

# Environmental Impact and Drainage Geochemistry of the Abandoned Keban Ag, Pb, Zn Deposit, Working Maden Cu Deposit and Alpine Type Cr Deposit in the Eastern Anatolia, Turkey

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## 1. Introduction

This study includes the effect on the environment of abandoned and working mine deposits which are lead, zinc, silver and copper deposit in Keban, working copper deposits in Maden and chromite deposit in Alacakaya. These are the largest metallogenic province of Turkey (Figure 1).

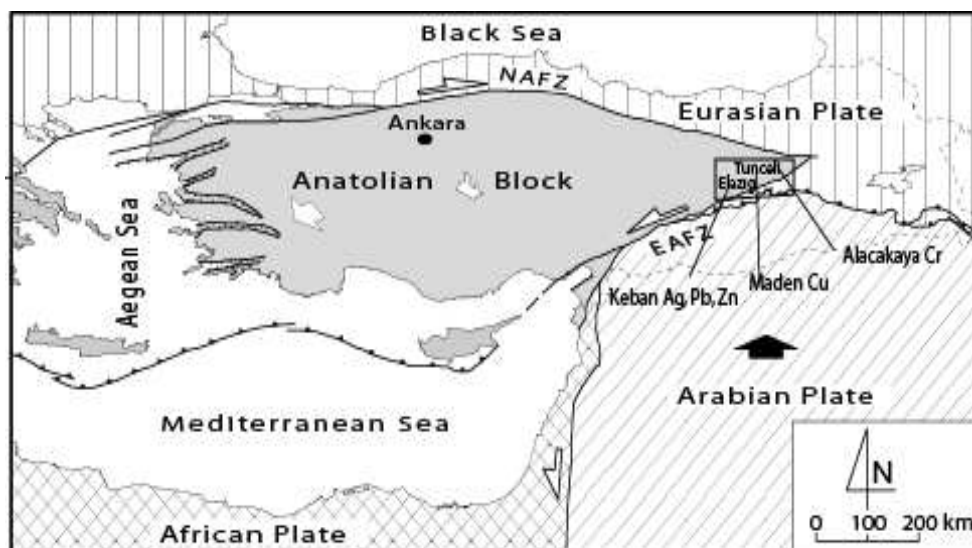


Fig. 1. Location map of the study area.

The Keban region was one of the most important base metal areas of eastern Turkey. The Keban area has been an important mining area since B.C. Archaeological studies revealed that ancient miners have mined the Keban area for gold, copper, lead, silver and iron. During twentieth century, the mining activity was restricted to iron, lead, zinc, silver and fluorite. The Keban mine was operated for Pb and Zn production at various times between the 1940s and the late 1980s. There were several prospect pits and mining tunnels in the area. However, mining ceased in 1988 and the site was abandoned. The west and east Euphrates slag sites account for on average 2.16 ppm Au, 66.41 ppm Ag, 2.38 % Pb, and 0.52 % Zn (Kalender & Hanelçi, 2001). The Euphrates River and its tributaries, in particular, Karamağara Stream, drain the former metal-mining areas, which have been contaminated by the release of heavy metals from old mining operations within the Keban mining district. Many geological studies have been conducted around the Euphrates River (Kalender & Hanelçi, 2001; Kumbasar, 1964; Kineş, 1969; Zisserman, 1969; Köksoy, 1975; Kipman, 1976; Akıncı et al., 1977; Balçık, 1979; Yılmaz et al. 1992; Çelebi & Hanelçi, 1998; Çalık, 1998; Kalender, 2000; Kalender & Hanelçi, 2001; 2002, Bölücek, 2002). However, none of these studies have addressed the issue of environmental contamination in the area. In this study will be presented geochemical results from several sampling media (sediments, mine-drainage waters, spring waters, river waters, moss, and algae) from the Keban mining district.

Maden copper deposit was important ore deposit of Turkey. Mining activity had been operated from 4000 B.C. up to the recent (Seeliger ve diğ., 1985, Tızlak, 1991). The mine was run by Rome, Seljuk and Ottoman Empires (1860-1915) and the Republic of Turkey. Maden copper mining operations have been transferred with the establishment of Etibank in 1935. Due to exhaustion of economic reserves were decided to close the facilities in 1995. However, Ber-Oner Mining has operated of the waste from 1995 to 2005. Since 2007, Maden copper mining waste has been operated by Eti Holding and SS Yıldızlar Holding and produced 20 000 tons of copper a year. Many geological studies have been conducted around the Maden copper deposit area (Erdoğan, 1977; Özkaya, 1978; Özdemir & Sağıroğlu, 1998; Özdemir & Sağıroğlu, 2000; Kirat et al, 2008).

In this study will be stressed dissolution methods and metal dispersion patterns were determined suitable for such an area by stream sediment survey. The physical and chemical feature of the area indicate that the metallic contents of the stream sediments originate from physical events rather than chemical events. In this case, 180-106  $\mu\text{m}$  sediment fraction were analysed. In addition to surface and seepage water samples were collected from the area and several elements were analyzed and data were evaluated in term of pollution. After study was conducted to evaluate the influence of anion (sulfate) and metals (copper, iron, manganese, zinc and nickel) on the reduction by these bacteria. Furthermore, the sulphate reducing bacterium methods were evaluated to selectively precipitate metals and reduction sulphate from Maden (Elazığ) copper Deposits AMD seepage waters in two samples locations. Initial and final metals and sulphate concentration before and after experiments, were measured and finally evaluated influence of bacteria.

Guleman ophiolite made up of tectonites which comprises dunite and chromite bearing hazburgites and cumulates which contain dunites, wehrlite, clinopyroxenite, gabbros,

diabase dykes, sheetdyke complex and basic volcanites are other constituents of the ophiolite. This area has been studied by Erdoğan, 1977; Erdoğan, 1982; Başpınar, 2006. There are thirty rock samples of Guleman Ophiolite were analyzed by Başpınar in 2006 and ten groundwater samples were analyzed by Kalender in 2010. This study includes correlation of both analysis results of data.

This study mainly focus on the concentrations and distributions of heavy metals and potentially toxic elements in the various sampling media impacts on environment pollution in the three different ore deposit

## 2. Keban Ag-Pb-Zn deposit

### 2.1 Sampling and analytical methods

Water, stream-sediment, algae samples were collected from the study area. Water samples were taken from natural springs (LK 1, LK 2, LK 3, LK 4, LK 6, LK 7, LK 8, LK 9, LK 10), mine-drainage waters (LK 5: fluorite production gallery; LK 8: Pb-Zn underground-mine production workings) and the Euphrates River (LK 11). Algae samples were collected from the bed of the Euphrates River (AK 13, AK 14, AK 18) and only one moss sample. Sediment samples were collected from the Euphrates River bed (LZ 120, LZ 150, LZ 160, LZ 170), from Karamağara Stream (LZ 270, LZ 310, LZ 330, LZ 340, and LZ 350) and from precipitates at the gallery mouth (LZ 370) (Figure 2). All of the sampling work was done in June 2002 (Kalender & Bölücek, 2004; Bölücek, 2007).

Water samples were collected into 250-ml polyethylene containers and filtered through 0.5 µm membrane filter paper (4.5 cm diameter). Temperature and pH measurements were conducted at the sampling sites. 5 ml concentrated HNO<sub>3</sub> (MerckTM ultra pure) was added to the samples for metal analyses. Samples were stored in the laboratory at +4°C until they were analyzed. For each sediment sample, 2 kg of sediment was sampled from a depth of about 10 cm by sieving to 2 mm mesh size. For analyses, samples dried in the laboratory were sifted using stainless steel sieves to mesh sizes between -80 and +140. The samples were subjected to partial-digestion involving the use of a cold solution of 0.3 % NaCN and 0.1 NaOH to extract weakly-bound elements from clay, organic matter, and amorphous Mn and Fe hydroxides (Kelly et al., 2003). Green algae *Cladophora glomerata* in sample AK 14 is a typical species in rivers; it is found together with macroalgae (Entwistle, 1989; Power, 1992). *Cladophora glomerata* is found mainly in volcanic areas (Whitton et al. 1998). The presence of *Cladophora glomerata* is used as an indicator of good-quality water. Aksın et al. (1999) examined the Keban stream algae and determined 70 taxa from the *Clorophyta*, *Cyanophyta*, *Bacillariophyta*, and *Dinophyta*. These workers reported that diatoms are the dominant group of organisms among the pelagic and benthic algae population because of the rapid water flow of Keban Stream. Algae species living in the Euphrates River differ from those in Keban Stream due to the temperature and low current velocity in the former. They are quite common in the river beds having low current velocity, that receive little light, and that have temperatures above 10°C (Schönborn, 1996). The temperature of the Euphrates (12.4–12.7°C) is suitable for the growth of this type of algae. Investigations indicate that the amount of this organism will increase with increasing temperature. The size of *Didymodon tophaceus* is around 0.5–5 cm. It is composed of circular cells that widen toward the base, and is mainly

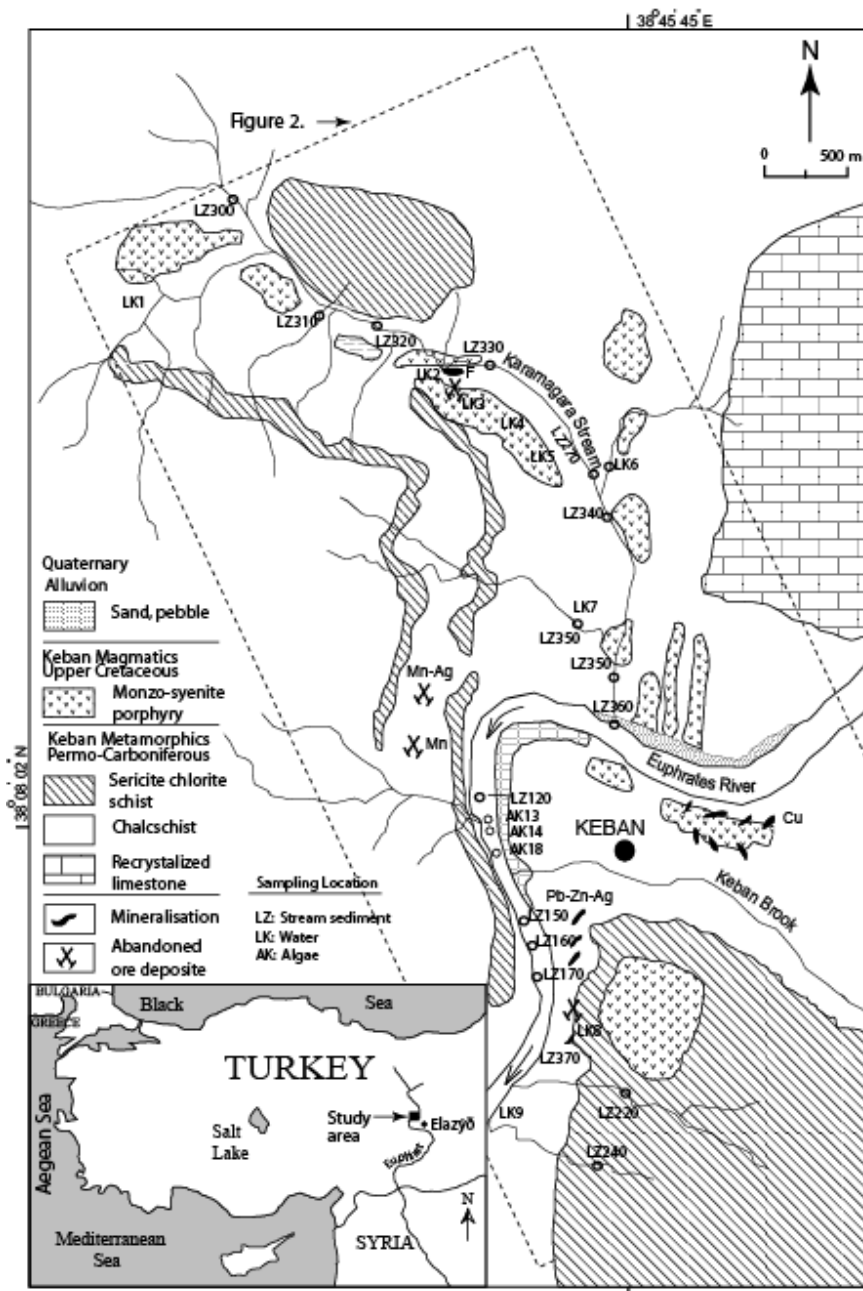


Fig. 2. Simplified geological map of the study area Kalender & Hanelçi, (2001; 2002) and locations of sampling sites (natural spring waters: LK 1-LK 4, LK6, LK 7, LK 9, LK 10; mine-drainage waters: LK 5, LK 8; Euphrates River water: LK 11).

olive green but turns brown in its lower parts. Moss and algae samples were washed using distilled water and dried in air in the laboratory. 0.5 gr sample batches were digested to dryness at a temperature of 95°C for one hour after adding 2 ml of HNO<sub>3</sub> and then 3 ml of a 2:2:2 HCl:HNO<sub>3</sub>:H<sub>2</sub>O mixture. A total of 38 elements in the water samples were analyzed by ICP/MS (inductively coupled plasma/mass spectrometry); F in water was analyzed by ion electrode. Sediment samples were analyzed by ICP/MS, except for Au and Hg which were determined by atomic absorption (AA) after MIBK extraction and flameless AA, respectively. The algae and moss samples were analyzed by the ICP/ES (inductively coupled plasma emission spectrometry) and ICP/MS methods.

## 2.2 Results and discussion

It was determined that Mg, Ca, S, Fe, F, Mn, Zn, Mo, Ba, Pb, U, Ni, Cd, Co, Ag, Cu, Sb and Se contents of groundwater are above the standards of drinking water and it is also enriched in some toxic elements such as Al, Cd, Cr, Fe, K, Mg, Mn, Na, Pb, Sb, SiO<sub>2</sub>, Tl and Zn. The springs particularly issuing from the mine galleries are probably the main source of pollution parameters. Analyses of weak leaching elements of -80 +140 mesh size sands collected from some main river and creeks indicate high As, Cu, Zn, Mo and Ag contents, various algae samples are characterized with high Cu, Pb, Zn, Ag, Cd and Cr concentrations. In this study will be determined the source and impact on environment of pollution in water, stream sediment and plants.

Element concentrations in different water samples are variable, with the Ba, Ca, Cd, Ce, Co, Cr, Cs, Mg, Mo, Pb, Rb, S, Se, U, Zn contents of most of these samples being above the world averages encountered in ground water (Table 1). The high metal concentrations in the samples originated from waters moving through the old mine adits or unexploited mineralized areas. This conclusion is supported by the compositions of waters collected from the adits (LK 5, LK 8).

In Table 2, the results of chemical analyses are compared to various standards in order to evaluate the drinking quality of waters. The concentrations of Cd, Pb, Tl, Cr, and Sb measured in these samples were higher than 0.005 mg/l<sup>-</sup>, 0.015 mg/l<sup>-</sup>, 0.002 mg/l<sup>-</sup>, 0.05 mg/l<sup>-</sup>, 0.006 mg/l<sup>-</sup>, respectively, which exceed the limits allowed for drinking waters (USEPA, 2002; WHO, 1993; Canada MAC, 2001; EEC, 1992). According to international standards, the concentrations of some other elements (Al, Fe, K, Mg, Mn, Na, SiO<sub>2</sub>, Zn, and F) are significantly higher than the maximum permissible levels and, therefore, these waters should not be used for drinking. In light of these data, it is concluded that contamination of these waters by heavy metals and other toxic elements through mining, production galleries, and slag sites also causes environmental contamination.

Spearman correlation coefficients were calculated and their values at a significance level of  $\alpha=0.05$  are summarized in Table 3. Spearman correlation coefficients given in brackets for the element pairs are: As-Cs (0.68), As-Re (0.65), Cd-Co (0.75), Cd-Cu (0.64), Cd-Fe (0.66), Cd-Mn (0.89), Cd-Zn (0.88), Se-S (0.85), Se-Re (0.86). Se, a chalcophile element found in appreciable amounts in polymetallic sulfide ores, easily dissolves in water by oxidation of sulfides and shows significant correlation with S and Re.

Elements	Median	Mean	Detection Limits	St. Dev.	Maximum	Groundwater World Average
As	2.5	3.3	0.5	2.91	11	2
B	20	27.4	5	13.23	58	10
Ba	43.345	44199	0.05	24.21	76.82	20
Br	46	124	5	195	654	20
Ca	89825	163275	0.05	154884	455325	50000
Cd	0.115	2.475	0.05	5.17	14.82	0.03
Ce	0.115	0.504	0.01	1.2	3.9	-
Cl	4000	10800	1	14413	49000	20000
Co	0.11	2.219	0.02	4.89	14.82	0.1
Cr	12.75	53.96	0.5	127.79	416.3	1
Cs	0.43	0.71	0.01	0.82	2.48	0.02
Cu	2.55	3.64	0.1	3.03	10.2	3
Fe	31	166	10	356.36	1171	100
In	47.5	45.3	0.01	7.85	57	7
K	2745.5	6410	0.05	8189	27565	3000
La	0.065	0.74	0.01	2.09	6.69	0.2
Li	6.5	13	0.1	14.32	41	3
Mg	27742	73133	0.05	94490	307178	7000
Mn	4.64	4421	0.05	13559	43000	15
Mo	15.9	34.38	0.1	39.96	109	1.5
Na	4228.5	15716	0.05	26916	90025	30000
Nd	0.055	0.18	0.01	0.38	1.25	-
P	22	24.7	20	5.4	33	20
Pb	10.75	15.86	0.1	14.58	47	3
Rb	14.54	21.94	0.01	24.89	82.28	1
Re	0.04	0.46	0.01	1.19	3.84	-
S	36000	138700	1	176251	399000	30000
Sb	0.575	1.49	0.05	2.24	7.26	2
Sc	5.135	5.38	1	1.49	8.29	-
Se	1.15	2.05	0.5	2.07	7.5	0.4
Si	19	18.5	40	5.43	29.6	16
Sn	0.425	0.992	0.05	1.26	4.3	0.1
Sr	1082.63	2008	0.01	2125	5668	400
Tl	1.31	4.36	10	8.51	27.75	0.002
U	17.58	17.71	0.02	14.08	32.02	0.5
Y	0.04	0.15	0.01	0.33	1.09	-
Zn	101.55	2466	0.5	5881	18573	20
F*	-	-	-	-	2200	100

Table 1. Statistical parameters for chemical composition of water samples ( $n=10$ ,  $\mu\text{g l}^{-1}$ , \*  $\text{mg l}^{-1}$ ). Elemental contents in groundwater are from Rose et al., 1979; Concentrations higher than the normal values for water are shown in bold.

Elements	Median	Mean	Std. dev.	Guidelines	Maximum values and sample code
Al	0.064	0.64	1836	0.05-0.2*	5.872 (LK-5)
Cd	0.0001	2.475	5.17	0,005*	0.014(LK-5);0.009 (LK-8)
Cr	0.013	0.054	127.79	0.1*	0.416(LK-2)
F	-	2200	-	1.5**	2200(LK-5)
Fe	0.031	0.166	356.36	0.3*	1.171(LK-8)
K	2.745	6.41	8189	12****	27.565 (LK-5)
Mg	27.742	73.133	94490	50****	307.178 (LK-9);163.114(LK-8);88.830 (LK-5)
Mn	0.005	4.421	13559	0.05*	43 (LK-5);0.1(LK-4);1.1(LK-8)
Na	4.228	15.716	26916	20*	90.025(LK-9);243 (LK-8)
Pb	0.011	0.016	14.58	0.0 15*	0.047(LK-10);0.018(LK-5);0.019(LK-2); 0.034(LK-1)
Sb	0.006	0.001	2.24	0.006*	0.007(LK-8)
Si <sub>02</sub>	19	18.05	5.43	10***	29.6(LK-5)
Tl	0.001	0.004	8.51	0.0005-0.002*	0.028(LK-5);0.0065(LK-4);0.002(LK-8);0.004(LK-3)
Zn	0.101	2.466	5881	5*	18.573(LK-5);5.2(LK-8)

Table 2. According to different drinking water guidelines that elements exceed of maximum contaminant level (MCL), n=10 mg/l<sup>-1</sup>. \* = USEPA: United State Environmental Agency \*\* = WHO: World Health Organization Guidelines, \*\*\* = Canada MAC: These limits are established by Health Canada; \*\*\*\* = EEC: Europium Economy Community.

	pH	Al	As	Ba	Ca	Cd	Cl	Co	Cs	Cu	Fe	K	Mg	Mn	Pb	Re	S	Se	Zn
pH	1.00																		
Al	-0.15	1.00																	
As	-0.38	0.07	1.00																
Ba	0.50	0.10	-0.90	1.00															
Ca	-0.78	0.06	0.53	-0.64	1.00														
Cd	-0.57	0.51	0.47	-0.44	0.62	1.00													
Cl	-0.02	-0	0.51	-0.49	0.55	0.27	1.00												
Co	-0.57	0.21	0.22	-0	0.62	0.75	0.37	1.00											
Cs	-0.79	-0	0.68	-0.67	0.80	0.5	0.27	0.31	1.00										
Cu	-0.41	0.85	0.08	-0.07	0.21	0.64	-0.10	0.58	0.04	1.00									
Fe	-0.19	0.09	0.06	0.03	0.37	0.66	0.37	0.82	-0	0.4	1.00								
K	-0.56	0.04	0.07	-0.67	0.81	0.46	0.6	0.29	0.90	0.01	0.03	1.00							
Mg	-0.22	0.21	0.55	-0.56	0.73	0.6	0.87	0.45	0.43	0.19	0.48	0.69	1.00						
Mn	-0.79	0.3	0.43	-0.53	0.82	0.89	0.25	0.76	0.67	0.48	0.58	0.53	0.54	1.00					
Pb	0.32	0.72	-0.30	0.28	-0.50	0.15	-0.38	0.05	-0.6	0.65	0.10	-0.61	-0.30	-0.10	1.00				
Re	-0.63	0.04	0.65	-0.74	0.89	0.5	0.69	0.51	0.80	0.06	0.22	0.84	0.73	0.72	0.50	1.00			
S	-0.61	-0.1	0.55	-0.61	0.93	0.41	0.72	0.50	0.64	0.09	0.33	0.73	0.81	0.64	-0.61	0.86	1.00		
Se	-0.43	-0.4	0.39	-0.46	0.68	0.11	0.63	0.22	0.42	-0.20	0.17	0.44	0.56	0.43	-0.70	0.73	0.85	1.00	
Zn	-0.27	0.49	0.55	-0.47	0.56	0.88	0.5	0.60	0.44	0.48	0.61	0.59	0.69	0.69	0.10	0.6	0.43	0.10	1.00

Table 3. Correlation coefficients (n=10); significant at α=0.05.

The negative correlation (-0.70) between Pb and Se indicates different solubility behavior of the Se and Pb under surficial oxidizing conditions. The negative correlations between Pb-S (-0.61) element pairs may indicate that Pb compounds with S (e.g., lead sulfo-salts) are quite

sensitive to dissolution. However, their enrichment in the waters is attributed to formation of complex Pb–Mn and Pb–Cr oxides (oxyhydroxide complexes). Negative correlation between Al and pH (Table 3) indicates that the amount of aluminum dissolved in water increases with increasing acidity. As seen in the underground spring, the presence of  $\text{CaF}_2$  in the water affects Al solubility by forming  $\text{AlF}_6^{-3}$  type complexes.

The elemental contents of water, syenite porphyry, fluorite, molybdenite, silver-manganite and stream sediments are given in Table 4. To date, no analyses have been done for As, B,

Elements	**Fluorite molibdenite	**Silver manganite	***Syenite porphyr	Detection Limits	Stream Max.	Sediment Min.	Mean	Detection Limits
Al	47900	2700	46300	100	<10	<10	<10	%0.01
As	168	328	-	1	99999	0.245	13.712	0.1
Ba	10600	774000	2516	5	1.57	0.01	0.67	0.5
Br	11.64	21	-	0.1	<5	<5	<5	5
Ca	250000	148400	26200	100	20	5	12	5
Cd	16.75	3	-	0.1	-	-	-	-
Cl	-	126	-	0.1	85	10	29	10
Co	7.35	6	9.86	0.2	0.061	0.002	0.021	0.1
Cr	33.05	34	-	0.5	0.12	0.05	0.08	0.5
Cu	163	82	173	0.1	13.57	0.3	6.1	0.01
Fe	22800	84800	5200	100	12	5	5.86	0.01
K	4900	950	73400	100	172	19	59	0.01
Mg	18900	76600	5800	100	<5	<5	<5	0.01
Mn	3200	51900	3300	100	0.5	0.1	0.33	1
Mo	2500	-	-	0.1	12.75	13	2.94	0.01
Na	1500	270	15500	100	-	-	-	0.001%
P	200	43600	20	10	3	1	1.44	0.0001%
Pb	5500	6100	98.18	0.1	0.12	0.01	0.03	0.01
Rb	89	15	181	0.1	-	-	-	-
S	2500	3700	-	5	-	-	-	-
Sb	89	61	-	0.1	0.04	0.005	0.014	0.02
Se	25.84	7	-	0.5	1.34	0.07	0.41	0.01
Si	181200	35800	617800	100	-	-	-	-
Sn	45.55	65	-	1	-	-	-	-
Sr	700	-	673	0.5	2.47	0.02	1.4	0.5
Tl	4.08	10	-	0.1	-	-	-	0.02
Zn	872	456	163	1	14303	0.38	1665	0.1
U	49.71	6	-	0.1	-	-	-	0.05
F(n=4)	183000	571	-	100	6120	460	2542	100

Table 4. Content of elements in mineralizations and syenite porphyry and stream sediments in ppm (\*\*= Çelebi ve Hanelçi, 1998, n=21, ppm; \*\*\* Kalender, 2000, n=22, ppm).



Br, Cd, Ce, Cl, Cs, La, Li, Mo, Nd, S, Sb, Sc, Se, Sn, Tl, U, and F in the syenite porphyries. The F, Mo, Mn, and Ag in the water samples were derived from fluorite ( $\text{CaF}_2$ ), molybdenite ( $\text{MoS}_2$ ), pyrolusite ( $\text{MnO}_2$ ) and Ag-sulfosalts while their Cd, Co, Cr, Cu, Fe, Sb, Se, Sn, and Z contents originated from dissolution of chalcopyrite ( $\text{CuFeS}_2$ ), arsenopyrite ( $\text{FeAsS}$ ), enargite ( $\text{Cu}_3\text{AsSbS}_4$ ), and loellingite ( $\text{FeAs}_2$ ). The Na, Al, Ca, K, and  $\text{SiO}_2$  concentrations of the waters resulted from the dissolution of the syenite porphyries themselves (Bölücek & Kalender, 2009).

Bioaccumulation values were calculated from two algae and one moss species. Bioaccumulation is a parameter that describes bioconcentration as the ratio of the concentration of a chemical species an organism to the concentration in the surrounding environment. Bioaccumulation factor (BAF) is calculated as follows:

$$\text{BAF} = (\text{whole body concentration of X}) / (\text{exposure media concentration of X})$$

The element contents and BAF values of the species are given in Table 5. *Bangia atropurpurea* (red algae) in the samples (AK 13 and AK 18) from the Euphrates river bed ( $T=13^\circ\text{C}$ ,  $\text{pH}=8$ ) was first described by Kishler & Taft (1970), in Lake Erie. This species is generally common in marine environments, gulfs and bays (estuarine). However, it is also found in continental waters where climatic conditions are suitable. *Bangia atropurpurea* is commonly found in iron-rich alkaline ( $\text{pH}=8-8.7$ ) fresh waters. When compared to *Cladophora glomerata*, it has a higher capacity for absorption of Cu, Pb, Ni, Mn, Au, Cr, Mg and S. *Bangia atropurpurea* contains 6 fold Cu, 26 fold Ni, 2.7 fold Mn, 11.5 fold Au, 20.5 fold V, and 77 fold Cr compared to *Cladophora glomerata*. As is well-known, bioaccumulation is the net accumulation of a chemical by an aquatic organism as a result of uptake from all environmental sources. Thus, BAF values in this study were calculated for green and red algae samples according to the elemental contents of river water and, for moss samples, according to the elemental contents of spring and mine-drainage waters collected from the same locations (Table 5). The chemical concentrations in tissues of aquatic organisms and water can be defined in terms of chemical partitioning between different biological or chemical phases. BAF values in *Bangia atropurpurea* for Mo, Cu, Ag, Sb, P, Mg, Ba, and  $\text{SO}_4$  are higher than those *Cladophora glomerata*, whereas BAF values for Zn, Co, V, Ca, La, B, Al, Hg, and Se are higher in *Cladophora glomerata* than those in *Bangia atropurpurea*. Total BAF (total concentration of the chemical in tissue / total concentration of chemical in water) values for *Bangia atropurpurea* are higher than those for *Cladophora glomerata* (Table 5). In sample AK-14 in comparison to *Bangia atropurpurea*, *Cladophora glomerata* has higher capacity of absorption for Cd, Bi, B, Hg, Se, Fe, Co, Ag, and Zn (Table 5). Particularly, the Hg (13 fold) and Cd (3.8 fold) contents of *Cladophora glomerata* may indicate that these algae may have a direct effect on the ecosystem. The moss, *Didymodon tophaceus* (Brid.) Lisa generally grows on Paleozoic limestones and dolomites, and is generally observed along banks and hilly areas close to river bed with gentle slopes. The highest BAF values in this study were observed in moss (*Didymodon tophaceus*) sample MK 20, indicating that the moss tissues have an ability to absorb heavy and toxic metals from mine-drainage waters. In this study, it was observed that there is considerable pollution of the waters and stream sediments in the Euphrates River. However, the presence of water plants have a positive effect on the aquatic ecosystem by absorbing the heavy metals and toxic elements (Pb, Hg, Cd, Cr, and As). Therefore, algae and moss can be used to remove some of the heavy metals and toxic elements from mining-waste water.

Elements	Detection Limits	LK13	LK 14	LK 18	LK 20	LK 8	LK 11
		<i>Bangia atropurpurea</i>	<i>Cladophora glomerata</i>	<i>Bangia purpurea</i>	<i>D. Tophaceus (Brid.) Lisa</i>	<i>Derebaca Gallery</i>	<i>Eupharate River</i>
Mo	0.01	0.38	0.26	0.33	0.36	0.001	0.003
Cu	0.01	13.15	1.54	9.26	68.61	0.002	0.003
Pb	0.01	1.75	<0.01	1.85	269.76	0.004	0.0002
Zn	0.1	155.4	267	117.9	3051.3	5.19	0.003
Ag*	2	11	70	8	1575	-	<0.05
Ni	0.1	6.3	0.1	2.6	25.1	-	<0.0002
Co	0.01	0.49	0.65	0.28	6.96	0.007	0.000008
Mn	1	22	15	41	1034	1.076	<0.00005
Fe	0.001%	730	930	390	3450	1.171	<0.01
As	0.1	6.3	13.9	13.3	123.5	0.011	0.003
U	0.01	0.27	0.39	0.15	6.86	0.04	0.0074
Au*	0.2	3.3	<0.2	2.3	17.3	<0.05	<0.05
Th	0.01	0.1	0.11	0.04	0.03	-	<0.00005
Sr	0.5	41.4	53.3	56.6	307.8	2.181	0.842
Cd	0.01	0.21	0.57	0.15	12.22	0.009	<0.00005
Sb	0.02	0.03	<0.02	0.19	0.98	0.007	0.001
Bi	0.02	0.05	145	0.02	0.09	-	<0.00005
V	2	11	226	11	12	-	0.001
Ca	0.01%	10400	13800	9800	46900	436.67	55.37
Pb	0.01	3020	840	4210	2060	0.02	0.023
La	0.01	0.29	2.21	0.12	1.02	0.0003	0.00001
Cr	0.1	4.98	0.05	3.87	3.87	0.011	<0.0016
Mg	0.0001%	2130	1830	2080	2091	163.11	18.56
Ba	0.1	8.2	22.3	12.6	30.3	0.016	0.026
Ti	1	14	13	14	7	-	<0.01
B	1	12	347	9	336	0.034	0.1
Al	0.001%	300	400	200	300	0.013	0.01
Na	0.001%	840	830	460	420	24.36	21.06
K	0.001%	300	300	1200	10600	10.047	1.82

Table 5. Content of elements in moss, algae and water in the Euphrate River,\* = ppb; the other elements are given ppm.

### 2.3 Conclusions

The present study focused on the environmental geochemistry samples of water, stream sediment, algae and moss from the Keban mine district. The average concentrations of Mo, Cu, U, Sb, Mg, Hg, Se ve SO<sub>4</sub>, Sr, V, Ca, P, Ba, B, Na, and Sc in Euphrates River water collected from near the former mining district were found to be elevated relative to average element concentrations reported for river waters. The concentrations of Al, Cd, Cr, F, Fe, Mg, Mn, Na, Pb, Sb, SiO<sub>2</sub>, Tl, and Zn in water samples collected near the mineralized locations were higher than the maximum permissible standards for drinking water and, thus, it was determined that these waters are not drinkable. Consequently, these waters, which are used for drinking and agricultural purposes in rural areas, may pose a serious risk to public health. The high concentrations of As, Mo, Se, Cu, Zn, and Pb in the Karamağara Stream and Euphrates River sediments and waters suggest that both mechanical and chemical dispersions are dominant in the area. The element concentrations

in tissues of green and red algae collected from the Euphrates River bed were compared with those in moss collected from the mouth of the mine adit. The concentrations of Cu, Pb, Ni, Mn, Au, V, and Cr in *Bangia atropurpurea* were found to be higher than those in *Cladophora glomerata*, but Zn, Co, Fe, Cd, Hg, Se, Ga levels in *Cladophora glomerata* are much higher than those in *Bangia atropurpurea*. The Cu, Pb, Zn, Mn, Ag, Ni, Co, Fe, As, U, Sr, Cd, Ca, K, Mg, Ba, and Au contents of *Didymodon tophaceus* (Brid.) Lisa are higher than those of the algae. Total BAF values for *Bangia atropurpurea* are higher than for *Cladophora glomerata*, while the total BAF values of the moss are highest.

These geochemical results suggest that chemical leaching–precipitation reactions are taking place near the Keban mine slags. The spatial distributions of metals in the sampling media of the Keban mining district suggest that the causes of the contamination are primarily the previous mining activities and to a lesser extent natural weathering products of the various types of mineralized zones in the area.

### 3. Maden copper deposit

#### 3.1 Sampling and analytical methods

The second study area is Maden Copper deposit in which the water and stream sediment geochemistry were studied (Figure 3; Figure 4). The water samples were collected from

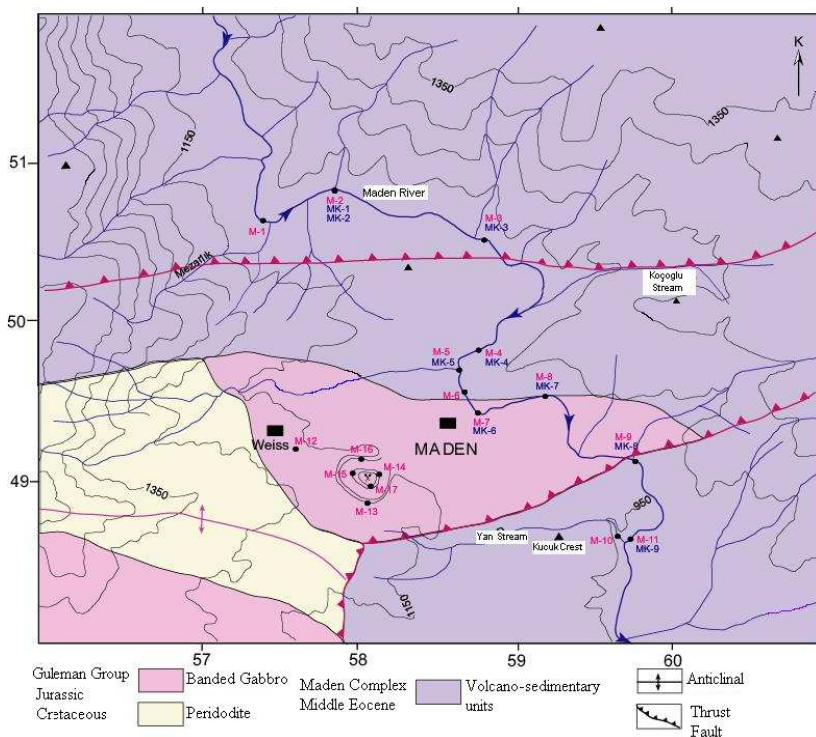


Fig. 3. Geology map of the Maden copper deposit and sediment samples location (MK: stream sediment samples, M: water samples; modified Kirat et al.2008; Kalender et. al. 2010).

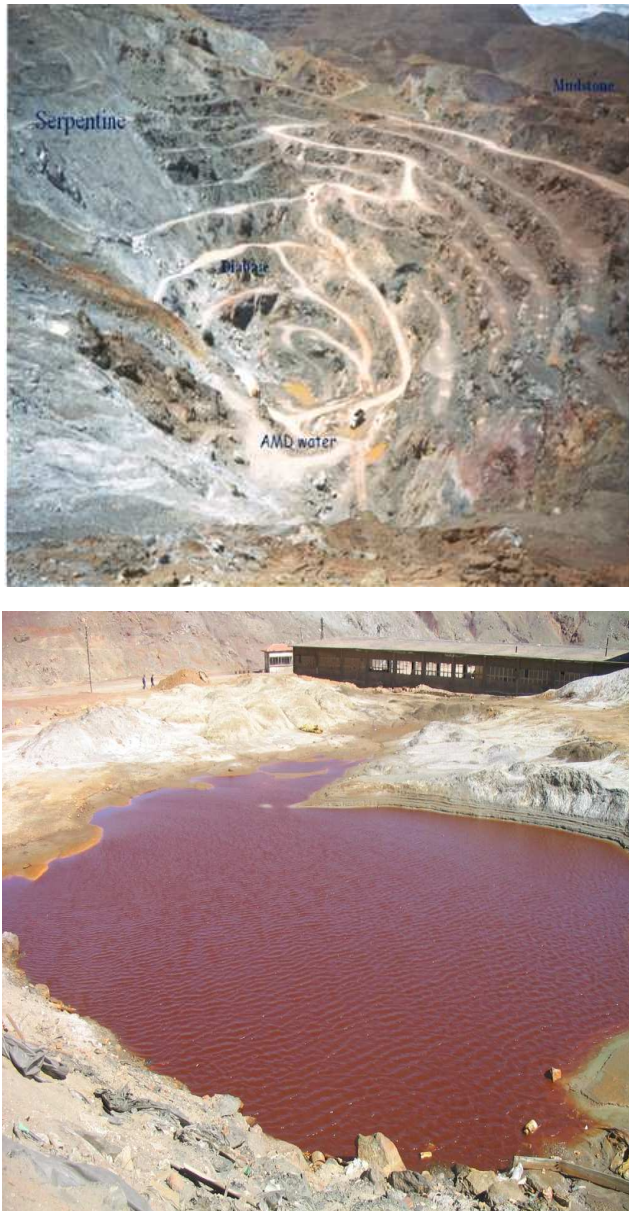


Fig. 4. AMD waters in the Maden copper deposit.

M1- M11 (spring water samples; M12-M17 seepage water samples; M18-M24 waste water samples from copper flotation) and sediment samples from Maden Stream sediment then sediment samples were sieved in different size sediment fractions (range 850 to  $-500 \mu$ ; 500 to  $-180 \mu$ ; 180 to  $-106 \mu$ ; 106 to  $-75 \mu$ ;  $<75 \mu$ ) analyzed by ICP-OES and IC (for  $\text{SO}_4$ ).

### 3.2 Results and discussion

The water samples taken from the vicinity of copper deposits within the scope of this study were determined for the metal content.

The waste waters from copper flotation (M18-M24) has increased over the metal content than the other samples. However, the mean values of analysis of water for all the sample points are given in Table 6 and these values are compared with drinking water standards. According to Table 6 Al, Ca, Fe, Mg, Mn and Zn values are higher than drinking water contents. Kalender & Bölücek (2007) indicated that metal contents are higher than maximum contaminat levels for drinking water and quite high enough to be dangerous to agriculture and stock raising and, thus to human health.

Elements	Max.Conta- minant Level (mg <sup>l</sup> <sup>-1</sup> )	Water samples	
		Mean (mg <sup>l</sup> <sup>-1</sup> )	Max. (mg <sup>l</sup> <sup>-1</sup> )
Al*	0.20	20.90	53.125
Ca	10-100	125.26	478.832
Cd	0.003	0.042	0.156
Co	1	10.42	21.546
Cu	1	107	314.962
Fe	0.2	9.65	22.106
Mg	125	486.47	491.564
Mn**	0.05	7.72	27.253
Ni	0.02	0.90	3.513
Pb	0.0015	0.0092	0.0388
Se	0.01	0.058	0.075
Zn	5	51.02	43.304
SO <sub>4</sub> ***	400	162	13224

Table 6. Drinking water maximum contamination level, (\*: EEC, \*\*: USEPA, \*\*\*: EQS fresh water, the others from WHO, standard values taken from Pais & Jones, 2000; Siegel, 2002). n=24.

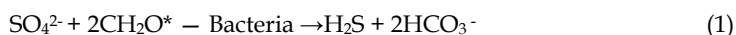
Within the scope of this study, Cu, Fe, Mn, Zn, Ni and SO<sub>4</sub> values of two seepage water in location no M15-M16 which had the highest metal concentration were analyzed before and after sulfate-reducing bacteria experiment (Figure 3 and 4; Kalender et.al. 2010).

Table 7 presents Cu, Fe, Mn, Zn, Ni and SO<sub>4</sub> values analyzed before and after adding bacteria to AMD water samples (M15, M16). It was found that in M15 and M16 locations, Cu values decreased from 151 µg<sup>l</sup><sup>-1</sup> to average 5.82 µg<sup>l</sup><sup>-1</sup>, from 1447 µg<sup>l</sup><sup>-1</sup> to average 29.1 µg<sup>l</sup><sup>-1</sup>; Fe values decreased from 132.2 µg<sup>l</sup><sup>-1</sup> to average 2.43 µg<sup>l</sup><sup>-1</sup>, from 517 µg<sup>l</sup><sup>-1</sup> to average 9.92 µg<sup>l</sup><sup>-1</sup>; Mn values decreased from 75.7 µg<sup>l</sup><sup>-1</sup> to average 19.33 µg<sup>l</sup><sup>-1</sup>, from 1695 µg<sup>l</sup><sup>-1</sup> to average 449.46 µg<sup>l</sup><sup>-1</sup>; Zn values decreased from 34.4 µg<sup>l</sup><sup>-1</sup> to average 0.45 µg<sup>l</sup><sup>-1</sup>, from 3212 µg<sup>l</sup><sup>-1</sup> to average 40.22; Ni values decreased from 4.3 µg<sup>l</sup><sup>-1</sup> to average <0.1, from 70.4 µg<sup>l</sup><sup>-1</sup> to average 4.49 µg<sup>l</sup><sup>-1</sup>; SO<sub>4</sub> values decreased from 1417.8 µg<sup>l</sup><sup>-1</sup> to average 788.38 µg<sup>l</sup><sup>-1</sup> and from 1719.2 to average 925.22 respectively.

Before Experiment						
Sample code	Cu	Fe	Mn	Zn	Ni	SO <sub>4</sub>
M15	151.1	132.2	75.7	34.4	4.3	1417.8
M16	1447	517	1695	3212	70.4	1719.2
Detection Limits	0.1	10	0.05	0.5	0.2	0.1mgL <sup>-1</sup>
After Experiment						
	Cu	Fe	Mn	Zn	Ni	SO <sub>4</sub>
M15-1-0.2	1.81	2.30	18.92	0.34	0.55	784.2
M15-2-0.2	1.70	2.40	19.23	0.37	<0.1	794.7
M15-1-2	2.63	2.60	19.45	0.42	<0.1	778.4
M15-2-2	2.7	2.72	19.98	0.48	<0.1	786.2
M15-1-20	13.51	2.25	18.9	0.52	<0.1	785.3
M15-2-20	12.6	2.28	19.5	0.56	<0.1	798.5
M16-1-0.2	36.18	9.07	423.5	30.2	3.6	924.4
M16-2-0.2	35.20	10.6	426.2	36.5	4.7	919.3
M16-1-2	23.12	10.7	452.5	40.5	4.5	920.5
M16-2-2	25.6	10.96	460.2	43.80	5.6	925.6
M16-1-20	26.7	8.87	462.2	44.66	4.33	932.5
M16-2-20	27.9	9.32	472.2	45.67	4.2	929.3

Table 7. pH values and metal contents ( $\mu\text{g l}^{-1}$ ) of acidic seepage waters in two different sample collection locations before and after bacteria experiment M1.; 1: G20, 0.2 ml; M1.; 2: NO132, 0.2 ml; M1, 1: G20, 2ml; M1; 2: NO132, 2ml; : M1; 1: G20; 20 ml; M1, 2: NO132, 20ml; M2.; 1: G20, 0.2 ml; M2.; 2: NO132, 0.2 ml; :M2, 1: G20, 2ml; M2; 2: NO132, 2ml; M2; 1: G20; 20 ml; M2, 2: NO132, 20ml.

According to Table 8, alkalinity values of M15 and M16 locations were found to be 164 and 143 ppm before bacteria cultivation. EC (electrical conductivity) value of the mentioned acidic seepage waters was found to be 2056-2200  $\mu\text{S/cm}$ . These values must have resulted from high metal content in the solution. *Desulphovibrio desulfurican* (G 20 - NO 132) sulfate-reducing bacteria used in the tests in the present study can convert the sulfate produced from the Maden main deposit ( $\text{SO}_4^{2-}$ ) in the water which is rich in  $\text{SO}_4$  into sulfur ( $\text{S}^2$ ). The bacteria can form bicarbonate ( $\text{HCO}_3$ ) in the presence of an organic carbon source using sulfate as an electron donor under anoxic and reducing conditions (Bechard et al.,1995; Dalsgaard & Bak, 1994; Fyson et al.,1995).



$\text{CH}_2\text{O}^* =$  Ordinary organic molecule (lactate or acetate)

During the process of sulfate-reducing, firstly  $\text{HS}^-$  is formed.  $\text{HS}^-$  forms hydrogen sulfur ( $\text{H}_2\text{S}$ ) by reacting with free hydrogen ion (1). Then, hydrogen sulfur reacts with metals and form insoluble metal complexes and thus metals removal occurs. Produced bicarbonate provides higher alkalinity and pH in the medium when compared to the initial values. Electrical conductivity (EC,  $\mu\text{S/cm}$ ) which is lower than the initial value, suggests decreased metal concentration in the solution (Table 8). Sulfate-reducing *Desulphovibrio desulfurican* is not active in conditions with a pH lower than 5 (Egiebor & Oni, 2007). For this reason,

Sample code	Sulphate reducing bacteria	ml	pH	EC $\mu\text{S/cm}$	Alk ppm
Before experiment					
M15			5.1	2056	164
M16			2.5	2200	143
After experiment					
M15	G20	0.2	8.7		
	G20	2	7.8	2000	250
	G20	20	6.2		
	NO-132	0.2	8.2		
	NO-132	2	7.8	2009	238
	NO-132	20	7.2		
M16	G20	0.2	8.6		
	G20	2	8.5	2083	279
	G20	20	8.2		
	NO-132	0.2	7.8		
	NO-132	0.1	7.6	2030	252
	NO-132	1	7.2		

Table 8. The effects of two types of bacteria cultivated to different media on pH, EC and alkalinity values.

reaction was realized in newly created neutralization conditions. Since suitable pH value for the survival of the bacteria was 7.8, a pH value of the solution was set to 7.8. After the incubation of the bacterium, pH values increased from 5.1 to 8.7 in M15 location and from 2.5 to 8.6 in M16 locations (Table 7; 8). It was found that the bacterium 0.8 increased pH value.

Reduction of manganese and iron can make significant contributions to neutralization process.

It was observed that Fe value increased approximately 57 times while Mn values decreased 4 times. Heterotrophic bacteria like *Desulfovibrio* analyzed in the study can directly reduce iron and manganese by using iron as the last electron acceptor in anaerobic conditions. When  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$ , removal of iron from AMD becomes easier.  $\text{Fe}^{2+}$  reacts with the sulfide formed after sulfate reduction and as a result, contributes to removal of iron and increase of alkalinity (Akçıl & Koldaş, 2006). The fact that Zn value decreased approximately 100 times suggests that like Fe, Zn also reacted with sulfate. When hydrogen sulfur gas ( $\text{H}_2\text{S}$ ) which is removed from Maden waste sites during sulfate reduction, permanent alkalinity values can be determined. Ni values in sulfate containing solution varied from 5.6  $\mu\text{g/l}$  to below detection limit.

Element distributions in different sediment size fractions are presented in Table 9. The fact that the elements in the study area were in the form of primary sulfides indicates that chemical degradation is low. Aqua regia is a quite good solvent for these types of samples (Allcott & Latin, 1978; Rubeska et al. 1987). This mixture can also dissolve colloidal metals, oxide sediments and minerals and many elements can be analyzed by dissolving of only one sample. As the metal distribution dissolved with this method decrease in current flow

Elements	Detection Limits	-20+35	Size fractions -35+80	-80+140	-140+200	-200
As	0.1	31.52	47.84	73.28	63.1	59.64
B	1	6	6	6.6	6.6	5.4
Ba	0.5	55.26	69.86	82.9	93.08	110.36
Bi	0.02	0.428	0.638	1.146	1.142	1.324
Cd	0.01	0.376	0.494	0.988	1.054	1.134
Co	0.1	292.28	302.08	310.8	253.8	297.42
Cu	0.01	1419.35	2153.28	3877.24	4261.61	5198.03
Cr	0.5	227.48	237.38	216.54	198.82	179.98
Ga	0.1	6.42	6.44	6.22	6.24	6
La	0.5	6.44	6.56	6.48	6.54	7.3
Mn	1	1068	1170	1266.2	1292.4	1642.8
Mo	0.01	7.34	8.352	8.878	7.864	7.664
Ni	0.1	151.46	164.54	198.64	205.16	195.26
Pb	0.01	82.04	126.28	270.37	284.16	318.98
Sb	0.02	1.87	3.13	7.064	7.306	6.878
Sc	0.1	8.3	8.54	8.5	8.56	8.2
Se	0.1	2.06	2.9	6.86	7.48	8.08
Sr	0.5	40.94	41.4	47.06	54.9	68.66
Te	0.02	0.21	0.31	0.65	0.72	0.75
Th	0.1	0.92	0.92	0.98	1	1.04
Tl	0.02	0.19	0.25	0.43	0.45	0.51
U	0.05	0.32	0.36	0.68	0.74	0.62
V	2	105.2	120	111.2	99	92.6
Zn	0.1	832.64	760.98	533.4	472.74	485.44
ppb						
Ag	2	301.4	477	1071.2	1133	1441.8
Au	0.2	27.56	64	960.3	124.22	283.3
Hg	0.1	40	64	170.2	198.4	280
%						
Al	0.01	2.06	2.14	2.29	2.39	2.33
Ca	0.01	1.56	1.52	2.03	2.65	3.68
Fe	0.01	8.76	9.37	9.15	7.52	6.96
K	0.01	0.08	0.08	0.10	0.11	0.11
Mg	0.01	2.19	2.28	2.74	2.71	2.35
Na	0.001	0.01	0.01	0.02	0.02	0.02
P	0.001	0.04	0.04	0.04	0.05	0.05
S	0.02	0.32	0.55	2.18	1.28	1.15
Ti	0.01	0.12	0.13	0.12	0.12	0.11

Table 9. Stream sediment element concentrations in different size fractions along the Maden River sediment size fraction=mesh; by Aqua regia (3HCl+HNO<sub>3</sub>) digestion method.

direction, according to Rose et al. (1979) it suggests that mechanical distribution is effective in the region. For this reason, it can be stated that physical processes are more effective than



chemical processes in distribution of element in stream sand. Higher enrichment of As, Co, Cr, Mo, Ni, Sb, Zn and particularly Au values in -80 mesh sediment grain size when compared to -200 mesh grain size suggest that these elements were enriched by attaching on silica, that this dissolution method is not effective in dissolving silica and particularly in releasing Au.

### 3.3 Conclusion

Metal concentration is high in the vicinity of Maden copper deposit both in surface and ground waters and in stream sand samples. For this reason, two locations which particularly have high metal contents were determined and the change in sulfate was tried to be observed through anaerobic purification method. However, the decrease in Cu, Fe, Ni, Mn and Zn values along with sulfate after anaerobic purification experiments indicated that bacteria can decrease the concentrations in water by precipitation of metals.

As a result of analysis indicate that water samples are above the standards of fresh water and it is also enriched in some toxic cations and anion such as Cu, Fe, Mn, Zn, Ni and SO<sub>4</sub>. Cu 151.1-1447 mg l<sup>-1</sup> (EQS fresh water max contamination level (mcl) 0,16 mg l<sup>-1</sup>), Fe 132.2-517 mg l<sup>-1</sup> (mcl 1 mg l<sup>-1</sup>), Mn 75.7-1695 mg l<sup>-1</sup> (mcl 0.30), Zn 34.4-3212 mg l<sup>-1</sup> (mcl 0,125), Ni 4.3-1447 mg l<sup>-1</sup> (mcl 0.20 mg l<sup>-1</sup>). SO<sub>4</sub> values reach to 1417.8 mg l<sup>-1</sup> and 1719.2 mg l<sup>-1</sup> (mcl 400 mg l<sup>-1</sup>) in different location in acide mine drainage waters. That is why the sulphate reducing bacteria experience was done in these water samples *Desulfovibrio desulfuricans* can initiate some metal precipitation in the parallel to indirect sulfide-mediated precipitation. Initial and final metals and sulphate concentration before and after experiments, were measured and finally evaluated influence of bacteria in different ratio (0.2; 2; 20 ml) in AMD waters at two different sample locations (M15 and M16) . The experimental results show that, Cu, Fe, Mn, Zn, Ni and SO<sub>4</sub> values have been decreased by using sulphate reducing bacteria, Cu values, range of 96 to 98 % ; Fe values, 98 %; Mn values, range of 73 to 74%; Zn values, 98 %; Ni values, range of 93.62 to 97.67% ratio and SO<sub>4</sub> values, range of 44.36 to 46.18% ratio, respectively.

Initial, metals are dissolved due to <pH in AMD waters, but after bacteria experiments metals are precipitated as complex compound due to >pH (>7 at the neutralize pH condition) and high alkalinity. Consequently, in this study bacteria experiments observed that SRB (sulphate reducing bacteria) affected on both precipitation of the metals and the sulphate reducing in the AMD waters from the Maden copper deposit. These data will be evaluated including in literature and investigated impact on environment pollution.

In stream sediment samples reach to high concentrations Zn values -500 μ, Fe values -180 μ, As values -106 μ; Cu, Pb and Cd values <75 μ in size fraction. These values were correlated with average of diabase according to NIST and observed to high concentration of the Cu, Pb, Zn, As, Cd and Fe values. It was found that metal concentrations in stream sand samples increased mostly by mechanical transportation, however metal content in various water samples increased chemically in high reducing conditions.

### 4. Alacakaya chromite deposit

Thirth study area is Alacakaya alpine type chromite deposit in which the water geochemistry was studied (Figure1).

#### 4.1 Sampling and material method

The water samples were collected from natural springs and ground water in the chromitite deposit area. The samples were taken using a hand pump and water sampler and filtered using 0.5  $\mu\text{m}$  membrane filter paper (4.5 cm diameter); subsequently, 5 ml of prepared 65% concentrated  $\text{HNO}_3$  solution were added to 250 ml of each water sample and the samples were stored in the laboratory at 4°C until analysed. Analysis were done in Kanada ACME Labs. by ICP-OES method. Detection limits and the results of the water samples analyses are given in Table 10.

#### 4.2 Result and discussion

There are many waste place in chromite mining area (Fig. 5). The waste is an important factor on ground water contamination by leaching. The second effect is surface waters seepage to the deep and after mixing to ground waters (Fig. 6A). Figure 6B shows serpentine formation in the study area. The spring and ground water element contents in the Alacakaya chromite mining area are showed in Table 10. When element contents are correlated to natural ground water chemical composition, Al, Fe and Mn values are high. Maximum Mg, Al and Mn values are 1912.706  $\text{mg l}^{-1}$ , 672.72  $\text{mg l}^{-1}$  and 125.56  $\text{mg l}^{-1}$  in groundwater samples in the Guleman Ophiolites, Upper Cretaceous. According to Rose et al. (1979) natural groundwater element contents were pointed out as Mg 7000  $\text{mg l}^{-1}$ , Al 10  $\text{mg l}^{-1}$  and Mn 15  $\text{mg l}^{-1}$ . However, the same element contents are correlated to drinking water maximum contamination levels that all metal contents are above drinking water maximum contamination levels (Table 10). The average concentration of Cr in the basaltic and ultramafic rocks the average concentration is 200 ppm. The average concentration of Mg in basaltic rocks the average concentration is 45000 ppm. The average concentration of Ni in the basaltic rocks is 150 ppm (Krouskopf, 1979). The results of rock samples analysis are given in Table 11.



Fig. 5. Waste in the Alacakaya Cr deposit.



Fig. 6. Seepage waters from surface to deep (A) in the gallery; serpentinite and chromitite (B).

Element	Mean	Max	Min	Dedection Limits	Ground-water	Max. allowed values	Drinking water (MCL)
Al	75.576	672.72	0.005	1	10	50a	0.20
As	0.003	0.002	0.001	0.5	2	50a	-
B	0.1	0.31	0.03	20	10	-	-
Ba	0.01	0.018	0.003	0.05	20	50b	-
Ca	139.14	463.78	13.47	50	5000	-	10-100
Cd	0.03	0.16	0.0005	0.05	0.03	5b	0.005
Co	5.6	39.35	0.001	0.02	0.1	-	1
Cu	74	447.75	0.002	0.1	3	1000a.b	1
Cr	0.05	0.23	0.001	0.5	1	50a	0.1
Dy	0.02	0.18	0.001	<0.01	-	-	-
Fe	31.83	302.03	0.1	10	100	300a.b	0.3
Mg	252.88	1912.71	2.88	50	7000	50000b	50**
Mn	14.8	125.56	0.003	0.05	15	50b	0.05
Na	7.4	21.26	1.7	50	30000	20000b	20
Nd	0.07	0.65	0.0005	<0.01	0.08*	-	-
Ni	0.95	6.3	0.002	0.50	-	-	0.02
P	1.2	11.12	0.02	20	20	-	-
Pb	0.01	0.06	0.001	10	3	15b	0.015
Rb	0.002	0.013	0.003	0.01	1	-	-
S	0.6	4408	11	1000	30000	-	-
Y	0.09	0.85	0.004	<0.01	0.06*	-	-
Zn	10.18	60.48	0.03	0.50	20	5000a.b	5

Table 10. Element concentrations of the spring and ground water samples (in mgL<sup>-1</sup>); element contents of natural ground water (in mgL<sup>-1</sup>) from Rose et al. (1979); \*= Jenssen & Verweij 2003; \*\*= EEC; a- Ley 18284 (1969) Codigo Alimentario Argentino; Modificaciones (1988) and (1994); b- USEPA 1980, 2000. MCL= maximum contamination level; n= 10.

Major oxide (%) and minor element (ppm)	Harzburgite	Dunite	Pyroxenite	Detection Limits
SiO <sub>2</sub>	44.56	43.3	49.56	0.01
Al <sub>2</sub> O <sub>3</sub>	0.63	0.46	6.33	0.01
Fe <sub>2</sub> O <sub>3</sub>	9.35	9.1	5.4	0.04
MgO	42.85	43.4	17.46	0.01
CaO	0.69	0.59	18.28	0.01
Na <sub>2</sub> O	0.04	0.02	0.17	0.01
K <sub>2</sub> O	<0.04	<0.04	<0.04	0.01
TiO <sub>2</sub>	<0.01	<0.01	<0.01	0.01
P <sub>2</sub> O <sub>5</sub>	<0.01	<0.01	<0.01	0.01
MnO	0.12	0.11	0.12	0.01
Cr <sub>2</sub> O <sub>3</sub>	1.14	0.51	0.41	0.002
Co	110.9	11.5	46.2	0.001
Ni	2634	2682	231	20*
Cu	14.5	25.4	32.7	0.0001
Zn	36	58	42	0.0001
Rb	0.6	<0.5	<0.5	0.5*
Nd	<0.4	<0.4	0.7	0.4*
Dy	<0.05	<0.05	0.65	0.005*
Y	0.2	0.3	6.6	0.01*

Table 11. Major oxide and minor element concentrations of harzburgite, dunite and pyroxenite from the Alacakaya chromitite deposit area from Başpınar (2006), Detection limits in %; \* = ppm.

The high metal concentration in both spring and ground water samples indicated that source of contamination is lithological units (harzburgite, dunite, pyroxenite and alteration produce serpentinite) due to surface erosion, leaching and tectonism.

Talc is an alteration mineral. Altering serpentine ( $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) can also form talc. Serpentine commonly contains chrysotile asbestos, a carcinogen listed by the EPA. That is why; groundwater geochemistry was investigated in the Alacakaya chromite deposit area (Kalender, 2009).

#### 4.3 Conclusion

These studies show that the major and minor elements may be useful geochemical tracers but they have dramatically effect on environmental pollution especially in mining area. The present studies have demonstrated that the distribution and behavior of toxic and non toxic element content in the different media (water, sediment, and plants) may be bonded to high concentrations in geological units.

This study focuses on environmental effect of the metal pollution in the different origin ore deposits.

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## 6. References

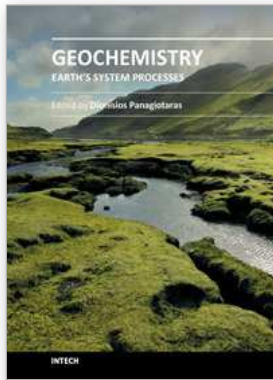
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