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Use of Heavy Metal Content and Modified Water Quality Index to Assess Groundwater Quality in a Semiarid Area

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Abstract: Groundwater is a major source of drinking and agricultural water supply in arid and semiarid regions. Poor groundwater quality can be a threat to human health especially when it is combined with hazardous pollutants like heavy metals. In this study, an innovative method involving entropy weighted groundwater quality index for both physicochemical and heavy metal content was used for a semiarid region. The entropy weighted index was used to assess the groundwater's suitability for drinking and irrigation purposes. Thus, groundwater from 19 sampling sites was used for analyses of physicochemical properties (electrical conductivity—EC, pH, K^+, Ca^{2+}, Na^+, SO_4^{2-}, Cl^-, HCO_3^-, TDS, NO_3^-, F^-, biochemical oxygen demand—BOD, dissolved oxygen—DO, and chemical oxygen demand—COD) and heavy metal content (As, Ca, Sb, Se, Zn, Cu, Ba, Mn, and Cr). To evaluate the overall pollution status in the region, heavy metal indices such as the modified heavy metal pollution index (m-HPI), heavy metal evaluation index (HEI), Nemerow index (NeI), and ecological risks of heavy metals (ERI) were calculated and compared. The results showed that Cd concentration plays a significant role in negatively affecting the groundwater quality. Thus, three wells were classified as poor water quality and not acceptable for drinking water supply. The maximum concentration of heavy metals such as Cd, Se, and Sb was higher than permissible limits by the World Health Organization (WHO) standards. However, all wells except one were suitable for agricultural purposes. The advantage of the innovative entropy weighted groundwater quality index for both physicochemical and heavy metal content, is that it permits objectivity when selecting the weights and reduces the error that may be caused by subjectivity. Thus, the new index can be used by groundwater managers and policymakers to better decide the water's suitability for consumption.

Keywords: heavy metal; water quality index; groundwater pollution; entropy weight

1. Introduction

Groundwater plays a major role in supplying water for drinking, agricultural, and industrial uses [1–3]. For arid and semiarid regions, groundwater resources are especially important in terms of quantity and quality. Under these climatic conditions, groundwater overconsumption has led to decreased quality or contamination that may impose hazards to society [4,5]. Especially, heavy metals are important to monitor due to their toxicity.

There are various methods for dealing with heavy metal pollution in groundwater resources. These could be pumped and treated [6], be absorbed [7] by various kinds of absorbents [8], captured by nanoparticles [9] in micromixers [10,11], and removed by more natural solutions like wetlands [12]. However, implementing any remedy measure needs sufficient understanding of the situation and reliable inclusive assessment of the potential risk. Evaluating water quality is of paramount importance in this sense.

Many methods such as multivariate statistical techniques (e.g., cluster analysis, principal component analysis, and factor analysis) [13,14], hydro-geochemical evaluation [15,16], heavy metal indices (e.g., heavy metal pollution index, degree of contamination, heavy metal evaluation index, contamination factor, and health risk assessment) [17–19], and water evaluation indices [13] have been developed for assessing water quality considering physicochemical parameters. Grading water quality indicators largely depends on indicator concentration and the rate of relative toxicity. One of the most applicable methods is Water Quality Index (WQI) that summarizes the quality of water for drinking and other purposes [3,20,21]. This index provides a single number as a measure of overall water quality at a specific location and time. However, WQI needs weights for the different chemical elements. These are usually assigned subjectively by experts [15,22]. Additionally, various water quality indices have been proposed for evaluation of water quality based on heavy metals [23,24]. One of these indices is heavy metal pollution index (HPI). This method considers maximum desirable limit and maximum permissible limit of each heavy metal for water quality characterization. According to recent regulatory guidelines, a number of heavy metals are now being considered under the nonrelaxation category [25]. Hence, HPI cannot be calculated using the latest regulatory guidelines. However, a modified heavy metal pollution index (m-HPI) method [26] overcomes this and other limitations of previous methods. This index is based on only highest desirable concentration (I_i) and does not depend on the maximum permissible concentration (S_i). Furthermore, similar indices are the heavy metal evaluation index (HEI), the Nemerow index (NeI), and the ecological risks of heavy metals in groundwater [23,25–27].

Although several studies have assessed the groundwater quality based on heavy metal pollution for different purposes [4,23,28–31], there are only a few studies in arid and semiarid regions [22,24,32]. Considering this, the main objective of the current study is to test an innovative method involving entropy weighted groundwater quality index (EWQI) for both physicochemical and heavy metal content in a semiarid region that can be used by decision and policymakers for improving water resources management. Thus, the EWQI was used and compared to other pollution indices such as m-HPI, HEI, NeI, and ERI to evaluate the status of the overall pollution level of groundwater in the study area with respect to physicochemical properties (electrical conductivity—EC, pH, K^+, Ca^{2+}, Na^+, SO_4^{2-}, Cl^-, HCO_3^-, TDS, NO_3^-, F^-, biochemical oxygen demand—BOD, dissolved oxygen—DO, and chemical oxygen demand—COD) and nine important heavy metals (As, Ca, Sb, Se, Zn, Cu, Ba, Mn, and Cr). The outcomes provide essential information on the suitability of the water source for different uses. The results can be used by decision-makers as a guide for managing the aquifer from both quantitative and qualitative viewpoints.

2. Materials and Methods

2.1. Study Area

The Imam Zadeh Jafar Aquifer is located in Gachsaran City, southwest Iran, between longitude 50°50′ and 51°09′ E and latitude 30°13′ and 30°28′ N (Figure 1). The average elevation of the area is 720 m above mean sea level. The mean annual precipitation and temperature are 395 mm and 23 °C, respectively. The average thickness of the aquifer is approximately 80 m. The geological material is composed of course material like cobblestone, sandstone, gravel, and sand in the northern parts, gravel, and sand in central parts, and finer material like silt and clay in the southern parts [33]. There are no clay lenses within this unconfined aquifer.

Generally, groundwater is the only resource of water for drinking and irrigation purposes in the study area. However, there are several industrial pollution sources such as slaughterhouses, industrial parks, and beverage and asphalt plants in the study area. Another important contaminant source in the area is agriculture. The intense agricultural activity has led to overuse of pesticides, herbicides, and fertilizers. Groundwater polluted with heavy metals may have severe effects on public health. Hence, monitoring and studying the potential sources of water pollution from metal sources are necessary in the study area.

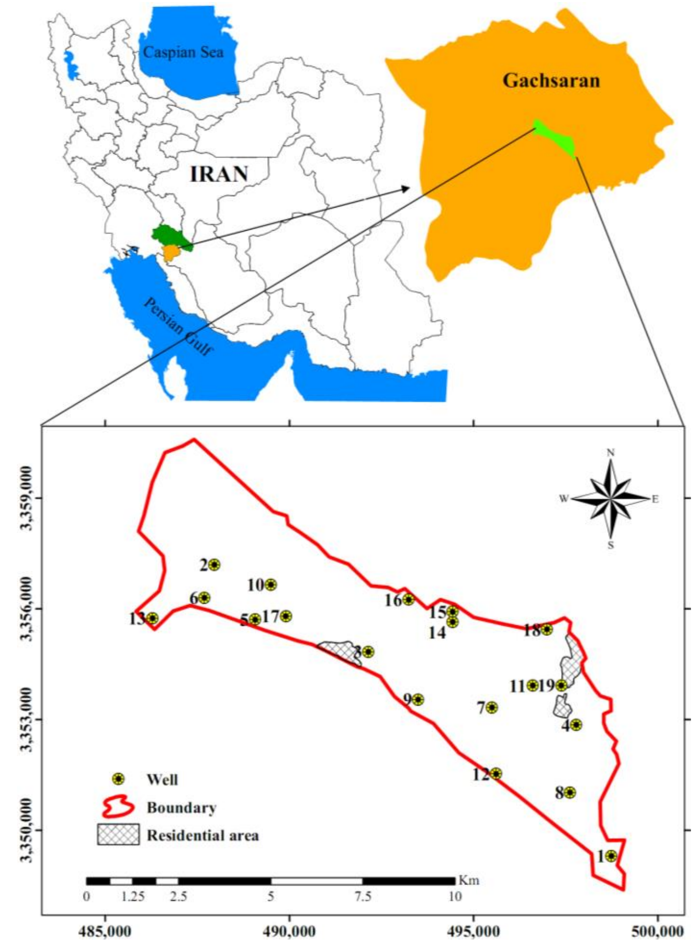

Figure 1. The Imam Zadeh Jafar Aquifer located in Gachsaran City, southwest Iran.

2.2. Sample Collection and Analytical Procedure

In 2009, nineteen existing wells were selected in the region and sampled for different groundwater quality parameters. The wells are used for drinking, irrigation, and industrial purposes depending on location in the region (Figure 1). Electrical conductivity (EC) and pH were measured on site. Other parameters such as potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), sulfate (SO_4^{2-}), chloride (Cl^-), bicarbonate (HCO_3^-), total dissolved solids (TDS), nitrate (NO_3^-), fluoride (F^-), biochemical oxygen demand (BOD), dissolved oxygen (DO), chemical oxygen demand (COD), arsenic (As), cadmium (Cd), antimony (Sb), selenium (Se), zinc (Zn), copper (Cu), barium (Ba), manganese (Mn), and chromium (Cr) were analyzed in the laboratory. Additionally, the concentration of other heavy metals such as Pb, Ni, Hg, and Fe was analyzed as well; however, the content of these was insignificant or close to zero. Hence, these elements were not included in the study. The analytical method for each chemical parameter is presented in Table 1. The accuracy of the chemical analysis was validated by calculating charge balance errors (CBE) using:

$$CBE = \frac{\sum \text{ cations} - \sum \text{ anions}}{\sum \text{ cations} + \sum \text{ anions}} \times 100 \tag{1}$$

where CBE is in percent and concentration of all cations and anions are in meq/L. The ion balance error for all groundwater samples ranged from 1 to 6.2%.

Table 1. Water quality parameters, associated units, and analytical method used.

Parameters	Unit	Analytical Method
Potassium	mg/L	Flame photometer
Sodium	mg/L	Flame photometer
Magnesium	mg/L	Titrimetric
Calcium	mg/L	Titrimetric
Sulfate	mg/L	Spectrophotometric
Chloride	mg/L	Titrimetric
Bicarbonate	mg/L	Titrimetric
pH	pH unit	pH meter
EC	µS/cm	Electrometric
Total dissolved solids	mg/L	Electrometric
Nitrate	mg/L	Spectrophotometric
Fluoride	mg/L	Spectrophotometric
Biochemical oxygen demand	mg/L	Dichromate method
Dissolved oxygen	mg/L	Winkler method
Chemical oxygen demand	mg/L	Winkler's aside method
Arsenic	mg/L	Atomic Absorption Spectrophotometer
Cadmium	mg/L	Atomic Absorption Spectrophotometer
Antimony	mg/L	Atomic Absorption Spectrophotometer
Selenium	mg/L	Atomic Absorption Spectrophotometer
Zinc	mg/L	Atomic Absorption Spectrophotometer
Copper	mg/L	Atomic Absorption Spectrophotometer
Barium	mg/L	Atomic Absorption Spectrophotometer
Manganese	mg/L	Atomic Absorption Spectrophotometer
Chromium	mg/L	Atomic Absorption Spectrophotometer

2.3. *Water Quality Index (WQI) and Entropy Weight Method*

Water Quality Index (WQI) is a useful method that has been widely used for assessing groundwater quality for drinking water use, with reference to hydro-geochemical parameters and heavy metal pollution [34]. The index provides a single number that is considered as an overall quality index of a sampled water. This can provide insights for deciding if the water needs to be used with special care or caution or if it needs treatment [28,35]. Herein, World Health Organization (WHO) standards (2011) [36] were used to compute quality rate of the hydro-geochemical parameters and heavy metals.

An essential step for using WQI is to assign weights. A common way to assign these weights is to allocate them subjectively based on experience [22] or reference literature [37]. This can lead to over or underemphasizing some parameters and affecting the outcome. In order to avoid subjectivity, entropy-weighted water quality index (EWQI) is employed in this paper [15,22]. Improving objectivity results in reduction of errors that may be caused by subjectivity when choosing the weights [38].

The entropy method was first proposed by Shannon [39] for reducing subjectivity in allocating weights to parameters of different nature. Shannon entropy expresses the degree of uncertainty concealed in a probabilistic or uncertain event [22]. When a parameter is precisely predicted and shows little change, the Shannon entropy weight will be small. Hence, a large change in concentration of a parameter will lead to a larger Shannon weight. This is especially important in water quality assessment when sudden changes occur in the water quality. Otherwise, the natural situation for aquifer water quality is to be almost constant [40,41].

Calculation of entropy weighted water quality index (EWQI) follows four steps according to the below. The first step is to construct the performance matrix. The initial matrix X shows a summary of chemical analysis data when m ($i = 1, 2, \ldots, m$) wells are monitored to evaluate the water quality, and each well has n measured parameters ($j = 1, 2, \ldots, n$). Then, x_{ij} represents the value of parameter j in the ith well. The matrix X can be obtained as:

$$\mathrm{X} = \begin{bmatrix} x_{11} & x_{12} & \ldots & x_{1n} \\ x_{21} & x_{22} & \ldots & x_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ x_{m1} & x_{m2} & \ldots & x_{mn} \end{bmatrix} \tag{2}$$

The second step is to normalize the performance matrix. This step is essential for eliminating errors when there are different units of measurement for different parameters and different quantity grades [22]. To do so, in normalized matrix of v_{ij}, each array is divided by the sum of arrays for each column:

$$v_{ij} = \frac{x_{ij}}{\sum_{i=1}^{m} x_{ij}} \tag{3}$$

The third step is to calculate the entropy value. The entropy value of the jth measured parameter is calculated as [42]:

$$z_j = -\frac{1}{\ln(m)} \sum_{i=1}^{m} v_{ij} \ln\left(v_{ij}\right) \tag{4}$$

where z_j is the entropy value of the jth parameter.

The fourth step is to calculate the objective weights of each parameter using:

$$W_j = \frac{1 - z_j}{\sum_{i=1}^{n} 1 - z_j} \tag{5}$$

where W_j is the weight for the jth parameter. Another quality scaling factor according to [36] is:

$$q_j = \left[\frac{V_j - V_{id}}{S_j - V_{id}}\right] \times 100 \tag{6}$$

where q_j is the quality rating for the jth water parameter, V_j is the measured jth parameter, S_j is the standard permissible value for the jth parameter assigned by WHO [43], and V_{id} is the ideal value of jth parameter in pure water (i.e., 0 for all other parameters except for pH = 7). The overall water quality index can thus be estimated by combining the quality scaling factor with the unit entropy weight using:

$$\mathrm{EWQI} = \sum_{i=1}^{n} W_j \times q_j \tag{7}$$

Based on the results of EWQI, water quality can be classified into five classes for drinking water purposes (Table 2).

Table 2. Classification of groundwater quality according to entropy weighted groundwater quality index (EWQI) range.

Range	Type of Water
<50	Excellent
50–99.99	Good
100–199.99	Poor
200–299.99	Very poor
>300	Unsuitable for drinking

2.4. Evaluation of Groundwater Quality for Irrigation Purposes

We examined irrigation water suitability of the sampled groundwater for Sodium Adsorption Ratio (SAR; in association with electrical conductivity), sodium percentage (Na%), total dissolved solids (TDS), permeability index (PI), total hardness (TH), and magnesium ratio (MR) as calculated by the following formulas,

1. The Sodium Adsorption Ratio (SAR) was calculated by [44]:

$$\mathrm{SAR} = \frac{\mathrm{Na}^+}{\sqrt{\frac{\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)}{2}}}\mathrm{meq/l} \tag{8}$$

2. The sodium percentage is computed with respect to relative proportions of cations present in water using:

$$\mathrm{Na\%} = \frac{(\mathrm{Na}^+ + \mathrm{K}^+)}{(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^+ + \mathrm{K}^+)}\frac{\mathrm{meq}}{\mathrm{l}} \times 100 \tag{9}$$

3. Doneen [45] classified irrigated water based on permeability index (PI) according to:

$$\mathrm{PI} = \frac{\mathrm{Na}^+ + \sqrt{\mathrm{HCO}_3^-}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2} + \mathrm{Na}^+}\mathrm{meq/l} \times 100 \tag{10}$$

4. Total hardness (TH) was calculated by [46]:

$$\mathrm{TH\ (as\ CaCO_3)mg/L} = \left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)\mathrm{meq/l} \times 50 \tag{11}$$

5. Magnesium Ratio (MR) was calculated by [46]:

$$\mathrm{MR} = \frac{\mathrm{Mg}^{2+}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}}\frac{\mathrm{meq}}{\mathrm{l}} \times 100 \tag{12}$$

We used ArcGIS software (10.3) (Esri, Redlands, CA, USA) to demarcate sampling locations and spatial distribution of groundwater quality indices throughout the study area. Inverse distance weighting was applied for interpolation [47].

2.5. Heavy Metal Pollution Indices

2.5.1. Modified Heavy Metal Pollution Index (m-HPI)

To improve the shortcomings of the heavy metal pollution index (HPI) and heavy metal evaluation index (HEI), Chaturvedi et al. [26] defined a modified heavy metal pollution index (m-HPI) for better evaluating water quality for drinking purposes. The m-HPI is calculated as:

$$\text{m-HPI} = \sum_{i=1}^{n} \text{m-HPI}^{i} \tag{13}$$

where n is the number of heavy metals considered in the evaluation. The m-HPI^i is the modified heavy metal pollution index for ith heavy metal ion defined as:

$$\text{m-HPI}^{i} = \omega_i Q_i \tag{14}$$

where ω_i is the relative weightage factor defined as:

$$\omega_i = \frac{W_i}{\sum_{i=1}^{n} Wi} \tag{15}$$

where W_i is the unit weighting factor defined as:

$$W_i = \frac{1}{I_i} \tag{16}$$

where I_i is maximum permissive level of ith heavy metal concentration (WHO standard). Sub index Q_i for the ith heavy metal is defined as:

$$Q_i = \frac{M_i - I_i}{I_i} \tag{17}$$

where M_i is the observed concentration of the ith heavy metal. The m-HPI can be divided into metals exceeding or not exceeding maximum permissible level. The former m-HPI is called positive index (PI of m-HPI) and the latter, negative index (NI of m-HPI). Thus, a pair of indices may be computed for each water sample. Based on both of indices, each sample's water quality related to heavy metal pollution is classified as follows: excellent ($-1 \leq$ NI ≤ 0 and PI = 0), very good ($-1 <$ NI ≤ 0 and $0 <$ PI $\leq U_L/2$), good ($-1 <$ NI ≤ 0 and $U_L/2 <$ PI $\leq U_L$), and unacceptable (NI ≤ 0 and PI $> U_L$), where U_L is upper limit of positive index.

2.5.2. Heavy Metal Evaluation Index (HEI)

As for m-HPI, HEI provides an overview of the water quality with respect to heavy metals. The HEI index is calculated based on maximum permissible concentration (MAC) for each target heavy metal using:

$$\text{HEI} = \sum_{i=1}^{n} \text{HEI}^{i} \tag{18}$$

where HEI^i is the pollution index corresponding to ith heavy metal calculated as:

$$\text{HEI}^{i} = \frac{M_i}{\text{H}^{i}_{\text{mac}}} \tag{19}$$

where $\text{H}^{i}_{\text{mac}}$ is the maximum permissible concentration of ith heavy metal. This method divides the water quality into three classes to demarcate the different level of contamination including: low (HEI < 10), medium (HEI = 10–20), and high (HEI > 20).

2.5.3. Nemerow Index (NeI)

This method is a multifactorial and integrated assessment approach where the index is calculated using [48,49]:

$$\mathrm{NeI} = \left[\frac{\left\{ (M_i/I_i)^2_{\mathrm{mean}} + (M_i/I_i)^2_{\mathrm{max}} \right\}}{n} \right]^{\frac{1}{2}} \tag{20}$$

where $(M_i/I_i)_{\mathrm{mean}}$ is the average value of (M_i/I_i) of all target heavy metals of a water sample and $(M_i/I_i)_{\mathrm{max}}$ is the maximum value of (M_i/I_i) among all target heavy metals detected in the water sample. This method classifies the water quality into four categories: insignificant (NeI < 1), slightly (1 ≤ NeI < 2.5), moderately (2.5 ≤ NeI < 7), and heavily (NeI ≥ 7) contaminated.

2.5.4. Ecological Risks of Heavy Metals in Groundwater

We used the ecological risk index (ERI) [50,51] to evaluate the potential ecological hazards associated with heavy metals in groundwater. The ecological risk index was calculated as:

$$\mathrm{ERI} = \sum_{i=1}^{n} \left[T_i \times \left(\frac{M_i}{I_i} \right) \right] \tag{21}$$

where T_i is the biological toxicity factor of the ith target heavy metal. The toxic-response factor of heavy metals is given as: As = 10; Cd = 30; Sb = 7; Cu = 5; Cr = 2; and Zn and Mn = 1 [52,53]. The index classifies the groundwater quality into four groups, low (ERI < 110), moderate (110 ≤ ERI < 200), considerable (200 ≤ ERI < 400), and very high (ERI ≥ 400) risk.

3. Results and Discussions

In the below, we group results in three main parts following a general statistical analysis. The first and second demonstrate the sustainability of groundwater for drinking and irrigation purposes, respectively. In the third, heavy metal pollution indices were used to identify status of the overall pollution level of groundwater resources in the study area.

3.1. Statistical Analysis

Descriptive statistics for observed water quality data are presented in Table 3. The table presents minimum, maximum, mean, standard deviation, permissible limits for drinking water set by World Health Organization, and entropy weight for each parameter used for EWQI assessment. Groundwater in this area is slightly alkaline to neutral, as the recorded pH ranges from 7.1 to 8.3, with a mean of 7.8. The pH is within the permissible limits (6.5–8.5) set by WHO standards for all samples. Electrical conductivity (EC) of the groundwater samples varied from 350 to 3270, with a mean of 1085. The total dissolved solids varied between 165 and 3440 mg/L. The order of cation occurrence was Ca^{2+} > Na^+ > Mg^{2+} > K^+ and the order of anions HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-. The average concentration of HCO_3^-, Ca^{2+}, SO_4^{2-}, Cl^-, Na^+, Mg^{2+}, NO_3^-, and K^+ were 259, 150, 140, 130, 54, 42, 20, and 1 mg/L, respectively. Furthermore, the maximum concentration of Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, F^-, BOD, and COD was 99.6, 732, 360, 355, 453, 46, 1.4, 7.8, and 7.1 mg/L, respectively. The maximum value exceeded the desirable limits for Mg^{2+} (30 mg/L), Ca^{2+} (75 mg/L), HCO_3^- (300 mg/L), Cl^- (250 mg/L), SO_4^{2-} (250 mg/L), NO_3^- (45 mg/L), F^- (1 mg/L), BOD (5 mg/L), and COD (5 mg/L) concentration for drinking purpose.

Table 3 illustrates that mean concentration of heavy metals As, Cd, Sb, Se, Zn, Cu, Ba, Mn, and Cr was 10, 3, 20, 10, 500, 50, 700, 100, and 50 µg/L, respectively. The maximum value of Cd, Sb, and Se was above the permissible limits for drinking water purposes.

Table 3. Descriptive statistics of chemical content in the groundwater samples.

Parameters	Unit	Min	Max	Mean	SD	WHO Standard (2011)	Entropy Weight (Wi)
EC	µS/cm	350	3270	1085	698.7	1500	0.01980
pH	pH units	7.01	7.68	7.36	0.18	6.5–8.5	0.00004
TDS	mg/L	165	3440	916.05	712.86	500	0.02545
K^+	mg/L	0.39	1.95	1.03	0.42	12	0.00835
Na^+	mg/L	4.83	190.21	54.90	60.88	200	0.05965
Mg^{2+}	mg/L	21.6	99.6	42.13	22.38	30	0.01288
Ca^{2+}	mg/L	52	732	150.32	156.72	75	0.03761
HCO_3^-	mg/L	213.5	359.9	259.09	41.54	300	0.00134
Cl^-	mg/L	28.4	355	130.42	116.51	250	0.04106
SO_4^{2-}	mg/L	12.96	453.12	140.93	126.97	250	0.03831
NO_3^-	mg/L	2	46	20.32	12.13	45	0.02167
F^-	mg/L	0.55	1.41	0.80	0.21	1	0.00341
BOD	mg/L	0	7.8	1.89	2.70	5	0.10412
COD	mg/L	0	1.2	0.71	0.37	10	0.01681
DO	mg/L	2.5	7.1	4.96	1.10	5	0.00272
As	µg/L	4.6	15.0	7.9	4.0	100	0.01282
Cd	µg/L	0.3	303.6	50.1	103.5	30	0.17146
Sb	µg/L	10.6	223.7	96.6	75.0	200	0.03357
Se	µg/L	6.0	133.0	25.9	28.9	100	0.04521
Zn	µg/L	37.0	4060.0	559.1	1073.5	50,000	0.11664
Cu	µg/L	8.0	101.0	31.8	27.7	500	0.03329
Ba	µg/L	219.5	2436.5	983.5	699.8	7000	0.02528
Mn	µg/L	1.7	402.7	56.5	116.8	1000	0.13860
Cr	µg/L	6.0	138.0	33.7	29.0	500	0.02990

3.2. Suitability of Groundwater for Drinking Use

Entropy Weighted Water Quality Index (EWQI)

To assess the groundwater quality, some researchers have used the EWQI [54–56]. The EWQI is an innovative tool that tests multivariable water quality data against specified water quality standards determined by the user [56]. Entropy weight improves WQI since it does not rely on subjective judgement in assigning weights. The entropy weights of hydro-chemical parameters show that the concentrations of Cd play the leading role in affecting the groundwater quality based on WQI index in the study area. EWQI range and type of water are presented in Table 4 and Figure 2. In total, 24 water quality variables were used for the EWQI. The calculated EWQI range was between 13 and 198. Among these, Table 4 illustrates that most of the samples were classified as excellent water (68%). Three wells were classified in the category good water for drinking purposes. However, as shown in Table 4 and Figure 2, the WQI for wells 8, 11, and 19 is classified as poor water. This figure represents the eastern part of the study area (Figure 2), whereas the value of chemical parameters such as Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, F^-, BOD, and COD, which were greater than the permissible limits for drinking purpose, belonged to the other samples. This indicates that heavy metals such as Cd, Sb, and Se play a major role in the groundwater quality assessment.

Table 4. EWQI for groundwater in the study area.

Well Number	EWQI Value	Classification
1	50.0	Good water
2	26.1	Excellent water
3	30.7	Excellent water
4	39.9	Excellent water
5	21.6	Excellent water
6	23.1	Excellent water
7	44.3	Excellent water
8	159.7	Poor water
9	24.9	Excellent water
10	13.0	Excellent water
11	172.5	Poor water
12	37.7	Excellent water
13	85.9	Good water
14	31.6	Excellent water
15	97.1	Good water
16	29.3	Excellent water
17	18.2	Excellent water
18	30.2	Excellent water
19	197.9	Poor water

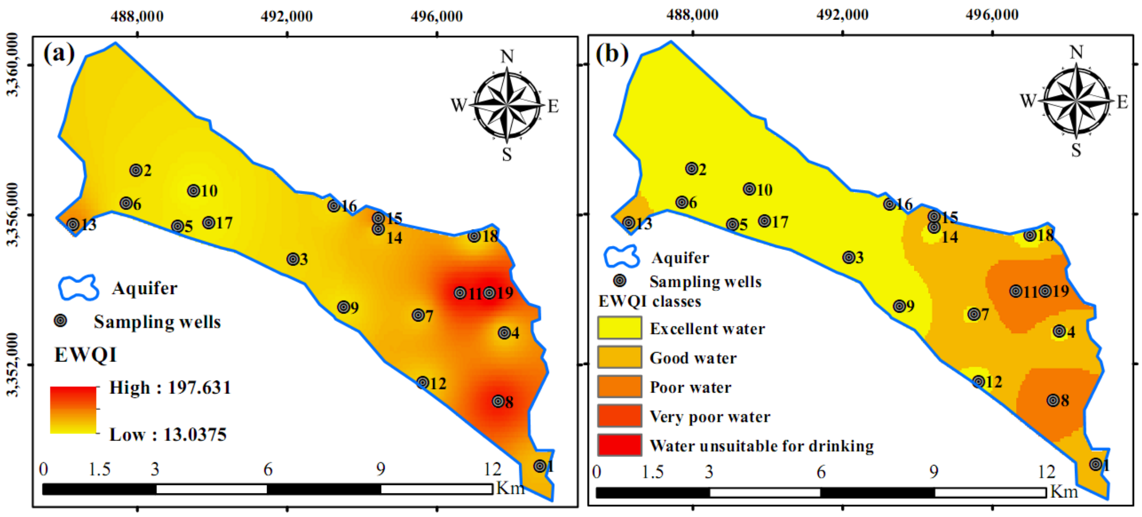

Figure 2. (**a**) Spatial distribution of EWQI score and (**b**) Classification of EWQI in the study area.

3.3. *Suitability of Groundwater for Irrigation*

3.3.1. The US Salinity Laboratory's Diagram and Sodium Percentage (Na%)

The SAR is a characterization of sodium hazards; it is an important parameter for determining the suitability of groundwater for irrigation purposes [1,57]. The rating of groundwater samples in relation to salinity hazard and sodium hazard can be explained by plotting the chemical data in a U.S. Salinity Laboratory (USSL) diagram. The plot of conductivity versus SAR in the Wilcox log diagram shows that out of the 19 samples, five samples fall in the medium salinity and low alkalinity (C2S1) category, which are suitable for irrigation purposes (Figure 3). Thirteen samples belong to the high salinity and low alkalinity (C3S1) category, which moderately fit irrigation purposes. This indicates that when using the water, attention should be paid on having proper drainage system and selecting proper crops that can tolerate salt, otherwise crops and soil may be damaged (Figure 3). Only one sample is categorized as very high salinity and low alkalinity (C4S1). Hence, this water is not suitable for irrigation.

The sodium percentage is an indicator to demonstrate the sodium hazard for irrigation purposes. Irrigation with a high Na content may deteriorate the soil structure and reduce its aeration and permeability, causing adverse impacts on crop growth. As shown in Figure 4, most of the groundwater samples fall in the excellent to good category, while well 13 (similar to the USSL), belongs to the unsuitable category for irrigation purposes.

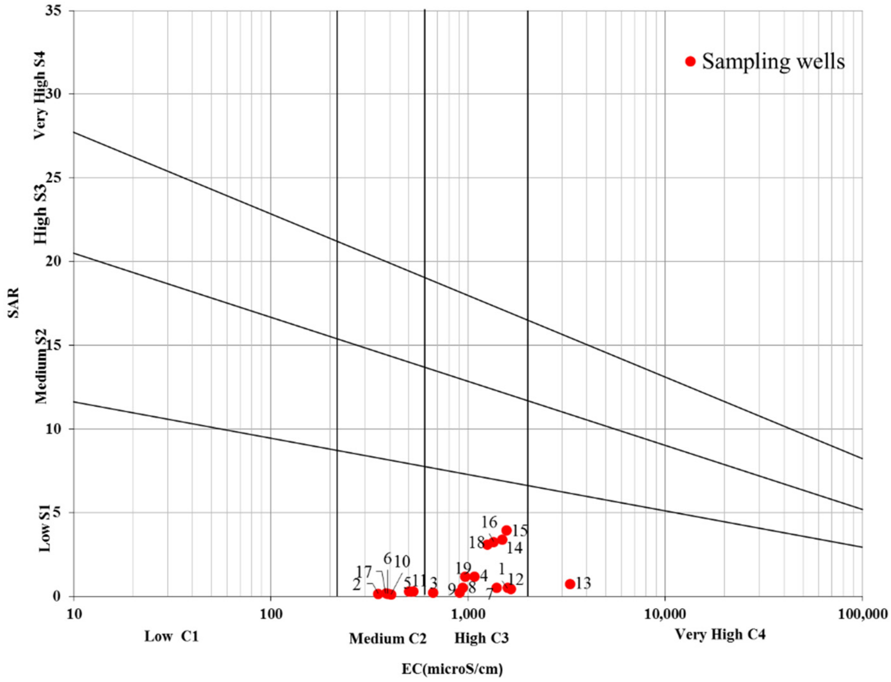

Figure 3. Wilcox log diagram of groundwater for the Imam Zadeh Jafar Aquifer.

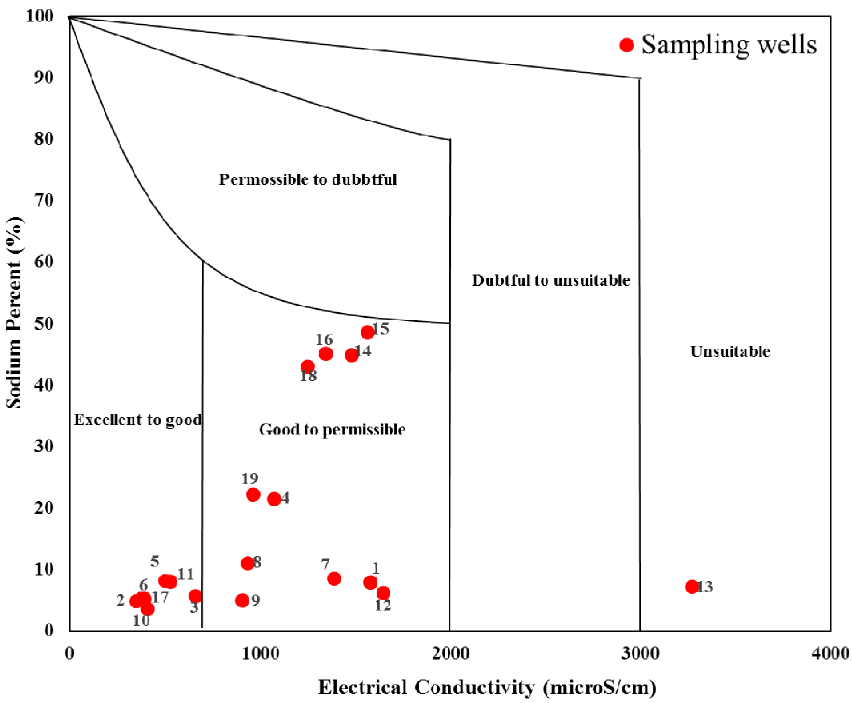

Figure 4. Rating of groundwater samples based on electrical conductivity (EC) and Na content.

3.3.2. Total Dissolved Solids (TDS)

A salinity problem exists if salt accumulates in the crop root zone to a concentration that causes a loss in yield. In irrigated areas, these salts often originate from a saline soil, high water table, or from salts in the applied water [58]. Yield reductions occur when salt accumulates in the root zone to such an extent that the crop is no longer able to extract sufficient water from the salty soil solution, resulting in a water stress for a significant period. If water uptake is reduced, the plant slows its rate of growth [59].

Groundwater in the study area shows a variation of TDS from 165 to 3440 mg/L. The spatial classification of TDS based on irrigation purposes is shown in Figure 5. Wells 12 and 13 are classified as unsuitable and questionable for irrigation, respectively. Wells 1, 2, 5, 6, 10, and 17 are classified as good to excellent. Other wells are classified as permissible for irrigation.

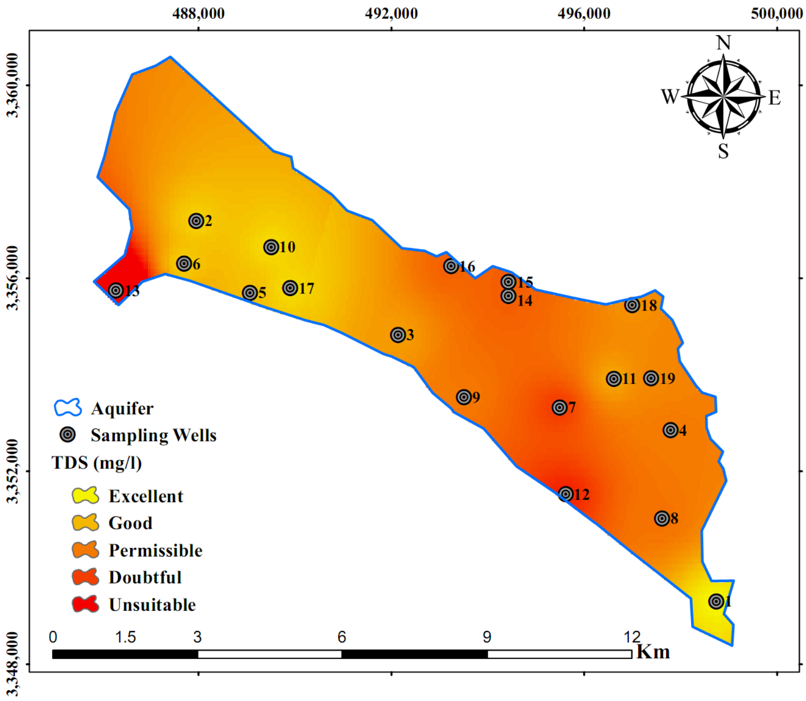

Figure 5. Spatial distribution of total dissolved solids (TDS) in the study area.

3.3.3. Permeability Index (PI)

Permeability index (PI) is an important parameter for groundwater use in agriculture. Sodium, bicarbonate, calcium, and magnesium concentrations in the soil may influence soil permeability [15]. In the study, the suitability of groundwater for irrigation based on PI was determined. This criterion categorizes the water into three classes. Based on the classification, water with PI > 75% (Class I) is good, 25–75% (Class II) is suitable, and PI < 25% (Class III) is unsuitable for irrigation [15]. As can be seen in Figure 6, all samples fall in Class I. This indicates that all wells are suitable for irrigation based on PI in the study area.

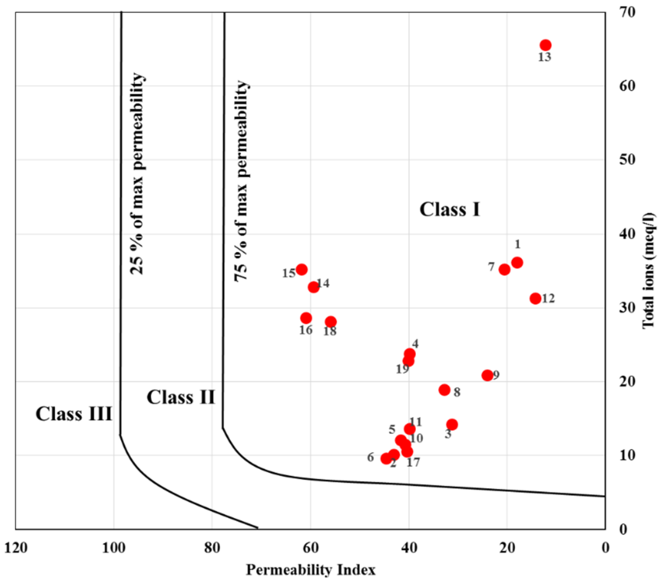

Figure 6. USSL Classification of irrigation water in study area, based on permeability index.

3.3.4. Total Hardness (TH)

Total hardness (TH) is caused primarily by the presence of cations such as calcium and magnesium and anions such as carbonate and bicarbonate [60]. The maximum permissible limit of TH for drinking purposes is 500 mg/L and the most desirable limit is 100 mg/L as per the WHO standard (2011). However, for irrigation purposes, up to 1000 mg/L of hardness is accepted [61].

Total hardness is commonly classified in terms of degree of hardness as (1) soft: 0–75 mg/L; (2) moderate: 75–150 mg/L; (3) hard: 150–300 mg/L; and very hard >300 mg/L. In the groundwater samples, TH varied from 225 to 2245 mg/L with an average of 551 mg/L. Figure 7 shows the spatial distribution of total hardness in the studied aquifer. As seen from the figure, TH in well 12 and 13 is classified as unacceptable for irrigation. In addition, the TH in wells 1 and 7 is more than 500 mg/L. A high level of TH in water can cause cardiovascular diseases, stunted growth, reproductive failure, and many more diseases due to the prevalence of magnesium and calcium in water [62].

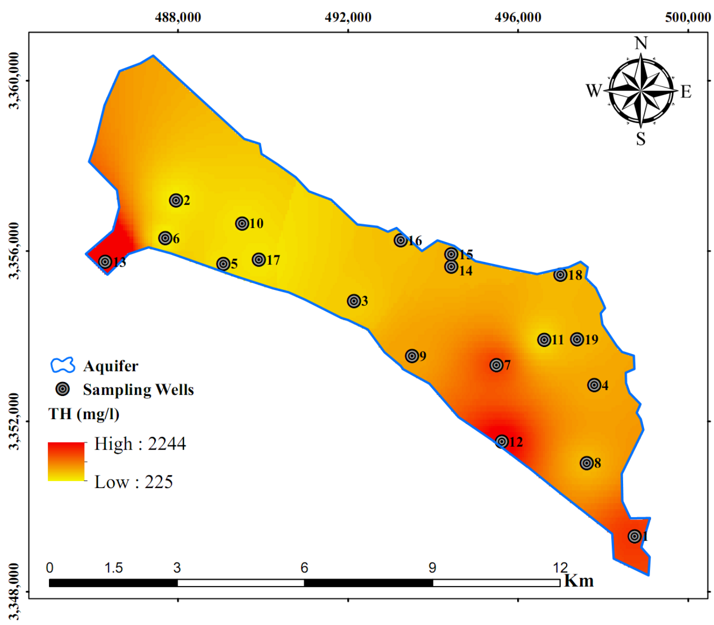

Figure 7. Total hardness (TH) in groundwater samples in study area.

3.3.5. Magnesium Ratio (MR)

Magnesium ratio is important for assessing suitability of water for irrigation. Magnesium damages soil structure when water contains a lot of sodium and high salinity [63]. If magnesium ratio exceeds 50, the water is considered to be harmful to crops and hence it is unsuitable for irrigation [64]. The residual Mg/Ca ratio [65] and the method established by Szabolcs and Darab (1964) [66] can be used to estimate the magnesium ratio (MR) for irrigation. According to this indicator, water with an MR greater than 50% is not suitable for irrigation [67]. The MR values obtained in this study ranged from 18 to 47%. This indicates that all wells are suitable for irrigation.

3.4. Heavy Metal Pollution Assessment

All m-HPI, HEI, NeI, and ERI indices were used to evaluate heavy metal pollution in groundwater samples for the study area. The values and spatial distribution of indices are presented in Table 5 and Figure 8, respectively. Heavy metal pollution evaluated by m-HPI method indicated more serious contamination than that of EWQI method. The values of m-HPI based on PI were in the range of 0–4.78 in the study area (Figure 8a). Based on the m-HPI water quality scale, nearly 16% of the samples were unacceptable for drinking whereas approximately 5–52% of samples were ranked as excellent to very good in the study area. The worst pollution status was recorded for wells 8, 11, and 19, which are in the eastern part of the area. The high m-HPI may be due to wastewater from industrial activities and domestic sewage. The m-HPI values of the samples in the western part of the study area were found below the critical pollution index (excellent to very good).

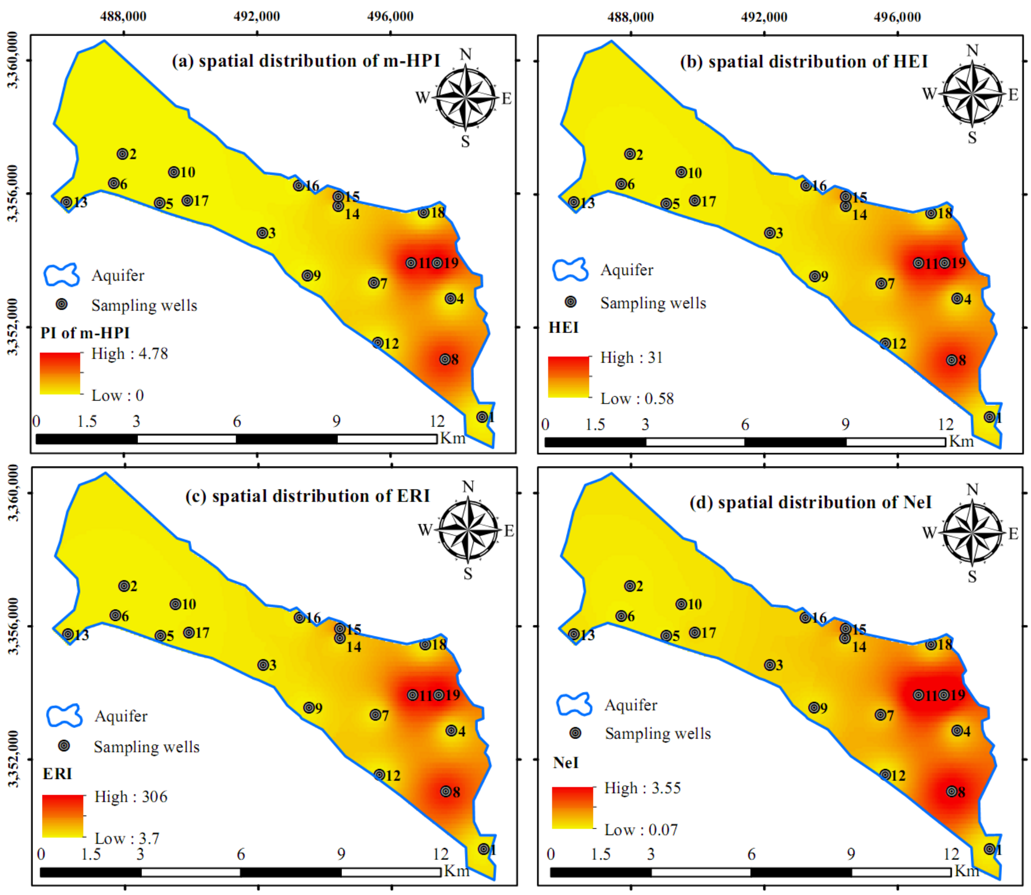

Figure 8. Spatial distribution of heavy metal indices: (**a**) modified heavy metal pollution index (m-HPI); (**b**) heavy metal evaluation index (HEI); (**c**) ecological risks of heavy metals (ERI) (**d**) negative index (NI) in the study area.

Table 5. Pollution evaluation indices of well water samples in the study area.

Well Number	m-HPI	PI	NI (m-HPI)	Classification	HEI	Classification	NeI	Classification	ERI	Classification
1	−0.92	0.000	−0.92	Excellent	0.68	Low	0.07	Insignificant	5.94	Low
2	−0.93	0.000	−0.93	Excellent	0.83	Low	0.13	Insignificant	5.93	Low
3	−0.86	0.009	−0.87	Very good	1.62	Low	0.39	Insignificant	14.78	Low
4	−0.84	0.003	−0.84	Very good	1.74	Low	0.37	Insignificant	16.10	Low
5	−0.95	0.000	−0.95	Excellent	0.57	Low	0.08	Insignificant	4.33	Low
6	−0.89	0.000	−0.89	Excellent	0.88	Low	0.09	Insignificant	6.82	Low
7	−0.67	0.052	−0.73	Very good	2.61	Low	0.47	Insignificant	23.76	Low
8	3.31	3.692	−0.38	Unacceptable	25.00	High	2.82	Moderately	248.49	Considerable
9	−0.91	0.000	−0.91	Excellent	1.02	Low	0.19	Insignificant	8.62	Low
10	−0.93	0.000	−0.93	Excellent	1.08	Low	0.19	Insignificant	7.83	Low
11	3.88	4.324	−0.44	Unacceptable	28.07	High	3.25	Moderate	279.84	Considerable
12	−0.91	0.000	−0.91	Excellent	0.99	Low	0.12	Insignificant	7.34	Low
13	−0.86	0.000	−0.86	Excellent	1.95	Low	0.24	Insignificant	13.14	Low
14	−0.88	0.000	−0.88	Excellent	1.10	Low	0.16	Insignificant	9.90	Low
15	1.09	1.496	−0.41	Good	12.13	Medium	1.35	Slight	120.32	Moderate
16	−0.87	0.002	−0.87	Very good	1.44	Low	0.36	Insignificant	13.35	Low
17	−0.90	0.000	−0.90	Excellent	1.66	Low	0.32	Insignificant	11.44	Low
18	−0.83	0.002	−0.83	Very good	1.69	Low	0.36	Insignificant	15.81	Low
19	4.38	4.787	−0.41	Unacceptable	31.14	High	3.56	Moderate	308.54	Considerable

Additionally, the HEI, NeI, and ERI indices were used for a better understanding of the pollution status. The HEI, and NeI values ranged from 0.58 to 31 and 0.07 to 3.55 with mean of 6.11 and 0.76, respectively (Figure 8b,d). Based on water quality classification of HEI, approximately 79%, 16%, and 5% of sampling wells were classified as low, medium, and high heavy metal pollution, respectively. Based on the NeI index, one, three, and fifteen wells were categorized as slight, moderate, and insignificant heavy metal pollution, respectively.

The potential ecological risk of groundwater in the study area in terms of ecosystem services was assessed using the ERI method. The ERI values of the study area varied from 4 to 308 with a mean of 59 (Figure 8c). Like the HEI index, about 79% of sampling wells from the area were found to expose low ecological risk to the groundwater system. However, the other samples were classified in the category of moderate to considerable ecological risks. Due to higher occurrence and biological toxicity, Cd and Sb were the dominant contributors to the risk with an average contribution of nearly 91% and 6%, respectively.

The spatial distribution of each heavy metal is depicted in Figure 9. It shows that higher concentration of Cd occurred in wells 8, 11, and 19, with 0.024, 0.027, and 0.030 mg/L, respectively, which are used as agricultural, industrial, and drinking purposes, respectively (Figure 9b). The permissible limit of Cd for drinking purposes is 0.003 mg/L based on WHO standards (2011). These areas are contaminated with sewage water as well as industrial effluents. Exposure to high concentration of Cd may cause liver and kidney damage as well as producing acute health effects [68,69].

Furthermore, high concentration of Sb is exhibited in wells 3 and 4 with agricultural use and in wells 16 and 18 with drinking water use that is much higher than 0.02 mg/L, which is the permissible limit of Sb for drinking purposes as recommended by WHO (2011). However, the highest Se concentration was found in well 7 with 0.013 mg/L, which is used for agricultural purposes, while the permissible limit for drinking purposes is 0.01 mg/L. Although all wells 3, 4, 7, 16, and 18 based on WQI, m-HPI, HEI, NeI, and ERI indices are classified as excellent, very good, low, insignificant, and low, respectively, the concentration of Sb and Se was above the permissible limits for drinking purposes. Antimony is a dangerous substance with chronic toxicity and potential carcinogenicity [70]. Sb poisoning can cause liver cirrhosis, muscle necrosis, nephritis, and pancreatitis. According to this fact, monitoring the concentration of these heavy metals is an essential measure to protect residents who use these sources of groundwater.

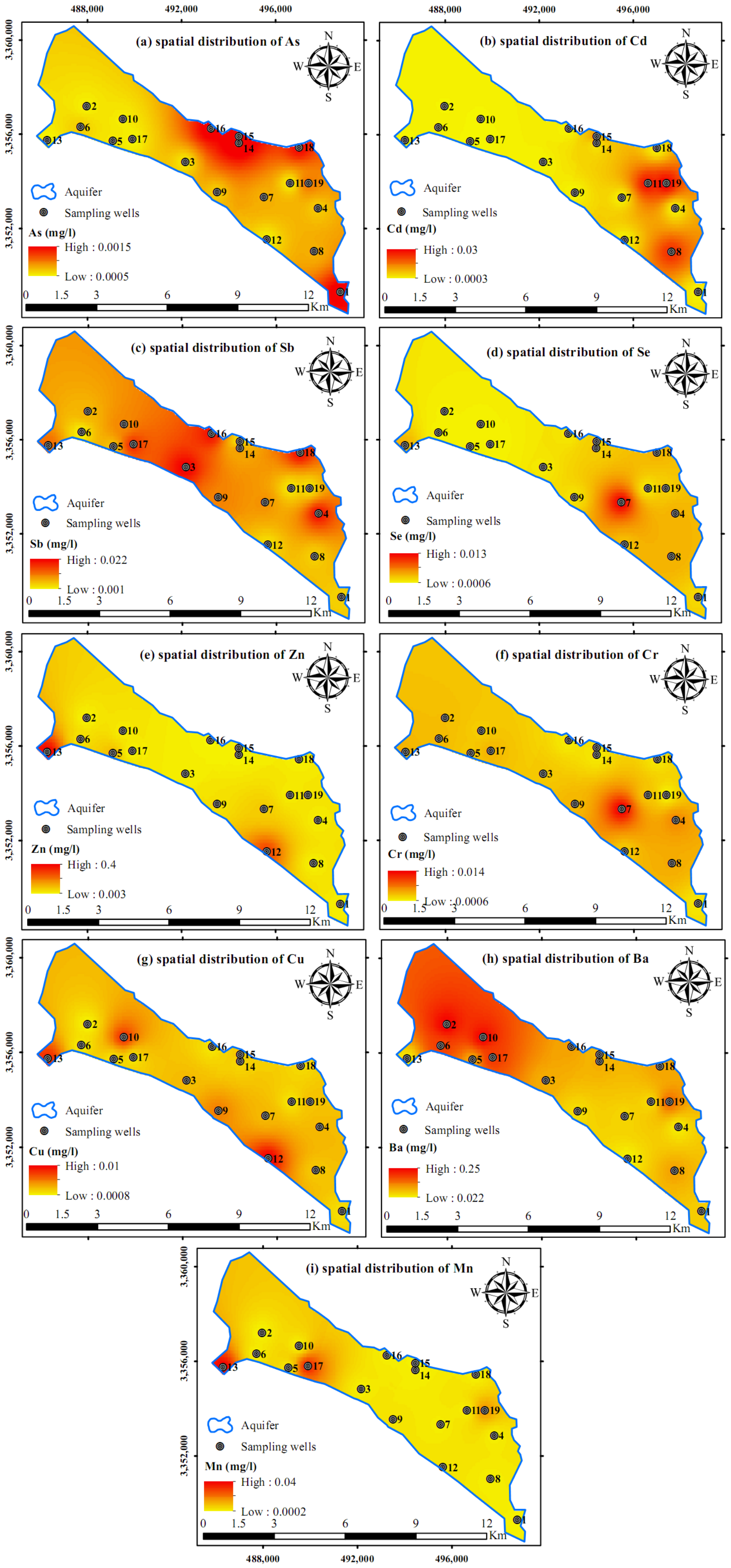

Figure 9. Spatial distribution of heavy metals for samples collected in the study area.

4. Conclusions

In this study, an innovative method involving entropy weighted groundwater quality index for both physicochemical and heavy metal content was used for a semiarid region. Using this index, the suitability of the groundwater for drinking and irrigation purposes was assessed for the Imam Zadeh Jafar Aquifer in southwestern Iran. We used the entropy method for assigning weights to water quality parameters in the WQI calculation to prevent subjectivity. This provides more reliability for the final output from the WQI. The entropy weights showed that concentration of Cd plays a substantial role in affecting the groundwater quality. Based on the EWQI, well 8, 11, and 19 were classified as poor water, while other wells were classified as excellent for drinking purposes.

Regarding water quality for irrigation, EC and SAR results reveal that all samples except for well 13 fall in C3S1 followed by C2S1 category. This denotes that the water is well suited for irrigation. However, MR and PI outcomes indicate that all samples are suitable for irrigation purposes. The results of TDS and TH show that well 12 and 13 are unsuitable for irrigation.

Heavy metal pollution indices, m-HPI, HEI, NeI, and ERI, showed that a majority of investigated wells have medium level of pollution in the study area. However, the values of these four indices in most parts of the area were below the critical levels. Wells 8, 11, and 19, are classified as unsuitable for drinking purposes due to an excessive amount of Cd. Additionally, well 7 was polluted by Se, while concentration of Sb in wells 3, 4, 16, and 18 showed higher than the permissible limits. According to the results, the regional groundwater system is most likely impacted by anthropologic and industrial activities in the area. Heavy metal pollution indices showed reliability in characterizing the groundwater pollution with respect to heavy metals. Entropy weights helped with avoiding personal judgement in calculating the weights in all stages that could lead to more transparency and reliability of the results. However, continuous monitoring of groundwater quality with respect to heavy metals is needed. Monitoring is especially important here due to a sharp increase in population.

The current study shed light on a potentially vital problem. Groundwater is under pressure in many parts of the world, especially in arid and semiarid regions. It is important to develop methods that reduce the complexity of data to clearly understandable numbers that managers and decision makers can readily use. Evaluating performance of remediation technologies is beyond the scope of this paper. However, this study can help with further planning of potential future remediation measures. Besides remediation measures, regulative processes are important to develop, especially in the developing world. However, this study may be used as a basis for further managerial actions in the field.

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