\right) \quad (12)$$

If HI, HQ > 1, it is probable that there are adverse effects on human health originated from heavy metal. However, if HI, HQ < 1, it means no negative effect [44]. Carcinogenic risk (CR) means to carry a potential risk by being exposed to a carcinogen for life. CR was calculated with the following equation (Eq. (13)):

Table 4
Toxicological parameters of the investigated metals used for health risk assessment [40,42]

	K_p	$RfD_{ingestion}$	RfD_{dermal}	
		μg/kg/d	μg/kg/d	ABS_g (%)
Al	1×10^{-3}	1,000	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	No data
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
Hg	1×10^{-3}	0.3	0.021	7
Pb	1×10^{-4}	1.4	0.42	11.7

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

In this study, CR was calculated just for As. Because, As is the only carcinogenic element among heavy metals analyzed. Cancer slope factor (CSF) values for ingestion and dermal exposure are respectively, 0.0015 and 0.00366 μg/kg/d [29]. USEPA [40] suggested acceptable or tolerable carcinogenic risk range as 10^{-6} and 10^{-4}. On the other hand, when CR ≥ 10^{-4}, it is highly possible that harmful effects on human health rise.

3. Results and discussion

3.1. Heavy metal concentration

Being exposed to toxic metals (Hg, As, Cd, and Pb) acutely and chronically may cause harmful effects for human health. Skin, respiratory, reproductive, immunological, neurological, lung cancer, genotoxic, and mutagenic effects constitute human health problems associated with heavy metal poisoning. WHO indicated that metals like Cr, Ni, Cu, Fe, Zn, Co are biologically important, but others such as Hg, As, Cd, Pb, U have not known physiological significance in humans and also even their low concentrations are toxic [30]. The statistical data (annual average, standard deviation (SD), range) of the heavy metals measured in this study are shown in Table 5. Furthermore, Box and Jitter plot graphs in which metal concentrations identified in rivers were compared with WHO's drinking water standards are shown in Fig. 3. Fig. 2 shows average concentrations of heavy metal parameters in descending order (Zn > Al > Fe > Mn > Cu > Ni > Pb > As > Hg > Cr > Cd > Co > U). The reason why Zn, Mn, and Cu are at relatively high levels in this area maybe because of widespread use of fertilizers and metal-based pesticides in agricultural areas [45].

Aluminum, which makes up about 8% of the Earth's crust, is the most abundant element in nature and can be found naturally in drinking water. However, it is slightly

Table 5
Statistical summary of heavy metal concentrations in rivers (Mean ± SD range)

	PS	BS	AS	YS	GLS	HR	GS
Al (µg/L)	167 ± 100	238 ± 47	254 ± 53	143 ± 132	197 ± 84	179 ± 11	267 ± 59
	86–297	205–308	207–315	20–290	78–274	77–312	221–351
Cr (µg/L)	1.01 ± 0.31	1.03 ± 0.15	1.28 ± 0.19	0.93 ± 0.34	1.06 ± 0.37	1.56 ± 1.43	1.41 ± 0.21
	0.75–1.46	0.85–1.2	0.99–1.42	0.57–1.38	0.60–1.46	0.52–3.67	1.26–1.73
Mn (µg/L)	18.12 ± 7.64	13.32 ± 5.75	9.96 ± 1.38	12.06 ± 4.13	14.39 ± 5.61	13.21 ± 4.5	5.90 ± 1.29
	11.14–28.55	8.43–19.56	8.9–11.85	8.87–17.93	9.68–21.85	8.41–18.28	4.58–7.67
Fe (µg/L)	21.12 ± 12.97	28.34 ± 4.52	32.17 ± 7.79	16.51 ± 11.8	40.55 ± 14.81	22.17 ± 16.25	32.38 ± 4.9
	10.27–38.23	23.66–33.33	25.25–40.69	6.15–32.55	28.88–62.23	9.44–44.48	27.99–38.44
Co (µg/L)	0.36 ± 0.06	0.29 ± 0.02	0.30 ± 0.02	0.47 ± 0.15	0.33 ± 0.03	0.30 ± 0.02	0.30 ± 0.05
	0.30–0.43	0.27–0.31	0.28–0.33	0.33–0.65	0.31–0.37	0.28–0.33	0.260.38
Ni (µg/L)	3.31 ± 2.46	5.52 ± 4.85	5.04 ± 3.63	4.76 ± 4.68	3.26 ± 1.67	2.76 ± 1.07	2.75 ± 1.22
	1.25–6.87	1.42–12.10	1.88–9.49	1.91–11.70	1.60–5.58	1.50–3.84	1.24–4.03
Cu (µg/L)	5.44 ± 2.38	3.43 ± 0.5	6.98 ± 6.84	7.75 ± 2.37	9.06 ± 6.42	5.73 ± 4.68	4.03 ± 0.98
	3.38–8.87	2.97–4.13	2.71–17.16	4.92–9.93	4.78–18.44	3.15–12.75	3.01–5.21
Zn (µg/L)	744 ± 376	1,178 ± 244	1,417 ± 424	600 ± 219	1,412 ± 781	700 ± 411	1,292 ± 543
	340–1,106	953–1,502	816–1,727	406–897	471–2,384	286–1,221	659–1,979
As (µg/L)	2.09 ± 0.84	1.81 ± 0.35	3.20 ± 0.87	2.04 ± 1.43	1.73 ± 0.72	1.54 ± 0.52	1.73 ± 0.25
	1.22–3.23	1.41–2.26	2.16–4.3	0.61–3.88	0.96–2.70	0.95–1.99	1.50–2.08
Cd (µg/L)	0.46 ± 0.2	0.32 ± 0.03	0.28 ± 0.01	0.28 ± 00	0.42 ± 0.18	0.52 ± 0.38	0.32 ± 0.02
	0.28–0.75	0.29–0.34	0.27–0.30	0.28–0.29	0.28–0.68	0.30–1.1	0.30–0.35
Hg (µg/L)	0.71 ± 0.11	1.48 ± 1.06	0.71 ± 0.33	0.72 ± 0.26	2.18 ± 3.41	1.16 ± 1.47	1.34 ± 0.88
	0.60–0.83	0.68–3.05	0.40–1.18	0.45–1.07	0.20–7.29	0.37–3.37	0.72–2.62
Pb (µg/L)	1.96 ± 0.77	1.48 ± 0.20	1.78 ± 0.41	3.57 ± 3.41	3.11 ± 1.83	2.02 ± 0.80	2.58 ± 0.28
	1.13–2.82	1.30–1.76	1.39–2.33	1.45–8.68	1.94–5.81	1.07–2.79	2.22–2.92
U (µg/L)	0.21 ± 0.1	0.16 ± 0.02	0.50 ± 0.26	0.48 ± 0.21	0.15 ± 0.03	0.47 ± 0.24	0.18 ± 0.03
	0.12–0.35	0.13–0.19	0.26–0.92	0.28–0.68	0.12–0.18	0.21–0.72	0.14–0.20

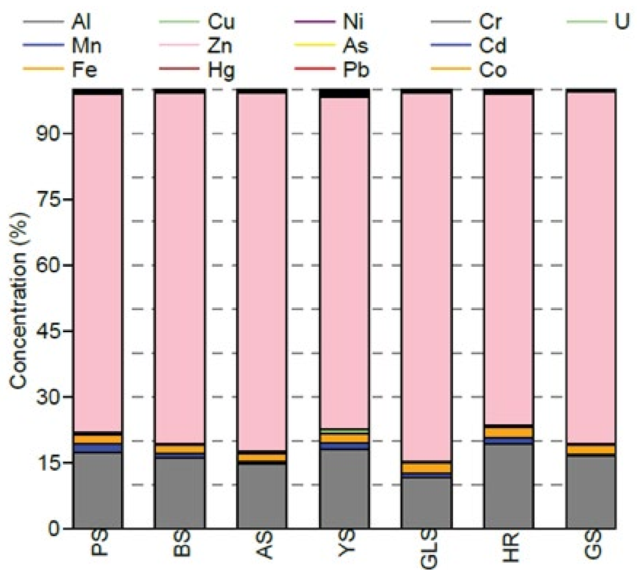

Fig. 2. Percentage of heavy metal concentrations (µg/L) in rivers.

soluble in water. It has been reported that being exposed to high amounts of aluminum may cause Alzheimer's disease in humans. In terms of individual metal concentrations, maximum value of Al in all rivers in this study exceeded limit value (200 µg/L) suggested by WHO for drinking water [36]. In terms of average Al values, only Batlama Stream (238 µg/L), Aksu Stream (254 µg/L) and Görele Stream (267 µg/L) were over limit values of WHO, the others are below the limit (Table 5, Fig. 3). In their study at Harşit River, Bayram and Önsoy [46] recorded the mean, minimum, and maximum Al values as 34–4–71 µg/L in the sub-basin which is approximately at the same point with this study area. As a result, this can indicate to policymakers that Al concentration in Harşit River has increased significantly in the last decade due to intensive stone and gravel quarry activities.

Although mercury is at higher levels in local mineral deposits and groundwater, it is usually in surface water at concentrations below 0.5 µg/L as an inorganic form. The measured values in all rivers, except the maximum value recorded at Gelevera Stream (7.29 µg/L) within the scope of the study, did not exceed the 6 µg/L level suggested by WHO.

As shown in box plot graphics in Fig. 3 of other heavy metals identified in rivers, concentrations of Mn, Fe, Cu, Zn, Ni, As, Pb, Cr, Cd, never exceeded limit values suggested by WHO for drinking water. Similarly, in a study conducted in Kızılırmak, the longest river in Turkey (1,355 km), it was reported that metal concentrations identified for Zn, Cu, B, Cr, Ni, Pb, Hg, As, Se, Sb, Mn, Cd, and Al complied with water quality standards of USEPA [47]. On the other hand, in

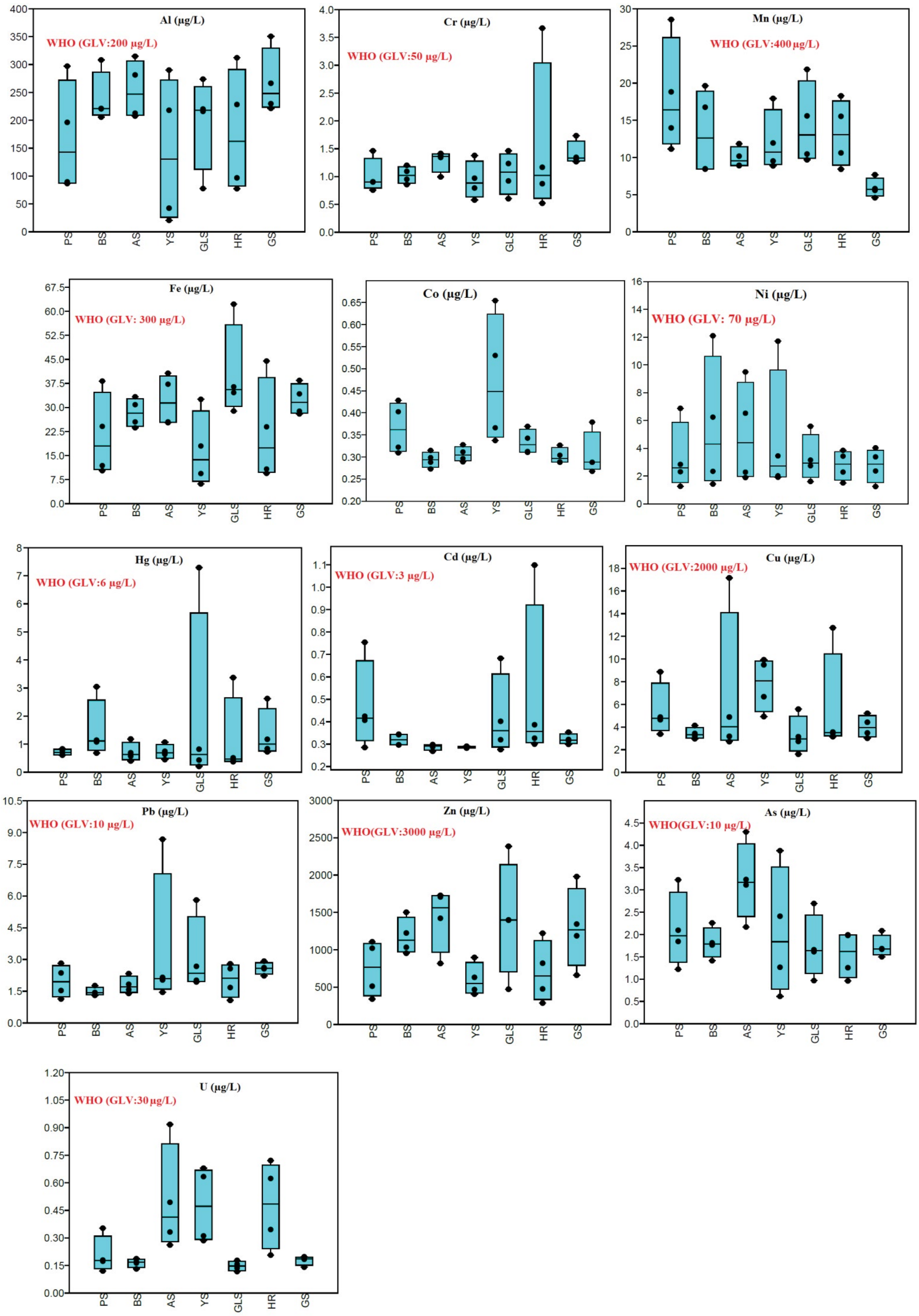

Fig. 3. Comparison of average metal levels (µg/L) at different sampling sites (GLV: Guideline).

Table 6
Water pollution indices

Sample station	WQI	HPI	HEI	Reference
Pazarsuyu Stream (Giresun, Turkey)	15.25	65.55	1.99	This study
Batlama Stream (Giresun, Turkey)	19.76	65.43	2.53	This study
Aksu Stream (Giresun, Turkey)	21.57	69.23	2.76	This study
Yağlıdere Stream (Giresun, Turkey)	14.26	69.43	1.94	This study
Gelevera Stream (Giresun, Turkey)	20.71	59.68	2.71	This study
Harşit River (Giresun, Turkey)	16.21	62.25	2.1	This study
Görele Stream (Giresun, Turkey)	20.91	66.01	2.75	This study
Aksu River (Antalya, Turkey)	35.6–337.5	–	–	[51]
Bogacayi River (Antalya, Turkey)	–	7.81–43.97	–	[53]

another study at Kirmir basin which is an important drinking source of Ankara, capital city of Turkey, it was determined that concentrations of Fe, Mn, As, and Al exceeded limit values in water quality standards [48].

3.2. Integrated approach of pollution through index analysis

WQI values calculated in rivers are close to each other and no fluctuations were observed. The lowest WQI, was found at the Yağlıdere Stream as 14.26 and the highest WQI was found in the Aksu Stream as 21.57 (Table 6). Based on these results, as WQI values of all waters are <50, they are in excellent water category. As similar studies in the literature, in a work at Gandaki, Indrawati, and Dudh Koshi some of the rivers in Himalayan WQI values were calculated as 37.23 (excellent), 30.93 (excellent), and 66.31 (good water quality), respectively [49]. Water qualities of rivers, consequently, their WQI values change depending on the contamination sources with which they interact. Such as, in Rambiara Stream which is the main drinking water source of Kashmir people, WQI values were between 43.47 and 48.74 range and in excellent water quality category. The lowest WQI value was recorded especially in places close to glacier source and covered with heavy forest vegetation as well as anthropogenic pressure was minimum [50]. WQI values of Aksu River, which is in southern-west of Turkey and exposed to city hall's waste, industrial discharge, and agricultural runoff at some points, differentiated between 35.6 (excellent) and 337.5 (undrinkable) [51].

Heavy metal pollution index (HPI) was used to evaluate the general contamination status of water in terms of heavy metals. In this study, not much difference between HPI values was observed. While minimum HPI value in Gelevera Stream was found as (59.68), maximum HPI value in Yağlıdere Stream was recorded as (69.44) (Table 6). As a result, HPI values of all waters didn't exceed critical or admissible value (<100) for safety of the drinking water [52]. In similar studies, it was reported that HPI values in Boğaçayı River (Antalya, Turkey) was between 7.81 and 43.97 [53]. And again, in a study at Mahananda River (North Bengal, West Bengal, India), it was seen that HPI values were under admissible values both in the pre-monsoon and the post-monsoon as in this one. Yet, in localities where HPI values are high, it was identified that river water is under threat due to anthropogenic activities such as agricultural irrigation and inner-city discharge [32]. In order to determine contamination load in rivers, heavy metal evaluation index (HEI) was also calculated. There was no significant difference between HEI values as in WQI and HPI, and these three indices showed a similar fluctuation. HEI was calculated minimum in Yağlıdere Stream as 1.94 and maximum in Aksu Stream as 2.76 and it was specified that all values were <10 (Table 6). According to these results all rivers are in low contamination category in terms of HEI [39].

Nemerow pollution index (P_n) provides not only individual information taking standard value into consideration about contamination degree of contaminators but also ensures focus on main contaminators [54]. In this study, P_n values ranged between 0 and 1.43 and to this index it was confirmed that only Al has an effect on heavy metal load of all rivers ($P_n > 1$). P_n values of all of the other metals were calculated as ≤1; therefore, they do not make up general contamination load. Consequently, it may be suggested that the main source of the metals in rivers is lithological but no dense heavy metal contamination anthropogenically. However, it was recorded that P_n values of all monitoring areas in Qilihai Natural Reserve, which is seriously affected by human acts, were more than 1 [33]. Besides, the degree of contamination (C_d) was used to estimate the degree of metal contamination as a reference. C_d is calculated when sum of each component's contamination factors exceeds admissible upper limit [55]. In this study, among the heavy metals only Al exceeded admissible upper limit. Therefore, C_d was calculated in only Batlama, Aksu, and Görele Streams as 0.19, 0.27, and 0.34, respectively. Because of $C_d < 1$, these rivers are in low contamination class [37].

3.3. Potential risk assessment for human health

Consuming drinking water containing metals with higher concentration than the maximum allowable concentration is harmful to health and can cause various cancers. When human health risk is evaluated, not only density of metal in drinking water but also water consumption rate is taken into consideration. Daily water consumption may change according to occupation and climate zone. In this study non/carcinogenic effects of heavy metals on human health (for adults and children) were determined. For this purpose, HQ, HI, and CR values were calculated on the basis of ADD and RfD values of each metal (Table S1). As $HQ_{ingestion}$, HQ_{dermal} and

HI values examined in all waters for metals were assessed using the guideline value <1, it can be said that using them as drinking waters for children as well as adults does not have potential danger, which is also a low possibility. These kinds of studies are conducted around the world, especially in Asia. For instance, it was reported that in Himaya River in Nepal, health risk (HQ and HI) of the residents depending on being exposed to toxic metals is low or none [49]. On the other hand, in a study conducted in Azaj River basin in India, it was stated that $HI_{ingestion}$ and HI_{dermal} values exceed the risk values and could cause health risk for the locals [56].

In case of getting arsenic exposure from drinking water for a long time, health problems like cancer, hypertension, skin lesions, diabetes, neuropathy may occur [11]. In this study, carcinogenic risk (CR) caused by only arsenic both for children and adults was calculated with CSF (Table S1). It was determined that CR calculated for children was higher than that of adults (Fig. 4). This shows that when children live in the same environmental conditions as adults, they are more vulnerable than adults [16]. It was seen that CR results identified for arsenic were between (10^{-4} and 10^{-6}) limit values suggested by USEPA. These values indicate that oral and dermal uptake of arsenic in rivers does not constitute a significant cancer risk. It observed that only in Aksu Stream, arsenic is slightly over the limit values both for children (1.46E-04) and adults (1.32E-04). This indicates a relatively low risk of cancer. It is thought that the origin of the arsenic in the study area may be related to geological structure as well as pesticides with arsenic commonly used for hazelnut agriculture [57,58]. In a similar study, it was reported that risk evaluation for dissolved arsenic in Barekese reservoir in Ghana was in admissible range of USEPA, yet, when arsenic is incepted, cancer risk for children was slightly higher [11]. It was reported that CR results especially based on arsenic in waters in mining areas was higher than admissible limit [35].

4. Conclusions

Rivers are significant natural resources for all living creatures, not only for today but for the future. In this study WQI, HPI, HEI values were found as 14.26–21.57, 59.68–69.44, and 1.94–2.76, respectively. $HQ_{ingestion}$, HQ_{dermal}, and HI results were calculated lower than 1, the threshold value. CR results were slightly above the limit values in both children (1.46E-04) and adults (1.32E-04) only for arsenic in Aksu Stream. This is the first study in which effects of the heavy metal contents of rivers in the region on water quality and human health were evaluated with a lot of indexes (WQI, Pn, HPI, HEI, Cd, HI, HQ, CR) simultaneously. Furthermore, it is thought that making evaluations just by observing metal concentrations doesn't give a clear idea about serious health danger. Therefore, index analysis was needed. Even if seasonally four samples are taken from discharge points of the rivers, it is thought that data will be reference for future studies. Results indicated that metal contamination in surface river water in north-eastern Turkey (Giresun) carries a low risk for local people.

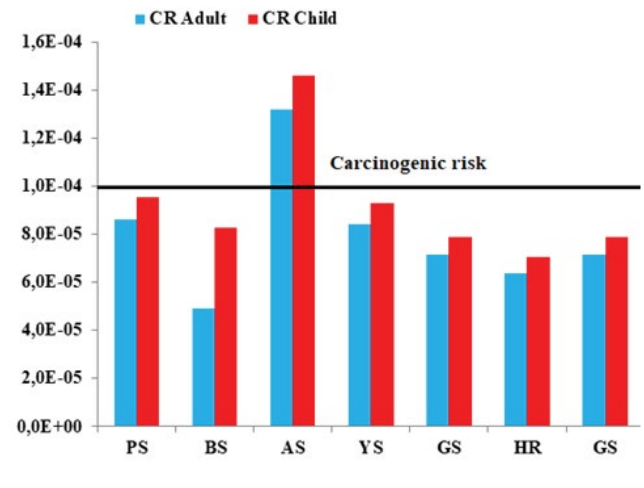

Fig. 4. Cancer risk (CR) values caused by arsenic in adults and children (ingestion and dermal sum).

Rivers in the study area are mostly contaminated with climatic and anthropogenic (agricultural activities, household waste) nonpoint source pollutants. In addition, inorganic mineral input of the basin is based on geological structure, non-point sources and surface flows. These sources may be natural as well as stone/gravel quarries. As a result of examinations, it was seen that there were active stone/gravel quarries in all the rivers' basins. Consequently, it can be said that water quality of the rivers in the study area are in good condition for now in terms of heavy metal content. However, it is an undeniable truth that they are under anthropogenic pressure. The most important environmental problems of the region are domestic solid wastes, stone/gravel quarries in the basins, excessive fertilizer and pesticide use. For protection of water quality and sustainable basin management, solid/liquid treatment facilities should be established, local people should be informed about the use of agricultural fertilizers and pesticides, basin-based protection status should be applied, and clean freshwater basins should be protected by monitoring activities.

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Supplementary information

Table S1
Hazard quotient and cancer risk for each element of the streams

	$HQ_{ingestion}$		HQ_{dermal}		HI		Cancer risk (Ingestion + Dermal)	
Element	Adult	Child	Adult	Child	Adult	Child	Adult	Child
Pazarsuyu Stream								
Al	4.53E-03	5.08E-03	1.30E-04	1.65E-05	4.66E-03	5.09E-03		
Mn	1.30E-03	1.46E-03	2.91E-03	3.70E-03	4.21E-03	1.83E-03		
Fe	1.21E-05	1.35E-05	2.33E-05	2.99E-06	3.53E-05	1.65E-05		
Cu	2.21E-03	2.48E-03	1.05E-04	1.35E-05	2.32E-03	2.49E-03		
Zn	1.47E-02	1.65E-02	1.15E-03	1.47E-04	1.59E-02	1.67E-02		
Hg	4.73E-03	5.30E-03	5.22E-03	6.69E-04	9.95E-03	5.97E-03		
Ni	1.89E-04	2.12E-04	7.09E-06	1.64E-05	1.96E-04	2.28E-04		
As	1.89E-01	2.12E-01	1.13E-03	1.45E-04	1.90E-01	2.12E-01	8.63E-05	9.55E-05
Pb	4.68E-03	5.24E-03	7.20E-05	9.24E-06	4.75E-03	5.25E-03		
Cr	1.25E-04	1.40E-04	2.08E-03	2.67E-04	2.20E-03	4.07E-04		
Cd	1.31E-03	1.47E-03	2.84E-03	3.64E-04	4.15E-03	1.84E-03		
Co	3.43E-02	3.84E-02	3.72E-04	4.75E-05	3.47E-02	3.84E-02		
Batlama Stream								
Al	6.46E-03	7.24E-03	1.84E-04	2.36E-05	6.64E-03	7.26E-03		
Mn	9.51E-04	1.07E-03	2.14E-03	2.75E-04	3.09E-03	1.34E-03		
Fe	1.62E-05	1.81E-05	3.12E-05	4.01E-06	4.74E-05	2.21E-05		
Cu	1.40E-03	1.56E-03	6.62E-05	8.49E-06	1.46E-03	1.57E-03		
Zn	2.24E-02	2.51E-02	1.82E-03	2.33E-04	2.43E-02	2.54E-02		
Hg	9.87E-03	1.11E-02	1.09E-02	1.40E-03	2.07E-02	1.24E-02		

Table S1 (*continued*)

	$HQ_{ingestion}$		HQ_{dermal}		HI		Cancer risk (Ingestion + Dermal)	
Element	Adult	Child	Adult	Child	Adult	Child	Adult	Child
Ni	3.15E-04	3.53E-04	1.18E-05	2.73E-05	3.27E-04	3.81E-04		
As	1.07E-01	1.20E-01	9.80E-04	1.26E-04	1.08E-01	1.20E-01	4.91E-05	8.27E-05
Pb	3.53E-03	3.96E-03	5.44E-05	6.98E-06	3.59E-03	3.96E-03		
Cr	1.28E-04	1.43E-04	2.12E-03	2.72E-04	2.25E-03	4.15E-04		
Cd	9.14E-04	1.02E-03	1.97E-03	2.53E-04	2.89E-03	1.28E-03		
Co	2.76E-02	3.09E-02	3.00E-04	3.83E-05	2.79E-02	3.10E-02		
Aksu Stream								
Al	6.89E-03	7.72E-03	1.96E-04	2.51E-05	7.09E-03	7.75E-03		
Mn	7.11E-04	7.97E-04	1.60E-03	2.05E-04	2.31E-03	1.00E-03		
Fe	1.84E-05	2.06E-05	3.55E-05	4.55E-06	5.38E-05	2.51E-05		
Cu	2.84E-03	3.18E-03	1.35E-04	1.73E-05	2.98E-03	3.20E-03		
Zn	2.70E-02	3.02E-02	2.19E-03	2.81E-04	2.92E-02	3.05E-02		
Hg	4.73E-03	5.30E-03	5.22E-03	6.69E-04	9.95E-03	5.97E-03		
Ni	2.88E-04	3.23E-04	1.08E-05	2.49E-05	2.99E-04	3.48E-04		
As	2.90E-01	3.24E-01	1.73E-03	2.22E-04	2.91E-01	3.24E-01	1.32E-04	1.46E-04
Pb	4.25E-03	4.76E-03	6.54E-05	8.39E-06	4.32E-03	4.77E-03		
Cr	1.58E-04	1.77E-04	2.63E-03	3.38E-04	2.79E-03	5.15E-04		
Cd	8.00E-04	8.96E-04	1.73E-03	2.22E-04	2.53E-03	1.12E-03		
Co	2.86E-02	3.20E-02	3.10E-04	3.96E-05	2.89E-02	3.20E-02		
Yağlıdere Stream								
Al	3.88E-03	4.35E-03	1.10E-04	1.42E-05	3.99E-03	4.36E-03		
Mn	8.61E-04	9.65E-04	1.94E-03	2.49E-04	2.80E-03	1.21E-03		
Fe	9.43E-06	1.06E-05	1.82E-05	2.33E-06	2.76E-05	1.29E-05		
Cu	3.16E-03	3.53E-03	1.49E-04	1.92E-05	3.30E-03	3.55E-03		
Zn	1.14E-02	1.28E-02	9.26E-04	1.19E-04	1.24E-02	1.29E-02		
Hg	4.80E-03	5.38E-03	5.29E-03	6.79E-04	1.01E-02	6.05E-03		
Ni	2.72E-04	3.05E-04	1.02E-05	2.36E-05	2.82E-04	3.28E-04		
As	1.85E-01	2.07E-01	1.10E-03	1.42E-04	1.86E-01	2.07E-01	8.42E-05	9.32E-05
Pb	8.52E-03	9.55E-03	1.31E-04	1.68E-05	8.66E-03	9.56E-03		
Cr	1.15E-04	4.16E-03	1.91E-03	2.46E-04	2.03E-03	4.40E-03		
Cd	8.00E-04	8.96E-04	1.73E-03	3.64E-04	2.53E-03	1.26E-03		
Co	4.48E-02	5.01E-02	4.86E-04	6.20E-05	4.52E-02	5.02E-02		
Gelevera Stream								
Al	5.35E-03	5.99E-03	1.52E-04	1.95E-05	5.50E-03	6.01E-03		
Mn	1.03E-03	1.15E-03	2.31E-03	2.97E-04	3.34E-03	1.45E-03		
Fe	2.32E-05	2.60E-05	4.47E-05	5.73E-06	6.79E-05	3.17E-05		
Cu	3.69E-03	4.13E-03	1.75E-04	2.24E-05	3.86E-03	4.15E-03		
Zn	2.69E-02	3.01E-02	2.18E-03	2.80E-04	2.91E-02	3.04E-02		
Hg	1.45E-02	1.63E-02	1.60E-02	2.06E-03	3.05E-02	1.83E-02		
Ni	1.86E-04	2.09E-04	6.99E-06	1.61E-05	1.93E-04	2.25E-04		
As	1.57E-01	1.75E-01	9.37E-04	1.20E-04	1.57E-01	1.75E-01	7.14E-05	7.90E-05
Pb	7.43E-03	8.32E-03	1.14E-04	1.47E-05	7.54E-03	8.33E-03		
Cr	1.31E-04	1.47E-04	2.18E-03	2.80E-04	2.31E-03	4.27E-04		
Cd	1.20E-03	1.34E-03	2.59E-03	3.33E-04	3.79E-03	1.68E-03		
Co	3.14E-02	3.52E-02	3.41E-04	4.36E-05	3.18E-02	3.52E-02		

Table S1 (*continued*)

	$HQ_{ingestion}$		HQ_{dermal}		HI		Cancer risk (Ingestion + Dermal)	
Element	Adult	Child	Adult	Child	Adult	Child	Adult	Child
Harşit River								
Al	4.86E-03	5.44E-03	1.38E-04	1.77E-05	5.00E-03	5.46E-03		
Mn	9.44E-04	1.06E-03	2.12E-03	2.72E-04	3.07E-03	1.33E-03		
Fe	1.27E-05	1.42E-05	2.44E-05	3.14E-06	3.71E-05	1.73E-05		
Cu	2.33E-03	2.61E-03	1.11E-04	1.42E-05	2.44E-03	2.63E-03		
Zn	1.33E-02	1.49E-02	1.08E-03	1.39E-04	1.44E-02	1.51E-02		
Hg	7.73E-03	8.66E-03	8.52E-03	1.09E-03	1.63E-02	9.76E-03		
Ni	1.58E-04	1.77E-04	5.91E-06	1.37E-05	1.64E-04	1.90E-04		
As	1.39E-01	1.56E-01	8.34E-04	1.07E-04	1.40E-01	1.56E-01	6.36E-05	7.03E-05
Pb	4.82E-03	5.40E-03	7.42E-05	9.52E-06	4.90E-03	5.41E-03		
Cr	1.93E-04	2.16E-04	3.21E-03	4.12E-04	3.40E-03	6.28E-04		
Cd	1.49E-03	1.66E-03	3.21E-03	4.12E-04	4.69E-03	2.08E-03		
Co	2.86E-02	3.20E-02	3.10E-04	3.96E-05	2.89E-02	3.20E-02		
Görele Stream								
Al	7.25E-03	8.12E-03	2.06E-04	2.64E-05	7.45E-03	8.14E-03		
Mn	4.21E-04	4.72E-04	9.48E-04	1.22E-04	1.37E-03	5.94E-04		
Fe	1.85E-05	2.07E-05	3.57E-05	4.58E-06	5.42E-05	2.53E-05		
Cu	1.64E-03	1.84E-03	7.77E-05	9.97E-06	1.72E-03	1.85E-03		
Zn	2.46E-02	2.76E-02	1.99E-03	2.56E-04	2.66E-02	2.78E-02		
Hg	8.93E-03	1.00E-02	9.84E-03	1.26E-03	1.88E-02	1.13E-02		
Ni	1.57E-04	1.76E-04	5.89E-06	1.36E-05	1.63E-04	1.90E-04		
As	1.57E-01	1.75E-01	9.37E-04	1.20E-04	1.57E-01	1.75E-01	7.14E-05	7.90E-05
Pb	6.16E-03	6.90E-03	9.48E-05	1.22E-05	6.26E-03	6.91E-03		
Cr	1.75E-04	1.96E-04	2.90E-03	3.72E-04	3.08E-03	5.68E-04		
Cd	9.14E-04	1.02E-03	1.97E-03	2.53E-04	2.89E-03	1.28E-03		
Co	2.86E-02	3.20E-02	3.10E-04	3.96E-05	2.89E-02	3.20E-02		