Identification of groundwater contamination sources of Lakan lead and zinc mine, Khomain, Iran

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Abstract

Altogether 20 groundwater samples were collected around the Lakan Pb and Zn mine in Iran. Samples were analyzed for 8 constituents including Fe, Pb, Hg, Mn, Zn, CN, SO_4 and Cl using standard method. The results show that the average concentrations of constituents were 0.01, 0.60, 0.10, 0.01, 0.40, 35, 0.01 and 5.95 mg/kg for Fe, Mn, Pb, Zn, Hg, SO_4, CN and Cl, respectively. The computed contamination index ranged between 2.38 and 443. It was concluded that contamination index shows a medium to high contaminated situation for Pb and Hg in groundwater around the tailings dam. Based on a multivariate analysis, four main sources of these hydrochemical data were identified. (1) Zn, Mn, TDS and SO_4 have both natural and anthropogenic sources; (2) Hg constituent represents a natural source and Pb shows a anthropogenic source due to Lakan mine; (3) CN and Fe have an anthropogenic source and mainly originated from the plant processing; (4) Cl represents a natural source.

Keywords: *Contamination index, WHO standard, multivariate analysis, Lakan Pb and Zn mine, Iran.*

Introduction

Excessive release of heavy metals such as Zn, Pb, Hg, Mn, and so on, contaminate the surface water and subsurface environment and contribute to groundwater pollution. Groundwater is often seriously polluted near mines of sulfide minerals. Pyrite (FeS_2), Galena (PbS), Sphalerite (ZnS) or Arsenopyrite (FeAsS) materials, containing residual sulfide minerals, are piled up as tailings. Concomitantly, large amounts of heavy metals are released that remain soluble due to acid mine drainage generation [1, 2]. Groundwater as an important environmental indicator of hydrochemical contamination receives heavy metals from various stationary sources [3] such as industrial plants, mining activities and natural geochemical resources. Mining activities therefore, make a significant contribution to groundwater pollution. For most hydrochemical components (e.g. Pb, Zn, Cu, As, Hg and CN) anthropogenic sources contributes more to pollution than natural source [4, 5, 6].
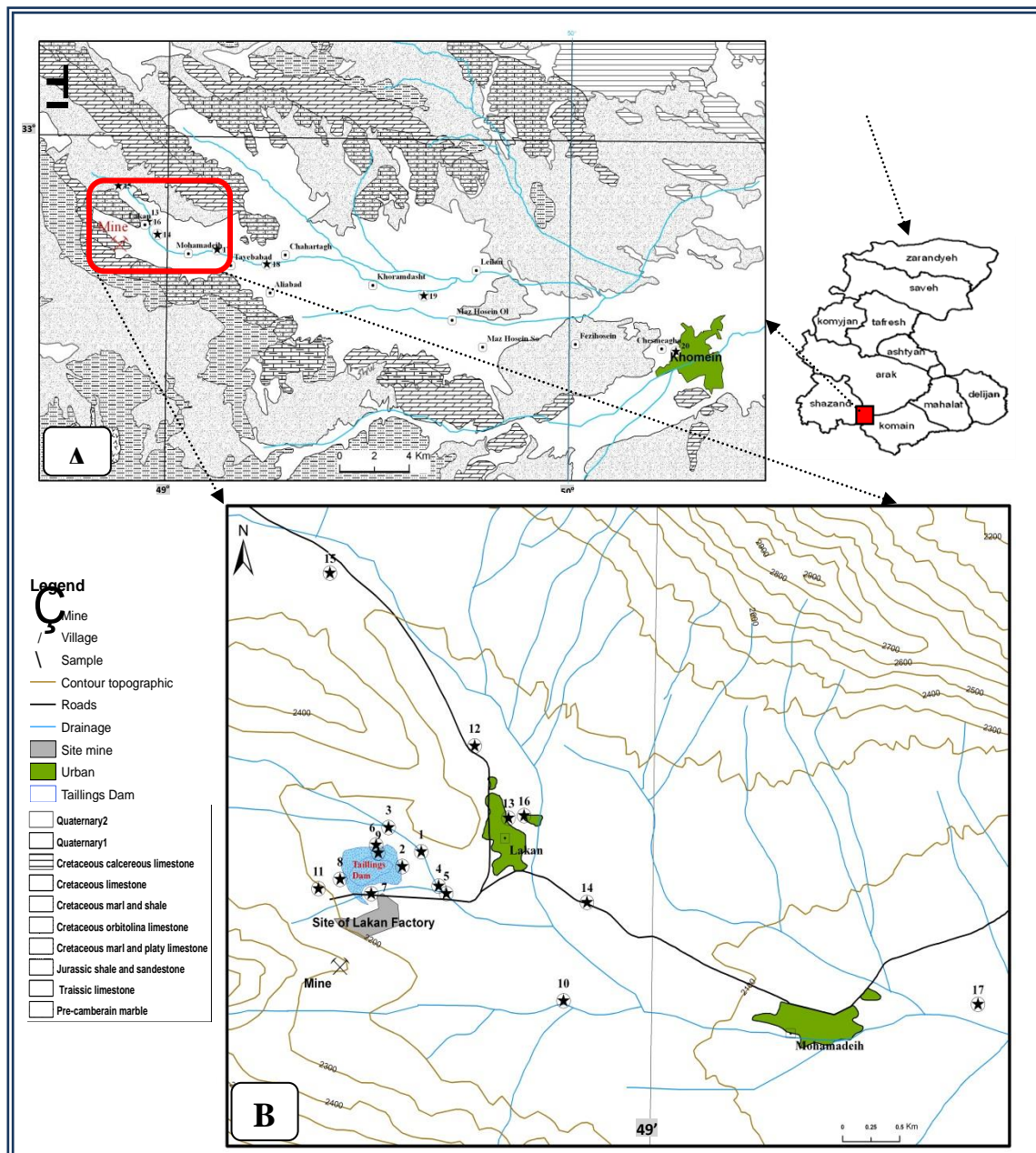
Lakan is a lead and zinc mine and industry. Mining activity and subsequent mineral processing operation has resulted in the release of substantial quantities of Pb, Cu, Zn and Cd to the mine environment [7].

The aims of this paper are (i) to analyze the total concentration of Fe, Pb, Hg, Mn, Zn, CN, Cl, TDS and SO_4 ions in the likely contaminated groundwater from a abandoned Pb–Zn mine located in Khomain, Iran; (ii) to carry out a preliminary assessment of groundwater pollution in the study area and (iii) to do a multivariate statistical analysis in order to examine the origin of hydrochemical components in groundwater.

2. Materials and methods
2.1. Hydrogeological setting of the study area
The study area is located near the city of Khomain, central Iran. The geological map of the study area is presented in Figure 1. The rocks of the area are composed of Cretaceous crystalline Limestone of the zone of the Sannandaj-Sirjan and low metamorphism rocks [8].

Figure 1. Geological map and sampling locations in the Lakan Pb and Zn mine
(A: 20 samples indicated in this map; B: 17 samples indicated in this map).

The shallow aquifer is developed into the Quaternary sediments. The bedrock of this formation is Cretaceous limestone. Groundwater drainage is observed to occur in westerly, while the aquifer is recharged by surface waters from the west and by lateral infiltration through carbonate rocks in the north and south of the region. Mining activities have started since 1990. During the operation period of the mine, mining wastes were discharged from the mine to 200 meters downstream in tailings site and directly to the main river which transported sulfides and trace elements to the groundwater. Groundwater was thus exposed to severe heavy metal pollution from the tailings materials.

2.2. Sampling and analytical methods
Twenty groundwater samples were collected around the Lakan Pb and Zn mine in February 2008 (Figure 1).pH was directly measured in the field using a pH-meter (PHH-65A model). Hydrochemical parameters of water samples including Fe, Pb, Hg, Mn, Zn, CN, Cl, TDS and SO_4 ions were measured by inductively coupled plasma mass spectrometer (ICP-MS) in the Uranium Conversion Facility Company (UCF). The results of the hydrochemical analyses are presented in Table 1.

2.3. Geoaccumulation index (Igeo)
The geoaccumulation index allows estimation of contamination comparing pre-mining and recent element concentrations. The geoaccumulation index is computed from the following Eq. 1:

$$Igeo = \log_2 (C_n/ 1.5B_n) \tag{1}$$

where, Cn is the measured concentration of the element in the groundwater sample and Bn denotes the permissible limit of World Health Organization (WHO) standard [9]. In the present work, geoaccumulation index was computed from the equation modified by Loska et al. (2004). Müller (1969) divided the geoaccumulation index into seven classes, they are [10]:
- Igeo≤ 0: practically uncontaminated
- 0< Igeo< 1: uncontaminated to moderately contaminated
- 1< Igeo< 2: moderately contaminated
- 2< Igeo< 3: moderately to heavily contaminated
- 3< Igeo< 4: heavily contaminated
- 4< Igeo< 5: heavily to extremely contaminated

- 5≤ Igeo: extremely contaminated

2.4. Contamination index
The quality of groundwater can be assessed by the use or calculation of environmental factors and indices, which include a wide range of parameters. Such factors may become a valuable tool for the assessment of environmental condition of an area. According to [13], contamination index (C_d) may be considered as such if the measured concentration of parameters and the upper permissible levels of a contaminant are taken into account. According to [13], contamination index is defined by Eq. 2 and Eq. 3:

$$C_d =\sum C_{fi} \tag{2}$$
$$C_{fi}=CA/ CN \tag{3}$$

where, C_d represents contamination index; C_{fi} denotes contamination factor, CA represents analytical value of the component and CN stands for upper permissible concentration of the component according to WHO (2011).Contamination index (C_d) is calculated individually for each water sample, as a sum of the contaminant factors of single component that exceed the maximum contaminant levels [14]. Hence, contamination index summarized the combinational effects of several quality parameters that may have harmful consequences to human health/the environment. The value scale for contamination index consists of 3 ranges; $C_d<1$ (low contamination), $1<C_d<3$ (medium contamination) and $C_d>3$ (high contamination) [6,15].

2.5. Statistical analysis
To identify the relationship among hydrochemical data in waters and their possible sources, correlation coefficient analysis, factor analysis (FA) and cluster analysis (CA) were performed using statistics software package (Statistica Version 8) [16]. The correlation coefficient measures the strength of inter-relationship between two hydrochemical data.

FA and CA are the most common multivariate statistical methods used in environmental studies [6, 17, 18].

FA has been widely used to reduce data and to a smaller number of independent factors (factor components) [19, 20]. FA started with a correlation matrix that describes the dispersion of the original variables and extracts the eigenvalues and eigenvectors [21]. An eigenvectors is a list of coefficients multiplying the original correlated variables to obtain new uncorrelated (orthogonal) factor analyses, which are weighted linear

combinations of the original variables. FA can reduce the number of correlated variables to a smaller set of orthogonal factor, making it easier to interpret a given multidimensional system by displaying the correlations among the original variables. FA and derivative methods have been widely applied to various environmental media, such as sediments [22, 23], soil [24] and water [25], to identify pollution sources.

CA classifies a set of observations into two or more mutually exclusive unknown groups based on combination of internal variables. CA is often coupled with FA to check results and to group individual parameters and variables [26]. The purpose of CA is to discover a system of organizing observations where a number of groups/variables share observed properties. A Dendrogram is the most commonly used method of summarizing hierarchical clustering. In the current study, CA was used to evaluate the sources similarities of hydrochemical data in waters.

Table 1 Hydrochemical analysis of water samples (concentrations are in mg/kg)

Sample No.	Fe	Mn	Pb	Zn	Hg	SO_4	CN	Cl	pH	TDS
1	0.68	0.12	0.03	0.04	1.5	36	0.034	0.34	8	57
2	0.50	0.09	0.14	0.6	0.8	57	0.019	0.03	8.1	47
3	0.29	0.06	0.01	0.01	1.1	16	0.028	0.01	8	31
4	0.12	0.06	0.05	0.15	0.1	234	0.019	6.10	8.1	229
5	0.18	0.10	0.21	0.86	4.4	338	0.032	7.60	6	425
6	0.26	0.06	0.09	0.31	1.8	70	0.014	0.62	7.8	99
7	0.01	0.38	0.08	2.78	0.2	333	0.010	8.70	8.5	470
8	0.08	0.14	0.19	0.84	1.3	287	0.010	11	8	380
9	0.01	0.01	0.01	0.01	1.1	25	0.010	2	8	144
10	0.01	0.52	0.14	0.68	0.6	236	0.008	5.80	8.2	346
11	0.03	0.01	0.01	0.01	0.8	26	0.010	1.90	8.2	182
12	0.01	0.37	0.08	2.79	1.50	307	0.006	6.70	8.4	473
13	0.01	0.01	0.10	0.01	0.01	10	0.048	2.80	7.8	164
14	0.01	0.01	0.10	0.01	0.01	23	0.010	11	7.4	276
15	0.01	0.01	0.10	0.01	0.01	8	0.010	2.20	7.7	147
16	0.01	0.01	0.10	0.01	0.01	12	0.010	6.90	7.7	199
17	0.01	0.01	0.10	0.01	0.01	19	0.010	5	7.9	200
18	0.01	0.01	0.10	0.01	0.01	35	0.010	9.50	7.5	263
19	0.01	0.01	0.10	0.01	0.01	31	0.010	12	7.7	230
20	0.01	0.01	0.10	0.01	0.01	200	0.010	52	7.5	476
Max.	0.68	0.52	0.21	2.79	1.40	338	0.048	52	8.5	476
Min.	0.01	0.01	0.01	0.01	0.01	8	0.006	0.01	6	31
Median	0.01	0.06	0.10	0.01	0.40	35	0.010	5.95	7.4	214
Reference value(WHO)*	0.3	0.05	0.015	5	0.002	250	0.05	250	-	-
Reference value(EPA)**	0.3	0.05	0.015	5	0.002	250	0.02	250	-	-
Reference value(IRAN)***	0.1	0.05	0.05	5	0.001	250	0.05	200	--	

3. Results and discussion
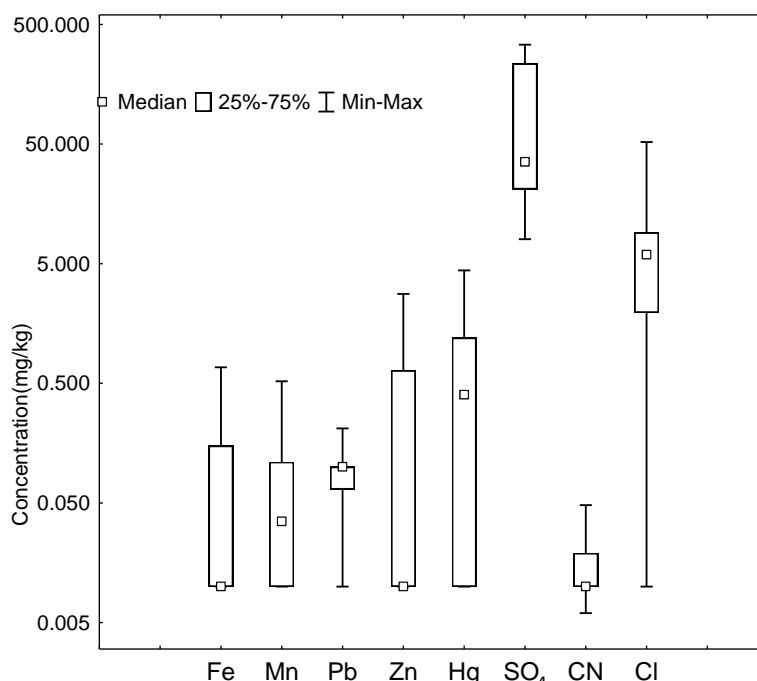### 3.1. Hydrochemical data
The level of the analyzed constituents in groundwater samples (Table 1) shows that in all the samples, Iron is low compared to the WHO standard limit in 18 locations (except samples 1 and 2).Manganese was found to be above the maximum permissible limit of WHO standard in only 10 locations. Lead exceeded the WHO standard limit in all the sampling locations (except samples 3, 9 and 11) while, Zinc, CN and Cl were found to be lower than the maximum permissible limit of WHO standard in all sampling locations. Mercury was found to be above the WHO standard limit in all the sampling locations. Sulfate ion was found to be within the WHO standard limit in all the sampling locations (except samples 5, 7, 8 and 12).

Figure 2 and Table 1 present the statistics of elemental constituents in groundwater of the study area. The result shows that the median concentrations of the examined parameters (Fe, Mn, Pb, Zn, Hg, SO$_4$, CN and Cl) were 0.01, 0.06, 0.1, 0.01, 0.40, 35, 0.01 and 5.95 mg/kg) respectively. Among the examined heavy metal constituents Pb, Hg and Mn show the highest mean while Fe and Zn remained the least. Between anions, sulfate ion recorded the highest value and Cl and CN are the least constituents.

High iron concentration is dominant in the groundwater samples around the tailings dam of Lakan Pb and Zn mine which is due to the local leachate from soils(samples 1 through 12) [27]. Investigations have also revealed excessive dissolved Pb and Hg concentrations in groundwater nearly 500 meter around and downstream the dam tailings dam (samples 1, 3, 5, 6, 9 and 12) (Figure 1).

Figure 2. Concentrations for constituents in groundwater samples around the Lakan Pb and Zn mine.

All samples display uncontaminated based on geoaccumulation index in Table 2 by Fe(except samples 1 and 2 are moderately contaminated); the samples in locations 3, 4, 6, 9, 11 and 13 through 20 are uncontaminated by Mn , samples 1, 2, 5, 7, 8, 10 and 12 are moderately contaminated; samples 4, 10 and 12 are uncontaminated by Pb and 17 other samples are moderately contaminated. All locations are uncontaminated by Zn, SO$_4$, CN and Cl and Hg shows a moderate contamination in all locations while location 5 is seriously contaminated. Based on box and whisker diagram (Figure 3), the study area is moderately contaminated by Pb and Hg but uncontaminated by Fe, Mn, Zn, SO$_4$, CN and Cl.

The computed contamination index (Table 3) for the sampling locations shows that samples 1 through 12 have the high contamination and samples 13 through 20 have high contamination by Fe, Mn, Pb, Zn and Hg as the contamination parameters (Figure 1 and Figure 4)[6].

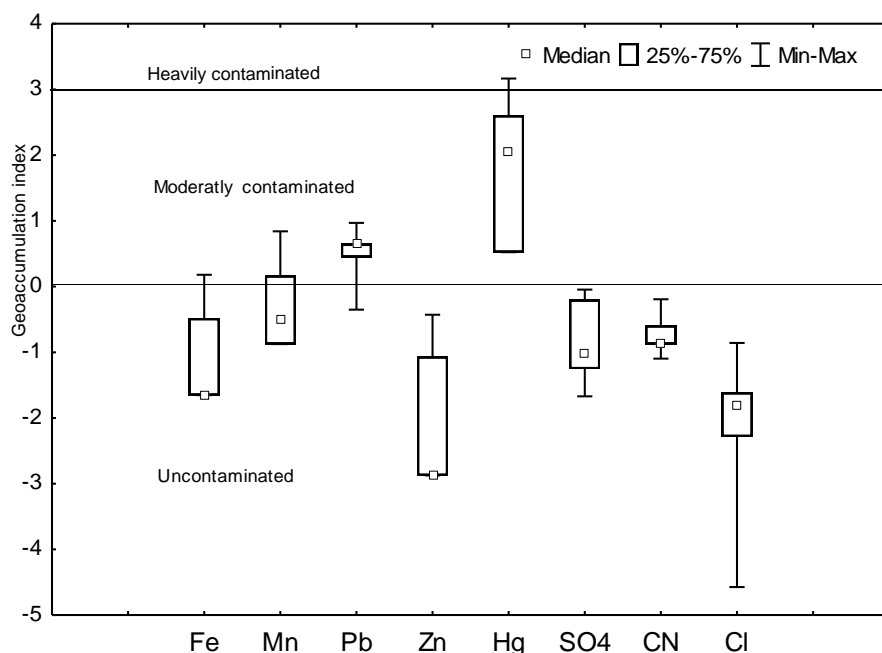### 3.2. Correlation coefficient analysis results

The correlation coefficients for hydrochemical data in the Lakan Pb and Zn mine are presented in Table 4. Inter-element relationships provide interesting information about the sources and pathways of the hydrochemical data. A significantly positive correlation at P< 0.05 was found between the hydrochemical data pairs Mn-Zn (0.762), Mn-SO$_4$(0.675), Zn-SO$_4$(0.746), Zn-TDS(0.623), SO$_4$-TDS(0.812), Cl-TDS(0.595) and Fe is also negatively correlated with TDS(-0.539) at P<0.05. These indicated that Mn-Zn, SO$_4$ and TDS were naturally derived from local rock unites [14]. Hg, Fe, Pb, and CN indicate moderately positive correlation and these show derived from anthropogenic sources (industrial or mineral processing in the vicinity of Lakan Pb and Zn mine) [14].

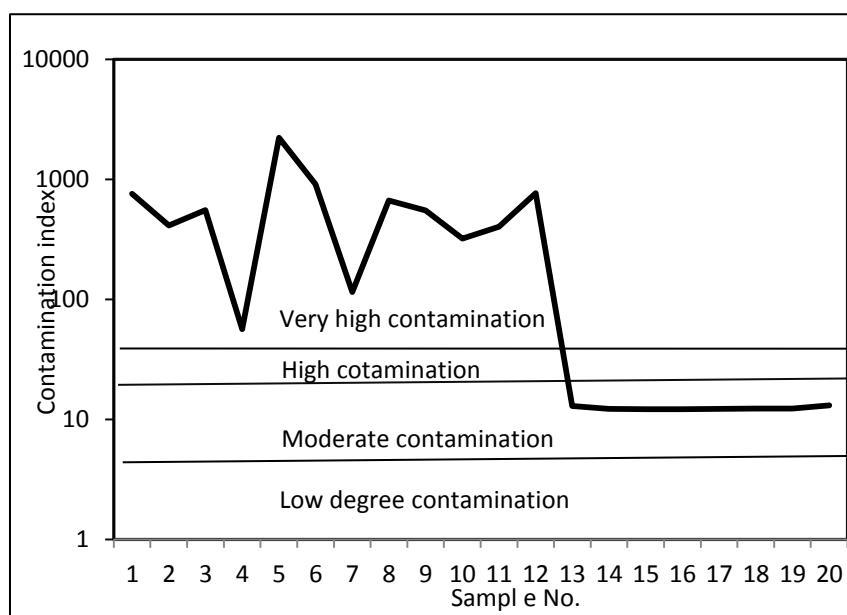**Table 2. Geoaccumulation index for constituents in groundwater samples around the Lakan Pb and Zn mine**

Sample No.	Fe	Mn	Pb	Zn	Hg	SO_4	CN	Cl
1	0.179	0.20	0.12	-2.27	2.7	-1.02	-0.34	-3.04
2	0.046	0.08	0.79	-1.10	2.43	-0.82	-0.60	-4.10
3	-0.19	-0.10	-0.4	-2.88	2.56	-1.37	-0.43	-4.57
4	-0.57	-0.10	0.35	-1.70	1.52	-0.20	-0.60	-1.79
5	-0.40	0.12	0.97	-0.94	3.17	-0.05	-0.37	-1.69
6	-0.24	-0.10	0.60	-1.38	2.78	-0.73	-0.73	-2.78
7	-1.65	0.70	0.55	-0.43	1.82	-0.05	-0.88	-1.63
8	-0.75	0.27	0.93	-0.95	2.64	-0.12	-0.88	-1.53
9	-1.65	-0.88	-0.4	-2.88	2.56	-1.18	-0.88	-2.27
10	-1.65	0.84	0.79	-1.04	2.30	-0.20	-0.97	-1.81
11	-1.18	-0.88	-0.4	-2.88	2.43	-1.16	-0.88	-2.30
12	-1.65	0.69	0.55	-0.43	2.70	-0.09	-1.10	-1.75
13	-1.65	-0.88	0.65	-2.88	0.52	-1.59	-0.19	-2.13
14	-1.65	-0.88	0.65	-2.88	0.52	-1.21	-0.88	-1.53
15	-1.65	-0.88	0.65	-2.88	0.52	-1.67	-0.88	-2.23
16	-1.65	-0.88	0.65	-2.88	0.52	-1.49	-0.88	-1.74
17	-1.65	-0.88	0.65	-2.88	0.52	-1.30	-0.88	-1.88
18	-1.65	-0.88	0.65	-2.88	0.52	-1.03	-0.88	-1.60
19	-1.65	-0.88	0.65	-2.88	0.52	-1.08	-0.88	-1.49
20	-1.65	-0.88	0.65	-2.88	0.52	-0.27	-0.88	-0.86

Table 3. Contamination factor (C_f) and contamination index (C_d) of groundwater samples around the Lakan Pb and Zn mine

Sampling No.	C_f					C_d	Conamination Index
	Fe	Mn	Pb	Zn	Hg		
1	2.27	2.4	2	0.008	750	151	High
2	1.67	1.8	9.33	0.12	400	82	High
3	0.97	1.2	0.67	0.002	550	110	High
4	0.4	1.2	3.33	0.03	50	11	High
5	0.6	2	14	0.172	2200	443	High
6	0.87	1.2	6	0.062	900	181	High
7	0.03	7.6	5.33	0.556	100	22	High
8	0.27	2.8	12.7	0.168	650	133	High
9	0.03	0.2	0.67	0.002	550	110	High
10	0.03	10.4	9.33	0.136	300	64	High
11	0.1	0.2	0.67	0.002	400	80	High
12	0.03	7.4	5.33	0.558	750	152	High
13	0.03	0.2	6.67	0.002	5	2.38	Medium
14	0.03	0.2	6.67	0.002	5	2.38	Medium
15	0.03	0.2	6.67	0.002	5	2.38	Medium
16	0.03	0.2	6.67	0.002	5	2.38	Medium
17	0.03	0.2	6.67	0.002	5	2.38	Medium
18	0.03	0.2	6.67	0.002	5	2.38	Medium
19	0.03	0.2	6.67	0.002	5	2.38	Medium
20	0.03	0.2	6.67	0.002	5	2.38	Medium

Figure 3 Geoaccumulation index for constituents in groundwater samples around the Lakan Pb and Zn mine.

Figure 4 Contamination index for groundwater samples around the Lakan Pb and Zn mine.

3.3. Multivariate statistical analysis results
3.3.1. Factor analysis results

FA was applied to identify sources of hydrochemical data in waters by applying varimax rotation. By extracting the eigenvalues and eigenvector from the correlation matrix, the number of significant factors and the percent of variance explained by each of them were calculated [20, 28]. Table 5 shows the results of the factor loadings with a varimax rotation, as well as the eigenvalues. The results indicate that there were four eigenvalues higher than one and

that these four factors explain 84.93% of the total variance. The first factor explains 40.14% of the total variance and loads heavily on Zn, Mn, SO_4 and TDS. Factor 2, dominated by Fe and CN, accounts for 23.29% of the total variance. Factor 3 is loaded by Cl, accounting for 13.90% of the total variance. Factor 4 is dominated by Pb and moderately by Hg, accounting for 7.60% of the total variance. The relations among the hydrochemical data based on the first and third factors are illustrated in Figure 5 in a two-dimensional space.

The factor scores were also estimated to find out the spatial variation of the factor representation and to identify the zone of its representation [17]. They are commonly obtained by weighted least square method. The positive zones indicate the dominance of that factor. The spatial representation for first factor with higher Mn, Zn, SO_4 and TDS related to samples 12, 7 and 10. Those are situated in the eastern part of the Lakan Pb and Zn mine, where the influence of both natural factors and anthropogenic activities (tailings dam) is preferably noted (Figure 6 and Figure 7). The s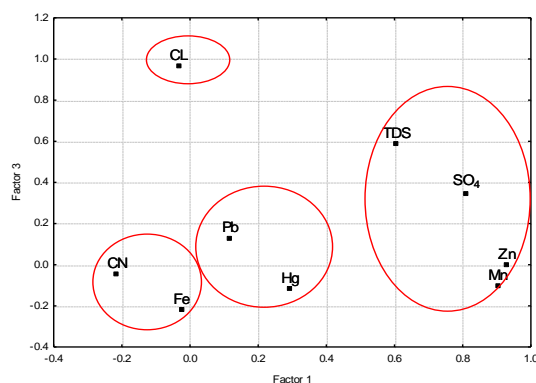patial representation of second factor (Fe and CN factor) in the samples 1, 5, 3, 2 and 6 are situated in the downstream the tailings dam (Figure 6 and Figure 7). They represent anthropogenic impact. The higher scores of third factor (Cl factor) in the samples 20 are situated away and in the eastern part of the Lakan Pb and Zn mine are represented in the regions of natural source. The spatial representation of forth factor (Pb and Hg factor) in the samples 5 and 8 are situated into and the downstream tailings dam (Figure 6 and Figure 7). They also represent anthropogenic impact.

Variable	Fe	Mn	Pb	Zn	Hg	SO$_4$	CN	Cl	TDS
Fe	1								
Mn	-0.031	1							
Pb	-.0109	0.198	1						
Zn	-0.106	0.762*	0.193	1					
Hg	0.385	0.165	0.322	0.244	1				
SO$_4$	-0.133	0.675*	0.462*	0.746*	0.430	1			
CN	0.486*	-0.199	-0.006	-0.213	0.319	-0.129	1		
Cl	-0.315	-0.083	0.201	-0.027	-0.206	0.288	-0.254	1	
TDS	-0.539*	0.496*	0.462*	0.623*	0.125	0.812*	0.354	0.595*	1

Table 4. Correlation matrix for hydrochemical data

Hydrochemical data	Factor				Variance (%)				
	Factor1	Factor2	Factor3	Factor4	Factor1	Factor2	Factor3	Factor4	Residual
Fe	-0.02	0.84*	-0.22	-0.16	0.04	70.56	4.84	2.56	22.00
Mn	0.90*	-0.07	-0.11	0.03	81	0.49	1.21	0.09	17.21
Pb	0.12	-0.05	0.13	0.92*	1.44	0.25	1.69	84.64	11.98
Zn	0.93*	-0.07	-0.01	0.07	86.49	0.79	0.01	0.49	12.52
Hg	0.29	0.41	-0.12	0.52*	8.41	16.81	1.44	27.04	46.3
SO$_4$	0.81	0.05	0.35	0.38	65.61	0.25	12.25	14.44	7.45
CN	-0.21	0.79*	-0.05	0.06	4.41	62.41	0.25	0.36	32.57
Cl	-0.03	-0.19	0.96*	0.05	0.09	3.61	92.16	0.25	3.89
TDS	0.60*	-0.33	0.48	0.37	36	10.89	23.04	13.69	16.38
% of variance explained	40.14	23.29	13.90	7.61					
% of cumulative variance explained	40.14	63.43	77.33	84.93					

Table 5. Rotated factor matrix for hydrochemical data of the Lakan Pb and Zn mine

Figure 5. FA results in the two-dimensional space, plot of loading of the first and third factor
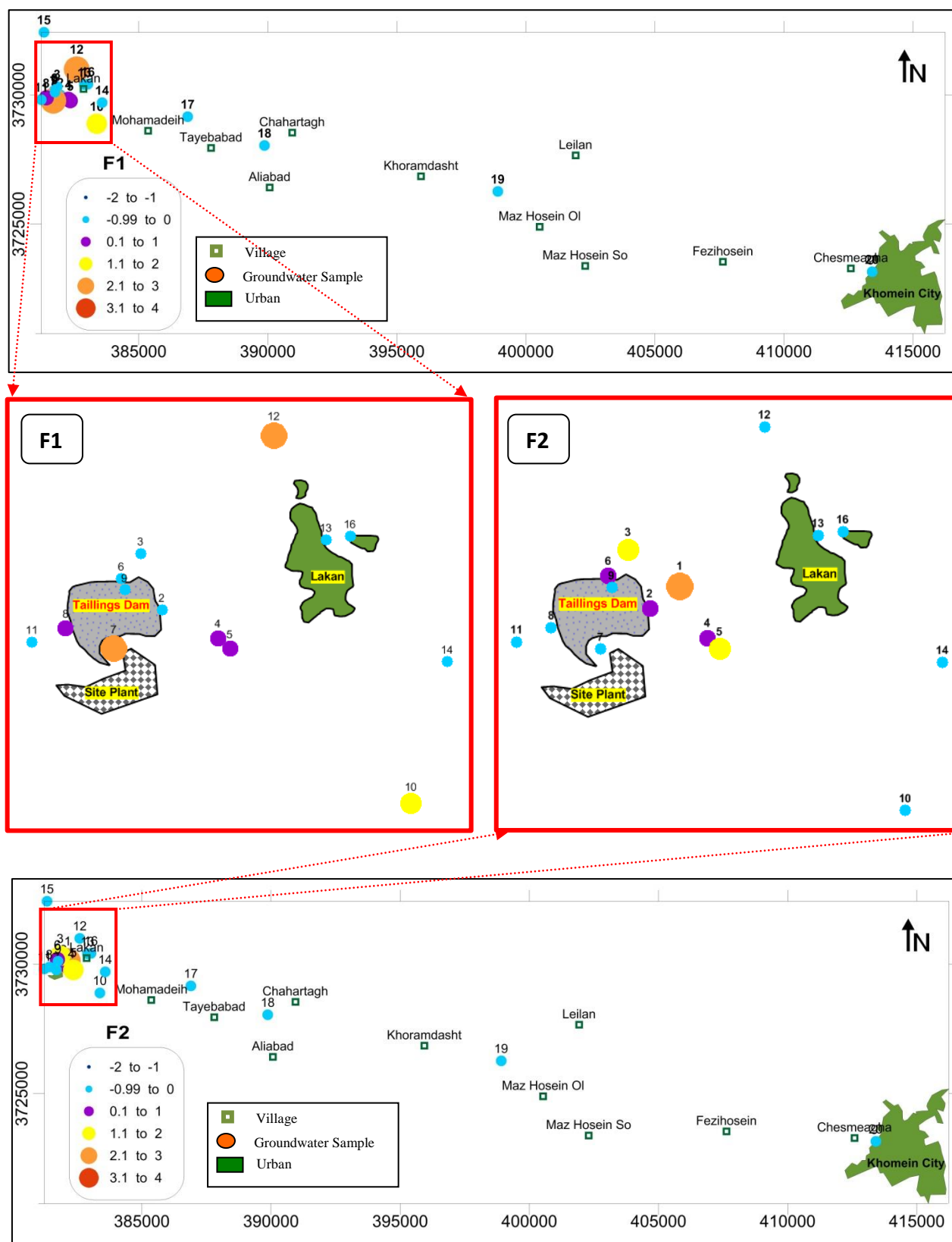
Figure 6. Geographical distribution of the factor scores (F1 and F2) in the study area.
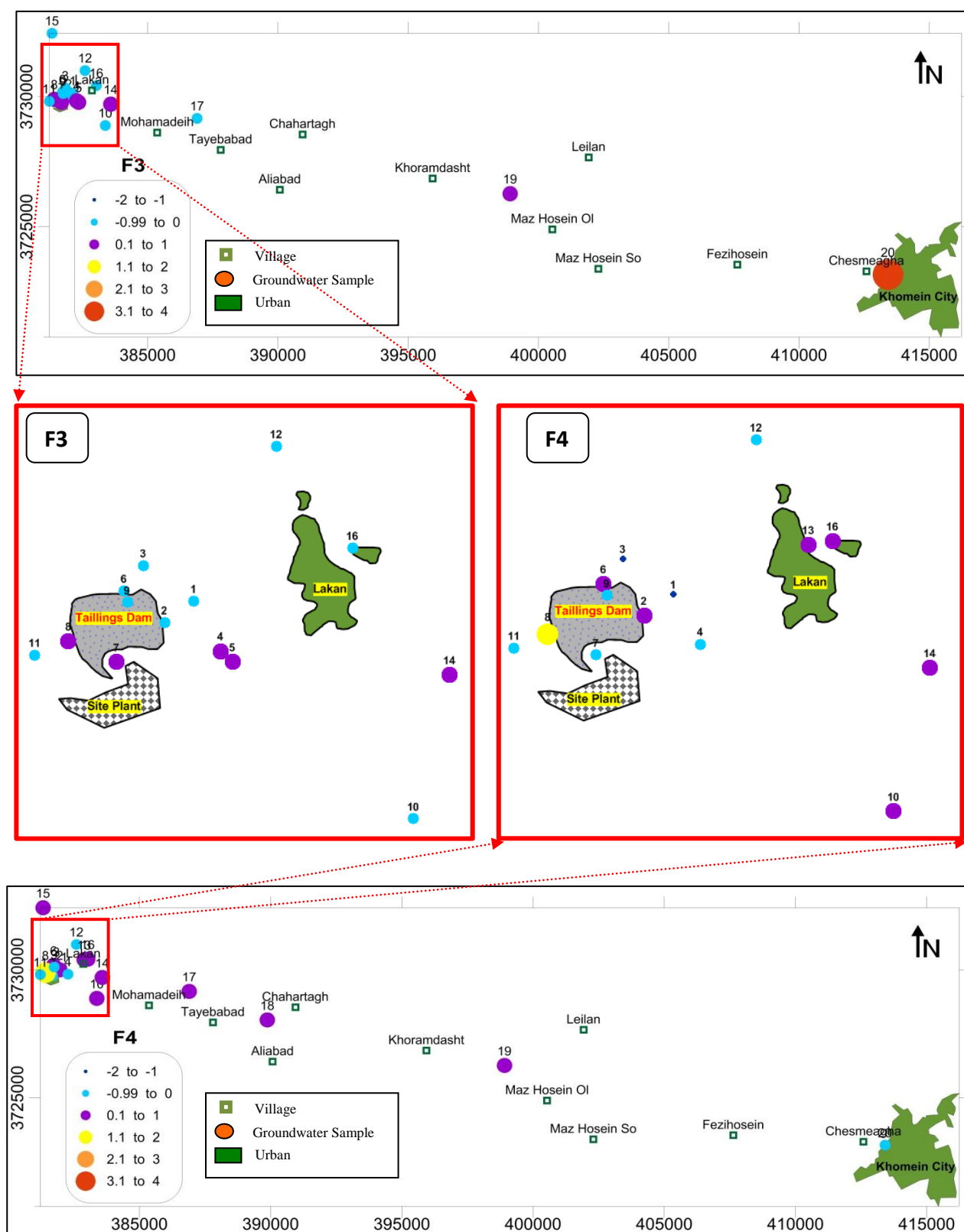
Figure 7. Geographical distribution of the factor scores (F3 and F4) in the study area.

3.3.2. Cluster analysis

The hydrochemical data concentrations (the variables) were standardized by means of Z-cores before CA and pearsons were calculated for similarities in the variables. Then hierarchical clustering by applying Ward's method was performed on the standardized data set. The CA results for hydrochemical data studied are shown in Figure 8 as a Dendrogram. Figure 8 displays four clusters: (1) TDS-SO$_4$-Zn-Mn; (2) Fe-CN; (3) Cl; (4) Pb-Hg, in full agreement with the FA results. It is observed, however, that clusters 2, 4 and clusters 3 and 1 join together at a relatively higher

level, possibly implying a common source.

The Dendrogram of the sample cluster analysis shows several groups of waters (Figure 9): Group A consists of 4 samples (1, 2, 3 and 6), corresponding to Fe and CN waters and affected by contamination of flotation process sources; group B comprises 9 samples, which correspond to non-contamination water (9, 11 and 13-19); group C consists of 7 samples (4, 5, 7, 8, 10, 12 and 20) corresponding to an anthropogenic source due to sulfide mineral oxidation within mine wastes and a natural source[29].
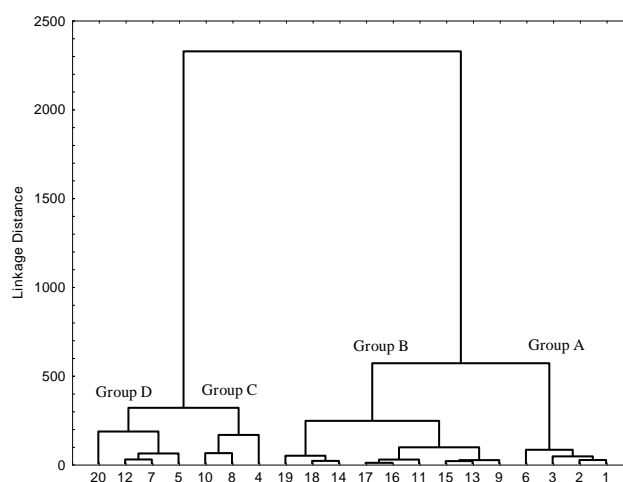

Figure 8. Dendrogram results Ward's method of hierarchical cluster analysis for 9 variables.

Figure 9. Dendrogram of sample cluster analysis for groundwater samples.

3.4. Hydrochemical data source identification

The extremely elevated concentrations of Fe and CN in some of the samples and Pb and Hg in all of the water samples suggest anthropogenic sources of these elements (processing plant in the Lakan Pb and Zn mine). While, elevated concentrations of Mn and Zn and slightly higher values of TDS and SO$_4$ are related to sulfide minerals oxidation in tailings materials of the Lakan Pb and Zn mine.

The correlation coefficient analysis results indicate that Mn, Zn, SO$_4$ and TDS have a similar source and Hg, Fe, Pb and CN have another similar source. FA and CA results are consistent with these interpretations. Four main sources can be indentified according to correlation coefficient analysis, FA and CA: (1) Zn, Mn, TDS and SO$_4$ have both natural and anthropogenic sources (of oxidation of sulfide minerals within mine wastes); (2) Hg and Pb constituents represent a natural source (geochemical anomaly) and anthropogenic source due to the Lakan Pb and Zn mine;(3) CN
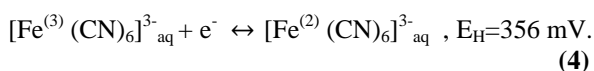
and Fe have an anthropogenic source and mainly originate from the processing plant; (4) Cl represents a natural source [7].

One group of hydrochemical data including Zn, Mn, TDS and SO$_4$ have strongly positive correlations in FA and correlation coefficient analysis and are classified together in CA. Higher concentrations of these elements were found in the water samples collected from the mine waste site. Zn, Mn, and SO$_4$ are normally regarded as an indicator for oxidation of mine wastes [23]. Sulfide minerals (such as ZnS and CuS) are formed under reducing conditions where sulfide is the dominant redox form of sulfur. Sulfide minerals are not stable in the presence of molecular oxygen (O$_2$); therefore it will oxidize and dissolve if exposed to earth surface conditions and high concentrations of sulfate are produced [1]. On the other hand, surface water and groundwater flowing through mineralized rock zones contain excessive amounts of heavy metals. Oxidation of sulfide minerals, in particular FeS$_2$ in

the presence of oxygen and moisture can produce sulfuric acid. The low-pH water can also leach heavy metals [30], as well as soluble calcium, magnesium, sodium and sulfate. These processes increase Zn, Mn, TDS and SO_4 in receiving waters.

A second group of elements consists of Hg and Pb. Hg and Pb concentrations in excess of the mean were found in the water samples from the mining area, in particular near the source rock or geochemical anomaly site. The host rocks of Pb and Hg are limestone and dolomitized limestone and are rich in Pb and Hg and this forms the Lakan Pb and Zn mine [7, 31]. Surface water and groundwater flow over these rocks and leach them; resulting in Pb and Hg rich waters.

A third group of elements consisting of Fe and CN correlated in FA and correlation coefficient analysis and clearly separate from the other heavy metals in CA. This separation between them and other heavy metals may suggest a mainly anthropogenic source. CN and Fe ions can be found in tailings dam and then in groundwater, while the close correlation between them is outstanding [32]. Furthermore, Cyanides are highly toxic and their toxicity is related to their physicochemical speciation after discharging to tailings dam. The free cyanide species (HCN, CN) is classified as the most toxic compound because of its high metabolic inhibition potential whereas metal–cyanide complexes (e.g. $Fe(CN)_{3-6}$, $Fe(CN)_{4-6}$) are considered relatively less toxic [33]. The iron–cyanide complex is called ferrocyanide, $[Fe^{(2)}(CN)_6]^{4-}$, which can be oxidized to ferricyanide, $[Fe^{(2)}(CN)_6]^{3-}$, in aqueous solution (Eq.4):

$$[Fe^{(3)}(CN)_6]^{3-}_{aq} + e^- \leftrightarrow [Fe^{(2)}(CN)_6]^{3-}_{aq} \text{ , } E_H = 356 \text{ mV.}$$
(4)

Generally, iron–cyanide complexes are of anthropogenic origin in soils. Industrial activities have led to contaminations with iron–cyanide complexes in soil and ground water. Iron–cyanide complexes are potentially hazardous, because they can be converted to extremely toxic free cyanide, CN_aq and HCNg,aq, in the presence of UV light. Various solid phases are known to absorb iron–cyanide complexes e.g. goethite, a-FeOOH, ferrihydrite, Fe_2O_3-nH_2O, n=1–3, amorphous Al oxide, soils, and activated carbon [34, 35].

The forth group of elements consists of Cl. This shows low mean concentration. Cl concentrations in excess of the median were found in water samples from the non-mining area, in particular near the Khomain city (40 kilometers of the Lakan Pb and Zn mine). However, concentration of Cl in most water samples close to mine and waste disposal site are lower than the corresponding value of Khomain city (sample 20). Water samples collected from the study area mainly originated from a natural source.

Conclusions

The concentrations and source of the hydrochemical parameters such as Fe, CN, Pb, Hg, Mn, Zn, SO_4, Cl and TDS in groundwater samples collected from the Lakan Pb and Zn mine, west of the Khomain city were investigated. The quality of groundwater samples of the study area was assessed based on contamination index. The adopted WHO standard shows that Pb and Hg were found to be above the maximum permissible limit of drinking water quality in the study area. The highest contamination index value was recorded at locations near to the tailings dam of mine and the lowest contamination value was recorded in outside from the study area and toward the Khomain city.

The authors recommended the development of an appropriate treatment system. It is also recommended that, mining effluents should be treated before discharging them to the land surface and natural water resources. This will safeguard the health of the people, especially those people who use groundwater for drinking.

Hydrochemical data were classified into two main groups according to their sources: natural and mining sources. Four main sources of different hydrochemical data in water samples of the Lakan Pb and Zn mine were identified according to FA and CA, coupled with correlation coefficient analysis. Fe and CN have mainly originated from the processing plant; Pb and Hg have naturally originated either from geochemical anomaly or tailings site. Zn, Mn, SO_4 and TDS indicate an anthropogenic source due to the sulfide minerals oxidation in mine waste disposal site and Cl has a natural source.

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