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Spatiotemporal variations in the levels of toxic elements in drinking water of Sivas, Türkiye, and an ecotoxicological risk assessment

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This study was conducted in 2022 to investigate the water variables of fountains used by people for drinking purposes in Şarkışla (Sivas, Türkiye). Five stations were selected from the most frequently used fountains. Sampling was carried out seasonally. Various physicochemical variables such as water temperature (WT), pH, electirical conductivity (EC), dissolved oxygen (DO), nitrite (NO_2), nitrate (NO_3), phosphate (PO_4), sulphate (SO_4), magnesium (Mg), calcium (Ca), total hardness (TH), chloride (Cl), salinity, total dissolved solids (TDS), arsenic (As), cadmium (Cd), zinc (Zn), manganese (Mn), and copper (Cu) were investigated. Additionally, the Nitrate Pollution Index (NPI), Groundwater Quality Index (GWQI), and Human Health Risk Assesment (HHRA) methods were applied to the data. One of the main objectives of this study was to conduct health risk assessments for people using water from drinking fountains and to identify both carcinogenic and non-carcinogenic metals. As a result of this research, NPI values indicated slight contamination, while no contamination was found based on GWQI values. The Mn and Cd were found to slightly exceed the permissible limit values. As, which exceeds the limit value in water, was found to pose a serious carcinogenic risk (CR) for both children and adults. High As values are from quaternary alluvial deposits and aquifer layers of Pliocene terrestrial layers. Considering the hazard quotient (HQ) and hazard index (HI) for the presence of Cd, it was determined that it poses a serious risk to humans and children through both ingestive and dermal exposure. At the end of the study, several recommendations for the sustainable use of drinking fountains water were provided.

Keywords Heavy metals, NPI, Groundwater pollution index, Health risk assessment, Türkiye

Water is the most valuable natural resource for sustaining life and protecting ecosystems. It is an excellent solvent due to the polar structure of its molecules[1,2]. While 70% of the Earth is covered by water, only 2.5% of it is fresh water. More than a third of the water used by humans comes from groundwater. Groundwater is reported to be pure, clean and drinkable in the in many parts of the world[3].

Turkey is located in the Central Anatolian climate zone. Sivas is situated in the middle of the Anatolian peninsula, in the Upper Kızılırmak section of the Central Anatolia Region. With an area of 28,488 km^2, it is the second largest province in Turkey. Sivas is bordered by Erzincan to the east, Malatya and Kahramanmaraş to the south, Kayseri to the southwest, Yozgat to the west, Tokat and Ordu to the north, and Giresun to the northeast. Şarkışla is the most populous district of Sivas Province and one of the 17 districts of Sivas, including the central district. It is located along the Sivas-Kayseri highway. The population of the district center is 22,000. Together with the villages and towns, the total population is around 37,000. Şarkışla is a developing district with a growing industry. Animal husbandry and agriculture are important sources of livelihood in the district[4].

It is determined that the Şarkışla Basin consists of volcanic and volcano-sedimentary rocks, folded formations and other Pliocene formations, which can be considered a typical geological feature of Central Anatolia[5]. From a hydrogeological perspective, the Sivas (Şarkışla) plain is the largest hydrogeological feature in the region, and most of the groundwater is supplied from the Pliocene aquifer. The highest arsenic concentrations are found in alluvial deposits and Pliocene layers, and a large part of the drinking water demand is met by these aquifers.

In Turkey, especially in Central Anatolia, fountains are an important source of drinking water for humans and animals[6]. A fountain is a concrete structure through which water from underground pipes flows into a container.

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Fountains, which are widely used by the public for drinking water supply, are mostly located in villages or along roadsides in rural areas[7]. In some cases, groundwater may contain toxic chemical compounds that pose health risks to humans. These compounds have harmful effects on the balance of the environment and the ecological system. Sometimes, these compounds are absorbed by organisms and transported through the food chain. They can accumulate in the human body and cause various diseases, including cancer[8,9] The potential risk of human exposure and adverse health effects should not be underestimated[10].

An HHRA (Human Health Risk Asessment) is conducted to identify and quantify past, present, and future exposures to various biological, physical, and chemical agents that may cause human health effects[8,11]. A health risk assessment evaluates the relevance of environmental pollution to human health and quantitatively estimates the risk of contamination through various exposure routes, including direct ingestion, skin contact, and inhalation[12–14].

Human health risk analysis is a critical area of research that examines the potential harmful effects of various exposures on human health. As societies encounter an increasing number of environmental, occupational, and lifestyle-related hazards, understanding the associated risks becomes essential. This process involves identifying potential hazards, assessing the extent of exposures, and evaluating the health consequences linked to them. By applying scientific methods and data-driven strategies, health risk analysis helps guide public health policies, shape regulatory frameworks, and ultimately protect populations from preventable health issues.

Scientists globally have used pollution indices to assess the health impact of heavy metal pollution and exposure to various pollutants in groundwater across countries like Thailand, Syria, India, China, and Turkey[12,13,15–20]. HHRA has been applied to many different aquatic environments in Turkey[13–16]. There are two studies on the high arsenic content of groundwater in Şarkışla, which constitutes the study area[21–24]. However, seasonal variation of arsenic content and HHRA were not analysed in these studies.

In this study, physicochemical variables from seasonal fountain water samples across Şarkışla were first evaluated against national and international criteria defined[25–28]. Secondly, the samples were assessed using the NPI and GWQI indices. These indices are methods that converts various water quality parameters into a single value revealing the quality of waters with this value[22]. Finally, an HHRA was applied to assess the effects of toxic metals found in the water samples on human health.

Materials and methods

The study area

Şarkışla is a district located 81 km from the center of Sivas. It shares borders with Sivas and Altınyayla to the east, Gemerek to the west, Kayseri to the south, and Yozgat and Yıldızeli to the north. Situated between 36° and 37° east longitude (36° 25′E) and 39° and 40° north latitude (39° 21′N), Şarkışla District is the subject of this study[4]. This research was conducted seasonally.

In Şarkışla, five different stations were selected from the fountains most intensively used by the public. The first station is Belkent Fountain, located at coordinates 39°20′47″N, 36°25′30″E. This station is situated away from settlements and agricultural areas. The second station is Karakaâ Fountain, positioned at coordinates 39°22′34″N 36°28′43″E, with many houses surrounding it. The third station is Döllük Fountain, situated at coordinates 39°20′45″N 36°27′31″E, close to a village and surrounded by agricultural lands. The fourth station is Pöyrek Fountain, located at coordinates 39°18′28″N 36°27′46″E, and is also surrounded by agricultural lands. Lastly, the fifth station is Kışla Fountain, located at coordinates 39°13′06″N, 36°28′55″E, surrounded by an abandoned village. The study area and sampling stations are depicted in Fig. 1.

Sampling and analysis

pH, WT, EC, TDS and DO of the water were measured during the field study. For the other variables, water samples were collected. The samples were taken following the method outlined by the American Public Health Association and transported under a cold chain[29]. The samples were prepared for analysis without delay. The concentrations of NO_3, NO_2, SO_4, PO_4, Ca, Mg, Cl, TH, and salinity of the water samples were analyzed[29]. Additionally, the concentrations of As, Cd, Zn, Mn, and Cu in the water were investigated. For this purpose, water samples were collected using polyethylene bottles and transferred to the laboratory with the addition of 0.1 N HNO_3 to lower pH levels to below 2. Analysis was conducted using an ICP-MS device at the accredited laboratories of Sivas Cumhuriyet University Advanced Technology Research and Application Center (CÜTAM), and measurements were recorded in parts per billion (ppb).

Each analysis was performed three times. The average value was taken and used for the analysis. The results were evaluated according to national and international water quality criteria as outlined in[25–28].

Statistical analyses

The similarity of the sampling stations and seasons in the distribution of the data was grouped by the Bray–Curtis cluster analysis with the Biodiversity Pro 2.0 programme[30]. The similarity of seasons in the distribution of the data was grouped Correspondence analysis with the Biodiversity Pro 2.0. programme[30]. The relationship between physicochemical parameters was evaluated using Pearson correlation analysis with IBM SPSS Statistics Version 2[30]. Spatial maps were created using ArcMap 10.3.1. package programme supported by GIS[8].

Water quality indexes

The NPI is an important method used to evaluate the contamination level of excess nitrate in groundwater and estimate its impact on human health[31,32]. They developed the NPI method to classify groundwater quality[33]. It is calculated using the following formula: A value < 0 means clean (unpolluted), 0–1 means slightly polluted, 1–2 means moderate polluted, 2–3 means significant polluted, and > 3 means very significant polluted[33,34]. In

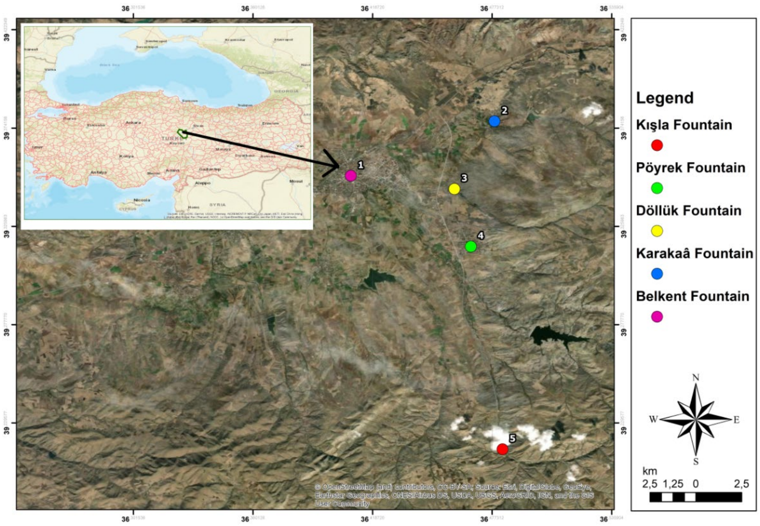

Fig. 1. Map of the study area and the locations of the stations Imagery Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, Aerogrid, IGN, and the GIS User Community. Figure generated using ArcMap Version 10.3.1. Software Openstreepmap, version number 19312, link www.openstreetmap.org.

	wi	Wi	Si (for drinking)
pH	4	0.16	6.5–8.5
TDS	4	0.16	1500
EC	1	0.04	2500
TH	2	0.08	500
PO_4	2	0.08	0.5
SO_4	4	0.16	250
Cl	3	0.12	250
NO_3	5	0.2	50

Table 1. Parametric values for the GWQI index[35].

the following equation, C_S represent the nitrate concentration of the water sample; HAV represent the value of affected human). The equation is shown 1 below.

$$NPI = \frac{C_S - HAV}{HAV} \tag{1}$$

The GWQI is widely used to identify and evaluate pollution in water. Variables such as pH, TDS, EC, TH, PO_4, SO_4, CI, NO_3 are used to calculate this index, ensuring that water quality is represented by a single value[35]. The resulting values are classified as follows: less than 50 as excellent, 50–100 as good, 100–200 as poor, 200–300 as very poor, and greater than 300 as unfit for drinking[35]. The values of the GWQI related to the parameters are given in Table 1. In the following equations, W_i represents the relative weight, w_i represents the weigth of each parameter, Q_i represents the quality rating, C_i represents the concentration of each chemical parameter in each water sampling in mg/l, Sl_i sub index of i^{th} parameters. The equations are in 2, 3, 4, and 5 below.

$$W_i = \frac{w_i}{\sum_i^1 wi} \tag{2}$$

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

$$Sl_i = W_i \times Q_i \tag{4}$$

$$WQI = \sum_{i=1}^1 Sl_i \tag{5}$$

Human health risk asssesment

In the study, health risk assessment methods were used[36]. While examining the risks of elements in water to human health, the amount absorbed through dermal and digestive processes was taken into account. Therefore, the daily intake of CDI through ingestion and dermal absorption (CDI through skin) were calculated using the equation suggested by the reference[36]. For non-carcinogenic risk analysis, As, Cd, Mn, Zn, and Cu were calculated among the toxic metals[36]. The equations are shown in 6, 7, 8, 9, 10, and 11 below.

$$CDI_{ingestion} = C_{water} \times \frac{(IR \times EF \times ED)}{(BW \times AT)} \tag{6}$$

$$CDI_{dermal} = C_{water} \times \frac{\left(SA \times K_p \times ET \times EF \times ED \times CF\right)}{(BW \times AT)} \tag{7}$$

$$HQ_{ingestion} = \frac{CDI_{ingestion}}{RfD_{ingestion}} \tag{8}$$

$$HQ_{dermal} = \frac{CDI_{dermal}}{RfD_{dermal}} \tag{9}$$

$$RfD_{dermal} = RfD_{ingestion} \times ABS_{gastrointestinal} \tag{10}$$

$$HI = HQ_{ingestion} + HQ_{dermal} \tag{11}$$

The carcinogenic risk analysis was calculated for As and Cd among the toxic metals. $CR_{ingestion}$ refers to the carcinogenic risk by ingestion, $CDI_{ingestion}$ refers to the chronic daily intake by ingestion, and $CSF_{ingestion}$ refers to the cancer slope factor by ingestion. CR_{derma}l refers to the carcinogenic risk by dermal absorption, CDI_{dermal} refers to the chronic daily intake by dermal absorption, and CSF_{dermal} refers to the cancer slope factor by dermal absorption[23]. Equations (12) and (13) were used to calculate the CR for ingestion and dermal absorption pathways, respectively.

$$CR_{ingestion} = CDI_{ingestion} \times CSF_{ingestion} \tag{12}$$

$$CR_{dermal} = CDI_{dermal} \times CSF_{dermal} \tag{13}$$

HI and HQ < 1 mean that there is no adverse effect on human health from toxic metals. However, if HI and HQ are > 1, there are likely to be adverse effects on human health from toxic metals[37–39]. According to the reference the carcinogenic risk range of 1×10^{-6} to 1×10^{-4} is recommended as the acceptable or tolerable risk range[40]. A CR value $> 1 \times 10^{-4}$ indicates a highly likely occurrence of harmful effects on human health, representing extremely high cancer risk. Values $< 1 \times 10^{-6}$ are classified as low risk. The symbols, units, values, and their respective references for the equations used in the health risk assessment are provided in Table 2.

Results and discussion

The seasonal values of 19 parameters measured in the 5 fountains most commonly used by the public for drinking and domestic purposes in Şarkışla are presented in Table 3.

Reference values used in the evaluation of physicochemical parameters are presented in Table 4.

The pH values of the waters ranged from 7.34 (winter season, station 1) to 8.63 (autumn season, station 5) (Table 3). The average pH value was 8, which falls within national and international limit values (Table 4). The measured values indicate that the fountain waters are alkaline in nature. A study conducted in China reported a groundwater pH value of 8.37[44]. Similarly, a study in India evaluated groundwater during the monsoon and post-monsoon seasons, reporting pH values ranging from 5.9 (monsoon season) to 6.0 (post-monsoon season)[13].

The EC values ranged from 290 µs/cm (winter season, station 5) to 696 µs/cm (summer season, station 1), with an average EC value of 414.7 µs/cm. EC is a parameter related to dissolved solids in water. A high EC value can be attributed to increased chemical weathering and a longer residence time of groundwater in the aquifer[45].

Definitions	Symbols/unit	Values
Metal concentration	C_W (ppb)	
Resident water intake ratio	IR (lt/day)	(2 for adults, 0.64 for children)[41,42]
Resident exposure frequency	EF (days/year)	(365)[41,42]
Resident exposure duration	ED (years)	(70 for adults, 6 for children)[41,42]
Body weight	BW (kg)	(70 for adults, 20 for children)[41,42]
Averaging time	AT (days)	(25,550 for adults, 2190 for children)[41,42]
Resident skin surface area	SA (cm^2)	(18.000 for adults, 6600 for children)[41,42]
Dermal permeability constant	Kp (cm/h)	(As: 0.001; Cd: 0.001; Mn: 0.001 Zn: 0.0006 Cu: 0.001)[43]
Resident exposure time	ET (hours)	(0.6 for adults, 1 for children)[41,42]
Unit conversion factor	CF (L/cm^3)	(0.01)[41,42]
Cancer slope factor	CSF (ppb/day)	(As:0.0015; Cd: 0.0061)[41]
Oral reference dose	$RfD_{ingestion}$ (mg/kg-day)	(As: 0.0003; Cd: 0.0005; Mn:0.14; Cu: 0.04; Zn:0.3)[43]
Dremal reference dose	RfD_{dermal}	(As:0.0003; Cd: 0.000025; Mn: 0,14; Cu: 0.04 Zn: 0.3)[43]
Gastrointestinal absorption (unitless)	$ABS_{gastrointestinal}$ (unitless)	(As:1; Cd:0.05; Mn: 1 Cu:1; Zn: 1)[43]

Table 2. Symbols, units, values, and references used in equations for health risk assessment.

Parameters/stations	Spring season					Summer season				
	1	2	3	4	5	1	2	3	4	5
pH	7.56	7.85	7.84	7.74	7.90	7.59	7.84	7.86	7.88	7.96
EC(µS/cm)	666	351	381	448	324	696	333	362	421	316
WT(°C)	10	10.5	11	11	9	19	17.3	17.9	17	16.5
DO (mg/l)	2.56	2.94	3.90	3.99	4.20	3.61	3.99	4.76	5.14	5.71
NO_2(mg/l)	0	0.001	0	0.001	0.001	0.01	0.01	0.01	0.01	0.01
NO_3(mg/l)	4.62	7.16	6.81	7.06	5.19	8.94	9.16	3.64	3.54	3.07
PO_4(mg/l)	0.58	0.71	0.61	0.71	0.67	0.44	0.55	0.57	0.52	0.52
SO_4 (mg/l)	2.29	0.14	0.12	0.80	0.08	2.81	2.46	0.28	2.01	0.81
Mg (mg/l)	14.34	8.97	7.75	11.12	8.24	13.90	8.68	6.53	11.31	8.73
Ca (mg/l)	86.57	56.91	50.50	65.73	49.69	84.16	52.90	43.28	64.12	51.30
T.H. (FS°	27.6	20	18.6	20	15.8	27	17.2	16.4	17.6	15.4
Cl (mg/l)	24	3.99	4.99	7.99	4.99	19.9	1.99	0.99	2.99	1.99
Salinity (‰)	0.06	0.02	0.03	0.04	0.05	0.03	0.02	0.01	0.01	0.008
TDS (mg/l)	247	135	140	155	110	290	143	161	187	151
As (ppb)	793	867	954	927	1035	968	1077	1121	1060	1061
Cd (ppb)	0.093	0.186	0.093	0.186	0.311	0.280	0.124	0.311	0.186	0.218
Zn (ppb)	3.72	6.71	3.64	3.25	3.30	2.70	2.30	1.18	1.04	1.55
Mn (ppb)	8.43	8.88	9.73	9.76	10.27	59.13	83.08	28.54	38.33	87.27
Cu (ppb)	1.21	0.88	0.88	0.74	1.10	1.31	1.37	1.41	1.47	1.34
Parameters/stations	Autumn season					Winter season				
	1	2	3	4	5	1	2	3	4	5
pH	7.59	8.36	8.54	8.58	8.63	7.34	8.02	8.33	8.28	8.42
EC(µS/cm)	647	346	375	389	323	584	324	330	388	290
WT(°C)	12	12.5	13	13	11	9	9.5	10	9.5	8.5
DO (mg/l)	1.52	1.90	3.04	2.85	2.47	4.76	6.28	6.66	5.90	5.75
NO_2(mg/l)	0.01	0.01	0.01	0.01	0.01	0.01	0.008	0.01	0.01	0.01
NO_3(mg/l)	4.99	2.57	3.12	4.97	2.42	5.02	1.00	2.07	3.82	0.72
PO_4(mg/l)	0.02	0.01	0.02	0.01	0.03	0.03	0.16	0.16	0.26	0.29
SO_4 (mg/l)	2.43	0.06	0.15	0.53	0.09	1.95	0.04	0.05	0.36	0.09
Mg (mg/l)	14.58	8.39	7.90	12.92	10.48	16.79	9.17	8.78	5.08	6.63
Ca (mg/l)	96.19	54.50	52.10	72.14	60.12	99.39	57.71	56.11	64.92	52.10
T.H. (FS°	36.2	20	19.6	19	17	30.6	20	20	44	24.8
Cl (mg/l)	14.99	7.99	2.99	3.99	5.99	20.99	0.99	3.99	7.99	6.99
Salinity (‰)	0.01	0.02	0.008	0.03	0.008	0.03	0.03	0.04	0.02	0.01
TDS (mg/l)	325	173	187	194	161	292	162	165	194	145
As (ppb)	1102	1223	1210	1136	1323	1119	1308	1106	1270	1265
Cd (ppb)	2.50	6.35	0.155	1.49	0.373	0.093	0.124	0.155	9.77	0.062
Zn (ppb)	2.21	3.97	3.03	2.69	5.11	4.61	5.06	3.17	3.04	3.36
Mn (ppb)	12.63	13.90	13.92	13.12	16.89	17.38	17.78	14.48	17.14	17.30
Cu (ppb)	1.43	1.23	1.00	0.77	1.35	1.40	1.26	1.28	1.38	1.39

Table 3. Physiochemical and heavy metal data analysed.

The WT values ranged from 8.5 °C (winter season, station 5) to 19 °C (summer season, station 1), with an average temperature of 12.36 °C. This indicates that the water temperature falls within national and international limit values (Table 4). Groundwater WT is an important physical parameter that influences various biological and chemical processes in the soil[46]. The results suggest that water temperature exhibits seasonal variation, with higher temperatures measured particularly during the summer and autumn seasons. A key factor contributing to this may be the increase in groundwater temperatures, both locally and globally, due to recently global climate change[47].

NO_2 values ranged from 0 mg/l (spring season, stations 1 and 3) to 0.01 mg/l (summer and autumn seasons, all stations; winter season, stations 1, 3, 4, and 5) (Table 3). The average NO_2 value was 0.007 mg/l. NO_3 values ranged from 0.72 mg/l (winter season, station 5) to 9.16 mg/l (summer season, station 2), with an average NO_3 value of 4.49 mg/l, which falls within national and international limit values (Table 4). The primary sources of NO_3 compounds are fertilizers containing NO_3 and domestic waste, which are converted to nitrate in the soil[48]. A study conducted in Aydın, Turkey, reported that nitrate concentrations in groundwater ranged from 0.063 to 42.22 mg/l. NO_3 is a key indicator of anthropogenic pollution in groundwater, particularly pollution

Parameters	Values and references
pH	(6.5 < pH < 8.5)[25]; (6.5–8)[26]; (6.5–8.5)[27]; (6.5–9)[28]
EC(μS/cm)	(400–2000)[25]; (2500)[28]
WT(°C)	(12–25)[25]
NO_2(mg/l)	(0.1)[25]; (3)[26] ; (1)[27]; (0.5)[28]
NO_3(mg/l)	(25–50)[25]; (50)[26]; (10)[27]; (50)[28]
SO_4 (mg/l)	(25–250)[25]; (500)[26]; (250)[27]; (250)[28]
Mg (mg/l)	(30–50)[25]
Ca (mg/l)	(100)[25]
Cl (mg/l)	(25–600)[25]; (250)[26]; (250)[27]; (250)[28]
TDS (mg/l)	(1500)[25]
As (ppb)	(50)[25]; (10)[26]; (10)[27]; (10)[28]
Cd (ppb)	(5)[25]; (3)[26]; (5)[27]; (5)[28]
Zn (ppb)	(100–5000)[25]; (3000)[26]; (5000)[27]
Mn (ppb)	(20–50)[25]; (50)[27]; (50)[28]
Cu (ppb)	(100–3000)[25]; (2000)[26]; (1300)[27]; (2000)[28]

Table 4. Physicochemical parameters and their reference values (National and International Criterias).

originating from fertilizers in agricultural areas. The use of fertilizers in agricultural areas and septic tanks in rural regions are the primary sources of nitrate contamination in groundwater. The study indicated that artificial fertilizers and animal waste are the most significant sources of NO_3 in groundwater[49]. Under natural conditions, nitrate concentrations in water typically do not exceed 10 mg/l, and concentrations above 10 mg/l are considered indicators of anthropogenic pollution[50]. Since the maximum NO_3 value measured in this study was 9.16 mg/L, it is likely that the NO_3 in groundwater is of natural origin.

PO_4 values ranged from 0.01 mg/l (autumn season, stations 2 and 4) to 0.71 mg/l (spring season, stations 2 and 4). As shown in Table 3, PO_4 concentrations were higher in the spring and summer seasons compared to other seasons. The variation in PO_4 concentration in groundwater is primarily due to agricultural areas where domestic wastewater is used as fertilizer, as well as industrial wastewater[51]. PO_4 containing fertilizers used in agricultural areas are the main source of phosphate in groundwater. PO_4 is generally adsorbed onto soil particles and mixes with groundwater when the soil's adsorption capacity is exceeded. This suggests that PO_4 containing fertilizers may have been applied unconsciously to agricultural areas in the study region, and excess phosphate could have leached into the groundwater through irrigation, as indicated by the literature.

SO_4 values ranged from 0.04 to 2.81 mg/l (summer season, station 1), with an average value of 0.87 mg/l. The values obtained in this study were well below the national and international limit values (Table 4). SO_4 is typically found in low concentrations in groundwater due to the reducing conditions that inhibit sulphide oxidation in the aquifer[52]. The low SO_4 concentration observed in this study supports this finding.

Mg values ranged from 5.08 mg/l (winter season, station 4) to 16.79 mg/l (winter season, station 1), with an average of 10.01 mg/l. Mg concentrations were higher in the spring and summer seasons compared to other seasons. This increase is likely due to the dissolution of Mg ions from underground aquifer layers as air temperatures rise, which then mix into the water, raising its concentration. Ca values ranged from 43.28 mg/l (summer season, station 3) to 99.39 mg/l (winter season, station 1), with an average of 63.52 mg/l (Table 3). Both Mg and Ca concentrations were found to be within the limit values (Table 4). TS values ranged from 15.4 FS° (summer season, station 5) to 44 FS° (winter season, station 4), with an average TS value of 22.4 FS°, placing the fountain waters in the medium hardness category. It is believed that the hardness of the tap waters is related to the underlying geology.

Cl values ranged from 0.99 mg/l (summer season, station 3; winter season, station 2) to 24 mg/l (Table 3), with an average value of 7.54 mg/l, which was found to be within national and international limit values (Table 4). Salinity values ranged from 0.008‰ (summer season, station 5; autumn season, stations 3 and 5) to 0.06‰ (spring, station 1), with an average salinity value of 0.02‰. Salinity is related to electrical conductivity, which reflects the total concentration of ionized substances in water. High electrical conductivity indicates high salinity, which can negatively affect drinking water taste and make it unsuitable for irrigation by reducing soil fertility[53].

TDS values ranged from 110 mg/l (spring, station 5) to 325 mg/l (autumn, station 1), with an average value of 185 mg/l, which was within the limit values (Table 4). TDS is a parameter that indicates the concentration of dissolved inorganic minerals and some organic chemicals in water[38]. A study conducted in Pakistan reported that TDS in groundwater ranged from 630 to 2944 mg/l[54]. In another study in India, TDS values were reported to range from 480 to 540 mg/l[13].

When the fountain waters were analyzed in terms of toxic metals, the average values for the stations were ranked as Cd < Cu < Zn < Mn < As, with As being the most toxic metal and Cd the least toxic. As concentrations ranged from 793 ppb (spring, station 1) to 1323 ppb (autumn, station 4), (Table 3) with an average value of 603 ppb, which is well above the national and international limit values (Table 4). The concentration of As should not exceed 50 μg/l[25]. However, As concentrations in the fountains consistently exceeded this limit across all seasons and at all stations.

As is a widely distributed element in aquatic environments, originating from both natural and anthropogenic processes[55,56]. Natural sources include geological weathering, erosion, hydrodynamic processes, volcanic activity, and atmospheric deposition, while anthropogenic sources are primarily linked to agricultural practices, mining, and industrial activities. As is considered a significant and widespread environmental pollutant that poses a human toxicity risk and is a global public health concern[57]. Groundwater As pollution represents a critical environmental challenge, posing substantial health risks to millions of people worldwide. Recently, several studies have reported groundwater As pollution in Turkey particularly in Western Anatolia[58–60].

There are several potential reasons for the high levels of As in groundwater. Studies have shown that shallow aquifers typically exhibit higher As concentrations than deeper aquifers[19,48]. According to some researchers, rock-water interactions are considered the primary cause of increased As release and deterioration of groundwater quality in aquifers[61]. In general, higher concentrations of naturally occurring As have been detected in groundwater, particularly in unconsolidated sediments, and have been linked to numerous adverse health risks worldwide[62,63].

Groundwater As pollution is known to cause serious effects on public health and the environment. The presence of As in drinking water can lead to various health problems, including cardiovascular disorders, skin lesions, skin cancers, immunological disorders and reproductive defects in humans[64,65]. As has been highlighted as one of the most important contaminants contributing to cancer worldwide[65]. The International Agency for Research on Cancer (IARC) has classified As and its compounds as a class 1 human carcinogen. In addition, genotoxic effects of As on human health have also been reported[66,67].

Previous studies in the region have reported that the geological formations of Central Anatolia consist of volcanic and volcano-sedimentary rocks, terrestrial sediments, gypsum, and Pliocene sedimentary rocks[68]. It has been reported that volcanism has accelerated the disintegration process by affecting water–rock interactions, which has caused an increase in the concentration of elements in the rocks[69]. In particular, the use of these waters by local people for drinking purposes may lead to an increase in the levels of some elements that are harmful to human health[70]. In light of this information, the high As levels in the groundwater in Şarkışla can be linked to the geology of the region. It has been reported that the amount of As in the Earth's crust varies between 2 and 5 mg/kg 5. This study shows that the amount of As in the groundwater is one-fifth of the As content found in the Earth's crust. Consumption of these waters for drinking or other purposes may pose a serious health risk to both children and adults.

Another study conducted in the region reported that high groundwater pollution in Şarkışla was caused by rocks containing sulfur[5]. It was noted that sulfur minerals, coal, hydrothermal deposits, volcanic rocks, petroleum, and fossil fuels are important sources of As[70]. Naturally occurring arsenic pollution in the groundwater of the Şarkışla Plain was also evaluated[5]. The study found that the highest arsenic concentrations ranged from 2.1 to 155 mg/kg in the alluvial and Pliocene layers. It was reported that alluvial and Pliocene rocks were the main aquifers in the study area and most of the drinking water was provided from this aquifer. It was determined that various interaction processes of rocks containing sulfur underground caused significant groundwater pollution in the study area. It was reported that the As levels detected in the study exceeded the recommended values for groundwater and that these waters should not be used[5].

The Cd values ranged from 0.062 ppb (winter season, station 4) to 9.77 ppb (winter season, station 2) (Table 3). The mean Cd concentration was 1.153 ppb, which was found to be well above the limit values in autumn season, station 2, and winter season, station 4. However, it remained within the limit values at other stations and during other seasons (Table 3). This situation may be attributed to anthropogenic influences in the village near station 2. In a study conducted in Syria, the average Cd concentration in groundwater was reported to be 0.27 µg/l[13,15]. In another study in India, Cd concentrations in groundwater were reported to range from 0.9 to 1.1 µg/l[13].

The Zn values ranged from 1.04 ppb (summer, station 4) to 6.71 ppb (spring, station 2). The average Zn concentration was found to be 1.46 ppb, which is well below the limit values at all stations[25,28]. A study conducted in India reported that Zn concentrations in groundwater ranged from 14.6 to 22.3 µg/l[13]. Another study in China reported that the average Zn concentration in groundwater was 92.05 µg/l[19].

The Mn values ranged from 8.43 ppb (spring, station 1) to 87.27 ppb (summer, station 5). The average Mn concentration was found to be 24.89 ppb. It was observed to exceed the limit values at all stations except station 3 during the summer (Table 4). A study conducted in India reported that the average Mn concentration in groundwater ranged from 15.7 to 50.5 µg/l[13].

The Cu values ranged from 0.74 ppb (spring, station 4) to 1.47 ppb (summer, station 4) (Table 3). The average Cu concentration was found to be 1.21 ppb. These values were well below the national and international limit values. Cu is an essential element, with typical intake from food ranging from 1–3 mg/day. In adults, the absorption and retention of copper depend on daily intake; therefore, copper overload is unlikely. However, acute gastric irritation may occur in some individuals at concentrations above 3 mg/L in drinking water[15]. A study conducted in Syria reported that the average Cu concentration in groundwater was 4.10 µg/l[15]. In another study conducted in India, it was reported that Cu concentrations in groundwater ranged from 1.9 to 8.7 µg/l[13].

They reported that the turnover rate of groundwater can be as short as a few months, but the renewal of water in underground aquifers can sometimes take 1 or even 10 years. Due to the lack of oxygen in groundwater, microorganisms living in this environment have a limited ability to break down heavy metals. The greatest danger of contaminated groundwater is the potential exposure to toxic effects on humans and animals that use this water 53.

Remote sensing methods, which have significantly advanced in recent years, can be used to assess both water quality and pollution levels[71,72]. In this study, maps showing the distribution of heavy metals at each station were created using a geographic information system (GIS). The heavy metal content of the fountains was analyzed using GIS, and the corresponding maps are presented in Fig. 2.

When analyzing the similarity of the stations in terms of physicochemical variables using the Bray–Curtis similarity index, it was found that Stations 2 and 3 exhibited the highest similarity, with a value of 97.61%. In contrast, Stations 1 and 5 showed the lowest similarity, with a value of 80.95%. Stations 2 and 3 are both located within the village, which likely explains their high similarity due to common anthropogenic influences.

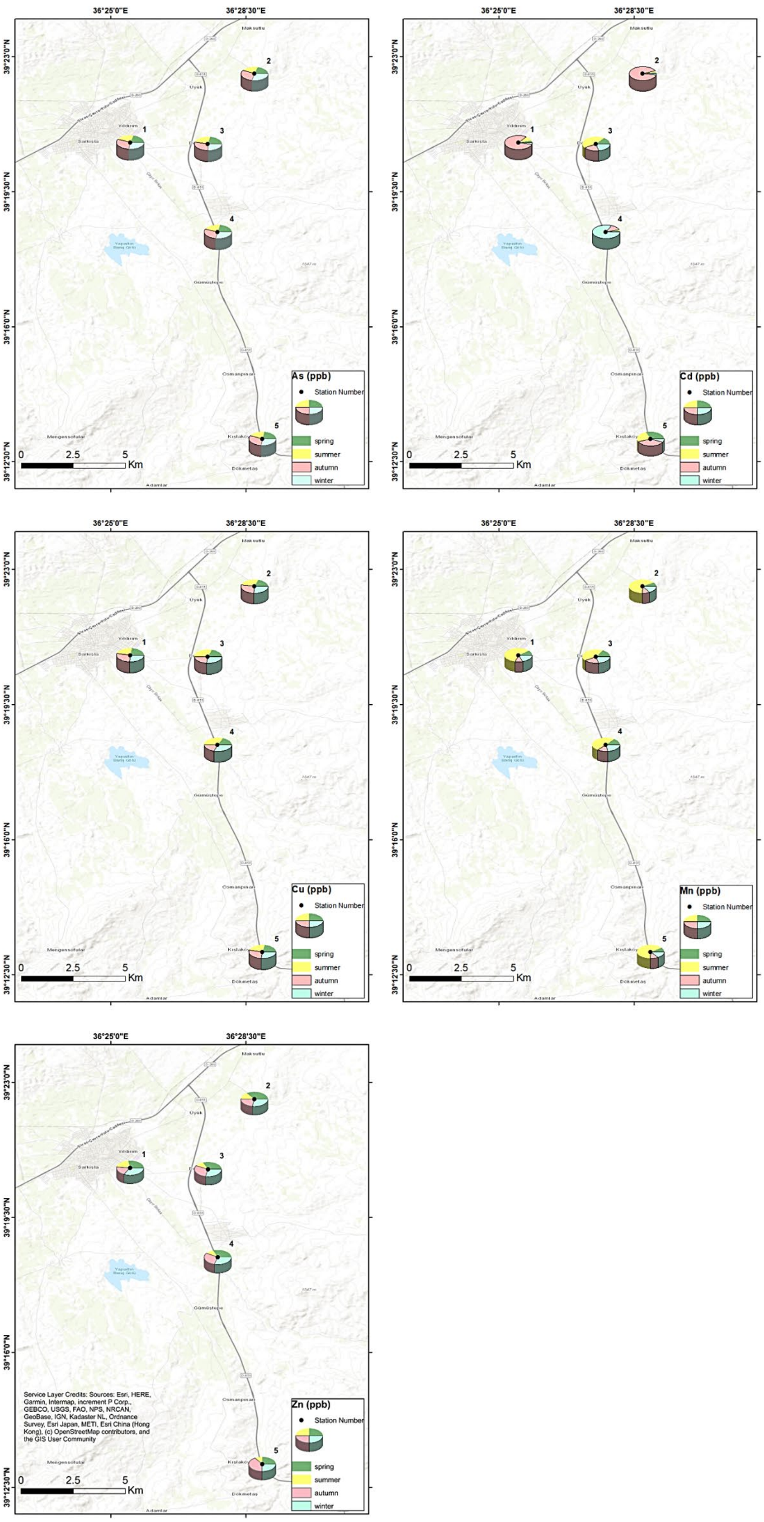

Fig. 2. Spatial and temporal distributions of heavy metals Imagery Source: Esri, HERE, Garmin, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), (**c**) OpenStreetMap contributors, and the GIS User Community. Figure generated using ArcMap Version 10.3.1.

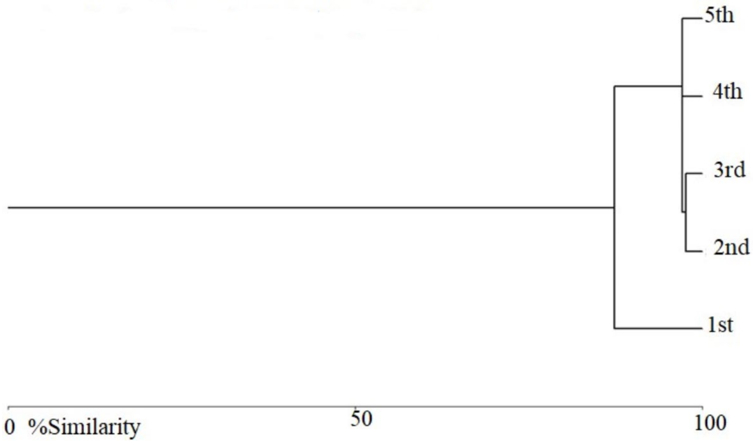

Fig. 3. The Bray Curtis Dendogram for stations.

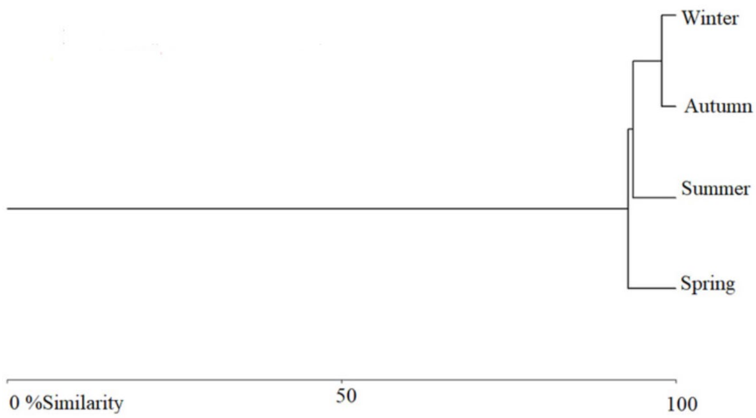

Fig. 4. The Bray Curtis Dendogram for seasons.

Conversely, Stations 1 and 5 are the most distant from each other, which likely contributes to their differences. A dendrogram illustrating the Bray–Curtis similarity between the stations is shown in Fig. 3.

When examining the similarity of the seasons based on physicochemical variables using the Bray–Curtis similarity index, it was found that autumn and winter were the most similar, with a similarity value of 97.83%. In contrast, spring and winter were the least similar, with a value of 88.48%. A Bray–Curtis similarity dendrogram illustrating seasonal similarity is shown in Fig. 4. Since both winter and autumn are rainy seasons, they may have influenced the water's physicochemical parameters in a similar way, which could explain the similarities between the two rainy seasons.

Correspondence analysis revealed that the summer, autumn, and winter seasons exhibited the highest similarity in terms of water variables, while the spring season was the most distinct, as shown in Fig. 5.

It was statistically found that Bray–Curtis similarity analysis and Correspondence analysis supported each other in evaluating seasonal similarity.

Additionally, Pearson correlation analysis was applied to normally distributed physicochemical values to establish reliable relationships between the data. All results from all seasons and stations were included in the analysis ($n = 20$). The relationships and correlation coefficients between the analyzed physicochemical variables are presented in Table 5, with significant relationships between two parameters highlighted in bold.

A significant positive correlation was found between WT and Zn, pH and EC, Ca and pH, As and TDS, EC and SO_4, EC and Ca, SO_4 and Ca, TDS and Ca, and TDS and SO_4. Similarly, a significant positive correlation was observed between NO_2 and Mn, PO4, and TH and Mg ($p < 0.01$), as shown in Table 5. A study conducted in Pakistan reported a correlation between pH and EC. Water with an acidic pH can disrupt the geological structure it passes through, dissolving chemical substances in underground layers and causing them to mix into the water. This increase in dissolved substances may lead to a rise in the EC value[13].

The study was also evaluated using two water quality indices, NPI and GWQI. According to the NPI values, the fountain water was determined to be slightly contaminated, as the calculated values for all stations were below 1. The highest NPI values were found at station 5 in winter, while the lowest were at station 2 in summer.

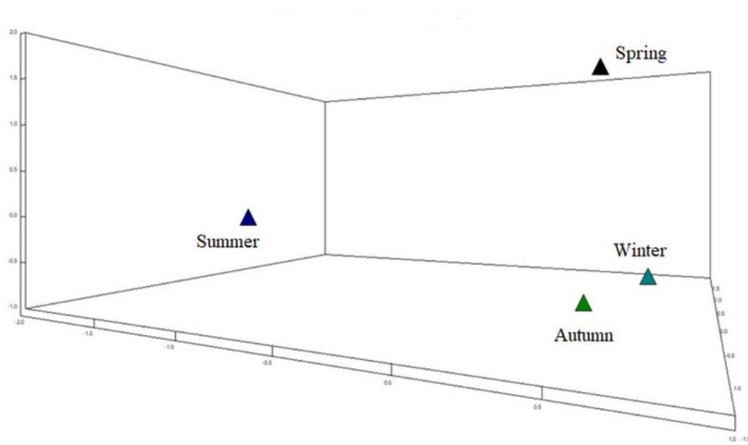

Fig. 5. The dendogram of Correspondence analysis for seasons.

n = 20	WT	pH	DO	NO_3	TDS	Zn	As	EC	SO_4	Ca
WT	1									
pH	−.004	1								
DO	−.078	.232	1							
NO_3	−.335	−.559*	−.190	1						
TDS	.028	−.463*	−.182	.172	1					
Zn	**.653****	−.087	−.189	.394	−.050	1				
As	−.151	−.240	.246	.328	**.587****	.010	1			
EC	−.081	**.667****	−.354	.423	<.001	.010	−.321	1		
SO_4	.452*	−.460*	−.234	−.019	**.767****	−.348	−.422	**.702****	1	
Ca	−.101	**.676****	−.350	.450*	**.814****	.055	−.238	**.954****	**.713****	1

Table 5. Pearson correlation analysis and correlation coefficients of fountains water. *Correlation is significant at 0.05 level ($p < 0.05$); **Correlation is significant at the 0.01 level (p˂0.01). No statistically significant correlation was detected.

This indicates that the NPI values are relatively close to each other in terms of both stations and seasons. According to the seasonal average values of the NPI index, the water quality was ranked as spring < summer < autumn < winter, and was classified in the 'slightly polluted water' category. When the NPI index values were examined in terms of station averages, they were ranked as 1 < 2 < 4 < 3 < 5. The NPI values by season are ranked as follows: in spring, 2 < 3 < 4 < 5 < 1; in summer, 2 < 1 < 3 < 4 < 5; in autumn, 1 < 4 < 3 < 2 < 5; and in winter, 1 < 4 < 3 < 2 < 5. The NPI values by station are ranked as follows: at the first station, summer < autumn < winter < spring; at the second station, summer < spring < autumn < winter; at the third station, spring < summer < autumn < winter; at the fourth station, spring < autumn < winter < summer; and at the fifth station, spring < summer < autumn < winter. The NPI index values for the stations are illustrated in Fig. 6.

When evaluated in terms of GWQI index values, the highest value was found at the second station in the summer, and the lowest at the second station in the winter. It was observed that GWQI values did not show any significant differences between seasons or stations. The seasonal average GWQI values were ranked as autumn < winter < summer < spring. Since GWQI index values were found to be < 50 in all stations and seasons, the water quality was classified as 'excellent.' These findings suggest that the fountain water is suitable for both drinking and irrigation purposes. The GWQI values by station averages were ranked as 3 < 5 < 2 < 1 < 4. The GWQI values by season are ranked as follows: spring; 3 < 5 < 1 < 2 < 4; summer; 5 < 4 < 3 < 1 < 2; autumn; 4 < 5 < 3 < 2 < 1; and winter; 2 < 1 < 3 < 5 < 4. When the GWQI values are ranked by station, they are as follows: at Station 1; winter < autumn < summer < spring; at Station 2; winter < autumn < spring < summer; at Station 3; winter < autumn < summer < spring; at Station 4; autumn < summer < winter < spring; at Station 5; autumn < winter < summer < spring. The seasonally calculated values for the stations are depicted in Fig. 7.

In this study, a HHRA was conducted separately for children and adults, taking into account the increased sensitivity of children to toxic metals. HI and HQ values, representing the intestinal and dermal effect coefficients, were calculated for As, Cd, Cu, Mn, and Zn in fountain water for both children and adults. Additionally, CR values were calculated for As and Cd, separately for both children and adults, based on the stations. All identified health risk assessment data, including HI and CR coefficients, are presented in Table 6.

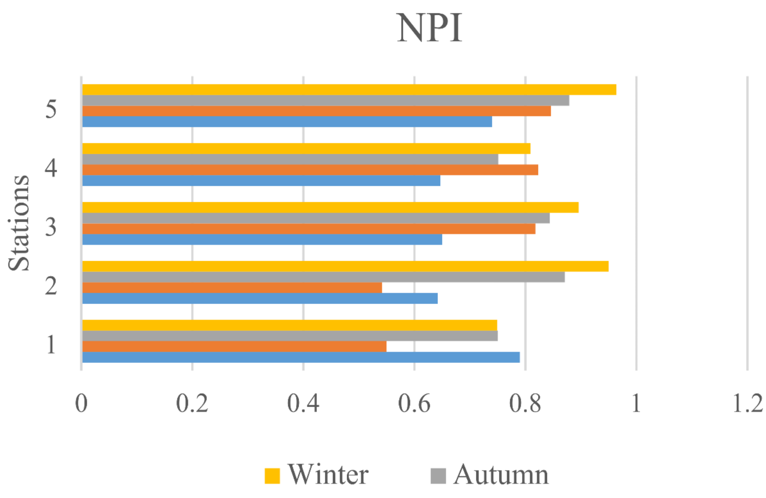

Fig. 6. The NPI values.

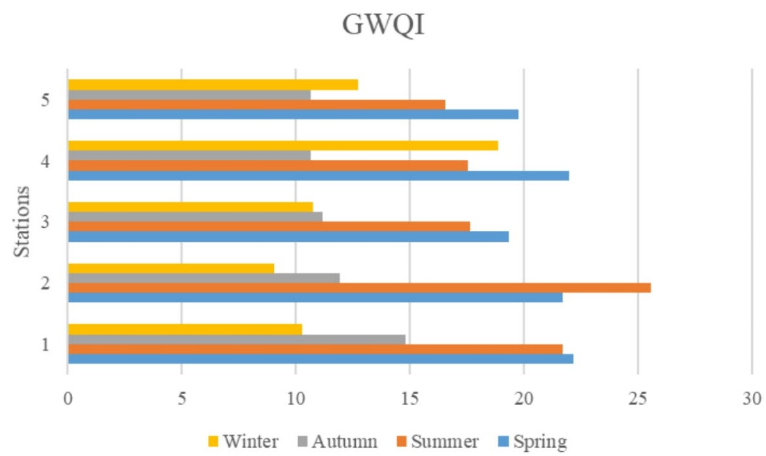

Fig. 7. The GWQI values.

In the study, both non-carcinogenic (HQ ingestion, HQ dermal, THI) and carcinogenic (CR) risks were calculated for children and adults as part of the human health risk assessment. The results are presented in Table 6. It was found that the water exhibited quite high HQ values for ingestion exposure in all seasons and at all stations. This was primarily due to the presence of arsenic (As) levels well above the limit values. When dermal exposure was evaluated, HQ values exceeded 1 for children across all seasons (except at Station 5) (Table 6). For adults, HQ values exceeded 1 in the spring season (except at stations 1, 2, and 3), summer season (except at station 2), autumn season (except at station 3), and winter season (except at stations 1, 2, 3, and 5). The highest HQ value for dermal exposure was recorded at station 4 during the winter season (Table 6). This elevated risk can be attributed to the station's proximity to agricultural areas. In winter, rainfall and snowfall recharge groundwater, carrying fertilizers left in agricultural fields. These fertilizers, which are often applied in excess and unconsciously, mix with rain and snowmelt, potentially increasing toxic metal concentrations in the groundwater.

The findings of this study revealed that water consumption via ingestion posed a greater health risk for both children and adults compared to dermal contact. These results are consistent with similar studies[23,54,73]. It was observed that the HQ values for both children and adults, through water ingestion in both dry and rainy seasons, were significantly higher than the acceptable non-carcinogenic risk level of 1 (Table 6). Additionally, children's total health index (THI) values were consistently higher than those of adults, indicating greater vulnerability. Similar findings have been reported in previous studies[23].

The carcinogenic risk results for both children and adults across all seasons were found to be above 1×10^{-4} and 1×10^{-6}, respectively. This indicates that the fountain water in all seasons could pose a carcinogenic health risk to humans. Upon reviewing Table 5, it was observed that the CR values for children were higher than those for adults, a finding consistent with previous studies[23,73]. The primary reason for this discrepancy is that children are more sensitive to carcinogenic risks than adults.

Risks		Carcinogenic risk		For child noncarcinogenic risks			For adult noncarcinogenic risk		
Seasons	Stations	Child	Adult	$HQ_{ingestion}$	HQ_{dermal}	THI	$HQ_{ingestion}$	HQ_{dermal}	THI
Spring	1	0.038801	0.034254	15.656	1.2289	16.885	14.01	0.574999	14.584
	2	0.042105	0.037412	31.647	2.4564	34.103	28.36	0.148006	28.508
	3	0.046589	0.041116	15.656	1.2289	16.885	14.01	0.57399	14.583
	4	0.0449776	0.039993	31.647	2.4554	34.102	28.36	1.147998	29.507
	5	0.050241	0.044641	53.032	4.1056	57.138	47.22	1.919502	49.139
Summer	1	0.047413	0.041779	47.702	3.6963	51.398	42.77	1.728	44.498
	2	0.052238	0.046414	20.986	1.6369	22.622	18.797	0.07533	18.872
	3	0.054422	0.048354	49.686	4.1056	53.791	44.547	1.91950	46.466
	4	0.051177	0.04571	31.647	2.4554	34.102	28.763	1.147998	29.910
	5	0.051519	0.045776	37.041	2.8778	39.919	33.204	1.34550	34.549
Autumn	1	0.059753	0.047896	428.152	33.0956	461.247	380.8	15.47	396.27
	2	0.060534	0.053819	1086.14	83.9204	1176.06	606	39.23	645.23
	3	0.058698	0.0522389	26.316	2.0462	28.363	23.577	0.950	24.527
	4	0.057904	0.049212	252.956	19.735	272.694	225.96	9.220	235.18
	5	0.064216	0.0570058	65.681	4.9240	70.605	54.774	2.30	57.074
Winter	1	0.054596	0.048356	15.656	1.2289	16.884	14.04	0.573999	14.613
	2	0.063487	0.056394	30.690	1.6369	32.326	18.795	0.765369	19.560
	3	0.053679	0.047695	26.316	2.04620	28.362	23.57	0.956766	24.526
	4	0.063499	0.055071	777.556	128.976	906.532	648.55	60.300	708.85
	5	0.061357	0.054433	10.325	0.81848	11.143	9.22	0.382665	9.602

Table 6. Carcinogenic and non-carcinogenic risk values for toxicants. *THI: Total hazard index.

The study was also compared with several studies conducted both in Turkey and internationally. For instance, a study in India evaluated groundwater samples collected from various depths for potential contamination with metal contaminants such as Al, Cd, Co, Cr, Cu, Fe, Mo, Mg, Ni, Pb, V, and Zn. The health risk assessment of the groundwater revealed non-carcinogenic health effects due to contamination by As, Cr, Co, Cd, Cu, Ni, Pb, and Zn, as well as carcinogenic health effects related to As, Cd, Cr, Cu, and Pb. The study reported average concentrations of As, Cu, Cd, and Zn at 136 µg/l, 8.1 µg/l, 0.55 µg/l, and 9.54 µg/l, respectively[20].

In their study conducted in the Meriç River basin (Turkey), various water quality indices and health risk assessment methods were employed. They reported that toxic elements such as As and Cd posed greater carcinogenic and non-carcinogenic health risks to children compared to adults. The study found that As had the highest HQ and CR values in the area, making it the most hazardous and toxic element. Additionally, it was noted that As concentrations in the river exceeded drinking water standards during the dry season, with ingestion being the primary exposure route[23].

They investigated the temporal and spatial distribution of potential toxic elements in the surface waters of Felent Creek (Kütahya, Turkey). The study attributed the elevated levels of As in the region to the mining activities taking place. They also emphasized that the health risks associated with As should be addressed[24].

Çorlu Stream (Edirne, Turkey) was evaluated for toxic metal content and water quality parameters. The study reported that domestic and industrial discharges significantly polluted the stream's water quality. It was noted that Cr and As, originating from waste discharges, could pose carcinogenic health risks to people in the region, particularly due to the proximity of leather factories[22].

Heavy metal pollution in the Angads Plain of Morocco was assessed, and potential sources were identified. Health risk assessments were conducted using indexed models and multivariate statistical techniques. The study found that As and Pb levels exceeded WHO limit values. While dermal exposure remained below the health risk limits, oral exposure exceeded the acceptable levels. The carcinogenic risk assessment indicated a potential for cancer development with lifelong exposure to groundwater[8].

They collected groundwater samples from the Angads aquifer to assess groundwater quality and associated human health risks. The study reported that the GWQI index indicated the water is not suitable for consumption. Additionally, it highlighted several activities in the area that are likely significant sources of NO_3 contamination. Long-term consumption of nitrate-contaminated groundwater was found to pose potential risks to human health[12].

A study conducted in the Bokoya massif, Morocco, aimed to assess groundwater pollution and evaluate the non-cancer risks associated with its consumption. The study reported that the deterioration in water quality was primarily due to strong mineralization caused by the dissolution of Paleozoic and Predorsal rocks, as well as high concentrations of anthropogenic NO_3 found in limestone formations. The assessment of non-carcinogenic risk from oral exposure to NO_3 indicated potential health risks for children, adult women, and adult men, with children being slightly more exposed to these risks[11].

In this study, the water quality parameters of drinking water fountains in Şarkışla were assessed using water quality indexes and health risk assessment methods. Based on the obtained data, values for pH, EC, water WT, DO, NO_2, NO_3, SO_4, Mg, Ca, Cl, TDS, Cd, Zn, Mn, and Cu were found to be within national and international limit values. When evaluated using index values, NPI values were found to be less than 1 at all stations, classifying the water as clean (unpolluted). Additionally, since the GWQI values were below 50, the water was classified as excellent. However, it can be concluded that the fountain water is significantly polluted with As, a toxic metal. The primary cause of this pollution can be attributed to the geological structure of the groundwater. According to the health risk assessment results for fountain water, non-carcinogenic health risks are expected for both children and adults at all stations and in all seasons. It has been determined that fountain water, due to its high As content, can pose significant carcinogenic health risks if consumed. Therefore, human consumption of this water should be prevented.

Conclusion

The findings of this study provide valuable data for the future management and sustainable use of groundwater in Central Anatolia, as well as for the protection of human health and safety. This study can be used as a reference for future research in the coming years. Additionally, several recommendations can be made to improve groundwater quality and ensure its sustainable use, including raising awareness among the local population about the importance of water conservation and pollution prevention. To protect public health, all living beings should be prevented from consuming contaminated groundwater. Emphasizing sustainable agricultural practices is essential to mitigate groundwater pollution. Local communities should be educated through training programs that emphasize the importance of groundwater protection and the harmful effects of pollution. The use of environmentally friendly products should be encouraged to minimize environmental impact. Additionally, local governments should prioritize the implementation of effective rainwater management strategies. Protective barriers should be established to prevent pollutants from reaching groundwater sources. Ongoing studies, similar to this one, should continue, with regular monitoring of groundwater quality in terms of its physical, chemical, biological, and toxicological properties.

Limitations of the study

The data of this study is limited to five stations located in Şarkışla district of Sivas province in the Central Anatolia region. The data obtained in this study is limited to various titrimetric and spectrophotometric methods at Şarkışla Aşık Veysel Vocational School. In addition, the analysis of heavy metals in this study is limited to the values measured using the ICP-MS device in the accredited laboratories of Sivas Cumhuriyet University Advanced Technology Research and Application Center (CÜTAM). The study can be further developed by examining other fountain waters in the region, expanding the study area and analyzing the waters using advanced research techniques.

Data availability

All data generated or analyzed during this study are included in this published article.

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Declarations

Competing interests
The authors declare no competing interests.

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