



Geochemical and Multivariate Statistical Evaluation of Trace Elements in Groundwater of Niğde Municipality, South-Central Turkey: Implications for Arsenic Contamination and Human Health Risks Assessment

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Abstract

This study was conducted to determine the concentrations of trace elements, their sources, and human health risks associated with arsenic contamination in groundwater of the Niğde Municipality, south-central Turkey. Fourteen groundwater samples were collected from groundwater supply sources fed by the Niğde water distribution system and were analysed for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, and Ba concentrations. Multivariate statistical analyses were applied to decipher the source and interrelationships among trace elements in groundwater. The groundwater is mainly tapped from Quaternary alluvial and volcanic aquifers of the Niğde Massif. The pH of groundwater is slightly acidic to neutral, which controls the solubility and mobility of the trace elements. The mean concentrations of the trace elements vary in the order $Zn > Fe > Ba > As > Cr > Ni > Se > Cu > Co > Mn > Al$. All of the trace element concentrations comply with the maximum permissible values provided by the Turkish Standards Institution and the World Health Organization, except Zn, Cr, and As. However, approximately 7.14% of the studied samples are contaminated with Zn and Cr, whereas 86% are contaminated with As. The As concentrations range from 9.47 to 32.9 µg/L with an average value of 16.8 µg/L. Contamination assessment indicates that the As contamination is dominant in the southern and southwestern parts of the area. The primary source of As in groundwater is attributed to geogenic processes involving weathering and dissolution of bed rocks and other factors, such as pH conditions, adsorption, and surface complexation. Three bimetallic complex associations are distinguished in groundwater: Fe-coordination group, As-coordination group and Ba-coordination group, all showing strong positive correlation with Cu and Ni. The As-coordination group is the most dominant in groundwater, which resulted in the high As content of groundwater. Multivariate statistical analyses indicate that As mobilization in groundwater is associated with pH, EC, Ni, Cu, and Ba depending on the redox conditions of the aquifer, controlled mainly by geogenic processes. The carcinogenic risk of arsenic affecting children and adults reaches 2×10^{-4} and 3×10^{-4} , respectively, exceeding the guideline value of 1×10^{-4} . The estimated hazard quotient for children is in the range of 1.79–6.21, whereas that of adults is 0.77–2.66, indicating that children in the municipality are more exposed to the noncarcinogenic effects of the consumption of high groundwater arsenic.

Water is vital for the livelihood and health of people and ecosystems and is a basic need in the development of countries (Adjei-Mensah and Kusimi 2019; Abanyie et al. 2020;

Spring 2020; Talukder and Hipel 2020). With the increasing population, industrialization, and global warming, the demand for water resources is increasing rapidly, and the usable water resources are decreasing (Sunkari et al. 2019a, 2020). The per capita water consumption in the world is approximately 800 m³ per year. Approximately 1.4 billion people, who correspond to approximately 20% of the world population lack sufficient drinking water and 2.3 billion people cannot access clean and potable water (Mekonnen and Hoekstra 2016). Estimates show that more than 3 billion people will face water scarcity by 2025 (Kulshreshtha 1998; Güneş Durak et al. 2011). Rapid population growth,

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scarcity of water resources, pollution of existing ground and surface waters, high consumption, insufficiency of water networks, competition in water use, and the increase of frequent droughts have increased the need to develop alternative plans for water management (Kolokytha et al. 2002; Çiner 2012).

Groundwater is globally preferred to surface water for drinking purposes due to the general perception that it is of better quality (Okogbue and Ukpai 2013; Sunkari et al. 2018, 2020). However, groundwater contains organic and inorganic compounds and microorganisms in suspended and dissolved form. Trace elements, such as lead, copper, iron, manganese, and arsenic, are among the most hazardous contaminants of groundwater as a result of their varying characteristics, including a wide range of sources, chemical stability, high toxicity level, bioaccumulation, and problems in remediation (Sun et al. 2016). They pose serious threats to humans and the environment (Barzegar et al. 2019). Trace elements may derive from weathering and dissolution of rocks, ion exchange processes, humic substances resulting from the degradation of plant and animal residues, pesticides, fertilizers, greywater irrigation, mining activities, industrial activities, urbanization, saltwater intrusion, and leachate from domestic and municipal wastes, inter alia (Turner et al. 2016; Sunkari and Danladi 2016; Barzegar et al. 2017; Dar et al. 2017; Khadra et al. 2017; Esmaeili et al. 2018; Bakyayita et al. 2019; Snousy et al. 2020).

According to Mora et al. (2017), trace elements can be categorized into essential (Cu, Zn, Mn, Fe, Cr, and Co) and nonessential (As, Pb, Cd) elements. Over dosage of the essential trace elements is detrimental to human health and high amounts of the nonessential trace elements can lead to terminal diseases (Calderon 2000). It is known that high trace element content in groundwater can lead to neurocognitive impairments, cardiovascular diseases, and cancers in humans (Embaby and Redwan 2019). For instance, arsenic is considered as one of the most hazardous trace elements in groundwater due to its elevated toxicity. Elevated concentrations have been largely linked to skin cancer and neurocognitive impairments among children in many countries (Rasool et al. 2016; Rwiza et al. 2016; Mayer and Goldman 2016; Mora et al. 2017; Lu et al. 2018; Bakyayita et al. 2019). Arsenic contamination of groundwater is a global problem and has been widely reported in several countries, including India (Ghosh et al. 2020), Pakistan (Ali et al. 2019), Bangladesh (Shamsudduha et al. 2019), China (Li et al. 2020), Mexico (Gómez-Hernández et al. 2020), and South Africa (Abiyi and Bhattacharya 2019). However, arsenic contamination of groundwater in Turkey has received limited attention by the scientific community in recent times (Çeliker et al. 2019). Review of the available literature revealed that geogenic arsenic contamination is a prevalent phenomenon in western Turkey (Gemici and Tarcan, 2004; Baba

et al. 2009; Gunduz et al. 2010; Yuce and Yasin 2012) and central Turkey (Altaş et al. 2011; Pasvanoğlu and Chandrasekharam 2011; Simsek 2013; Lermi and Ertan 2019). The arsenic loading in groundwater in these areas have been attributed to mineral dissolution, mixing with geothermal water and volcanic activities. However, arsenic mobilization in groundwater also can emanate from anthropogenic sources, such as pesticides, wood preservatives, and glass manufacture (Ahuja 2008).

Understanding the sources and contents of trace elements in groundwater has a stake in helping to sustainably manage groundwater resources. Several approaches are used in the literature to determine the source of trace elements in groundwater, including hydrochemical graphing, multivariate statistical techniques, and geochemical modeling approaches (Sun et al. 2016; Barzegar et al. 2019). Multivariate statistical techniques are widely used due to the easy nature of their application and the capability to process large datasets even in complex hydrogeological systems (Bingöl et al. 2013). Within the scope of applicability of the multivariate statistical techniques, factor analysis (FA) and hierarchical cluster analysis (HCA) have gained popularity in the scientific front for determining the source of groundwater contaminants (Yidana et al. 2010; Wu et al. 2014; Soltani et al. 2017; 2019; Lermi and Ertan 2019; Sunkari and Abu 2019; Zango et al. 2019). FA is used to determine potential hydrogeochemical processes controlling groundwater chemistry without requiring prior knowledge of the contaminant sources (natural or anthropogenic) and their general behaviour (Barzegar et al. 2019). HCA unravels the similarities between samples and sample suites. Correlation analysis is also widely used to elucidate the relationships between hydrochemical parameters, which facilitates easy identification of the potential sources of contaminants (Esmaeili et al. 2018). All these multivariate statistical approaches have been effectively used to identify the sources of trace elements in groundwater globally (Esmaeili et al. 2018; Lermi and Ertan 2019). For instance, Esmaeili et al. (2018) studied the sources of trace elements (Fe, Mn, Zn, Cr, Pb, Cd, Al, and As) in groundwater of the Qareh-Ziaeddin plain of North-western Iran using correlation analysis, HCA, and FA. They suggested that the principal controls of groundwater chemistry in the study area include evaporate dissolution, silicate weathering, denitrification, and cation exchange reactions. Additionally, by using FA, they confirmed the geogenic origin of the trace elements. Contamination of trace elements in groundwater usually exposes human populations to several health risks, and thus, a lot of studies not only determine the trace element contents and their sources but evaluate the associated human health risks that the populace is exposed to by estimating the daily intake of groundwater, carcinogenic, and noncarcinogenic risks with regard to the particular contaminant (Li et al. 2020; Shahab

et al. 2019; Tabassum et al. 2019; Zango et al. 2019; Zhang et al. 2019).

Lermi and Ertan (2019) studied the hydrochemistry of spring and well waters in the Niğde Province. Their study revealed that the dominant water type in the province is Ca–SO₄–HCO₃ water type with other mixed water types. They documented evidence of metal pollution, especially arsenic, and attributed it to intense water–rock interaction and mixing with geothermal waters. However, the study of Lermi and Ertan (2019) did not include communities under the current study and used limited multivariate statistical approaches in deciphering the sources of the groundwater constituents. Their study also did not assess the human health risks associated with arsenic contamination of the groundwater. Therefore, this study focuses on a complete understanding of the trace element loading in groundwater of the Niğde Municipality. The objectives of this study were to: (1) determine the hydrogeochemical characteristics of trace element composition in groundwater of Niğde Municipality, (2) identify the sources (geogenic and anthropogenic) of the trace elements, and (3) appraise the human health risks associated with arsenic contamination in the groundwater.

Study Area

Location and Climate

Niğde Municipality is located between latitude 37°10' in the south and 38°58' in the north, and longitude 33°10' in the west and 35°25' in the east. It is situated to the north of the area where the Bolkar and Aladag Mountains in the Central Taurus are found and in the northeast of the Central Anatolia Region. It is separated from Aksaray in the northwest, Nevşehir in the north, Kayseri in the northeast, Konya in the west, and Adana in the southwest. The Niğde Province, where Niğde Municipality is situated, has a surface area of approximately 779,522 ha. Bordered by the Misli Plain in the north and the Bor Plain in the south, it is split by mountains and streams. The study area is generally 1229 m above sea level. The area features dry and hot summers, warm and rainy Mediterranean air in the summer, and cold and partially rainy days in the winter. In January, low temperatures up to 0 °C are observed, whereas higher temperatures up to 22 °C are normally recorded around July. Average precipitation is 348.8 mm/year.

The study area is known for its agricultural productivity in Turkey, especially potato production. The farmers use several agrochemicals to increase yields of their field crops. There are several old mines, some of which are being reexplored for different deposit types. The area has quite a few factories, including cement, carbon dioxide, and

mineral-processing factories. There also are sites for harnessing geothermal water. Streams in the province, such as Alihoca, Horoz, Gümüş and Çakıt streams, have recently being reported to be extremely polluted with As, Cd, Sb, Zn, and Pb (Lermi and Sunkari 2020). Despite the existence of all these potential threats to groundwater quality, studies on the trace element content of groundwater are limited.

Geology and Hydrogeology

The study area is surrounded by a dome-like mountainous structure known as the Niğde Massif and Central Anatolia volcanic rocks, which vary in age from Paleozoic to Cenozoic (Fig. 1). The Niğde Massif is primarily composed of different metamorphic units arranged in a broad irregular dome (Gautier et al. 2002). The basement of the metamorphic units is composed of marble alternating with quartzite, schist, and gneiss (Fig. 1) that were subjected to various degrees of partial melting. The uppermost part of the metamorphic units is represented by recrystallized quartzites and marbles (Whitney and Dilek 1998). Granitoids are widespread in the area and show various degrees of deformation. Accordingly, the main intrusion is the Late Cretaceous Üçkapılı granitoid and its related dykes (Göncüoğlu 1986; Boztuğ 2000). It outcrops from the middle part of the Niğde Massif to the northeast with a few exposures in the western and southern fringes (Fig. 1). However, the southern part of the Niğde Massif is dominated by quartzite, marble intercalated with gneiss, and thin slices of ophiolitic rocks (Fig. 1), representing the zone of high-grade metamorphism (Floyd et al. 2000). This is confirmed by the high degree of deformation in the amphibolite facies (Gautier et al. 2002). Moreover, a massive ophiolite exposure is observed in the northern fringe and to the far east (Fig. 1). This part also is dominated by metagabbros with minor intrusions of the Üçkapılı granitoid (Fig. 1). Sediments and volcanic rocks belonging to the Central Anatolia Volcanic Province also surround the Niğde Massif (Clark and Robertson 2002). The metamorphic units in the north are partially altered and covered by Late Miocene—Pliocene ignimbrites and Tertiary alluvial sediments (Aydin et al. 2014). Some isolated ignimbrites are found within the massif. The central part of the area is overlain by older sediments with contrasting contact relationships (Fig. 1). The rocks in the area are affected by normal faults belonging to the Niğde Fault Zone and Tuz Gölü Fault Zone, which traverse the northeastern and southern fringes (Fig. 1).

The aquifer system in the area is dominated by recent alluvial sediments, volcanic products, and clay deposits (Celik and Afsin 1998). The alluvial sediments comprise of sand, silt, tuff, and gravel representing unconfined aquifer in the area (Şener et al. 2017). However, the volcanic products and clay deposits form the confined aquifer (Yuce

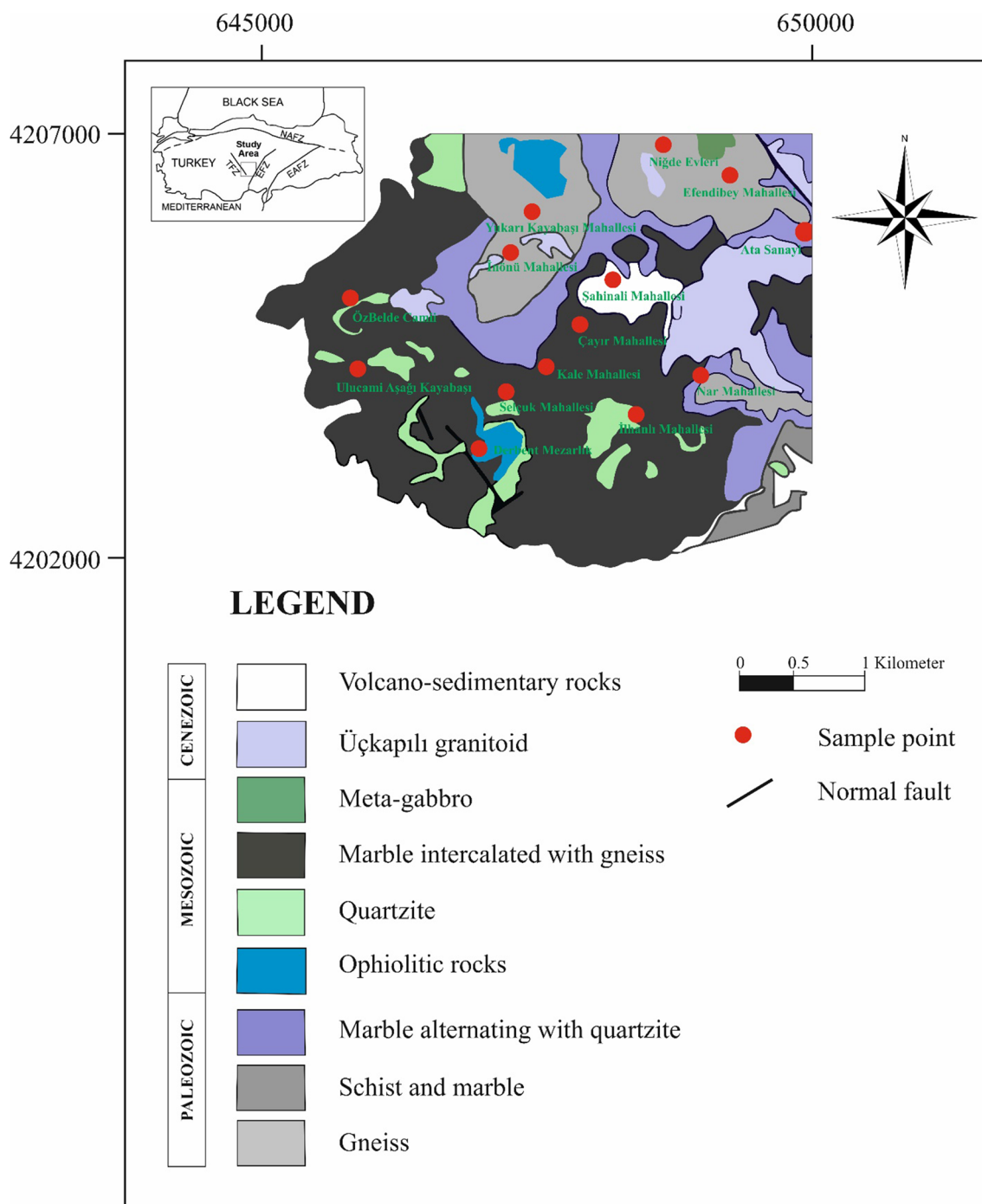


Fig. 1 Location and geological map of the Niğde Municipality and its vicinity with the sample points

2007). Recharge is from direct precipitation and subsequent infiltration into the aquifers through faults and fractures in the rocks, whereas groundwater is discharged by means of pumping from bore wells and springs. The aquifers are controlled by the architecture of the Niğde Fault Zone and Tuz Gölü Fault Zone (Lermi and Ertan 2019). The water requirement of the city is met by 47 deep well water drillings and distributed to private and public institutions, where the

samples for this study were collected. The water from deep well water drillings is collected in six water tanks in various points of the city and supplied to the people of the city after being subjected to chlorination. The total capacity of deep well water drillings is approximately 500 L/s. Due to the high arsenic concentrations, 14 of these wells were closed in 2008. The depth of the wells is in the range of 30–250 m, and the yield varies from a few liters to 60 L/s (Yuce 2007).

The transmissivity of the aquifers is estimated to be in the range of 300–900 m³/day/m based on pumping tests (Yurdağul 1998). Also, the storativity of the aquifers varies from 0.15 to 0.25 (Yurdağul 1998). In general, groundwater flows from NW to SE and NE to SW in the study area (Lermi and Ertan 2019).

Materials and Methods

Sample Collection and Analysis

In the spring season of 2017, a total of 14 groundwater samples were collected from groundwater supply sources in common areas used by the society, such as schools, mosques, markets, and health centers fed from the Niğde water distribution system using 500-ml polyethylene bottles. Before sample collection, each bottle was rinsed three times with the sampled groundwater before collecting the final sample to avoid cross-contamination from the bottles. The collected samples were stored in ice chests and immediately conveyed to the central laboratory of Niğde Ömer Halisdemir University and stored in a refrigerator under 4 °C to avoid bacterial activity and degradation of the samples (Okogbue and Ukpai 2013). The coordinates of the sample locations were measured using the Magellan eXplorist 610 GPS device. pH and Electrical Conductivity (EC) were measured instantaneously in the field using a potable handheld meter (WTW Multi 3320 SET 1 S41 TC 325 CO 325). In the laboratory, 0.1-µm nitrocellulose membrane Millipore filter was used to filter the samples in order to remove any suspended material. An aliquot of 100 ml was taken from each sample and acidified with HNO₃⁻ to preserve metals (Embaby and Redwan 2019). The acidified samples were analyzed for trace metals: Pb, Zn, Cr, Ni, Cd, Mn, Co, Cu, As, Se, Ba, Al, and Fe by means of inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce). The analysis followed the standard analytical procedures (APHA 2012) and resulted in < 0.01 µg/L detection limit for most of the trace elements. Pb and Cd concentrations were generally below their detection limits and thus are not used in the interpretations. Quality assurance and control of the trace element analysis were ascertained by the use of duplicates, blank reagent, and standard reference materials (USGS Geochemical Reference Materials). The accuracy (% of recovery) varied from 86.4 to 97.2% for all the analyzed trace elements. The analysis for each element in each sample was repeated thrice, and the standard deviation was calculated to establish the precision of the analysis. The precision (% of relative standard deviation for multiple replicate measurements) values were in the range of 1.97–2.51%, generally < 3%, which indicates a good precision for the analytical method used.

Data Processing

The results obtained from the trace element analysis were processed using AquaChem version 4.0. This involved plotting of bivariate diagrams to determine the element relationships. Spatial distribution maps of the trace elements were modelled using Surfer version 13. Kriging interpolation method was preferred over other spatial interpolation methods since it resolves the problem of surface estimation by employing spatial correlation and variograms (Sunkari and Abu 2019). The kriging interpolation was performed using Eq. 1:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(s_i) - Z(s_i + h)]^2 \quad (1)$$

where (h) denotes the spatial correlation between the measurement points, $N(h)$ represents the number of pairs of measurement points with distance h apart, $Z(s_i)$ and $Z(s_i + h)$ are the predicted and observed values at location s_i , respectively.

Multivariate Statistical Analysis

All the multivariate statistical techniques applied in this study were performed using SPSS Statistics software version 25. Pearson correlation analysis has been effectively used on hydrochemical data to decipher element relationships (Snousy et al. 2020). In this study, the Pearson correlation analysis was used in determining the linear relationship that exists between two elements. R-mode Factor Analysis (FA) through Principal Component Analysis (PCA) were used to transform the original data into a few uncorrelated latent variables (Sunkari et al. 2019b), which enhanced inference of the hydrogeochemical processes enriching and depleting the trace elements in groundwater. FA explicitly assumes the existence of latent factors underlying the observed data. PCA instead seeks to identify variables that are composites of the observed variables. Although the techniques can get different results, they are similar to the point where the SPSS Statistics software uses PCA as its default algorithm. In the FA, Varimax rotation was the rotation algorithm and factors with eigenvalues > 1 were extracted using Kaiser Criterion (Kaiser 1960). Hierarchical Cluster Analysis (HCA) with Average Linkage (Within Groups) as the linkage criterion also was employed to determine the element groupings or clusters based on their similarities.

Arsenic Contamination Assessment

In the current study, groundwater contamination was assessed using a single-factor water quality index from Eq. 2 (Zhang et al. 2019).

$$I_I = \frac{C_I}{C_0} \quad (2)$$

where C_I is the concentration of the contaminant (arsenic) in the groundwater and C_0 denotes the standard of the contaminant provided by the World Health Organization (WHO 2017). From the calculation, if the water quality index I_I is > 1 , then the groundwater is said to be contaminated with respect to the contaminant.

Human Health Risk Assessment of Arsenic

Exposure Assessment

The population of the municipality was grouped into two age groups; children (< 6 to < 16 years) and adults (≥ 16 years) based on their physiological changes. This helped in assessing the adverse health effects of arsenic in the groundwater on human consumers. Daily intake of groundwater with high arsenic concentration was estimated from the recommended model of the United States Environmental Protection Agency (USEPA 1989).

$$EDI = \frac{CW \times IR \times EF \times ED}{BW \times AT} \quad (3)$$

where EDI expressed in mg/kg/day is the estimated daily intake; CW is the concentration (mg/L) of arsenic in groundwater; IR represents the ingestion rate (L/d) with 0.85 L/d and 1.5 L/d as the values for children and adults, respectively (USEPA 2004); EF denotes the frequency of exposure (d/a), which is 365 days (USEPA 2004); ED is the exposure duration (years) of an individual to groundwater containing arsenic for a lifetime; BW indicates the average body weight (kg) where the value for children is 15 kg and that of adults is 61.75 kg (USEPA 2004); AT represents the average time of exposure (d). In this study, $AT = ED \times 365$ for noncarcinogenic effects and $AT = 77.434 \times 365$ for carcinogenic effects, because 77.434 is the average life expectancy of people in Turkey (Karacan et al. 2020). All the parameters for the calculations are shown in Table 1.

Table 1 Parameters of oral daily dose estimations in the two groups of the population

Parameters	Unit	Children	Adults	Source
IR	L/d	0.85	1.5	Zuo (2011)
BW	kg	15	61.75	USEPA (2004)
EF	d/a	365	365	USEPA (2004)
ED	a	6	30	USEPA (2004)
AT	d	77.434×365	77.434×365	Karacan et al. (2020)

Carcinogenic and Noncarcinogenic Risks

The carcinogenic risk of the intake of arsenic contaminated groundwater in the study area was estimated from the model of the USEPA (1989).

$$CR = EDI \times SF \quad (4)$$

From the above equation, CR represents the probability of a person developing cancer due to groundwater arsenic ingestion; EDI is the daily average exposure dose (mg/kg/day), and SF represents the carcinogenic slope factor (mg/kg day) $^{-1}$. The SF value of arsenic is 1.5 (USEPA 2018). Accordingly, the carcinogenic risk level is normally measured using the acceptable maximum risk standard to human health (Zhang et al. 2019). This study used 1×10^{-4} as the maximum acceptable risk level, and when the computed risk is above this value, then carcinogenic risk can be inferred.

To appraise the risk of non-carcinogenic effects, the hazard quotient model of the USEPA (1989) was used:

$$HQ = \frac{EDI}{RfD} \quad (5)$$

where 5 as explained before is the estimated daily intake or daily average exposure dose (mg/kg/day) and RfD is the reference dose of arsenic (mg/kg/day). The RfD of arsenic (3×10^{-4}) used in this study was taken from the archives of the integrated risk information system (IRIS) of the USEPA. When the non-carcinogenic risk value exceeds 1, then it is concluded that there is a health risk associated with the intake of arsenic-rich groundwater in the study area.

Results and Discussion

Trace Element Geochemistry

The trace element compositions and concentrations of physicochemical parameters of the studied samples as well as their statistical summaries are presented in Table 2. The pH values of groundwater varied from 6.35 to 7.46 with an

Table 2 Concentrations of trace elements, pH, and electrical conductivity (EC) in groundwater (all trace elements are measured in µg/L whereas EC is measured in µS/cm

Sample No.	Location	X	Y	pH	EC	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ba
N001	Ulucami Aşağı Kayabaşı	644,554	4,202,220	7.23	307	BDL	4.44	0.43	38.3	0.4	6.12	0.23	496	9.47	2.54	14.1
N002	Derbent Mezarlık	646,429	4,202,863	6.35	361	0.65	20.3	0.82	28.9	1.75	8.22	0.80	104	26.4	2.31	44.9
N003	Seçuk Mahallesi	647,058	4,203,083	7.08	340	0.83	3.66	BDL	34.6	0.30	5.44	0.45	38.4	10.2	0.56	19.5
N004	ÖzBelde Camii	644,539	4,203,422	7.27	301	36.4	82.3	0.17	81.5	0.36	9.46	0.37	56.8	13.0	0.91	29.1
N005	Yukarı Kayabaşı Mahallesi	646,741	4,205,280	6.99	352	0.43	3.34	0.11	42.7	0.37	6.65	0.33	18.5	13.7	0.69	29.3
N006	İnönü Mahallesi	646,591	4,205,125	7.43	356	0.87	4.07	0.33	35.1	0.33	6.74	0.49	65.8	9.83	1.20	13.8
N007	Şahinalı Mahallesi	648,390	4,204,786	6.58	291	23.0	3.03	0.27	74.1	0.21	4.41	0.40	63.5	11.8	1.00	6.52
N008	Efendibey Mahallesi	649,207	4,206,305	6.7	362	BDL	3.57	0.21	33.7	0.32	5.85	0.08	34.1	12.6	0.86	6.38
N009	Niğde Evleri	648,491	4,206,676	7.17	356	1.04	11.6	0.22	18.1	0.26	4.78	0.28	48.3	12.2	0.50	3.30
N010	İlhanlı Mahallesi	648,583	4,202,973	7.16	440	BDL	5.00	0.12	65.3	0.59	10.1	4.17	84.3	32.9	1.06	43.0
N011	Nar Mahallesi	649,231	4,203,310	7.46	434	0.21	3.22	0.03	60.4	0.55	8.36	0.69	23.4	31.4	0.56	31.2
N012	Ata Sanayi	650,775	4,205,499	7.05	487	1.27	3.26	0.04	63.7	0.54	8.50	0.46	11.5	31.4	0.86	33.3
N013	Kale Mahallesi	647,525	4,203,592	7.21	315	0.88	3.52	0.22	22.3	0.27	4.60	0.30	88.9	11.2	1.00	26.0
N014	Çayır Mahallesi	647,963	4,203,941	7.05	313	0.03	2.00	0.38	64.0	0.33	6.84	1.02	227	9.70	1.37	15.0
Minimum				6.35	291	0.03	2	0.03	18.1	0.211	4.41	0.08	11.5	9.47	0.50	3.30
Maximum				7.46	487	36.4	82.3	0.82	81.5	1.75	10.14	4.17	496	32.9	2.54	44.9
Average				6.93	358	0.01	11	0.24	47.3	0.47	6.87	0.72	97.1	16.8	1.10	22.5
Standard Deviation				6.94	58.0	0.01	21.1	0.21	20.2	0.39	1.83	1.02	127	9.16	0.62	13.3
TSE-266 (2005)				6.50–9.20	2000	200	50	50	300	NA	NA	1000	300	10	NA	NA
WHO (2017)				6.50–8.50	2500	200	50	50	300	200	20	1000	300	10	100	700
SABSL				None	None	None	1	None	None	None	None	None	1	12	None	None

SABSL Samples above standard limit, BDL below detection limit, NA not available

average value of 6.93 that represent slightly acidic to neutral conditions. The acidic to neutral pH has a major control on the solubility and mobility of many trace elements in groundwater (Taillefert et al. 2002; Snousy et al. 2020). Subtle changes in pH may cause trace elements to be deposited or re-transported into groundwater; therefore, trace element solubility depends on pH (Mollema and Antonellini 2016; Mora et al. 2017). With regard to the maximum permissible limit of 8.5 for pH in drinking water (WHO 2017), all of the studied samples are in compliance. Similarly, all the samples fall within the range (6.50–9.20) of the Turkish National standard for pH in drinking water (TSE-266 2005). The EC values ranged from 291 to 487 $\mu\text{S}/\text{cm}$ with an average value of 358 $\mu\text{S}/\text{cm}$, implying total compliance with the maximum permissible limit of 2500 $\mu\text{S}/\text{cm}$ and 2000 $\mu\text{S}/\text{cm}$ by WHO (2017) and TSE-266 (2005), respectively. Naturally derived trace elements in groundwater constitute approximately 1% dissolved constituents (Embaby and Redwan 2019). The average concentrations of the trace elements vary in the order $\text{Zn} > \text{Fe} > \text{Ba} > \text{As} > \text{Cr} > \text{Ni} > \text{Se} > \text{Cu} > \text{Co} > \text{Mn} > \text{Al}$.

The trace elements above the TSE-266 (2005) and WHO (2017) maximum permissible limits are zinc (Zn), arsenic (As), and chromium (Cr) (Table 2). Zn serves an anticorrosion effect when used in iron pipelines, and its oxidation may potentially contaminate the water. Sphalerite (ZnS) is the main ore for Zn with extractable 60–62% Zn (Greenwood and Earnshaw 1997). Zn also could be derived from biotite in granite and organic sources from limestone (Embaby and Redwan 2019). Mafecki et al. (2017) suggested that Zn is one of the mobile trace metals in groundwater as a result of its tendency to form soluble complexes under neutral and acidic pH. Zn also can be derived from anthropogenic sources through the use of agrochemicals (Khatri and Tyagi 2015). In this study, the Zn concentrations range from 11.5 to 496 $\mu\text{g}/\text{L}$ with an average value of 97.1 $\mu\text{g}/\text{L}$ (Table 2). Only one sample (N001) from Ulucami Aşağı Kayabaşı shows a higher Zn concentration (496 $\mu\text{g}/\text{L}$) that exceeds the WHO (2017) and TSE-266 (2005) guideline value of 300 $\mu\text{g}/\text{L}$. The high Zn concentration in this area is likely from the weathering and dissolution of sphalerite in the calc-silicate lithologies of the Niğde Massif (Çopuroğlu 1996; Tümüklü et al. 2018) in the southwestern part of the municipality where Ulucami Aşağı Kayabaşı is located. The slightly acidic to neutral pH of groundwater facilitated the formation of soluble Zn complexes that resulted in the high Zn content in groundwater. Ingestion of Zn-contaminated water can cause nausea, vomiting, abdominal upset, anaemia, and vertigo (Embaby and Redwan 2019). Severe Zn poisoning can lead to destruction of the pancreas and thus inhibit protein metabolism (Plum et al. 2010).

Arsenic (As) showed very high concentrations in groundwater in the range of 9.47–32.9 $\mu\text{g}/\text{L}$ with an average value of 16.8 $\mu\text{g}/\text{L}$, exceeding the maximum permissible limit of

10 $\mu\text{g}/\text{L}$ (TSE-266 2005; WHO 2017). Approximately 86% of the total samples studied are contaminated with As. The most affected areas are İlhanlı Mahallesi, Nar Mahallesi, and Ata Sanayi, which are all industrial areas. Natural forms of As in groundwater can come from sulphide minerals, such as arsenopyrite (FeAsS) and enargite (Cu_3AsS_4) (Embaby and Redwan 2019), which are common in the Niğde Massif (Çopuroğlu 1996; Hanılçı et al. 2019). However, As from these minerals is in trace quantities. Elevated As concentrations are found in coals, granites, and meta-argillites (Reimann and de Caritat 1998). Volcanic rocks also contain high As content such that when they weather and leach into aquifers, they can enrich groundwater with As. Anthropogenic sources of groundwater As include mining activities, industrial pollution, pesticides, and livestock feed additives (Etim 2017). The high groundwater As in the study area might be due to an interplay of geogenic and anthropogenic factors, including dissolution from volcanic rocks, sulphide minerals, industrial pollution, agrochemicals, and hydromorphic dispersion from ancient mines in the area.

Cr content in drinking water should not exceed 50 $\mu\text{g}/\text{L}$ (TSE-266 2005; WHO 2017). Naturally occurring Cr is derived from the weathering of Cr-rich rocks and volcanic activities (Okogbue and Ukpai 2013). The primary ores of Cr are chromite (FeCr_2O_4), Cr-bearing magnetite, and ilmenite. Rock-forming minerals, such as biotite, pyroxenes, potassium feldspars, amphiboles and olivine, also are some sources of natural Cr (Bricker and Jones 1995). Apart from the geogenic sources of Cr in groundwater, anthropogenic input from industrial activities also are culprits for high groundwater Cr (Selvam et al. 2017). In the present study, the Cr content varied from 2.00 to 82.3 $\mu\text{g}/\text{L}$ with an average value of 11.0 $\mu\text{g}/\text{L}$ (Table 2). This suggests that the Cr content exceeds the maximum permissible limit of 50 $\mu\text{g}/\text{L}$. However, only one sample (N004) from Özbelde Camii towards the western fringe of the study area shows Cr concentration in excess of the TSE-266 (2005) and WHO (2017) guideline value. The high Cr content in this area is likely from the weathering and dissolution of metamorphic rocks, such as gneiss in the area that are rich in Cr. Sharma et al. (2012) mentioned that Cr enrichment in groundwater can result in dermatological and gastrointestinal problems, as well as haematological dysfunction. The remaining trace elements, including Al, Mn, Co, Ni, Cu, Se, and Ba, are all within the maximum permissible limits (Table 2).

Spatial Distribution of Trace Elements

The spatial distribution maps of the various trace elements investigated in this study are presented in Fig. 2. The highest concentration of As is observed in the southern and southwestern parts of the study area (Fig. 2a). Groundwater supply sources in Derbent Mezarlık, Nar

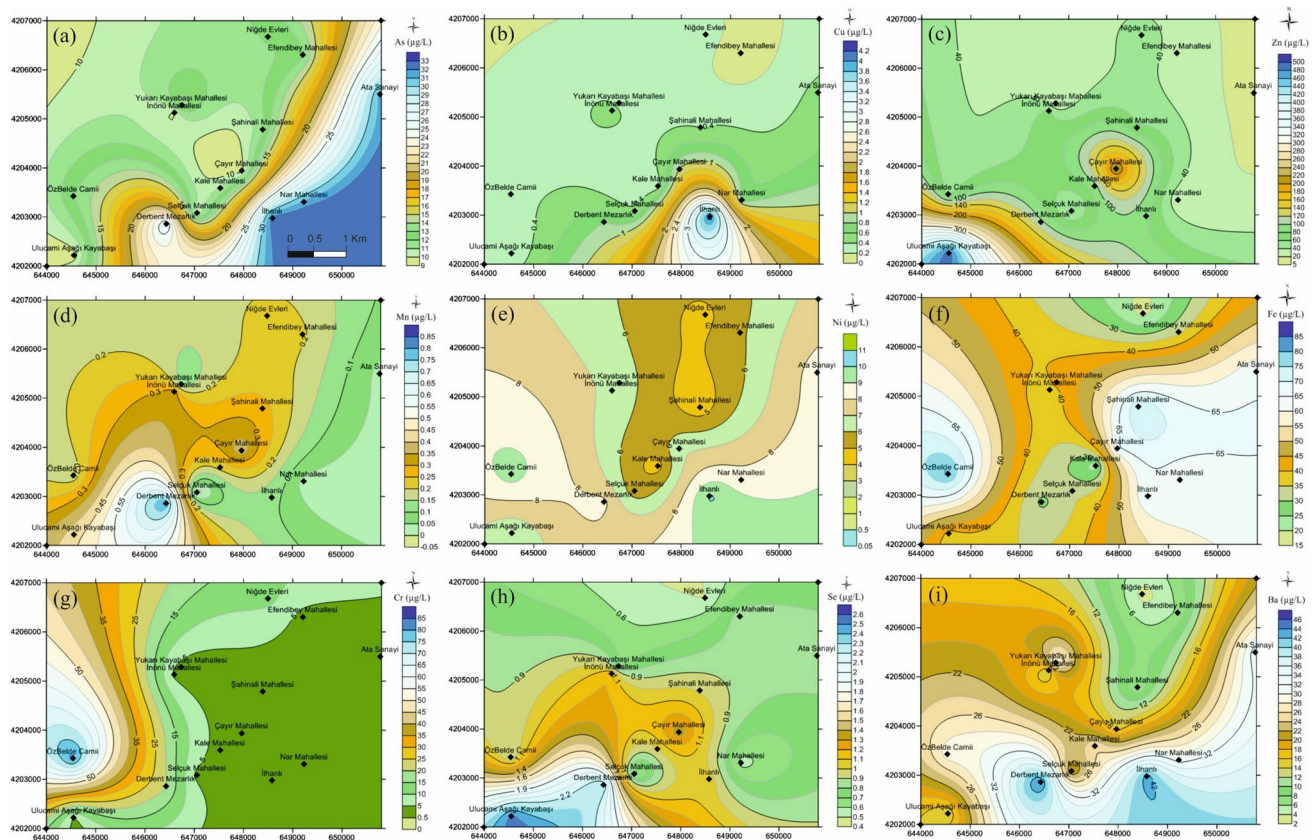


Fig. 2 Spatial distribution maps of trace elements in groundwater of the Niğde Municipality **a** spatial distribution of As ($\mu\text{g/L}$), **b** spatial distribution of Cu ($\mu\text{g/L}$), **c** spatial distribution of Zn ($\mu\text{g/L}$), **d** spatial

distribution of Mn ($\mu\text{g/L}$), **e** spatial distribution of Ni ($\mu\text{g/L}$), **f** spatial distribution of Fe ($\mu\text{g/L}$), **g** spatial distribution of Cr ($\mu\text{g/L}$), **h** spatial distribution of Se ($\mu\text{g/L}$), and **i** spatial distribution of Ba ($\mu\text{g/L}$)

Mahallesi, İlhanlı Mahallesi, and Ata Sanayi have very high As content $> 25 \mu\text{g/L}$ whereas the remaining in the other parts of the study area have As content $< 14 \mu\text{g/L}$ (Fig. 2a). The high As zones, mainly the southern and southwestern parts of the municipality, are all composed of slices of ophiolites and metamorphic rocks (marble, quartzite, gneiss) (Fig. 1). Although the Cu concentrations are generally within the acceptable standard, the highest Cu content in groundwater in the area is restricted to the central and southern parts of the study area, especially in İlhanlı Mahallesi ($4.17 \mu\text{g/L}$), Çayır Mahallesi ($1.02 \mu\text{g/L}$), and Derbent Mezarlık ($0.80 \mu\text{g/L}$) (Fig. 2b). These areas are overlain by volcano-sedimentary rocks and sequences of metamorphic rocks (Fig. 1). The highest Zn content is mainly observed in the southwestern and central parts of the study area (Fig. 2c), which are composed of metamorphic and volcano-sedimentary rocks (Fig. 1). Groundwater supply source in Ulucami Aşağı Kayabaşı in the southwestern part (Fig. 2c) contains the highest Zn concentration ($496 \mu\text{g/L}$), which exceeds the maximum permissible limit. Mn content of groundwater in the Niğde Municipality is very low in view of the guideline value

of $50 \mu\text{g/L}$. However, the highest Mn content is within the southern peripheral (Fig. 2d) region, particularly in Derbent Mezarlık ($0.82 \mu\text{g/L}$) where there are several pieces of ophiolitic outcrops. The Ni concentrations show a heterogeneous spread in the area with the highest values mainly in the southeastern (İlhanlı Mahallesi) and western (ÖZbelde Camii) fringes of the municipality (Fig. 2e) intruded by granites. A similar trend is observed in the Fe distribution map (Fig. 2f). Only groundwater supply source in ÖZbelde Camii shows a very high Cr content ($82.3 \mu\text{g/L}$) in the western part of the study area (Fig. 2g). The highest Se content in groundwater is limited to the southern and southwestern parts, especially in Derbent Mezarlık and Ulucami Aşağı Kayabaşı (Fig. 2h). However, high Ba content in groundwater is mainly observed in the southern (Derbent Mezarlık, Nar Mahallesi, İlhanlı Mahallesi) and southeastern (Ata Sanayi) fringes (Fig. 2i). Overall, trace element quality of groundwater in the western, southwestern, southern and southeastern parts of the Niğde Municipality is not entirely good and requires immediate redress from the stakeholders to safeguard the health and livelihood of the people.

Table 3 Pearson correlation analysis of the hydrochemical parameters (bold numbers indicate correlation coefficients ≥ 0.50)

	pH	EC	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ba
pH	1												
EC	0.16	1.00											
Al	-0.06	-0.43	1.00										
Cr	0.08	-0.27	0.80	1.00									
Mn	-0.53	-0.36	-0.06	0.07	1.00								
Fe	0.07	0.12	0.62	0.38	-0.27	1.00							
Co	-0.53	0.27	-0.17	0.11	0.66	-0.13	1.00						
Ni	0.17	0.56	0.14	0.43	-0.03	0.54	0.45	1.00					
Cu	0.08	0.42	-0.15	-0.09	-0.07	0.32	0.20	0.58	1.00				
Zn	0.09	-0.39	-0.14	-0.09	0.46	-0.07	-0.03	-0.11	-0.02	1.00			
As	-0.04	0.86	-0.19	-0.07	-0.11	0.31	0.55	0.72	0.56	-0.31	1.00		
Se	-0.30	-0.27	-0.12	0.01	0.83	-0.13	0.52	0.11	0.03	0.79	-0.04	1.00	
Ba	-0.04	0.51	-0.06	0.21	0.08	0.23	0.67	0.77	0.52	-0.18	0.75	0.18	1.00

Correlation Analysis and Bimetallic Complex Formation

The Pearson correlation analysis showed interelement relationships and is given in Table 3. Correlations with $p < 0.01$ were considered strong, whereas those with $p < 0.05$ were considered significant correlations. Moreover, correlation coefficients ≥ 0.50 were regarded as significant positive correlations forming the basis of the discussion in this section. From the Pearson correlation analysis (Table 3), pH shows weak positive correlation with EC, Cr, Fe, Ni, Cu, and Zn, implying that their enrichment might be related to a common process. However, pH shows negative correlation with most of the trace elements, especially with As ($r = -0.04$), indicating that pH and As may have different associations in the aquifer (Okogbue and Ukpai 2013). The negative correlation of pH with most of the trace elements might be as a result of high H^+ concentration that was absorbed by water–rock interaction of volcano-sedimentary rocks in the area (Pacheco and Van der Weijden 1996). Accordingly, most trace metals show progressive sorption at increasing pH, and thus, the heterogeneity of the trace elements may be pH dependent because of the fluctuating water content in the aquifer, which enhanced formation of suitable ligands (Pinheiro et al. 1996). It is known that metals get sorbed and form complex ligands at high pH (> 5) (Pinheiro et al. 1996). In this study, the various trace metals show heterogeneous compositions in groundwater with pH values generally > 5 , implying that metal complexes were formed in groundwater and the redox reactions in the aquifer control the general chemistry of groundwater and, thus, the trace element concentrations in groundwater.

EC displays strong positive correlation with As ($r = 0.86$), Ni ($r = 0.56$), and Ba ($r = 0.51$), indicating that the processes enriching these elements might be the same. It is worth

noting that the very strong positive correlation of EC with As reflects the influence of charged species in groundwater on the As content (Lermi and Ertan 2019). Also, the charged species may slow and reduce the formation of bimetallic complex associations (Battistel et al. 2016). On bivariate plots of EC versus some selected trace elements (Fig. 3), it is observed that the EC value increases with increasing trace element concentration, implying that the trace element enrichment is related to the abundance of charged species in groundwater. Al displays strong positive correlations with Cr ($r = 0.82$) and Fe ($r = 0.62$), which may be related to dissolution of meta-sediments rich in alumino-silicate minerals (Khaled 1995). The positive correlations observed in Mn with Co ($r = 0.66$) and Se ($r = 0.83$) point to the weathering and dissolution of mafic rocks in the area. Fe displays strong positive correlation with Ni ($r = 0.54$) also pointing to the mafic rock sources of these metals (MacDonald et al. 2006). Moreover, Co is positively correlated with As ($r = 0.55$), Se ($r = 0.52$), and Ba ($r = 0.67$), which may be an indication of leaching from recent sediments enriched in metals with an extensive pathway of water flow (Farrag et al. 2005; Redwan and Rammlmair 2017). Ni is positively correlated with Cu ($r = 0.58$), As ($r = 0.72$), and Ba ($r = 0.77$), reflecting the influence of mafic–ultramafic rock sources, such as meta-volcanic and ophiolitic rocks that are rich in chlorite minerals and detrital hornblende (MacDonald et al. 2006). Cu displays strong positive correlation with As ($r = 0.56$) and Ba ($r = 0.52$), suggesting weathering of hornblende and Cu-bearing minerals in granitoids in the area, which influenced groundwater chemistry (Embaby and Redwan 2019). Zn only displays very strong positive correlation with Se ($r = 0.79$), indicating hydromorphic dispersion from Zn deposits in the area. Similarly, As shows very strong positive correlation with Ba ($r = 0.75$), which is related to weathering and dissolution of altered hydrothermal barite deposits in

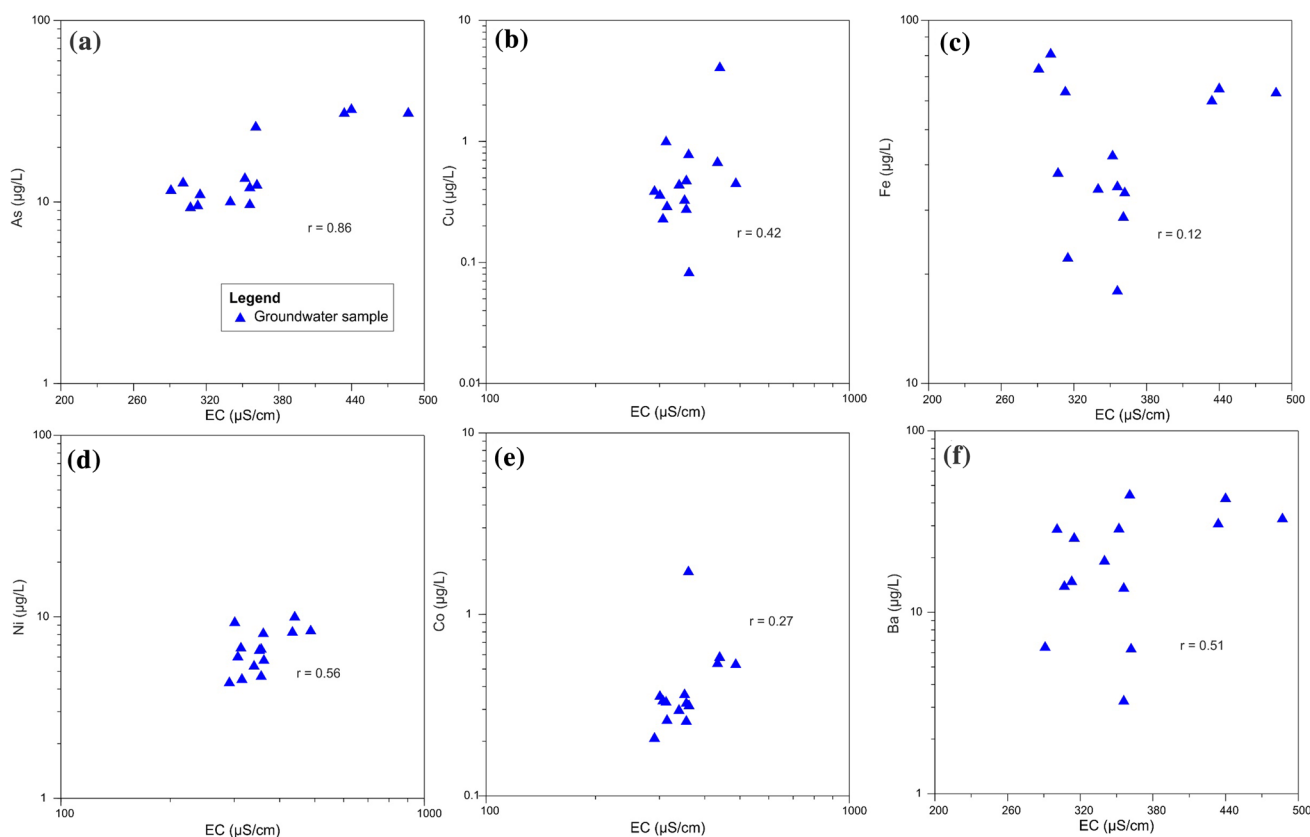


Fig. 3 Relationship between EC and selected trace elements in groundwater

the area (Cengiz 2014). The high Ba concentration is also likely from mixing with geothermal waters that contain Ba (Afsin et al. 2014).

Three bimetallic complex associations are distinguished in groundwater of the Niğde Municipality. The first group involves Fe-coordination that likely complexed with Cu ($r=0.32$) and Ni ($r=0.54$) (Fig. 4a, b). The second group comprises As coordination, which may have complexed with Cu ($r=0.56$) and Ni ($r=0.72$), similar to the first group (Fig. 4c, d). The third group constitutes Ba coordination that also peradventure, complexed with Ni ($r=0.77$) and Cu ($r=0.52$) compared with the first two groups (Fig. 4e, f). The As coordination group is the most dominant in groundwater, which resulted in the high As content of groundwater. This confirms the geogenic source of groundwater arsenic from weathering and dissolution of volcano-sedimentary rocks in the area. The reaction of the trace metals with negatively charged inorganic ligands may be minimal in the aquifer system, which accounts for the positively charged metal coordination pairs. However, to preserve the integrity of the bimetallic complex associations, the two metals in each group were possibly bridged by negatively charged ligands. Similar observations were recently made by Snousy et al. (2020) in Quaternary aquifers in Egypt.

Factor Analysis (FA)

The results of the FA are presented in Table 4. Four principal components/factors with eigenvalues > 1 were extracted from the R-mode FA (Table 4). These principal components/factors explain approximately 85.1% of the total variance of the dataset (Table 4). The R-mode FA reveals that various geochemical sources dependent on the aquifer lithology, control the groundwater chemistry in the study area, although not precluding anthropogenic input. Factor 1 explains approximately 30.5% of the total variance (Table 4) and is represented by pH, EC, Ni, Cu, As, and Ba (Fig. 5). The strong positive loadings of these parameters in factor 1 imply leaching from recent sediments in the area that contain high amounts of Ni, Cu, As, and Ba under influence from charged species considering the positive loading with EC (Farrag et al. 2005). The association of pH with trace elements in this group also suggests that redox processes in the aquifer play a significant role in the trace element mobilization in groundwater. Previous studies in the Niğde Province focused on identifying sources of trace elements in sediments of watersheds documented very high As concentrations (Yalcin et al. 2007; Keskin 2012, Lermi and Sunkari 2020). It is, thus, certain that the high As loading in

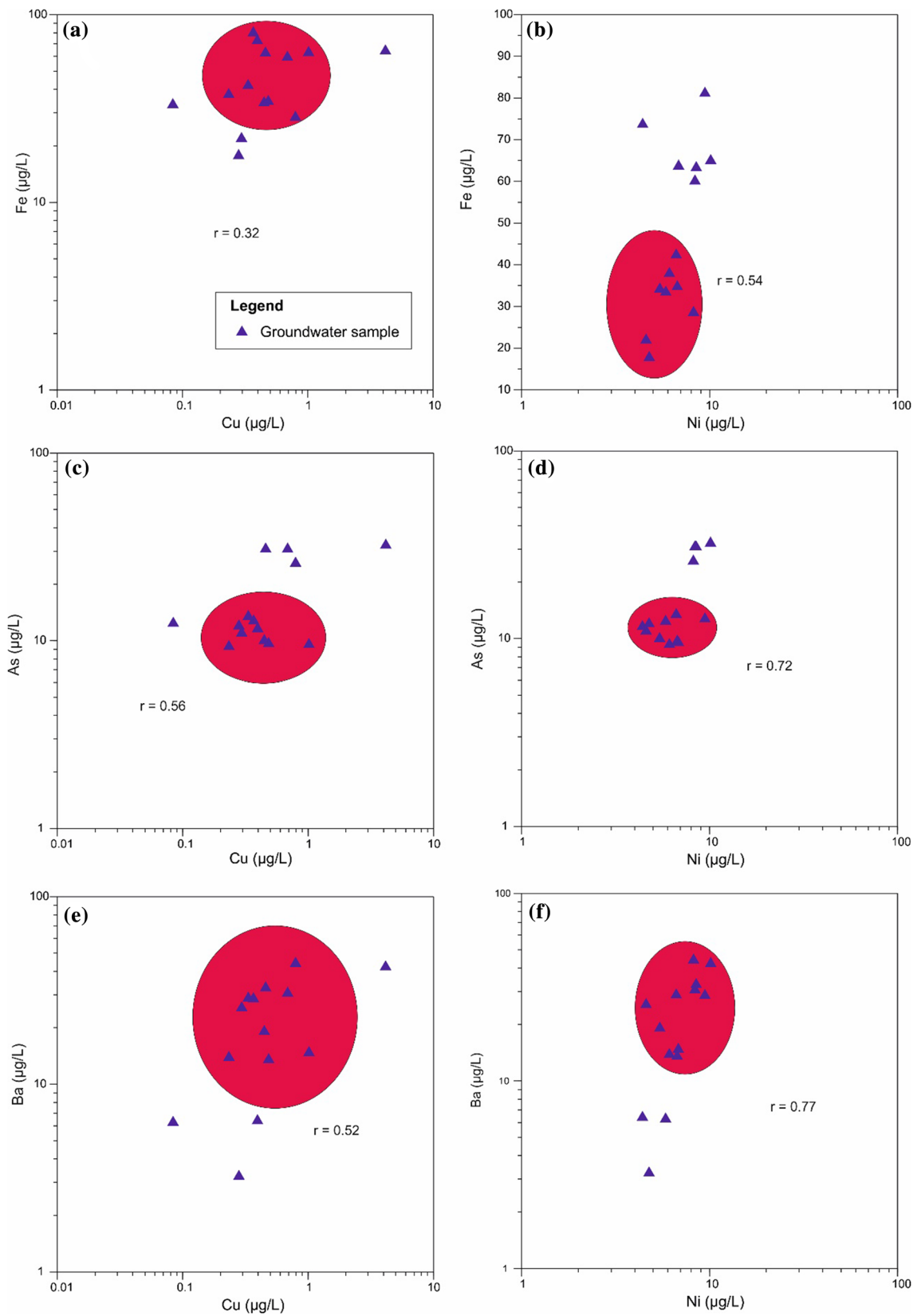
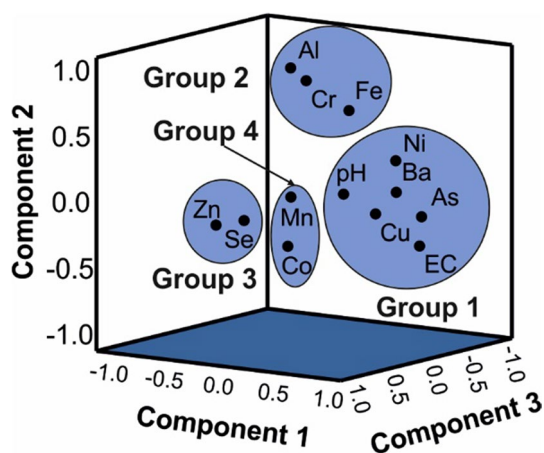


Fig. 4 Three bimetallic complex associations in groundwater; Group 1 **a** Fe versus Cu, **b** Fe versus Ni, Group 2 **c** As versus Cu, **d** As versus Ni, Group 3 **e** Ba versus Cu, and **f** Ba versus Ni

Table 4 Total variance explained from factor analysis

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.08	31.4	31.4	4.08	31.4	31.4	3.97	30.5	30.5
2	3.12	24	55.4	3.12	24.0	55.4	2.47	19.0	49.5
3	2.44	18.8	74.1	2.44	18.8	74.1	2.37	18.2	67.8
4	1.43	11.0	85.1	1.43	11.0	85.1	2.26	17.3	85.1
5	0.81	6.23	91.4						
6	0.50	3.86	95.2						
7	0.25	1.92	97.1						
8	0.16	1.20	98.3						
9	0.13	1.01	99.3						
10	0.05	0.41	99.7						
11	0.02	0.17	99.9						
12	0.01	0.07	100						
13	0.00	0.01	100						

**Fig. 5** Rotation plot from R-mode factor analysis

groundwater is from leaching of the As-rich sediments due to occasionally high precipitation (Nath et al. 2008). This process was also accompanied by weathering and dissolution of meta-volcanic/ultramafic rocks (MacDonald et al. 2006) in the area. Thus, factor 1 is assumed to be a reflection of weathering of both alluvial and volcanic/ultramafic aquifers in the area.

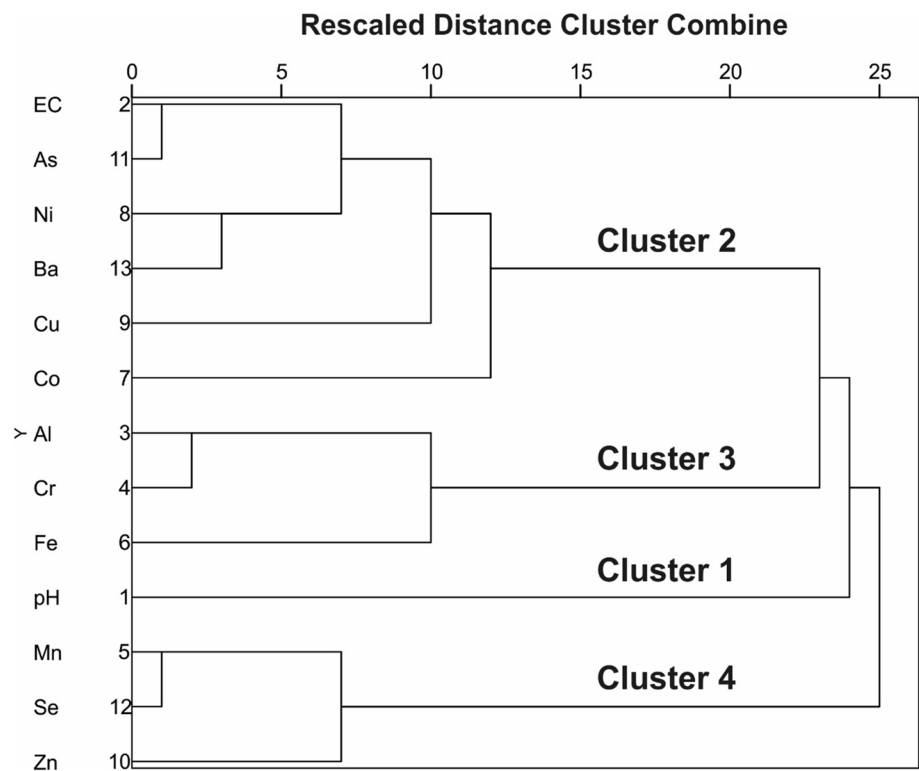
Factor 2 explains approximately 19.0% of the total variance (Table 4) and loads positively with Al, Cr, and Fe (Fig. 5). This factor indicates the role adsorption of Al and Fe on the surfaces of clay minerals in the area plays in groundwater chemistry (Snousy et al. 2020; Małecki et al. 2017). Moreover, Taillefert et al. (2002) mentioned that pH and Fe can control metal loading in groundwater. Therefore, the positive correlation of pH and Fe (Table 3) coupled with the positive loading of pH in factor 2 albeit not the major factor for its enrichment indicates the pH-dependent redox

processes in the aquifer. Factor 3 also explains 18.2% of the total variance of the dataset (Table 4) and is represented by Zn and Se (Fig. 5). The high positive loading of this factor is due to weathering of metamorphic rocks and allochthonous ultramafic units such as ophiolites in the area that contain hydrothermally altered Zn-rich minerals (Embaby and Redwan 2019). This is consistent with the findings of Çopuroğlu (1996) and Tümüklü et al. (2018) who reported widespread occurrence of sphalerite (ZnS) in the metamorphic rocks and allochthonous ultramafic units of the Niğde Massif. This factor is assumed to be a highlight of water–rock interaction in the mafic volcanic aquifers in the area. Factor 4, which accounts for 17.3% of the total variance, is a subgroup of factor 3 and is represented by Mn and Co. Weathering and dissolution of metamorphic and ultramafic rocks that contain hydrothermally altered Mn- and Co-rich minerals are the likely sources of Mn and Co in factor 4 just like factor 3.

Hierarchical Cluster Analysis

The hierarchical cluster analysis (HCA) revealed four main clusters and parameters in the same cluster were likely derived from similar processes (Fig. 6). Cluster 1 involves only pH but this cluster is a subcluster of cluster 2, which is represented by EC, Co, Ni, Cu, As, and Ba (Fig. 6). This confirms the geogenic source of As from weathering and dissolution of metamorphic and mafic–ultramafic rocks in the area that influenced the confined volcanic aquifer with contribution from the redox processes in the aquifer. Cluster 3 includes Al, Cr, and Fe (Fig. 6), corroborating the element association in factor 2 in the FA, hence their adsorption on clay mineral surfaces and subsequent release into groundwater. Several chemical processes such as complexation of Al and Fe through adsorption on the

Fig. 6 Dendrogram using Average Linkage (Within Groups) criterion to illustrate the clustering behaviour of the trace elements with pH and EC



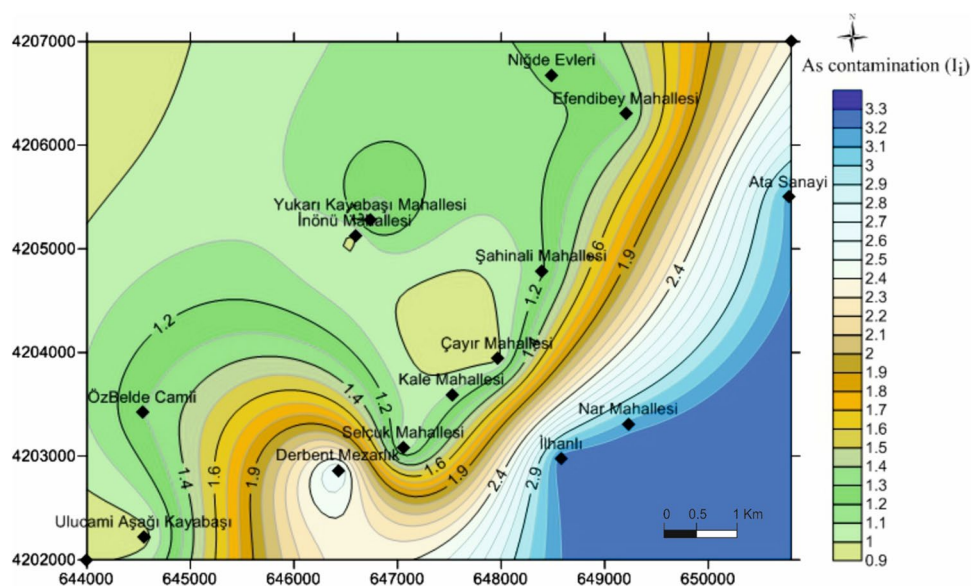
surfaces of oxyhydroxides, argillaceous sediments, and clay minerals can eliminate ionic species from solution (Małecki et al. 2017). Therefore, the very low concentrations of most of the trace elements imply that their removal mechanisms are very fast in the aquifer system. Cluster 4 involves Mn, Zn, and Se (Fig. 6), which agrees

with the same loading in factor 3 and partly in factor 4 in the FA. As explained earlier, this element association reflects weathering and dissolution of ultramafic rocks such as ophiolites that contain these elements. Certainly, the results of the FA are consistent with that of the HCA.

Table 5 Groundwater arsenic contamination and human health risks assessment in the Niğde Municipality

Sample	Location	Contamination assessment			Estimated daily intake (EDI)		Cancer risk (CR)		Hazard quotient (HQ)	
		As (mg/L)	I_i	Interpretation	Children	Adults	Children	Adults	Children	Adults
N001	Ulucami Aşağı Kayabaşı	0.00947	0.95	Uncontaminated	0.0005	0.0002	0.0001	0.0001	1.79	0.77
N002	Derbent Mezarlık	0.02636	2.64	Contaminated	0.0015	0.0006	0.0002	0.0002	4.98	2.13
N003	Selçuk Mahallesi	0.01019	1.02	Contaminated	0.0006	0.0002	0.0001	0.0001	1.92	0.83
N004	ÖzBelde Camii	0.01297	1.30	Contaminated	0.0007	0.0003	0.0001	0.0001	2.45	1.05
N005	Yukarı Kayabaşı Mahallesi	0.01370	1.37	Contaminated	0.0008	0.0003	0.0001	0.0001	2.59	1.11
N006	İnönü Mahallesi	0.00983	0.98	Uncontaminated	0.0006	0.0002	0.0001	0.0001	1.86	0.80
N007	Şahinali Mahallesi	0.01179	1.18	Contaminated	0.0007	0.0003	0.0001	0.0001	2.23	0.95
N008	Efendibey Mahallesi	0.01260	1.26	Contaminated	0.0007	0.0003	0.0001	0.0001	2.38	1.02
N009	Niğde Evleri	0.01220	1.22	Contaminated	0.0007	0.0003	0.0001	0.0001	2.30	0.99
N010	İlhanlı Mahallesi	0.03288	3.29	Contaminated	0.0019	0.0008	0.0002	0.0003	6.21	2.66
N011	Nar Mahallesi	0.03136	3.14	Contaminated	0.0018	0.0008	0.0002	0.0003	5.92	2.54
N012	Ata Sanayi	0.03137	3.14	Contaminated	0.0018	0.0008	0.0002	0.0003	5.93	2.54
N013	Kale Mahallesi	0.01118	1.12	Contaminated	0.0006	0.0003	0.0001	0.0001	2.11	0.91
N014	Çayır Mahallesi	0.00970	0.97	Uncontaminated	0.0005	0.0002	0.0001	0.0001	1.83	0.79
Safety Limits		0.01	1.00		5×10^{-8}	5×10^{-8}	1×10^{-4}	1×10^{-4}	1	1

Fig. 7 Groundwater arsenic contamination distribution map using the water quality index (I_i). Areas with I_i values > 1 are said to be contaminated with respect to arsenic



Arsenic Contamination and Human Health Risks Assessment

The water quality index I_i calculated for As contamination of groundwater reveals that samples with I_i values > 1 are contaminated with respect to As. Almost all parts of the study area are contaminated with As, because the I_i values are > 1 (Table 5; Fig. 7). The extremely high As contamination areas are restricted to the southern and southwestern parts of the area (Fig. 7). Only groundwater supply sources in Ulucami Aşağı Kayabaşı, İnönü Mahallesi, and Çayır Mahallesi in the central and southwestern fringes of the municipality are uncontaminated with As (Fig. 7).

The human health risks assessment indicates that children are more exposed to daily intake of water contaminated with As (Table 5; Fig. 8a). The estimated daily intake (EDI) of groundwater As for children varies from 0.0005 to 0.0019 mg/kg/day, whereas that of the adults varies from 0.0002 to 0.0008 mg/kg/day. This implies that children are more exposed to the health implications of drinking As-contaminated water. Adults (0.0001–0.0003) have higher carcinogenic risk of the intake of groundwater As than children (0.0001–0.0002) (Table 5; Fig. 8b). The higher carcinogenic risk in adults may be due to the difference in physiological characteristics with the children (Table 1). The proportion for carcinogenic risk areas in the study area is 50% for both children and adults. Only four groundwater supply sources in the study area (Derbent Mezarlık, İlhanlı Mahallesi, Nar Mahallesi, and Ata Sanayi) show higher carcinogenic risk ($CR > 1 \times 10^{-4}$) for both children and adults (Table 5). Arsenic levels are high enough that adults in the study area may be at risk for carcinogenesis or keratinization of the skin (Health and Environment 2016). Similar observations were made by

Zhang et al. (2019) in China, where adults have higher carcinogenic risk of groundwater As than children.

For the noncarcinogenic risk, hazard quotient (HQ) model from the USEPA was used where if the HQ value is > 1, noncarcinogenic risk is invoked. The estimations indicate that in contrast to the carcinogenic risk, children have higher noncarcinogenic risk than the adult population (Table 5; Fig. 8c). The estimated HQ for children is in the range of 1.79–6.21, whereas that of the adults is 0.77–2.66 (Table 5). The noncarcinogenic risk mainly emanates from the fact that children in the municipality consume more water than the adults consistent with the high daily intake of groundwater As for children. The statistical classification of the study area indicates that the proportion for noncarcinogenic risk areas is 100% for children and exactly 50% for adults. Barzegar et al. (2019) documented similar findings in Iran where children showed significantly higher noncarcinogenic risk for groundwater As.

Conclusions

Groundwater is the main source of water for domestic, industrial, and agricultural purposes in the Niğde Municipality of south-central Turkey. The area is dominated by metamorphic rocks, volcano-sedimentary rocks and granitoids that make up the Niğde Massif. This study determined the hydrogeochemical characteristics of trace elements in groundwater, identified sources of the trace elements, and appraised the human health risks associated with arsenic contamination in groundwater. Groundwater is contaminated with zinc, chromium, and arsenic. The arsenic contamination is the most dominant and affects approximately 86% of all the groundwater supply points in

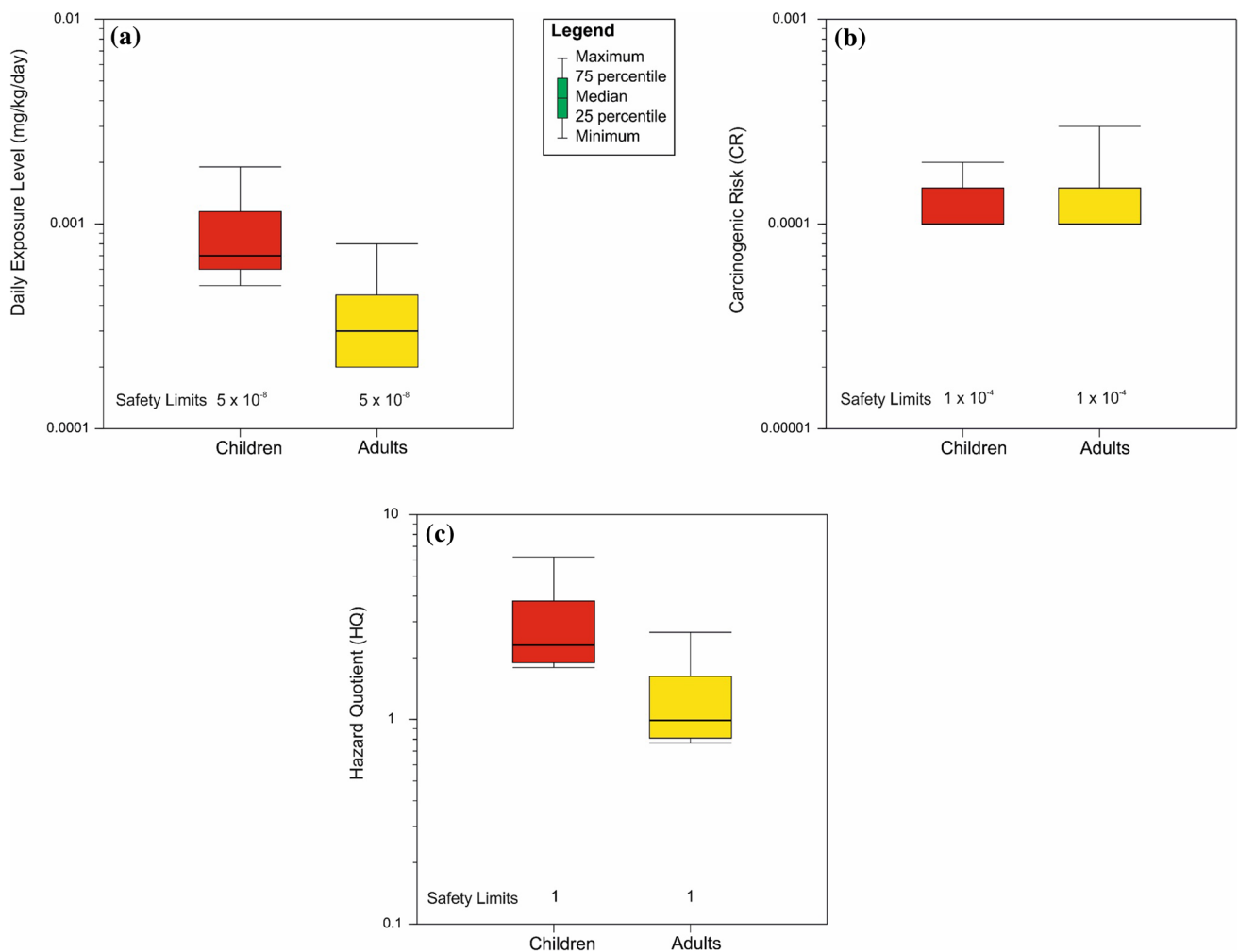


Fig. 8 Human health risks assessment among children and adults in the study area. **a** Daily exposure level of groundwater arsenic. **b** Carcinogenic risk (CR) associated with the intake of groundwater arsenic. **c** Noncarcinogenic risk using hazard quotient (HQ)

the water distribution system of the municipality. Groundwater supply sources in Derbent Mezarlık, Selçuk Mahallesi, ÖzBelde Camii, Yukarı Kayabaşı Mahallesi, Şahinalı Mahallesi, Efendibey Mahallesi, Niğde Evleri, İlhanlı Mahallesi, Nar Mahallesi, Ata Sanayi, and Kale Mahallesi all have arsenic concentrations greater than the guideline value of 10 mg/L. The arsenic mobilization in groundwater of these areas is largely due to weathering and dissolution of metamorphic, ultramafic, and volcano-sedimentary rocks in the area, as well as redox processes in the aquifer. Adults have higher carcinogenic risk than children as a result of consumption of the arsenic-contaminated water. However, children show higher hazard quotient than adults and thus are the hypersensitive population. A great deal of attention is needed by the stakeholders to help mitigate the groundwater arsenic contamination. It is recommended that the groundwater arsenic menace can be mitigated by

an integrated treatment process that involves intensive filtration, coagulation of the water using ferric chloride or alum, adsorption on pure zeolites, adsorption on zero-valent iron, and elimination by iron oxide-coated sand.

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Availability of Data and Material (Data Transparency) All data used in the study will be readily available to the public.

Code Availability (Software Application or Custom Code) All software applications used in this study were the licensed software applications used by Niğde Ömer Halisdemir University.

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interests.

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