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Research article

ASSESSING THE EFFECT OF HEAVY METAL CONCENTRATIONS (Fe, Pb, Zn, Ni, Cd, As, Cu, Cr) ON THE QUALITY OF ADJACENT GROUNDWATER RESOURCES OF KHORASAN STEEL COMPLEX

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ABSTRACT: Khorasan Steel Complex is in the north-east of Iran, located at a distance of 15 kilometers in the north-west of the Neyshabur city. The plant's annual steel production capacity is approximately 1.7 million tons and has annual production capacity of at least 420,000 tons of the slag as a by-product. According to Khorasan Steel Complex slag and dust composition, it has the potential of increasing environmental contaminants in the Neyshabur plain. In this study, eight heavy metal concentrations including Fe, Pb, Zn, Ni, Cd, As, Cu, Cr which have been detected in dust and slag, were measured in the selected samples of the complex adjacent groundwater resources. Then by using quality indices based on heavy metals, Cd, HEI and HPI, the impact on the quality of groundwater resources surrounding of the complex were measured and evaluated. Water samples were analyzed by atomic absorption spectrophotometry and the slag and dust samples were analyzed using X-ray fluorescence spectroscopy. The results show that the metal pollution of groundwater resources in the study area is much less than the threshold risk, but if the proper approaches are not taken to recycling the stored slag and dust, it is possible that over time and with increasing in concentrations of these elements in ground water, we have the environmental problems in the mentioned area.

Keywords: Heavy Metals, Ground Water, Khorasan Steel Complex, Heavy Metal Indices

INTRODUCTION

Nowadays, throughout the world, heavy metals have been taken into consideration due to their toxic effects even at low concentrations [6]. Heavy metals are considered as potential contaminants in the environment and excessive amounts of them which entering into a food source, can cause problems for human health [1]. These metals are toxic for living organisms and are stable in the environment and tend to accumulate in the tissues of plants and animals [3]. Industrialization, urbanization, agriculture and exploitation of natural resources (mining and energy exploration), are basic activities associated with living in contemporary societies that enter metals into natural cycles such as of water, soil and air cycles [9]. Among the cycles of nature, water cycle due to the dynamism and constant contact with soil and atmosphere is more exposed to the pollution. Water quality index (WQI) does not give the overall picture on the water quality just by itself [5], in this regard different indices were used to assess heavy metal pollution of water resources. Three indices of water quality including, Cd (Contamination Degree), HPI (Heavy Metal Pollution Index) and HEI (Heavy Metal Evaluation Index) were evaluated for water samples in this article. In this research a part of the Neyshabur plain has been studied that is in the possible influence of Khorasan Steel Complex environmental impacts. Khorasan Steel Complex is known as the largest integrated steelmaking plant in east of the country, Iran. Given that beside generation of iron and steel, different by-products such as slag, dust, sludge, metal shell and oxide layers are produced and these materials are depot in adjacent of the plant, this is likely to have an impact on water resources in the region.

Among these by-products, slag due to the greater volume of production, is more important and according to the volume of slag which stockpiled at the plant (about 4 million ton), the possibility of increasing toxic metal elements in water resources has elevated and has created many environmental concerns for the region. However, in the addition of slag, dust depot, due to being high in zinc and iron and also because of the physical conditions (light and fine particle size) can affect the environment.

MATERIALS AND METHODS

Geology of the study area

The study area is in the north-east of Iran and is located in the central part of Khorasan Razavi Province. Khorasan Steel Complex is located in Neyshabur's west plains catchment, at a distance of 15 km from the Neyshabur city. In terms of geographical location, it is within an area of 58 42´ E longitude and 36 21´ N latitude (Figure 1). Neyshabur plain is one of the most important plains of agricultural development and population density of Khorasan Razavi Province. The annual groundwater discharge of the plain aquifer is about 1.2 billion cubic meters. Neyshabur Plain groundwater resources includes 2396 deep and half deep wells, 908 springs and 832 qanats with various uses in agriculture, domestic, industrial and livestock. Existing wells in the study area have high depth water tables which are located at a depth of 120 meters in some cases. This makes it be less vulnerable to the impact of the contaminants. According to geological characteristics, Khorasan Steel Complex is located in south of Binalud highlands which is a part of eastern Alborz section. In the heights of Binalud, units are mostly including evaporite minerals and marl. Degradation product of these units are floodplain coarse sediment of present covenant that start from north parts of Steel Complex and continue to the central parts of Neyshabur plain and at the end gradually turn into fine sediments in the central plain. The part of the unconfined aquifer that is composed in the alluvial plain of the Neyshabur, is the subject of this research. Geological map of the study area and location of sampling points relative to the complex are shown in Figure 1.

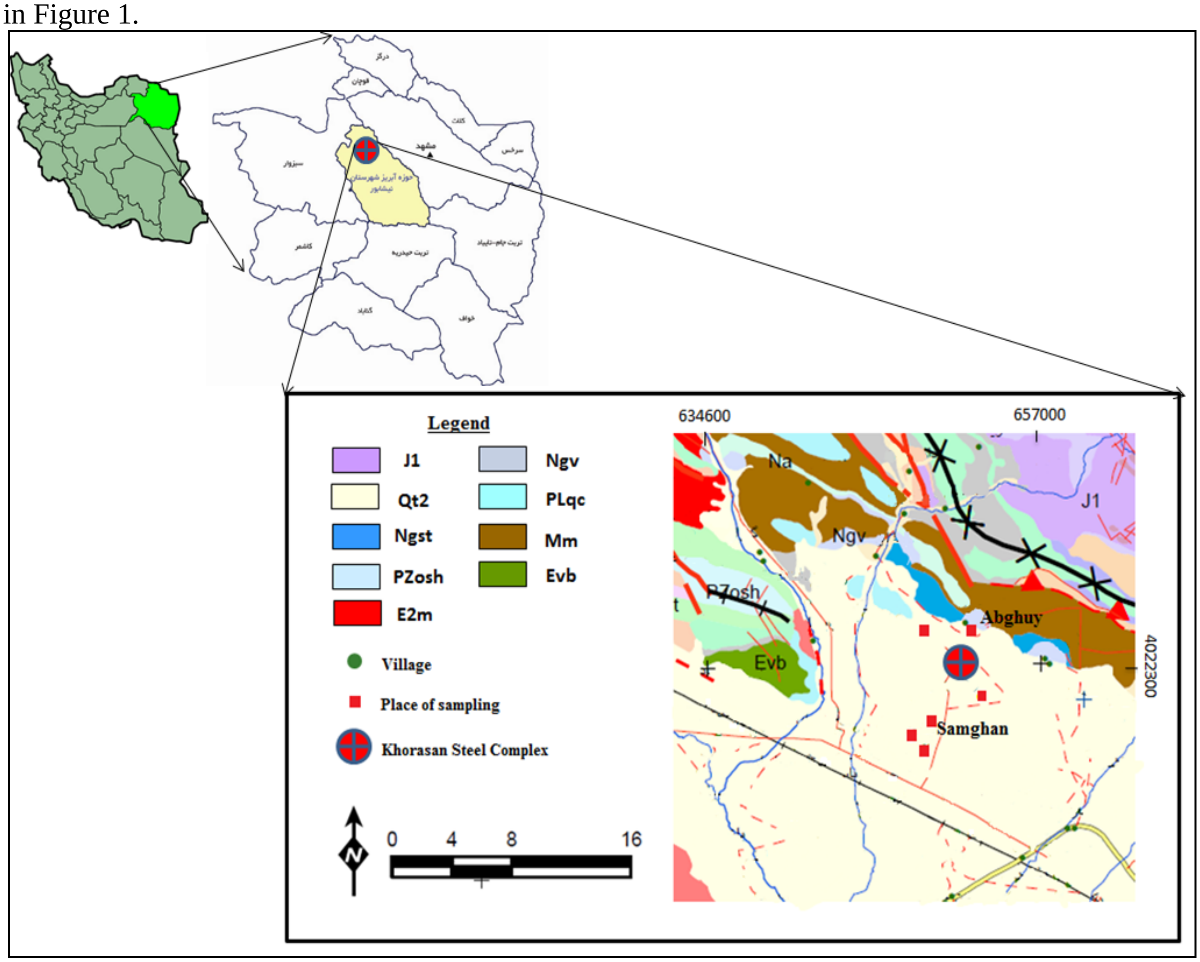

Fig 1. Geographical and geology of study area

In order to assess the heavy metal indices of the study area (surrounding areas of Khorasan Steel Complex), groundwater samples from various resources such as springs, wells and qanats were collected. Sampling from water resources of Abghuy village (located at 2 kilometer in upstream of the complex), Samghan village (located at 5.5 kilometer in downstream of complex) as well as existing wells on downstream lands of this complex was performed. Samples were collected based on Institute of Standards and Industrial Research of Iran, Standard 2347, for measuring parameters required in the calculations. To measure chemical parameters and heavy metals of each station, 250 ml of water was filtered, acidify and stored in polyethylene containers and then immediately transferred to the laboratory. It should be noted that separate samples were taken for analysis of chemical parameters and heavy metals.
To measure pH, temperature and electrical conductivity of the samples, respectively, during the sampling devices such as, thermometers, pH meters and EC meters were used (pH-meter- model E603 Metrohm, EC-meter GLP 32).
The other parameters were measured in the Water and Wastewater Laboratory for collected samples. For the measurement of heavy metals, 6 samples were transferred to laboratory equipped with (AAS), atomic absorption spectrophotometry device. To assess the contamination potential of the slag and dust and heavy metal emissions from storage area of Steel Complex, sampling and crushing (for slag samples) were done and then samples were transported to the laboratory for analysis using XRF (X-Ray Fluorescence). The results for 8 heavy metals (Fe, Pb, Zn, Ni, Cd, As, Cu, Cr) are presented in the table 2.

RESULTS AND DISCUSSION

Calculation of Water Quality Indices

To investigate the water quality, four indices were used individually in this study. Contamination Degree (Cd), Heavy Metal Pollution Index (HPI), Heavy Metal Evaluation Index (HEI) and Metal Index (MI) were calculated for the water samples of study area.

Contamination Degree (Cd)

In this index water samples are classified by calculating the degree of contamination in water samples [2]. Contamination degree by combining several parameters affecting water quality, investigates suitability of drinking water samples for domestic consumption. Contamination degree has to be calculated separately for each sample based on the exceeded parameters from standard values. Index is calculated by the following equation:

$$C_d \sum_{i=1}^{n} C_{fi}$$

Cfi in this regard can be obtained from the following equation:

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$$

Cfi: Contamination factor for the ith parameter
CAi: Measured value for the ith parameter,
CNi: Standard allowed value for the ith parameter,

In this study, the authors have used all measured heavy metals so that the contamination degree can be used for comparing with other indices. Although water samples with heavy metal concentrations below the permissible limit may not pose a threat to water quality but, the authors considers necessary to calculate the current condition of the water samples accurately and so, this makes it possible for future researchers to compare their results with the values of this investigation. To determine the quality of water samples by contamination degree, values are categorized into three groups, which include low contamination (Cd<1), moderate contamination (1<Cd<3) and high contamination (Cd>3). It should be noted that because this is the first study in the mentioned area, data are not normalized. To calculate this index, measured values of eight heavy metals such as Fe, Pb, Zn, Ni, Cd, As, Cu, Cr have been used. Calculated values of this index for the samples are presented in Table 5.

Heavy Metal Pollution Index (HPI)

This index was first suggested in 1996 that represents the overall quality of water which is based on heavy metals [11]. The index is calculated based on the weighting the parameters that the weight value is between zero and one, points the importance of the parameters. Weight of the samples can be considered as inversely proportional to the standard value for each element that have been calculated and considered for each parameter previously [10, 11, 12].

This index is calculated by the following equation:

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

Mi: Measured value for the ith parameter,
Ii: Ideal value for ith parameter,
Si: Standard value allowed for ith parameter,

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

Qi: Sub index calculated for the ith parameter,
Wi: weight assigned to the ith parameter
The calculated the index, weight and ideal values for the elements Fe, Pb, Zn, Ni, Cd, As, Cu, Cr are given in Table 1.

Table 1. Standard values, ideal values and weight of metals in the study area

Parameter	W	S	I	MAC	RV
Fe	0.005	300	200	200	50.0
Zn	0.0002	5000	3000	5000	5.0
Cu	0.001	1000	2000	1000	3.0
Pb	0.70	100	10	1.5	3.0
Cd	0.3	5	3	3	0.2
As	0.02	50	10	50	0.5
Cr	0.02	50	50	50	1
Ni	0.05	20	20	20	0.3

Water quality based on heavy metal pollution index can be divided into three categories including: low heavy metal pollution (HPI <100), heavy metal pollution on the threshold risk (HPI = 100) and high heavy metal pollution (HPI> 100) [11]. If the samples have heavy metal pollution index values greater than 100, water is not potable. Measured values of this index for the sample are presented in Table 5.

Heavy Metal Evaluation Index (HEI)

Heavy metal evaluation index is a way of estimating the water quality with focus on heavy metals in water samples [7]. The water quality index classify into three categories which include: low heavy metals (HEI <400), moderate to heavy metals (400 <HEI <800) and high heavy metals (HEI> 800). The index is calculated from the following equation:

$$HEI = \sum_{i=1}^{n} H_i / H_{mac},$$

Hi: Measured value for the ith parameter,
Hmac: Standard allowed value for ith parameter

Metal Index (MI)

This index expresses the overall quality of drinking water based on metal content like heavy metal evaluation index [13] and can be calculated by the following equation:

$$MI = \sum_{i=1}^{N} \frac{C_i}{(MAC)_i}$$

Ci: Measured value for the ith parameter,
MACi: Standard allowed value for ith parameter
According to this water quality index, water samples can be divided into three groups including: potable (MI <1), on the threshold of danger of drinking (MI = 1) and non-potable (MI> 1).

Both MI and HEI indices, measure with the use of the same equations, but the final classification varies. For the HEI index, the main problem related to the high amount defined for threshold risk (HEI = 400), which let the low and moderate contaminated samples to group with the high contaminated samples. In the case of index MI, that relies particularly on the quality of drinking water, classification considered less for a threshold risk (MI = 1).
It should be noted that the samples with lower metal index category are suitable for drinking but it is possible that a number of metals have enrichment in the water sample and with long-term usage it can create many problems for the human. Measured values of this index were similar to the HEI index values so are not recalculated. HEI index values are presented in Table 5.
The location of Khorasan Steel Complex within the north-west of Neyshabur plain, slag and dust position respect to the complex are shown in figure 2.

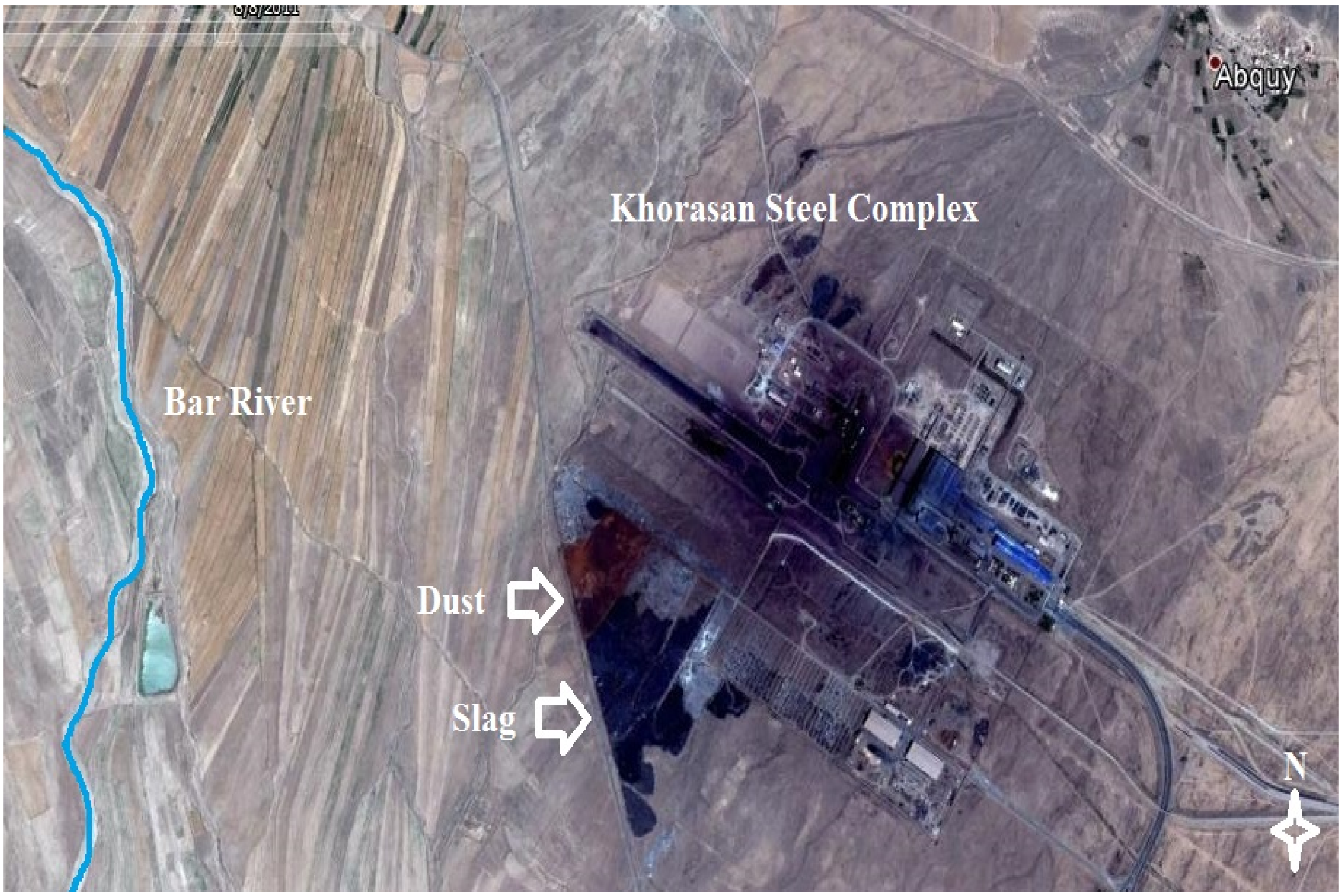

Fig 2. Khorasan Steel Complex and position of slag and dust

In order to examine the impact on groundwater resources in the surrounding areas of complex, slag and dust were analyzed and the values of eight heavy metals including Fe, Pb, Zn, Ni, Cd, As, Cu, Cr were measured and are given in Table 2.

Table 2. Analysis of the slag and dust for the elements Fe, Pb, Zn, Ni, Cd, As, Cu, Cr

ppm	Pb	Cu	Zn	Fe	Cd	As	Cr	Ni
slag	52	31	117	> 10%	0.28	3.7	142	23
dust	1182	331	14198	> 10%	21.7	17.3	157	40

The measured values for the eight metals with pH, temperature and electrical conductivity of the water samples taken at the stations shown in Figure 1, are listed in Table 3. To investigate how the distribution of the measured parameters in water samples is, descriptive statistical data are presented in Table 4.

Table 3. Parameters measured in water samples from the study area

No.	Fe	Zn	Cu	Pb	Cd	As	Cr	Ni	Temp	pH	E.C	Metal Load
Samp.1	83.0	6.2	2.0	1.19	0.23	4.03	4.32	1.6	11	7.97	4200	102.6
Samp.2	214.4	7.1	2.51	1.19	0.23	4.03	7.74	1.6	12	7.88	4850	238.83
Samp.3	175.4	7.5	2.66	1.449	0.23	4.25	16.12	1.6	12	7.6	5350	209.23
Samp.4	247.2	7.9	2.58	1.226	0.23	4.86	17.36	1.6	12	7.71	5100	282.98
Samp.5	531.0	8.3	9.90	1.586	1.12	5.41	25.88	2.36	13	7.9	14050	585.56
Samp.6	114.9	5.4	2.0	1.19	0.23	4.03	7.27	2.23	10	7.6	6050	137.28

According to the calculated values, all samples pH are slightly alkaline by the mean of (7.77) which can influence the presence of heavy metals in the water samples. In addition, the electrical conductivity of the water samples taken from the region is very high (6600 µS / cm) due to the presence of evaporite minerals such as marl in the highlands of the region. Average iron of the water samples (227 ppb) is near the standard level allowed for this metal (300 ppb) that reveal the importance of the iron element in environmental pollution of the area. Other elements have been measured in low doses.

Table 4 . Descriptive statistics for the water sample parameters of the study area

Parameter	Units	Min	Max	Mean	Median	Std. Deviation
Temp	C	10	13	11.67	12	1.03
pH	-	7.6	7.97	7.78	7.79	0.16
E.C	µS/cm	4200	14050	6600	5225	3699.73
Fe	ppb	83	531	227.6	194.9	160.59
Zn	ppb	5	8.3	7.10	7.3	1.09
Cu	ppb	2	9.9	3.61	2.54	3.1
Pb	ppb	1.19	1.59	1.31	1.21	0.17
Cd	ppb	0.23	1.12	0.38	0.23	0.36
As	ppb	4.03	5.41	4.43	4.14	0.58
Cr	ppb	4.32	25.88	13.11	11.93	8.13
Ni	ppb	1.6	2.36	1.83	1.6	0.36

Measured indices for the samples are given in Table 5. According to HPI, the maximum amount of heavy metal pollution in the samples is for Samghan village, located in 5.5 km downstream of the steel complex, with a value of (10.558) and the lowest heavy metal pollution index is for the sample of Abghuy village, located in 2 km upstream with the value (3.213). Mean value for HPI in the water samples, is (4.827) which is classified as low heavy metal pollution. According to HEI, the maximum estimated amount of metals in samples belongs to Samghan village sample (4.840) and the lowest value is for the Abghuy village (1.548). Based on this classification for this index, the average index for samples is (2.590) so water samples are estimating at low heavy metals level.
According to Cd, the highest degree of contamination is in the complex downstream village, Samghan (- 3.159) and the lowest degree of contamination has been determined for Abghuy village (- 6.209). The index average for the region is (- 5.409), which is classified as low degree of contamination class.

Table 5. Calculated indices for water examples of the study area

No.	HPI	Mean deviation	% deviation	HEI	Mean deviation	% deviation	Cd	Mean deviation	% deviation
Samp.1	3.213	- 1.614	- 33.44	1.548	- 1.042	- 40.23	- 6.451	- 1.042	- 19.264
Samp.2	3.569	- 1.258	- 26.06	2.274	- 0.316	- 12.20	- 5.725	- 0.316	- 5.842
Samp.3	4.022	- 0.805	- 16.68	2.418	- 0.172	- 6.64	- 5.582	- 0.173	- 3.198
Samp.4	4.059	- 0.768	- 15.91	2.665	0.075	2.89	- 5.335	0.074	1.368
Samp.5	10.558	5.731	118.73	4.840	2.25	86.87	- 3.159	2.25	41.597
Samp.6	3.541	- 1.286	- 26.64	1.798	- 0.792	- 30.57	- 6.209	- 0.8	- 14.79
Maximum	10.558			4.840			- 6.209		
Minimum	3.213			1.548			- 3.159		
Mean	4.827			2.590			- 5.409		

In order to investigate the relationships between measured parameters, the correlation matrix was drawn by the software SPSS-Version 20. Based on calculations performed at the 1% level, there is a direct correlation between the heavy metals including iron, copper and cadmium; So that any increase or decrease in each of them cause the other two elements to be affected. Besides, the three metals including iron, copper and cadmium have a direct and positive relationship with the electrical conductivity of water and are affected by this factor. The amount of zinc is directly related to the temperature and the amount of arsenic and chromium are directly relevant to each other. According to the relationship stated, calculated indices such as Cd, HEI and HPI were also directly affected by iron, copper, cadmium, and electrical conductivity. A case study approach was used for the classification of water based on metal content (mg / l) and the pH. This method was originally developed and presented in 1992 [8] and then was modified in 1999 [4].

Table 6. Correlation matrix for the measured parameters and calculated indices

	Fe	**Zn**	**Cu**	**Pb**	**Cd**	**As**	**Cr**	**Ni**	**Temp**	**pH**	**E.C**	**HPI**	**HEI**	**C_{deg}**
Fe	1													
Zn	.778	1												
Cu	$.952^{**}$	.624	1											
Pb	.782	.667	$.840^{*}$	1										
Cd	$.925^{**}$	.555	$.996^{**}$	.811	1									
As	$.916^{*}$	.794	$.855^{*}$	.711	$.830^{*}$	1								
Cr	$.889^{*}$	$.853^{*}$	$.815^{*}$	$.854^{*}$	.769	$.932^{**}$	1							
Ni	.550	-.057	.674	.466	.716	.467	.410	1						
Temp	$.812^{*}$	$.966^{**}$	.695	.705	.632	.737	.792	-.020	1					
pH	.277	.171	.349	.014	.375	.164	-.071	-.060	.340	1				
E.C	$.918^{**}$	.513	$.983^{**}$	$.819^{*}$	$.986^{**}$	$.823^{*}$	.789	.795	.573	.232	1			
HPI	$.952^{**}$	.622	$.998^{**}$	$.846^{*}$	$.994^{**}$	$.872^{*}$	$.835^{*}$	.695	.680	.301	$.988^{**}$	1		
HEI	$.993^{**}$	.777	$.964^{**}$	$.844^{*}$	$.937^{**}$	$.924^{**}$	$.921^{**}$	.570	.803	.220	$.936^{**}$	$.968^{**}$	1	
C_{deg}	$.993^{**}$	.777	$.964^{**}$	$.844^{*}$	$.937^{**}$	$.924^{**}$	$.921^{**}$	.570	.803	.220	$.936^{**}$	$.968^{**}$	1.000^{**}	1

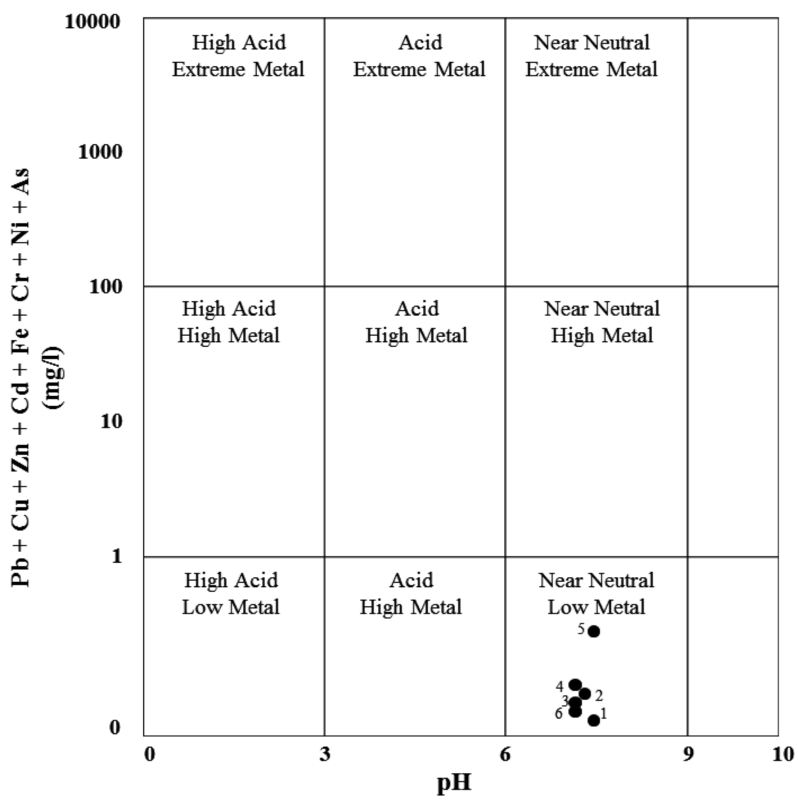

Figure 3. Diagram of water classification based on the metal content and pH

In this method, the metal content in the sample is calculated from the total amount of metal elements, in this study, it results of eight metals including Fe, Pb, Zn, Ni, Cd, As, Cu, Cr. The condition of 6 samples is shown in Figure 3. Based on the plot, 100% of samples classified as close to neutral pH and low metal content water.

CONCLUSIONS

In order to assess the impact of Khorasan Steel Complex activities on groundwater resources of adjacent plain, 6 groundwater samples were taken. Eight elements including Fe, Pb, Zn, Ni, Cd, As, Cu, Cr in the samples were measured and were used in calculating Cd, HEI and HPI indices. Based on the results, the maximum value for the indices were in the sample of downstream of complex (HPI = 10.558, HEI = 4.840, Cd = - 3.159) and the lowest indices were calculated for the sample in the complex upstream (HPI = 3.213, HEI = 1.548, Cd = -6.209). Heavy metal pollution is not observed in any cases. According to the water indices, water samples of the study area have been identified suitable for drinking but based on the correlation matrix, iron has a great role in the quality of water samples. Relying on the fact that the Khorasan Steel Complex is at the end of its first decade of operation and almost 4 million tons of slag and dust have been depot around the complex, and considering the fact that the water level in aquifer of the study area is over 100 meters and sufficient time has not passed away to increase pollutants in water resources, we can expect that over the time the impact of contaminants resulting from the plant would be more tangible. According to the point that long-term and continuous consumption of water resources containing heavy metals, will cause problems for human health, in this regard, it is recommended that more detailed examinations of the Khorasan Steel Complex activity be done on the water resources of the region by sampling alternatively.

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