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Evaluating the potential impact of Agdarband coal mining on water quality, NE Iran

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Abstract

The evaluation of geochemical composition of coal mine drainage in Agdarband shows that the concentration of some elements (especially iron and aluminum) in the surface water is more than the standard. The evaluations imply that the large quantities of these elements have anthropogenic origin and they are resulted from coke washing plant in the area. Calcium, potassium and also Sodium in the samples of taken water from Kashaf-rud are more than the standard which is often due to Lithogenic origin and also it is corresponded to the kind of limestone formations in Agdarband. The pollution indices (HPI and MI) reveal the surface water of Agdarband is polluted and non-potable. The Pearson coefficient and cluster diagram show a high correlation between Fe, Al, Mn, pH and HCO₃⁻ in a same group and Na, K, Cl⁻, SO₄⁻², Ca, and NO₃⁻ in the other group. The three-dimensional graph of the main analysis compound also confirms the correlation between these groups. There is a large quantity of iron in coal mine drainage which is due to the pyrite oxidation and high quantity of aluminum as a result of biochemical reactions of the fluid sulfate.

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Introduction

Coal is the largest source of energy for the generation of electricity worldwide, as well as one of the largest worldwide anthropogenic sources of carbon dioxide releases (Kronbauer *et al.*, 2013). Mining and consuming coal are the main environmental concerns especially in the late years. Most of the concerns are related to acidic mine drainage (AMD), acidic rains, the increase of carbon dioxide levels in atmosphere and the revival of open-pit mines in the end of mining operations. The first two concerns are due to 0.2 to 7 percent amounts of sulfur existing in all coals (Tiwary, 2001). Using more coal makes more pollution and environmental impacts in the nature. Despite government's attempts to decrease environmental pollutants, we can observe the increasing damages on our nature and environment. In the event that this process goes on, the future of the world will be in a severe danger. One of the severe dangers of coal mining is pollution of the surface and underground water. The main environmental problems about water sources in the areas where coal mining's are done are related to AMD, coal washing factories, the suspended solid resulted from diggings and transporting coals and soluble salt and iron. When these materials are entered into the healthy and clean waters of the region it affects the quality of waters and makes them polluted. Acidic waters may dissolve the heavy metals in themselves (Younger, 2004). Coal mine of Agdarband is about seventy five years which are extracted. It has four tunnels that two tunnels are currently active. The mine contains a coal washing factory, the water from this factory is pour into kashaf-rudriver. These materials can cause plants and animals to be contaminated and make problems for the people's health that are living in the area. Hence it is necessary to examine the water quality to determine the amount and levels of water pollution resulted from heavy elements. In this study we have tried to evaluate the impact of Agdarband coal mining on water quality and distribution of heavy elements in area. For evaluating the amount of water pollution, the metal index (MI),

pollution index of heavy metal (HPI), correlation coefficient, cluster analysis and main analysis compound have been used.

Materials and methods

Regional geology

Agdarband is located in north-east of Iran, between $61^{\circ} 30' E$ longitude and $35^{\circ} 30' N$ latitude. This area is considered as a part of structural geology of KapehDagh. KapehDagh consists of 5000 to 7000 meters sediments which deposited in a sea shallow basin (Ruttner, 1984). Triassic formation in Agdarband area is called Agdarband formation by Ruttner (1984). Ruttner (1991) has considered four parts for Agdarband: Sefidkooch limestone formation, Nazarkardeh formation, Sina volcanic formation and Miyankohi shale formation (Ruttner, 1991). The Sefidkooch formation with 200 meters thickness contains light-gray and blue-gray lime stones that in some parts it contains nodules (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). Sina volcanic formation has a diameter between 400 to 700 meters and including the sequence of sandstone, shale, and marl which is rich in fossils. The Miyankohi formation outcrops in the core of the syncline "Agdarband" and contain coal-bearing shale, shale, sandstone and volcanic rocks (Fig.1). Agdarband coal mine is located in this section which Plant fossils indicates the Norian age for it (Ruttner, 1993).

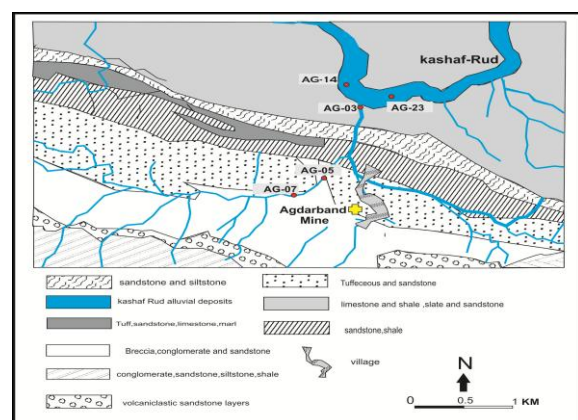


Fig. 1. Geology map of the Agdarband area after Ruttner (1993).

Analytical methods

In order to determine the chemical properties, 250^{cc} water was taken from eight parts separately in two polyethylene containers. Physical parameters such as salinity, pH, Temperature, TDS, and EC are measured insitu. Each of two samples was labeled and one of them preserved with 5cc nitric acid to decrease pH and prevent the precipitation of heavy metals.

The other ones are sent to environmental laboratory of Islamic Azad-university in Mashhad to examine the amounts of TSS, AlkT, Alkp, TH, and Turbidity. The results of measuring physical parameters are shown in (Table 1). Five water samples of the area were sent to mineral processing research center (IMPRC) to measure the amounts of heavy metals like anion and cation in water by ICP-EAS method (Table 2).

Table 1. Descriptive characteristics of physical parameters characteristics of the water samples from Agdarband area.

Sample	LON	LAT	Location	T (°C)	PH	TDS	EC	Salinity	Turbidity	TH	ALKT
AG3a	60 51 32.2	35 59 52.4	Kashaf-Rud	27	8.34	10340	14860	7380	106	450	186
AG3b	60 51 32.2	35 59 52.4	mine drain	32	7.9	630	886	6.11	2.07	450	96
AG3C	60 51 32.2	35 59 52.4	out fall	31	7.19	1530	2180	1.02	849	483	166
AG5	60 51 21.2	35 59 28.5	coal washing	27	8.4	720	1003	515	OVER	343	210
AG7	60 50 55	35 59 23.8	Kiln place	30	8.03	765	1098	8.03	13.9	350	124
AG14	60 51 30.6	35 59 59.4	River bed	32	8.12	1600	2260	1100	59	152	450
AG19	48 32.160	36 01 37.4	Entrance bridg	22	7.92	1440	2.1	1010	57.8	316	-
AG23	60 51 46.8	35 59 54.9	Last turn of Kashaf-Rud	21.7	7.96	1400	2120	1020	68.1	400	110

Table 2. Descriptive characteristics of heavy metal concentrations (mg/Kg), and comparison with potable water standards.

sample	AG-3	AG-5	AG-7	AG-14	AG-23	WHO	Iran's standard instituted	Europe council 1986	Standard 1053
AS	<0.05	<0.05	<0.05	<0.05	<0.05	0.01	0.05	0.05	-
AG	<0.01	<0.01	<0.01	<0.01	<0.01	NS	NS	-	-
AL	2.4	7.07	0.55	3.58	1.63	0.2	-	-	0.2
Ca	112	73	59	138	131	100	250	100	250
Cd	<0.02	<0.02	<0.02	<0.02	<0.02	0.0003	-	0.005	-
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	0.005	-	0.05	-
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	2	1	0.1	1
Fe	1.21	9.06	0.76	4.55	2.2	0.3	0.3	-	0.3
K*	2.8	6.3	5.7	14.6	12.2	-	-	12	-
Mn	<0.02	0.21	<0.02	0.18	0.09	0.4	0.5	0.02-0.05	0.5
Mg	29	23	24	36	35	50	50	30-50	50
Na	61	194	135	270	232	200	200	175	200
Ni	<0.02	<0.02	<0.02	0.02	<0.02	0.07	NS	5	-
pb	<0.05	<0.05	<0.05	<0.05	<0.05	0.01	0.005	0.05	-
Zn	<0.02	0.07	<0.02	<0.02	<0.02	3	3	0.1	3
NO ₃ ⁻	41	9	8	42	26	45	50	-	50
CL ⁻	18	13	19	330	180	250	400	25	400
SO ₄ ⁻²	230	274	298	508*	358	450	400-600	250	400
CO ₃ ⁻	0	0	0	0	0	-	-	-	-
HCO ₃ ⁻	180	200	195	125	140	-	-	-	-

Results and discussions

Studying the physical parameters of water samples taken from the area indicates that the samples contains standard amount of pH. Since the TDS values for potable water should be between 500 to

1000 mg/L(DeZuane, 1997), it is obvious that the studying samples have high level TDS of recommended value by EPA. For instance in sample Ag32, Ag19, Ag14 the amount of TDS was within 1200, which is nonpotable.

Also, the electrical conductivity (EC) of the samples is higher than European council (1986). The samples of the area's water have more hardness than the standard, therefore it is considered in the range of hard water (TH>300). This high hardness may result from limestone formation especially Sefidkooch and Nazarkarde. Nitrate and chloride levels in samples are less than the recommended standards of World Health Organization (WHO). While, sulfate and magnesium levels in samples are 508 and 36 mg/l respectively which make the water nonpotable.

Assessing the contamination of water

In order to assess the contamination of water, the concentration of heavy metals compared with WHO standard for drinking water were in almost all locations. An index for assessing the water contamination was applied. The index used is metal index (MI). The MI index was preliminarily defined by Tamasi and Cini (2004). This index can be expressed as the following equation:

$$MI = \sum \frac{Ci}{(MAC)}$$

Where C is the concentration of each element solution, MAC –Maximum Acceptable Concentration for each element, and subscript i is the ith sample. The higher the concentration of metal compared to its respective MAC value, the worse the quality of the water. If the concentration of certain element is higher than respective value (that is, MI > 1), the water can not be used according to this index (Tamasi and Cini, 2004). Table 3 shows the evaluated amounts of metal index based on standard WHO. Metal index reveal that all samples contain higher amounts of elements than standard which make the

water non-potable. The high concentration of iron and aluminum cause high MI value in water samples. For example in AG5 sample amount of aluminum and iron are more than 11 times as much the standard. The high concentration of iron in mine drainage can be attributed to the presence of pyrite oxidation (FeS₂) in coal (Fig. 2). The secondary biochemical reactions in sulfated environment, with the presence of Thiobacillusferrooxidans can release high quantity of aluminum in water sources (Toler, 1982). Calcium, potassium and sodium are also high in the water samples. This concentration can be attributed to lithogenic source (limestone formation).

By evaluating the pollution index of heavy metals (HPI) we can determine the effect of heavy metals on human health. It is defined as W_i taken as inversely proportional to the recommended standard (S_i) for each parameter. HPI model is given as

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

Where Q_i = subindex of the ith parameter. W_i is the unit weightage of ith parameter and n is the number of parameters considered. The subindex (Q_i) of the parameter iscalculated by

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

where M_i is the monitored value of heavy metal of ith parameter, I_i is the ideal value of the ith parameter and S_i is the standard value of the ith parameter in ppm. Generally, the critical pollution index of HPI value for drinking water is 100 (Prasad and Bose, 2001). The HPI values show that the samples are contaminated and non-potable (Table 3).

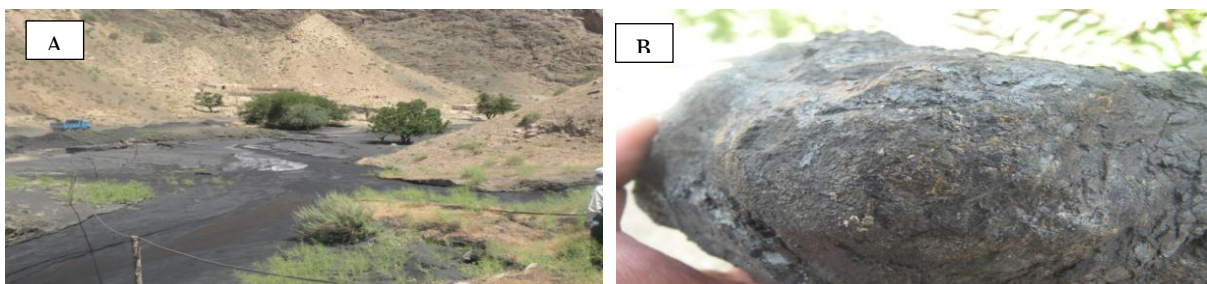


Fig. 2. A) Coal ash permeates the soils along the Agdarbandriver, B) Pyrite minerals in coal.

Assessing the correlation of heavy metals

For further examination about correlation in water samples, their Pearson correlation coefficients were calculated. Pearson correlation matrixes of elements with three parameters PH, TDS, and EC are shown in table 4. Pearson correlation coefficients calculated show that there is more positive correlation between iron and aluminum ($r=0.969$, $P < 0.01$). Also there is a high positive correlation between magnesium and calcium that indicates they have a common source (lithogenic source). Among anions, SO_4^{-2} and Cl^- have the highest correlation.

The techniques most commonly used in environmental studies, included in multivariate statistical methods, are cluster analysis (CA) and principal component analysis (PCA) (Mendiguchía *et al.*, 2007, Tariq *et al.*, 2006, Tokahoglu *et al.*, 2002). The CA technique comprises an unsupervised classification procedure that involves measuring either the distance or the similarity between objects to be clustered. The CA shows the relations between the elements (Fig 3). This diagram shows that there is a significant correlation

between the elements Al and Fe. These elements correlate with the group of Mn, HCO_3 , pH, TDS and EC. In contrast, K has a good correlation with Na, Cl^- and SO_4^{-2} . This group has a strong correlation with Ca, Mg and NO_3^- . Principal component analysis is a technique whereby a complex data set is simplified by creating one or more new variables or factors, each representing a cluster of interrelated variables within the data set. Results obtained with the application of the principal component analysis are presented in Fig. 4. PCA reveals that Fe, Al, Mn, HCO_3 and pH in first compound, Ca, Mg, NO_3^- , K, Na, Cl^- and SO_4^{-2} in the second compound and TDS and EC in the third compound are related together in each compound (Table 5). This result is compatible with the results from cluster analysis. The results of the statistical analysis of the heavy metal data indicate the elements in first compound have a same source and originate of the waste water of coal-washing factory (anthropogenic source). In addition, the second compound elements have the same source and originate from the limestone of Agdarband area (lithogenic source).

Table 3. MI and HPI index in water samples of studied area.

Sample	AG23	AG14	AG7	AG5	AG3
MI	3.1	6.2	1.4	11.4	3.6
HPI	772.77	1658.74	263.29	3283.16	869.51

Correlations

	Al	As	Ca	Cr	Cu	Fe	K	Mg	Mo	Ni	Pb	S	Sn	Zn
Al	1													
As	.062	1												
Ca	-.883**	-.200	1											
Cr	.325	-.192	-.571	1										
Cu	-.355	.344	.498	-.680*	1									
Fe	.658*	.744**	-.783**	.263	-.158	1								
K	.788**	-.707*	-.133	-.161	-.050	-.616*	1							
Mg	.709**	-.355	-.763**	.701*	-.803**	.306	.555	1						
Mo	-.383	.779**	.380	-.582*	.783**	.226	-.599	-.827**	1					
Ni	.305	-.346	-.565	.741**	-.746**	.113	.069	.810**	-.757**	1				
Pb	.411	.881**	-.541	.031	.227	.898**	-.618*	-.009	.546	-.119	1			
S	.001	.986**	-.110	-.281	.456	.682*	-.682*	-.456	.855**	-.452	.866**	1		
Sn	.684*	-.406	-.564	.029	.323	-.346	.745**	.250	-.321	.064	-.274	-.403	1	
Zn	.371	.792**	-.518	.069	.311	.812**	-.551	-.014	.523	-.068	.968**	.797**	-.157	1

** . Correlation is significant at the 0.01 level (2-tailed).
 * . Correlation is significant at the 0.05 level (2-tailed).

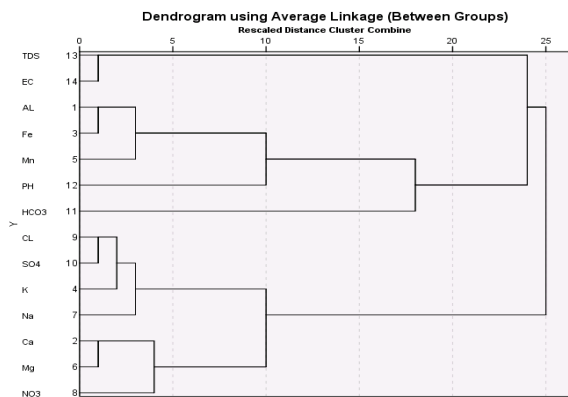


Fig. 3. Results of cluster analysis of heavy metals and associated parameters in Agdarbands water samples. Cluster analysis was performed using Pearson's method.

Table 5. Principal component analysis based on the measured variables in Agdarbands water samples.

	Component		
	PC1	PC2	PC3
AL	-.037	.727	.683
Ca	.763	-.480	.379
Fe	.087	.855	-.507
K	.986	.131	-.094
Mn	.465	.759	.456
Mg	.863	-.464	.131
Na	.880	.464	-.064
NO3	.459	-.687	.548
CL	.980	-.100	.082
SO4	.946	.073	-.037
HCO3	-.941	.322	-.084
PH	-.537	.256	.796
TDS	-.414	-.742	.528
EC	-.413	-.745	.524

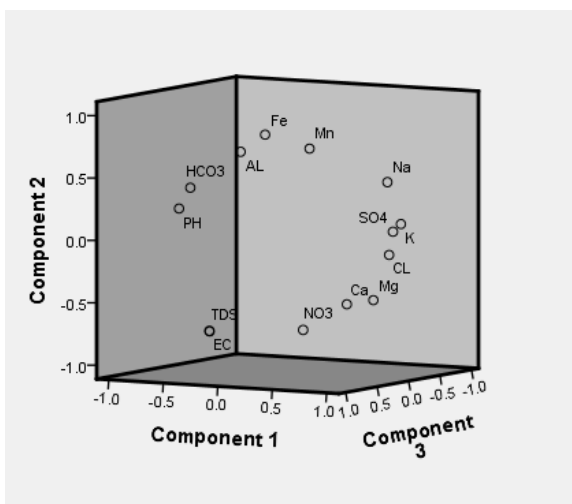


Fig. 4. Loadings of the rotated eigenvectors, vertical axis are the relevant component: PC1, PC2, PC3.

Conclusion

Our study reveals that TH, sulfate and magnesium levels in samples are higher than the recommended standards of WHO. In contrast, they have low levels in Nitrate and chloride. Pollution index value shows that all samples are polluted. MI in some cases reaches to eleven times higher than the standard values. The pollution index of heavy metals (HPI) shows that they have quantities more than 100 and as a result the surface water is non-potable. The evaluation of correlation between elements indicate that there is a significant correlation between Al, Fe, Mn, PH and HCO₃. This correlation is also seen between K, Na, Cl⁻, SO₄²⁻, Ca, Mg and NO₃⁻. Ideed, EC and TDS have the least correlation with the mentioned elements. The dendrogram of elements or CA analysis confirms this correlation. According to statistical analysis and the PCA it can be find the first compound elements (Al, Fe, Mn, PH and HCO₃⁻) have the same origin which results from anthropogenic source (the wastewater of coal washing factory). The origin of the second compound elements (K, Na, Cl⁻, SO₄²⁻, Ca, Mg and NO₃⁻) is the same and results from the limestones of Agdarband.

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