

Assessment of Heavy Metal Pollution in the Groundwater of the Northern Develi Closed Basin, Kayseri, Turkey

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Abstract This study was carried out to assess the groundwater pollution in the northern Develi Closed Basin by using the heavy metal pollution index (HPI). Samples from 10 wells and 5 springs were collected in dry and wet seasons and concentrations of Pb, Zn, Cr, Mn, Fe, Cu, Cd, As and B were determined. In both seasons, for more than half of the samples, As, B and Fe concentrations exceeded the Turkish drinking water guideline values. Due to the occurrence of these metals in high concentrations in some samples HPI values are up to 1740. The source of these metals is geogenic and attributed to the interaction of these waters with highly altered volcanic and pyroclastic rocks. The overall HPI for wet and dry periods are reported as 360 and 440, respectively. Accordingly, the pollution level in the groundwater of this area is unacceptable.

Keywords Geogenic water pollution · Heavy metal pollution index · Groundwater · Kayseri · Turkey

Groundwater is a significant source of drinking water, which is withdrawn not only as a drinking water supply, but also to supply water for irrigation, livestock, industry and domestic purposes. In fact, more than 2 billion

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people worldwide depend on groundwater for their daily supply (Kemper [2003](#page-7-0)). Increasing stresses on water supplies resulted in groundwater contamination issues in many parts of the world (Lugoli et al. [2011](#page-7-1); Guler et al. [2012](#page-7-2); Huang et al. [2013](#page-7-3); Yolcubal et al. [2016](#page-8-0) and many others). Until the recent past, water quality concerns have been neglected since adequate and good quality water supplies have been available and also the adverse effects of some heavy metals on human health were not fully understood. Today, heavy metal pollution of groundwater is considered as one of the most substantial environmental problems since heavy metals are highly toxic to humans even at low concentrations (Marcovecchio et al. [2007;](#page-7-4) Varghese and Jaya [2014;](#page-8-1) Abou Zakhem and Hafez [2015](#page-7-5); Bhuiyan et al. [2016](#page-7-6)). It is difficult to evaluate the water contamination by only elemental concentrations (Nimick and Moore [1991](#page-7-7)), therefore water quality indices are used to assess the overall effects of pollution and to commentate on the influence of the individual pollution parameters (Prasad and Sangita [2008](#page-7-8); Bhuiyan et al. [2016](#page-7-6)). There are several different methods developed to calculate water quality indices and these methods usually depend on the available data and the solicited results (Horton [1965](#page-7-9); Nishida et al. [1982](#page-7-10) and others). Heavy metal pollution index (HPI) is one of these methods which is proven to be a powerful way to evaluate the heavy metal pollution in surface water and groundwater (Mohan et al. [1996;](#page-7-11) Prasad and Jaiprakas [1999;](#page-7-12) Prasad and Sangita [2008;](#page-7-8) Milivojević et al. [2016\)](#page-7-13). The HPI is a practical and easy to understand guiding tool that can be used by environmental managers, decision makers and users of a groundwater system (Prasanna et al. [2012](#page-7-14)). It represents the composite influence of the selected pollution parameters and the total quality of groundwater with respect to heavy metals (Prasad and Jaiprakas [1999](#page-7-12)). Not only groundwater

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quality, but also its suitability for drinking purpose can be evaluated by using the HPI.

The Develi Closed Basin is located in Central Turkey within the borders of the Kayseri province (Fig. [1a](#page-1-0), b). The basin is closed in character due to the mountainous parts surrounding the plain part (Fig. [1b](#page-1-0)) The study area is located in the northern part of the Develi Closed Basin, which hosts one of the most important bird paradises of Turkey, Sultansazligi wetland. The wetland area is protected according to the International Ramsar Agreement since 1994. The area attracted researchers and different studies were carried out around the wetland area in the last 10 years mainly to propose an approach to the hydrologic sustainability of the wetland (Dadaser-Celik et al. [2007\)](#page-7-15), to put forward the spatial changes in the wetland by analyzing the satellite images (Dadaser-Celik et al. [2008\)](#page-7-16), to calculate the water budget in the area (Yildiz and Gurer [2009\)](#page-8-2), to determine the factors affecting the severe contraction that the wetland suffered over the years (Bayari and Yildiz [2012\)](#page-7-17), to simulate the water levels in the wetland area by using an artificial neural network (Dadaser-Celik and Cengiz [2013\)](#page-7-18) and to determine the evaporation from the wetland area (Yildiz and Gurer [2014\)](#page-8-3). All of these studies concentrated on the wetland area and none of them focused on the heavy metal pollution issues, although the protection of the wetland from possible pollution sources depend on the identification of these sources. In the northern part of the basin, groundwater flow is towards the wetland area and the ground-water quality is more of an issue. Yildiz [\(2007\)](#page-8-4) reported that although the groundwater of the study area does not seem to affect the wetland system in the short-term due to the occurrence of clay layers below the wetland area, in the long term there might be an interaction between the surface waters and groundwater. Hence, this study was carried out to exhibit and to investigate the heavy metal pollution in the groundwater of the northern Develi Basin. There are no remarkable anthropogenic point sources related to industrial and/or mining activities that can cause pollution in the northern Develi Basin and the pollution source is assumed to be geogenic. In order to assess the degree of this geogenic pollution in the basin,

Fig. 1 a Location map of the Kayseri province (Source Google Earth), **b** map showing the location of the study area in the Develi Closed Basin, **c** geological map of the study area (Modified from Donmez et al. [2005\)](#page-7-19)

a geochemical survey was carried out and groundwater samples were collected in two different seasons.

Materials and Methods

The Develi Closed Basin is located in central Turkey (Fig. [1](#page-1-0)a). The total drainage area of the basin is 3190 km^2 , however, the present study was carried out in the northern part of the basin in an area which is approximately 761 km² (Fig. [1](#page-1-0)b). The study area has a terrestrial climate with hot, dry summers and cold winters. According to the long-term measurements carried out at the Kayseri meteorological station between 1929 and 2008, the average annual temperature and precipitation are around 10.6°C and 380.2 mm, respectively. The highest elevation is the summit of Mount Erciyes with 3917 m elevation above sea level, which is located in the northeastern part of the area (Fig. [1](#page-1-0)c). Actually, Mount Erciyes is the highest peak in Central Anatolia. The bottom of Çöl Lake is the lowest elevation in the area (1071 m) (Fig. [1](#page-1-0)c).

The study area is characterized by formations of volcanic origin formed during the latest stages of Mount Erciyes volcanism in between the Miocene and Quaternary (Donmez et al. [2005\)](#page-7-19). The geologic units outcropping in the area are Miocene volcanics, Upper Miocene sedimentary rocks, Pliocene volcanic rocks and Quaternary volcanic and sedimentary units (Fig. [1](#page-1-0)c). Lower Miocene sedimentary rocks consist of gray, red colored sandstones, mudstones and pebble stones. The Upper Miocene andesites are the products of a viscous magma and are in porphyritic texture. Upper Miocene basalts are comprised of plagioclase, olivine and clinopyroxene phenocrystals. Upper Miocene pyroclastic rocks are comprised of grey–purple colored tuffs and ign-imbrites (Donmez et al. [2003](#page-7-20)) whereas the sedimentary rocks are composed of brown to red colored pebble stones, sandstones, mudstones with gypsum, anhydrite and ignimbrite levels (Donmez et al. [2005](#page-7-19)). Pliocene aged rocks are the pyroclastic rocks composed of tuffs and agglomerates, being the products of an andesitic lava, the basaltic rocks which are dark colored and have a vesicular texture and the andesitic rocks which are dark colored and massif (Turkecan et al. [1998](#page-8-5)). Pliocene units are overlain by Quaternary aged volcanic glasses, pyroclastic rocks (pumices and volcanic ashes), massif and dark colored olivine basalts and grey–black colored andesites (Turkecan et al. [1998\)](#page-8-5). Quaternary alluvium units cover the plain parts of the area and comprised of clay, sand and pebbles. Groundwater occurs under both unconfined and confined conditions in the altered and fractured parts of volcanic rocks (SHW [1995](#page-7-21)).

Samples from 10 groundwater wells whose depths vary between 101 and 215 m, and 5 springs were collected in both wet (October 2013) and dry (March 2014) seasons (Table [1](#page-3-0)). All of the wells are equipped with an electrical submersible pump. During sampling from the wells, extensive purging procedure has been completed to ensure that more than three times the well volume has been discharged while monitoring the indicator field parameters (pH, temperature and electrical conductivity) with a Hach HQ40d multi-analyzer. Sampling was carried out only after the field parameters were stabilized to guarantee that the sample represents the groundwater from the aquifer. Sampling from the springs was carried out directly from the outlet of the spring. The samples were collected in acid washed polyethylene bottles (250 ml), they were passed through 0.45 um filters to remove sediment particles, acidified to $pH < 2$ (65% HNO₃) after filtering and kept refrigerated at 4°C prior to analyses. Duplicate samples were collected from each sampling point for quality assurance/quality control and the average of replicates are presented as the analysis results. The analyses were carried out in ISO-certified State Hydraulic Works (SHW) laboratories in Kayseri by using a Bruker Aurora M90 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) following standard methods given by United States Environmental Protection Agency (EPA Method 200.8). Before introducing the heavy metals in question to the MS, they were ionized in ICP by argon and then quantified by their mass/charge ratio. The analytical data quality was ensured by performing periodic measurements of the calibration standards, analysis of laboratory reagent blanks, replicates and internal standards. All of the standards used were traceable to the U.S. Department of Commerce, National Institute of Standards and Technology (NIST). Analyses were carried out in duplicates and the results are expressed as the mean. The detection limits were found to be 0.04 μ g/l for Pb, 0.83 μ g/l for Zn, 0.17 μ g/l for Cr, 0.25 µg/l for Mn, 1.23 µg/l for Fe, 0.10 µg/l for Cu, 0.09 µg/l for Cd, 0.64 µg/l for As and 0.01 mg/l for B. Analytical precision was reported as $\pm 5\%$ for all metals.

Statistical analysis hierarchical agglomerative clustering (HAC) was carried out by using Excel Statistical software. HCA was performed by using Ward's method for linkage (Ward [1963](#page-8-6)) and squared Euclidean distance as a measure of similarity. Besides, HCA was conducted in R-mode where clusters of variables are searched (Bhuiyan et al. [2016](#page-7-6)). A dendrogram was then used for visual inspection of the results (Davis [1986;](#page-7-22) Guler [2002\)](#page-7-23) (Fig. [2](#page-4-0)). Prior to analysis, data was log-transformed and standardized to assure that the influence of every each metal would be equal in the analysis (Guler et al. [2002\)](#page-7-23).

The HPI was calculated using Eq. [1](#page-4-1) by Mohan et al. [\(1996](#page-7-11)). It was developed by assigning a weighting for each selected parameter (W_i) between zero and one, depending on the relative importance of the parameter in quality considerations. W_i is usually defined as inversely proportional to the recommended standard (S_i) for each

The World Health Organization drinking-water quality guidelines together with Turkish standards (WHO 2008; ITASHY 2005) are also presented in this table The World Health Organization drinking-water quality guidelines together with Turkish standards (WHO [2008](#page-8-7); ITASHY [2005](#page-7-24)) are also presented in this table

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 (b) ₄₅ (a) 40 35 40 35 30 inkage Distance 30 Linkage Diistance 25 25 20 20 15 15 10 10 5 5 $\mathbf 0$ $\mathbf 0$ ξ ů٩ 운 පි ٩ŝ ö ඁඁ ភ $\mathbf a$ ö දී m පි ₹ ٩ 넫 운 පි

Fig. 2 Dendrogram obtained by cluster analysis of heavy metal contents in groundwater samples **a** in October 2013 **b** in March 2014. The *dashed line* represents the position of the phenon line

parameter (Horton [1965](#page-7-9); Mohan et al. [1996;](#page-7-11) Prasad and Sangita [2008\)](#page-7-8).

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

where n is the number of the parameters considered, W_i and Q_i are the unit weight and the sub-index of the *i*th parameter, respectively. The sub-index was calculated using Eq. [2](#page-4-2):

$$
Q_i = \sum_{i=1}^{n} \frac{|M_i - I_i|}{S_i - I_i} \times 100
$$
 (2)

where M_i , I_i and S_i are monitored value of the metal, desirable maximum and standard values of the *i*th parameter, respectively. Prasad and Sangita [\(2008](#page-7-8)) reported that the critical pollution index value is 100.

Results and Discussion

Concentrations of nine metals in two different seasons (dry and wet) are presented in Table [1](#page-3-0) together with pH, Electrical Conductivity (EC), WHO [\(2008](#page-8-7)) and ITASHY [\(2005](#page-7-24)) guideline values. According to Table [1,](#page-3-0) pH of the waters is near neutral ranging between 6.5 and 7.8 in dry season and between 6.8 and 7.4 in the wet season. Electrical Conductivity values vary from 63 to 1543 and from 61 to 1532 in dry and wet seasons, respectively. The lowest EC is observed in a spring (SP4) and the highest one is observed in a well (w4). Concentrations of some metals (As, Fe and B) in most of the samples exceed the desirable limits prescribed by WHO [\(2008](#page-8-7)). In fact, for As, 60% of the samples in both the dry and wet seasons exhibit concentrations above the guideline values $(10 \mu g/l)$, the maximum concentrations reaching up to 593 µg/l in dry season and 774 µg/l in the wet season. The mean concentrations tend to increase from dry (164 µg/l) to wet (188 µg/l) seasons. Such high concentrations of As in drinking water represent an enormous threat to human health (Nriagu [1994\)](#page-7-25). Moreover, Imamul Huq et al. ([2006\)](#page-7-26) stated that arsenic contaminated irrigation water may have a negative effect upon both food safety and crop production. Imamul Huq [\(2008](#page-7-27)) also put forward that irrigation water with high levels of As can cause contamination of agricultural soils due to the accumulation of As in soil. The Canadian Guidelines for dis-solved arsenic in irrigation water is 100 µg/l (CCME [1993](#page-7-28)). Accordingly, 60% of the samples exceeds these guidelines and not suitable for irrigation, although most of these wells are already utilized to supply water for especially sugar beets (Yildiz [2007\)](#page-8-4).

The mean concentrations of Zn, Fe and B also show an increasing trend from dry to wet seasons. B concentrations in 20% (same for both seasons) and Fe concentrations in 46.7% (33.3% for wet season) of the samples have concentrations above the limits recommended by ITASHY [\(2005](#page-7-24)). The increase in the mean Fe concentrations is especially attention striking since they have almost been doubled in between the two seasons (Table 1). In contrary to As, B, Fe and Zn, concentrations of Pb, Cr, Mn and Cu show a decreasing trend in between dry and wet seasons.

According to the dendrogram obtained as a result of hierarchical agglomerative clustering of October 2013 data, there are three clusters formed. Cluster 1 contains As and B, Cluster 2 includes Pb, Cu, Mn and Zn; Cluster 3 includes Cr, Cd and Fe (Fig. [2](#page-4-0)). The dendrogram prepared for March 2014 is different from the aforementioned one since Cluster 1 is formed by Cu, Pb, Zn, Fe and Mn, Cluster 2 consists of Cd and Cluster 3 consists of As, B and Cr. As is highly correlated with B in both dry and wet seasons. Fe shows correlation with Cr and Cd in dry season, but in the wet season Fe is highly correlated with Mn, Zn, Pb and Cu. Mn, Zn, Pb and Cu are correlated in both seasons. The considerable increase/decrease in Fe, As, B and Mn concentrations between two seasons changes the correlation systematics. The controls on dissolved As, Fe and Mn concentrations in the groundwater are often complex. In order to find out the distribution of the aqueous species and the precipitation state of the solids (saturation index) in the samples, the computer program PHREEQC (Parkhust and Appelo [1999](#page-7-29)) utilizing database llnl was used. This program relies on an ion-association aqueous model and is able to carry out aqueous geochemical calculations (Somay et al. [2008](#page-8-8)). In this manner, As (V) is dominant in all of the samples and the major As species are $HAsO₄⁻²$ and $H₂AsO₄⁻$ without any seasonal variations except for the percent change in the species occurrences, Mn (II) is dominant in all of the samples and the major species is in the ionic form as Mn^{2+} . In case of iron, Fe^{3+} components (Fe(OH)₃) are more abundant than Fe^{2+} components (FeHCO₃⁺ and Fe^{2+}) for most of the samples (i.e. W3, W4, W5, W9, W10, SP1, SP2 and SP4). This may be attributed to the oxidation of dissolved $Fe²⁺$ ions due to biological activities resulting in the precipitation of $Fe(OH)_3$, to temperature and pH or Ehcontrolled reactions with aquifer material or to the seasonal changes in the potential hydraulic conditions between the wetland area and the groundwater system. Dissolved iron can precipitate rapidly with increasing pH or Eh, therefore considerable seasonal changes of dissolved iron in groundwater can be observed (van der Grift et al. [2014](#page-8-9)). It should be noted herein that wells W1, W2, W3, W4, W5, W8, W9 draws water from the unconfined aquifer, whereas W10 draws water from both the unconfined and the confined aquifer due to the screens installed in both aquifers. W6 and W7, on the other hand, draw water from the confined aquifer. Among the samples, the oversaturation of the mineral phases containing iron includes goethite, magnetite and hematite. Further evaluation is required to reveal out the exact mechanisms of the dissolution/precipitation of Fe together with As, B and Mn in such a complex groundwater system where the extend and the thickness of the aquifer is highly variable due to the characteristics of the volcanic terrain.

There are no industrial or mining activities that can cause anthropogenic contamination in the study area; however the outcrops of young and altered products of Erciyes volcanism (Fig. [1](#page-1-0)) are enriched in various heavy metals, therefore the heavy metal pollution source of the groundwater is considered to be geogenic. Arslan et al. (2016) (2016) mentioned that there is a change in the chemical character of the groundwater between wet and dry seasons due to the water–rock interaction especially during the wet season. This interaction occurs as a result of the dissolution in the altered zone formed due to the weathering of the volcanic and the pyroclastic rocks of Erciyes volcanism under the influence of the tectonic components (faults) (SHW [1995](#page-7-21); Donmez et al. [2005](#page-7-19)). To be more specific, for sample W2, the water type in the dry season is $Ca-Mg-HCO₃$ and in the wet season it is $Ca-HCO₃$. For sample W5, the water type in the dry season is Na–Ca–Cl–HCO₃ and in the wet season it is Na–Cl–HCO₃. In the same manner, the spring SP3 sample is Na–Ca–Mg–HCO₃ type in dry season and the type changes to Na–Ca–HCO₃–SO₄ in the wet season. For SP4, the water type is Na–Ca–HCO₃ in dry season and Na–Ca–HCO₃–SO₄ in the wet season. Although there is a slight decrease in the mean electrical conductivity values of the samples between dry and wet seasons, some of the major ion concentrations between dry and wet periods increase, whereas some decrease.

As mentioned previously, HPI is considered as an effective tool used in the characterization of the composite influence of metals on the overall water quality (Sheyki and Moore [2012](#page-7-31)). In Tables [2](#page-6-0) and [3,](#page-6-1) the HPI calculations for groundwater of the study area and HPI of the individual sampling points are presented. In this study, Ii values are assumed to be zero for all of the metals that are considered and Si values are the highest permissible value for drinking water as specified by the drinking water quality guidelines for Turkey (ITASHY [2005](#page-7-24)). The HPI values calculated for both dry and wet seasons are more than three times higher than the critical value of the pollution index (100) suggested by Prasad and Sangita [2008](#page-7-8). Therefore, the level of pollution in the area is unacceptable in both seasons. The HPI in dry season (360) is slightly lower than the one in wet season (~440). Kumar et al. ([2012\)](#page-7-32) classified HPI into three categories as low $(<19$), medium $(19-38)$ and high (>38). According to this classification, in both dry and wet seasons, most of the samples (46.7% and 60%, respectively) fall in the high category. Some of the samples exhibit very high HPI values (as high as 1740) due to high concentrations of As, B and Fe in these samples (e.g. W4, W5, W7, W8, W9, SP-2 and SP-5). These high HPI values are due to the geogenic pollution source. For the rest of the samples, in dry season, 26.7% of the samples fall in both low and medium categories and in the wet season, 20% of the samples fall in both low and medium categories respectively.

In conclusion, in this study heavy metal pollution is examined and pollution index calculations are carried out for groundwater resources located in the northern part of the Develi Closed Basin. This is the first study focusing on the heavy metal pollution of groundwater resources around the Sultansazlığı wetland. The results indicate that

Table 2 Heavy metal Pollution Index (HPI) calculations for groundwater based on Turkish drinking-water standards (ITASHY [2005\)](#page-7-24) and World Health Organization guidelines for drinking-water quality (WHO [2008](#page-8-7))

Metals	Mean value (M_i) (μ g/l)		Standard permissi-	Highest desirable	Unit	Subindex (Q_i)		$W_i \times Q_i$	
	Oct. 2013	March 2014	ble value (S_i) (μ g/l)	value (I_i) (μ g/l)	weightage (W_i)	Oct. 2013	March 2014	Oct. 2013	March 2014
Pb	3.05	1.92	10.00		0.1000	30.480	19.247	3.048	1.925
Zn	63.44	75.42	-		-	-		-	
Cr	1.90	2.18	50.00		0.0200	3.809	4.352	0.076	0.087
Mn	58.58	55.10	50.00		0.0200	117.153	110.196	2.343	2.204
Fe	867.95	1443.48	200.00		0.0050	433.974	721.740	2.170	3.609
Cu	27.43	25.11	2000.00		0.0005	1.372	1.256	0.001	0.001
C _d	0.05	0.12	5.00		0.2000	1.000	2.333	0.200	0.467
As	153.00	188.41	10.00		0.1000	1530.013	1884.053	153.001	188.405
B	1002.00	1002.00	1000.00		0.0010	100.200	100.200	0.100	0.100

For October 2013 $\Sigma W_i Q_i = 160.94$, $\Sigma W_i = 0.45$, HPI = 360.45 For March 2014 $\Sigma W_i Q_i = 196.80$, $\Sigma W_i = 0.45$, HPI = 440.75

Table 3 Heavy metal pollution index (HPI) of groundwater at each sampling point in the northern Develi Closed Basin

for almost half of the samples As, B and Fe concentrations are much higher than the maximum permissible level for drinking water. For As, the highest concentration exceeds the drinking water standard about 77 times and is detected in the wet season in one of the samples (W4). The source of the heavy metals (As, B, Fe, Pb, Zn, Fe and Cu) occurring at substantially high concentrations in some of the groundwater samples is attributed to geogenic sources. To be specific about the geogenic sources, the volcanic rocks formed during the latest stages of Erciyes volcanism are products of a fast cooling magma and they are highly heterogeneous in nature. Some heavy metals present naturally in these rocks dissolve especially from the altered parts and incorporate into groundwater. The alteration in these volcanic rocks occurs due to various reasons including the

multi-phase volcanism in effect during the formation of these rocks and the existence of a pressure ridge in the area. The overall HPI for wet and dry periods are calculated as 360 and 440, respectively. For some of the samples (about 47%) HPI values are extremely high (up to 1740) due to presence of especially As, B and Fe in high concentrations. To summarize, it is concluded that geogenic sources contribute to the high scores of HPI in the study area and the pollution level in the groundwater is unacceptable. Therefore, the treatment of groundwater in this area is highly recommended before it is to be consumed and/or used for agricultural purposes.

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