

The environmental impacts of Aghdarband coal mine: pollution by heavy metals

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Abstract

Aghdarband coal mine, located in NE of Iran, with annual coal and waste production capacity of about twenty million and six thousand tons, respectively, causes the increase of the concentration of some heavy metals in the soil and surrounded sediments. This paper deals with geochemical distribution and environmental effects of the heavy metals on the sediments around the mine, using geochemical data and statistical analysis. Investigation of the correlations of soil chemical parameters based on Pearson correlation coefficients, cluster analysis and principal component analysis suggested that sulfur, arsenic, molybdenum and copper were distributed in the region under the effect of anthropogenic origin (coal washing plant). Also, magnesium, nickel, cadmium and chromium were caused by the lithogenic origin effect (ultramafic rocks) in soil and sediment of the region. These studies also revealed that the concentration and geochemical distribution of aluminum, manganese, antimony, cobalt, iron, zinc and lead was controlled by the acidic rocks (rhyolites, metamorphosed acidic tuffs) and the metamorphosed polytuff sediments (slate and phyllite) and the calcium element by the carbonate rocks. Calculation of the enrichment and geo-accumulation factors also shows that the soil of the region is polluted by the elements such as sulfur, arsenic, copper and lead. Zoning maps of elements concentration also showed that these elements have the highest concentration at the place of coal washing and coking plant, as the concentration was gradually decreased by moving away from these locations.

Keywords: Environmental Impacts, Pollution, Heavy Metals, Coal Mine, Aghdarband

Introduction

Coal is an important fuel, as it provides 27% of global energy and 36% of world electricity (Tiwary, 2001). In recent years, coal mining and use of this material causes environmental concerns. High density of nutrients and heavy metals such as Cd, Cr, Cu, Hg, S, As, Ni, Pb in soils around coal mines, causes environmental pollution and environmental problems for both animals and plants (Baba *et al.*, 2010; Belkin *et al.*, 2008; Bhuiyan *et al.*, 2010; Zhengfu *et al.*, 2010). The presence of heavy metals in soil caused by industrial activities or factory waste or dust is a great danger for the environment (Sun *et al.*, 2010). Aghdarband coal mine is located at the northeast of Iran at the geographic coordinates of E60° 52' 18.7" and N35° 59' 06.2". The village is placed at 141 km of SouthEast of Mashhad. This mine is an underground mining and has coal washing and coking plant. Drainage water caused by mining activities leaves the Aghdarband village out by some streams and flows toward the Kashfrud river (Fig. 1). In this paper, using geochemical data, we evaluate the correlation between the elements in the sediments of Aghdarband coal mine and by determining the pollution indices (indexes of geo-accumulation and the contamination factor) we

evaluate the environmental impact of the mine.

Regional Geology

The Triassic sequence of the Aghdarband window comprises four formations that together form the Aghdarband Group (Ruttner *et al.*, 1991). The lowest of these is the Sefidkuh Formation, which is an alternation of thickly bedded to massive yellowish limestone and thinly bedded light grey to bluish-grey limestone (Fig. 2). This formation is overlain by the Nazarkardeh Formation in the type section (Ruttner, 1993). Nazarkarde formation includes the thin lime stones of chert layers, tuff marl and shale with abundant fossil showing the age of lower Anisian that their thickness is more than 50 meters (Ruttner, 1991). The Nazarkardeh Formation is overlain by the Sina Formation, a sequence of rocks reportedly 400 m to 700 m thick, whose lower part comprises tuffaceous sandstone, limestone, marlstone and marl, and whose upper part comprises green tuffaceous shales and conglomerate. The Aghdarband Coal Bed represents the lowermost part of the overlying Miankuhi Formation. This formation forms the core of the Aghdarband syncline and consists of a monotonous sequence of brown-coloured shales with intercalations of siltstones and fine-grained

sandstones (Ghasemi-Nejad *et al.*, 2008). They are 200 m thick in the core of the Aghdarband syncline. Aghdarband coal mine is located in this section which Plant fossils indicates the Norian age for it (Ruttner, 1993). Coal rocks of Aghdarband region have been formed of two parts of macerals (often vitrinite) and minerals (mainly pyrite) (Fig. 3). Sulfide vein containing abundant pyrite have been developed between layers of coal (Fig. 4).

Methodology

In order to determine the chemical properties, 22 samples of soil and sediment were selected from different parts of the study area. Environmental soil samples were screened in the laboratory of Islamic Azad University, Mashhad, by the sieve shakers by the mesh of 10 (>2mm) as the soil texture and type

of sediment were detected. PH of the soil samples were determined using standard methods of EC EPA SW-846 Method 9045 and the CE was determined through extraction, soil to water ratio of 1 to 5, respectively (Table 1).

Twelve samples of soil and sediment have been selected for analysis of heavy metals and heavy element by ICP-MS method in the Zarazma laboratory, Tehran (Table 1). Using the two-variable or multivariate statistical methods, correlation factor, cluster analysis, and analysis of the principal component, paragenesis relations and correlation of different elements were also examined. Also the environmental quality and enrichment of soil was investigated by various parameters such as soil geochemical enrichment factors and land accumulation index.

Table 1. Geochemical analysis results (in ppm) of the samples in the Aghdarband coal-mining region.

Sample	Al	As	Ca	Cr	Cu	Fe	K	Mg	Mo	Ni	Pb	S	Sn	Zn	EC	pH
AG-06	58482	33.3	34956	39	33	46039	8269	3826	3.15	14	52	32111	2	89	3330	7.79
AG-09	61002	6.5	30970	71	31	27408	13788	7720	1.07	28	33	5119	2.5	79	8830	7.86
AG-13	54480	5.3	42958	60	21	25156	13563	8290	0.81	24	23	1730	2.2	55	535	8.08
AG-15	52709	4.2	34853	60	16	25332	13592	8129	0.34	31	18	325	2.1	49	440	8.47
AG-16	73844	4.3	36353	41	23	27222	16227	6930	0.77	16	22	2199	2.3	53	2110	8.19
AG-20	54930	5.6	37694	65	16	25683	13783	8551	0.35	33	19	558	2.2	51	2850	8.3
AG-22	52545	5.2	34199	104	17	27103	12177	7678	0.47	28	19	751	2.4	52	801	8.18
AG-27	61898	5.4	39416	60	20	24943	15585	8837	0.38	27	20	223	2.4	51	497	8.25
AG-29	63997	5	41335	74	21	25773	15318	8358	0.59	24	21	822	2.4	52	222	8.24
AG-32	71458	2.8	39855	60	21	27462	18053	8365	0.7	22	20	760	2.3	53	634	8.05
AG-33	81477	4.3	28078	46	30	26936	20586	7516	0.68	23	22	358	3.1	56	442	8.37
004(S590)	6814	2.3	98722	17	38	3623	-	924	2.08	11	5	1625	-	36	N	8

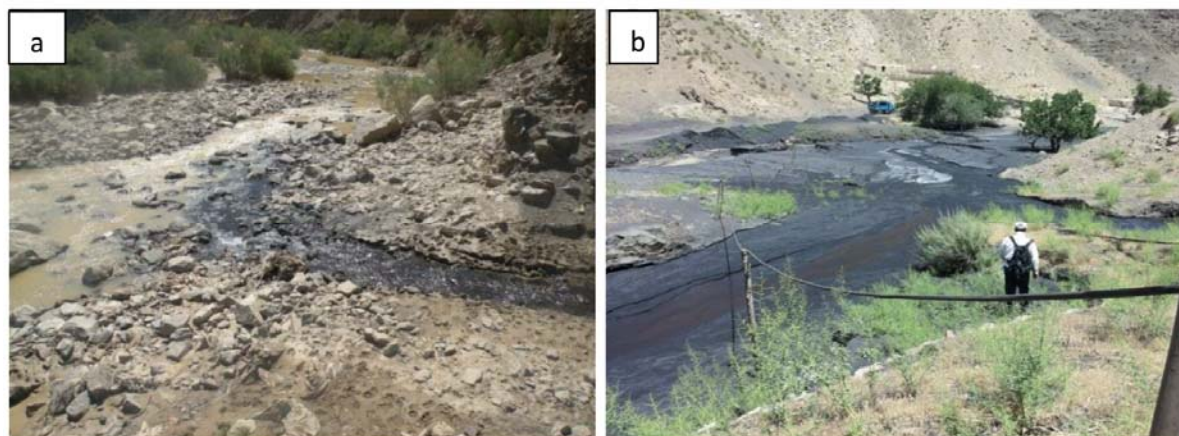


Figure 1. a: Mine drainage from Aghdarband coal mine (right) mixes with the waters of the Kashfrud River (left). b: Soil Pollution around the Aghdarband village as a result of coal mining activities

For this purpose, the SPSS22 software was used. The ArcGis 10.2 software was also used in order to determine the distribution of the elements based on interpolation method.

Discussion

Chemical characterization

pH is an important variable that controls the ion exchange, precipitation and dissolution reactions, redox, adsorption and complexation reactions. High or low pH values generally reflect the particular minerals or ions in the soil (Sparks, 2003). This parameter is influenced by the concentrations of cations such as Mg, Ca, K and Na that increase the soil pH by dissolution and leaching of the bedrock and entering the soil. Soils of the region had a pH in the range of 7.74 to 8.47, classified as to the low to medium alkaline soils. The regional soil, with the average values of electrical conductivity (EC) of 1880 has put in the category of neutral to slightly saline soils. Based on the classification of soil texture and the amount of sand, silt and clay obtained from screening method of soil and hydrometer, the texture of the most soils in the area is sandy to sandy silt.

Correlation analysis

Pearson correlation coefficient was calculated for further exploring the relationship between soil samples, (Table 2). In this table, the correlation

coefficients between the different elements are shown as positive (positive correlation) and negative (negative correlation) values. The correlation between the various elements in this table shows that sulfur element has a high positive correlation with arsenic, iron, molybdenum, lead and zinc, which indicate that all these elements may derive from the same source.

The correlation coefficient of these elements is 0.986, 0.682, 0.855, 0.866 and 0.797, respectively. Also sulfur shows a negative correlation ($p < 0.01$, $r = -0.682$) with the potassium. Tin element has a significant positive correlation with aluminum ($p < 0.01$, $r = 0.684$) and potassium ($p < 0.01$, $r = 0.745$) indicating that the origin of these three elements is common. Also chrome and nickel ($r = 0.741$, $p < 0.01$) and magnesium ($r = 0.701$, $p < 0.05$) are highly interdependent, reflecting the same origin for these three elements. Calcium has no positively correlation with none of the elements and shows the negative relationship with copper and tin. Having a different source (Sefidkuh Formation or Nazarkardeh Formation) can be a reason for the lack of correlation between these elements.

Cluster analysis (CA)

Cluster analysis helps us for clustering of the elements in terms of similarity or difference of elements.

Table 2. Pearson correlation coefficient matrix between soil pH and EC and heavy elements

Correlations																	
	Al	As	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Ni	Pb	S	Zn	Sn	EC	PH
Al	1																
As	-.191	1															
Ca	-.315	-.121	1														
Cr	-.506	-.381	.083	1													
Cu	.449	.579	-.520	-.495	1												
Fe	-.055	.977**	-.192	-.405	.628*	1											
K	.788**	-.707*	-.133	-.161	-.050	-.616*	1										
Mg	-.043	-.910**	.332	.452	-.672*	-.951**	.555	1									
Mn	.067	.356	-.402	-.001	.776**	.339	-.135	-.276	1								
Mo	-.030	.959**	-.158	-.452	.730*	.972**	-.599	-.936**	.465	1							
Ni	-.491	-.558	-.018	.603*	-.609*	-.650*	.069	.726*	-.084	-.692*	1						
Pb	-.073	.933**	-.239	-.400	.785**	.928**	-.618*	-.889**	.601	.976**	-.586	1					
S	-.137	.991**	-.146	-.413	.638*	.987**	-.682*	-.934**	.392	.984**	-.612*	.961**	1				
Zn	-.060	.812**	-.363	-.290	.834**	.816**	-.551	-.786**	.753**	.889**	-.455	.961**	.858**	1			
Sn	.684*	-.406	-.564	.029	.323	-.346	.745**	.250	.325	-.321	.064	-.274	-.403	-.157	1		
EC	-.105	.253	-.419	-.009	.535	.250	-.312	-.269	.656*	.349	.038	.518	.319	.706*	-.039	1	
PH	.087	-.624*	-.018	.098	-.639*	-.653*	.500	.584	-.631*	-.755**	.507	-.794**	-.689*	-.839**	.286	-.625*	1

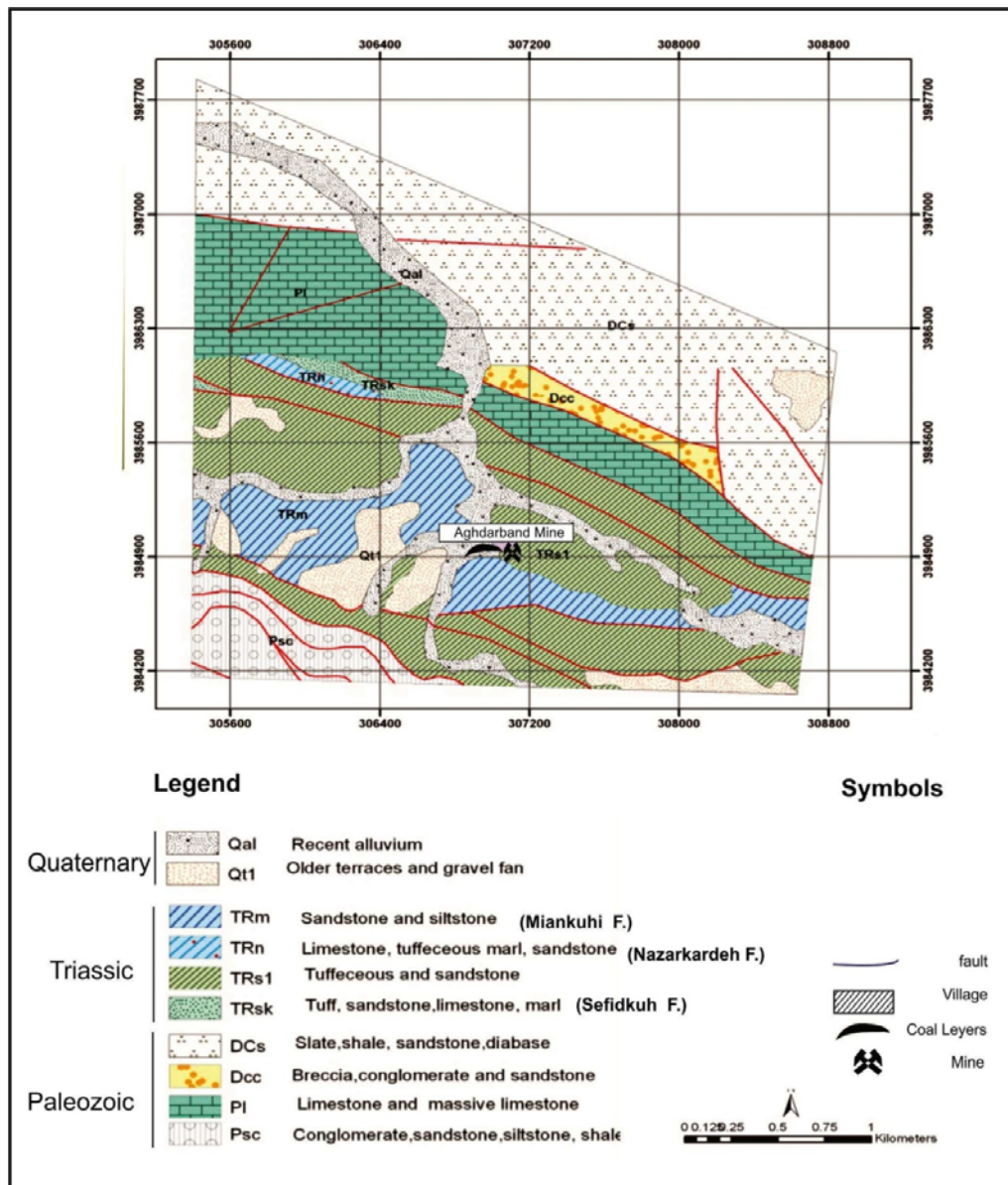


Figure 2. Geological map of the intended region with the distribution of analyzed samples in the studied area (after Rutter, 1993)

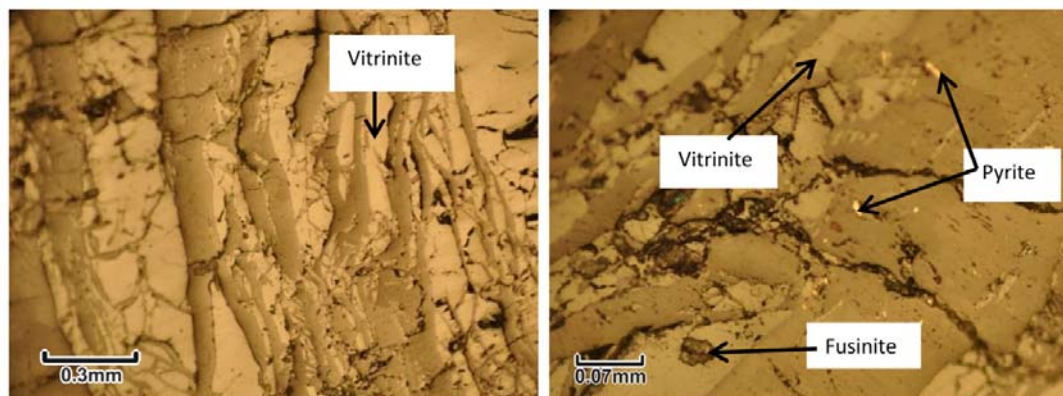


Figure 3. Photomicrographs (reflected light) of Macerals (including vitrinite and fusinite) and minerals (pyrite) in coal Aghdarband.

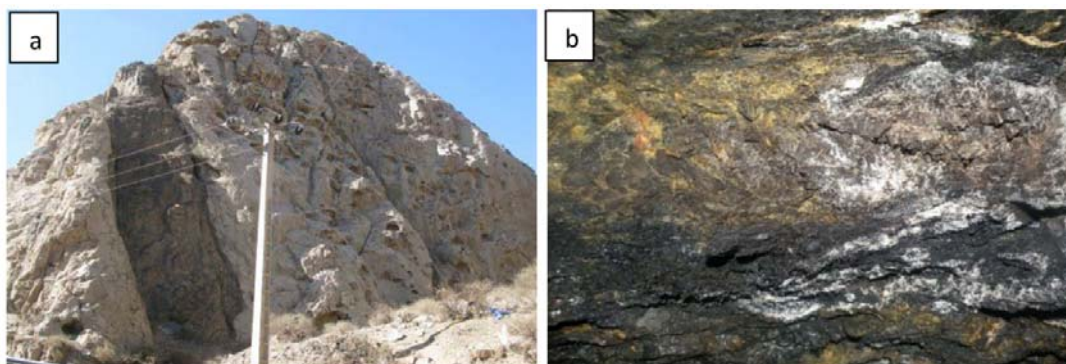


Figure 4. a: A light-gray limestone cut by younger black diabase dike b: Sulfide veins and pyrite in the coal

Due to its dendrogram, (Fig. 5), the two main clusters can be observed. As, S, Fe, Mo, Pb, Zn, Cu are placed in the first cluster and Al, K, Sn, Mg, Cr, Ni have been placed in another cluster.

Each of these two clusters is divided into subcategories that reflect their different origin. Due to the presence of sulfide, sulfur and pyrite veins in the coal layers, the source of the first cluster should be attributed to mining activities and anthropogenic origin. The second main cluster consists of chromium, nickel and magnesium in the waste soil of the mine. The same source (diabase dikes and ultramafic rocks origin) and low concentrations of these elements can be attributed to the lithological origin. Origin of the aluminum potassium and tin also can be found in the acidic rocks (rhyolites, tuffs metamorphosed acid) and the sediment of metamorphic rock (slate and phyllite). As mentioned in Pearson coefficients, the calcium forms a separated sub-category. It has the lithogenic source related to the limestone rocks of the region. According to this cluster analysis, the geochemical distribution of elements in sediment and soil of the region are controlled by two factors of anthropogenic and lithogenic. As the anthropogenic source, entrance of coal washing and leaching waste and washing of the tailings of the water stream, control the distribution and concentrations of arsenic, sulfur, iron, copper, lead and zinc of the region. The limestone rocks, volcanic rocks (rhyolites, metamorphosed acidic tuffs) and metamorphosed plate sediments (slate and phyllite) are known as the lithogenic source of the other elements.

Principal component analysis (PCA)

The purpose of this multivariate statistical method is to determine the main controlling variables among a set of data, or in other words determining

the least number of the variables with the most observed changes among the data series. As shown in Figure 6, principal component analysis suggests a three-component model for data. Some features such as the radius and ionic charge, the mobility, the behavior of the elements with the soil components (organic materials and clay minerals) existence of the shared resources and so on, are some of the issues causing the distribution of elements in different components. The first component is composed of arsenic, sulfur, molybdenum, copper, lead, zinc, and iron. As noted in the cluster component, accumulation of these elements at one section of the graph of analysis of the main component can be attributed to the source of coal washing waste in the region. Aluminum, potassium and tin accumulated in the upper part of the PCA graph and the lithogenic origin (acidic and metamorphic rocks) caused the correlation of these elements. Accumulation of magnesium, nickel and chromium elements are well known in the charts reflecting their lithogenic origin (ultramafic rock). Calcium with the lithogenic origin (limestone) in the PCA chart, as an independent group, does not show a good correlation with the other elements. This point was also observed in the calculation of Pearson coefficients and CA graphs.

Environmental and Geochemical Evaluation

A) Enrichment Factor (EF)

Using this factor, it is possible to value of one element than its natural value and use it for determining the enrichment of an environment by the other one (Moslempour & Shahdadi, 2013). By calculation of the coefficient, we can determine the source of pollution (lithogenic or anthropogenic). This factor can be obtained by the equation (1).

$$EF = \frac{M_x XFe_b}{M_B XFe_x} \quad (1)$$

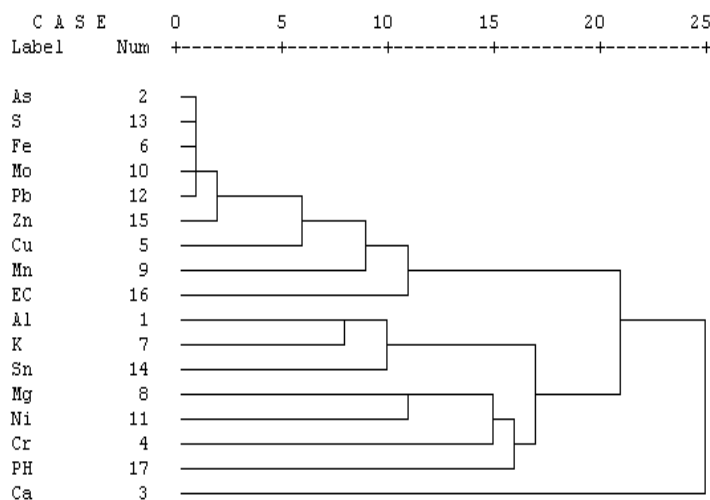


Figure 5. Hierarchical clustering results (dendrogram) of the heavy metal concentrations in soil samples from the Aghdarband coal mine

Component Plot in Rotated Space

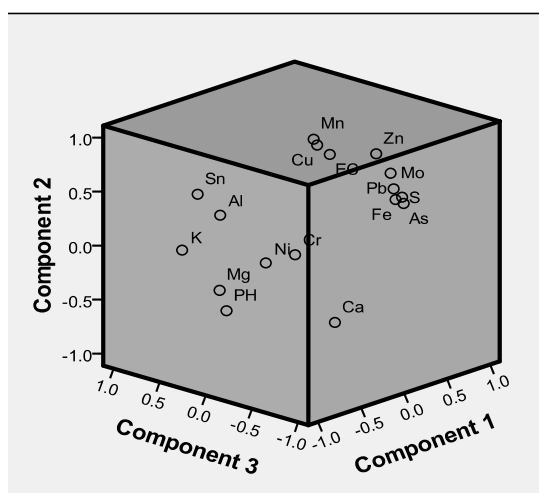


Figure 6. Variables in the coordinates of principal factors (Factor 1 vs. 2 vs. 3)

In this regard, (EF) is the enrichment factor, (XF_{eb}) is the concentration of the element evaluated in the environment (soil), (M_x) is concentration of the base element (AL) in the study range, (XF_{ex}) is concentration of the element in a base environment (earth crust) and (M_B) is the concentration of the base element (AL) in the base environment. The average of AL as the base element in the earth crust was considered as 82000 ppm (Hutzinger *et al.*, 2013). Enrichment factor is also calculated for soil samples (Table 3). According to this classification, sulfur enrichment is severe (Table 4). Arsenic is highly enriched and copper, molybdenum, lead and zinc have relatively little enrichment in soils of the area.

The other studied elements were not enriched. Most highly enrichment was related to the amount of sulfur in the sample AG06 as 129 ppm, that according to Chen classification it has enriched as infinite. The sulfur enrichment is reduced away from coal washing plant (Fig. 7). It seems that the sulfur of pyrite release in the presence of water and oxygen and has polluted the environment of rocks and soils around the mine. Also abundant sulfide veins in coal layer have increased this enrichment (Fig. 3). Coal possessing high levels of organic matter and maceral, are a proper place for absorbing elements such as As, Mn, Pb, Zn, Be, Br, Ba, Co, Sr, and Sb (Eskenazy and Stefanova, 2007; Song *et al.*, 2007). So enrichment of arsenic,

molybdenum, lead and zinc elements in the area can be attributed to the high cation exchange capacity (CEC) of the coal.

According to the classifications, enrichment

factors between 0.5 and 2 can be attributed to the geo-accumulation origin and values more than 2 can be attributed to the impact of anthropogenic activities (Hernandez *et al.*, 2003).

Table 3. Principal component analysis based on the measured variables in the Aghdarbands soil samples.

Component Score Coefficient Matrix			
	Component		
	1	2	3
Al	.057	-.043	.312
As	.123	-.037	-.048
Ca	.055	-.210	-.109
Cr	-.150	.160	-.193
Cu	.045	.142	.139
Fe	.132	-.044	-.011
K	-.033	-.014	.249
Mg	-.135	.046	-.027
Mn	-.073	.298	.002
Mo	.123	-.013	-.005
Ni	-.175	.164	-.160
Pb	.087	.061	-.025
S	.123	-.026	-.036
Sn	-.076	.154	.222
Zn	.035	.158	-.033
EC	-.088	.291	-.076
pH	-.031	-.120	.066

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Component Scores.

Table 4. Enrichment factors (EF) value of heavy metals in the Aghdarband soils

Element	Enrichment factors												
	As	Ca	Cr	Cu	Fe	K	Mg	Mo	Ni	Pb	S	Sn	Zn
EF-06	26.03	0.06	0.54	0.77	1.15	0.02	0.23	3.69	0.23	5.85	129.11	0.02	1.79
EF-09	4.87	0.26	0.94	0.70	0.66	0.14	0.45	1.20	0.45	3.56	19.73	0.12	1.52
EF-13	4.45	0.45	0.89	0.53	0.68	0.17	0.54	1.02	0.43	2.78	7.47	0.12	1.19
EF-15	3.64	0.46	0.92	0.42	0.70	0.22	0.54	0.44	0.58	2.25	1.45	0.15	1.09
EF-16	2.66	0.47	0.45	0.43	0.54	0.26	0.33	0.72	0.21	1.96	7.00	0.16	0.84
EF-20	4.66	0.37	0.95	0.40	0.68	0.17	0.55	0.44	0.59	2.28	2.39	0.12	1.09
EF-22	4.52	0.36	1.60	0.44	0.76	0.16	0.52	0.61	0.52	2.38	3.36	0.14	1.16
EF-27	3.99	0.40	0.78	0.44	0.59	0.20	0.50	0.42	0.43	2.13	0.85	0.13	0.97
EF-29	3.57	0.46	0.93	0.45	0.59	0.21	0.46	0.63	0.37	2.16	3.02	0.14	0.96
EF-32	1.79	0.79	0.68	0.40	0.56	0.44	0.41	0.67	0.30	1.84	2.50	0.25	0.87
EF-33	2.41	0.36	0.46	0.51	0.48	0.32	0.33	0.57	0.28	1.78	1.03	0.22	0.81
EF-04	15.43	0.00	2.01	7.65	0.78	0.00	0.48	20.94	1.58	4.83	56.08	0.00	6.21
AVERAGE	6.50	0.37	0.93	1.09	0.68	0.19	0.45	2.61	0.50	2.82	19.50	0.13	1.54

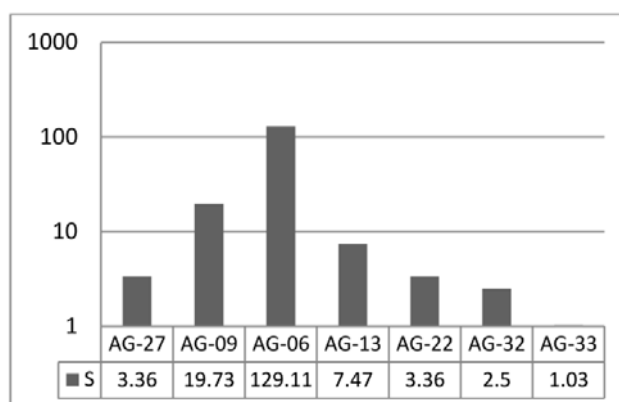


Figure 7. Enrichment factors (EF) value of sulfur away from Aghdarband coal washing plant

According to the mean values of enrichment factors of As, Mo, Pb and S elements, which have the enrichment factor more than 2, the origin of these elements can be attributed to mining activities. Also, according to Zhang and Liu (2002), values of enrichment factors between 0.5 and 1.5 indicated that the metal is completely of shell material or natural processes. Values greater than 1.5 indicate that the origins are closer to the anthropogenic activities (Zhang *et al.*, 2009). The other studied elements (Ca, Cr, Cu, Fe, K, Mg, Ni, Sn, Zn) with an average enrichment factor of less than 1.5 have the lithologic origin and their enrichment in the region soil is caused by physical and chemical weathering of minerals of the rocks in the region.

B) Geo-accumulation index (*I_{geo}*)

The geo-accumulation index suggested by Müller in 1969 can be used to determine the extent of contamination. It is computed using the following:

$$I_{geo} = \log_2 (C_n / 1.5B_n) \quad (2)$$

where C_n is the measured concentration of element n, B_n is the content of element n in average shale. 1.5 factor is embedded in the above equation as the correction factor of the base matrix in the equation. The average concentration of the element in shale is used as background concentration (Abraham and Parker, 2008; Goorzadi *et al.*, 2009). The index has been calculated for the elements in soils (Table 5). Based on these indices, Muller has classified the soils according to their contamination degree into 6 groups (Table 6). As could be seen, I_{geo} value was decreased as for $S > Pb > As$. Elemental sulfur in the study area possessed the highest geo-accumulation (3.16) and the average of (1.62). According to the Muller's classification in 1969, the degree of

contamination between 3 and 4 reflects the highly polluted (Muller, 1969). Lead element also with a geo-accumulation index of zero to one possessed a little pollution. The other metals owing the geo-accumulation values less than zero and the zero-emission, are considered as the non-polluting elements (Table 5). Therefore, due to the accumulation index values depicted in Table 5, in terms of environmental quality, the soils of the region are contaminated with sulfur and lead.

Environmental impact assessment by GIS

Geographic Information Systems (GIS) is one of the useful tools to support decision-making cases based on spatial data, with the basic application to gain data derivable by combination of the different layers of data with various approaches and methods. GIS geographic information system, provides the business capabilities to gather input, processing, deforming, image capturing, combining, searching, analyzing, modeling and removing all spatial data based on targets, in fact, the main objective of the integration of GIS is to coordinate the spatial data and their final assessment. In this study, zoning map of a number of elements was prepared using the ArcGis 10.2 software and the geological map of the region and information collected from soil samples collected from the study area (Fig. 8). Surveying the zoning maps of sulfur, lead and arsenic indicated that these elements have the maximum concentration in place coke ovens baking, which gradually decreases by getting far away. Copper zoning map also shows that this element has the highest concentration at the coal washing plant near the site. The results of the assessment findings are consistent with those of geochemical and environmental pollution.

Table 5. Classification of Enrichment Factors (EF) values of the Aghdarband soils based on Chen *et al.* (2007)

Description of soil quality	No enrichment	Minor	Moderate	Moderately severe	Severe	Very severe	Extremely severe
Enrichment Factors	EF<1	1-3	3-5	5-10	10-25	25-50	EF>50

Table 6. Geo-accumulation Index (I_{geo}) value of heavy metals in the Aghdarband soils.

Geo-accumulation Index (I _{geo})																
Element	Al	As	Ca	Cr	Cu	Fe	K	Mg	Mo	Ni	Pb	S	Sn	Zn	I _{geo}	Description of soil quality
AG-06	-1.0	0.6	-0.5	-1.8	-2.0	-0.7	-2.3	-2.6	-0.3	-2.9	0.8	3.2	-2.2	-1.1	3-4	Strongly contaminated
AG-09	-1.0	-1.8	-0.7	-0.9	-1.1	-1.4	-1.5	-1.5	-1.9	-1.9	0.1	0.5	-1.9	-1.3	0-1	Uncontaminated to moderately contaminated
AG-13	-1.1	-2.1	-0.2	-1.2	-1.7	-1.5	-1.6	-1.4	-2.3	-2.1	-0.4	-1.1	-2.0	-1.8	0>	Uncontaminated
AG-15	-1.2	-2.4	-0.5	-1.2	-2.1	-1.5	-1.6	-1.5	-3.5	-1.7	-0.7	-3.5	-2.1	-2.0	0>	Uncontaminated
AG-16	-0.7	-2.4	-0.4	-1.7	-1.6	-1.4	-1.3	-1.7	-2.3	-2.7	-0.5	-0.7	-2.0	-1.9	0>	Uncontaminated
AG-20	-1.1	-2.0	-0.4	-1.1	-2.1	-1.5	-1.5	-1.4	-3.5	-1.6	-0.7	-2.7	-2.0	-1.9	0>	Uncontaminated
AG-22	-1.2	-2.1	-0.5	-0.4	-2.0	-1.4	-1.7	-1.6	-3.1	-1.9	-0.7	-2.3	-1.9	-1.9	0>	Uncontaminated
AG-27	-1.0	-2.1	-0.3	-1.2	-1.8	-1.5	-1.4	-1.4	-3.4	-1.9	-0.6	-4.0	-1.9	-1.9	0>	Uncontaminated
AG-29	-0.9	-2.2	-0.2	-0.9	-1.7	-1.5	-1.4	-1.4	-2.7	-2.1	-0.5	-2.1	-1.9	-1.9	0>	Uncontaminated
AG-32	-0.8	-3.0	-0.3	-1.2	-1.7	-1.4	-1.1	-1.4	-2.5	-2.2	-0.6	-2.2	-2.0	-1.9	0>	Uncontaminated
AG-33	-0.6	-2.4	-0.8	-1.6	-1.2	-1.4	-1.0	-1.6	-2.5	-2.2	-0.5	-3.3	-1.5	-1.8	0>	Uncontaminated
AG-04	-4.1	-3.3	-12.4	-3.0	-0.8	-4.3	-	-4.6	-0.9	-3.2	-2.6	-1.2	-	-2.4	0	Uncontaminated
AVERAGE	-1.2	-2.1	-1.4	-1.3	-1.6	-1.6	-1.5	-1.8	-2.4	-2.2	-0.6	-1.6	-1.9	-1.8	0>	Uncontaminated

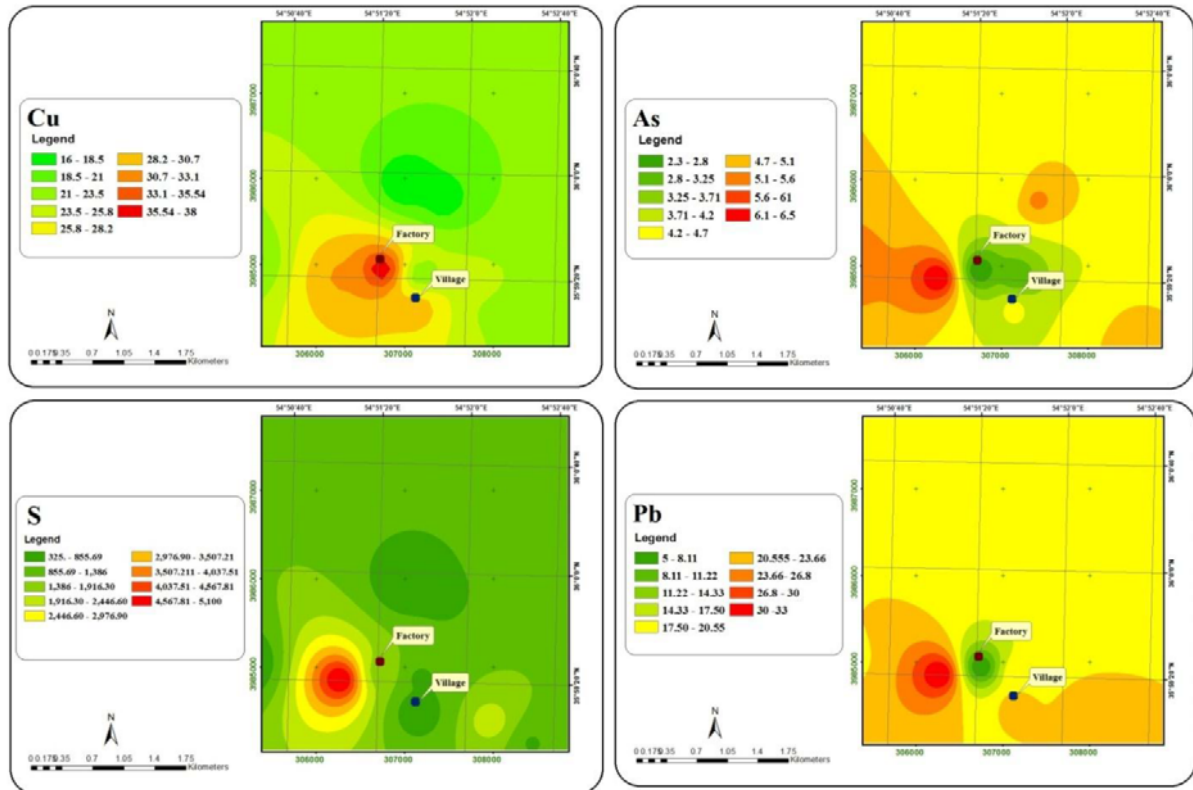


Figure 8. The distribution map of Cu, As, S and Pb elements in the studied area

Table 7. Classification of Geo-accumulation Index (I_{geo}) values of the Aghdarband soils based on Muller (1969)

Description of soil quality	Uncontaminated	Uncontaminated to moderately contaminated	Moderately contaminated	Moderately to strongly contaminated	Strongly contaminated	Strongly to extremely strongly contaminated
I _{geo} class	0	1	2	3	4	5
I _{geo}	0>	0-1	1-2	2-3	3-4	4-5

Conclusion

According to the results of Pearson correlation coefficient and principal component analysis, cluster analysis and reviewing of zoning maps, two different origins can be suggested for entering the elements to the soil of the region. Elements of sulfur, arsenic, molybdenum and copper have the anthropogenic origin (coal washing and coking wastewater), and elements such as magnesium, nickel, cadmium and chromium showed a lithogenic source (ultramafic rocks). The study shows that the concentration and geochemical distribution of elements including aluminum, manganese, antimony, cobalt, iron, zinc and lead

have been controlled by the nature of the acidic rocks (rhyolites, metamorphosed acidic tuffs) and metamorphosed plate sediments (slate and phyllite), while calcium is controlled by the carbonate rocks. Conducted calculations and amounts of enrichment factors revealed that sulfur and arsenic have the highest enrichment values in the region. The geo-accumulation index values also indicated that this factor was maximum for the sulfur at the grade of 3 or 4, ranging in the highly polluted region. According to this index, the lead showed a little pollution in the region. Zoning maps also confirmed the sulfur and arsenic contamination.

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