Bull. Environ. Contam. Toxicol. (2004) 72:482–489

DOI: 10.1007/s00128-004-0271-x

Environmental
Contamination
and Toxicology

Impact of Acid Mine Drainage from the Abandoned Halıköy Mercury Mine (Western Turkey) on Surface and Groundwaters

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Received: 26 September 2003/Accepted: 9 January 2004

Several abandoned mercury mines are located in western Turkey. Due to the low prices, low demand and increasing environmental concerns of mercury, the mines were abandoned gradually until early 1990s (Gemici and Oyman 2003). The acid drainage and the mine wastes create potential environmental problems around these mines. The abandoned Halıköy Hg mine that is located 5 km west of the town of Beydağ (İzmir) is one of the largest Hg deposits in western Turkey (Fig. 1). The Halıköy Hg mine operated from 1958 through the 1986 with a total production of 2045 t of mercury (Tokcan, 1987). No environmental recreation studies have been done since its abandonment and acid mine drainage and leachate from calcines, which are potentially hazardous for surface and groundwaters, presently flow from Halıköy Hg mine. Some of the shallow ground water wells that are used for drinking and agricultural purposes are not presently suitable for these purposes. Study area has a Mediterranean type climate which is characterized by arid, sunny summers and wet, cool winters. The mean precipitation value is around 700 mm. The mean temperature for summer and winter seasons are 27 and 8.5 °C, respectively. The mine area is rugged and highly sloped reaching 30°. The mine area is drained by an ephemeral stream and its small tributaries. The purpose of this study is to evaluate the influence of the abandoned Halıköy Hg mine on the environment and to determine the environmental pollution related to past mining activities using geochemical analysis of mine, surface and ground waters. Mine, surface and ground water samples were collected and analyzed to evaluate geochemical dispersion of Hg and other heavy metals in and around the mines.

MATERIALS AND METHODS

Unfiltered mine water samples (1, 2, 6 and 11) and some surface water samples (8 and 12) that were likely polluted by mining activities were sampled from the study area (Fig. 1b). Sample 1 was taken from the main adit with discharge of 40L/s of the abandoned Hg mine. Samples 6 and 2 are mine water samples draining the calcines with discharge rates of 3 L/s. Samples 11, 8 and 12 are from the surface water with a discharge of around 100 L/s at the location of sample 12. Samples 3, 4, 5, 9, 10 and 13 were taken from shallow wells with depths of around 10 to 15 m and from a spring sample (sample 7). Two samples were collected from each sampling location. One of the bottles was acidified with HNO_3 to determine metal

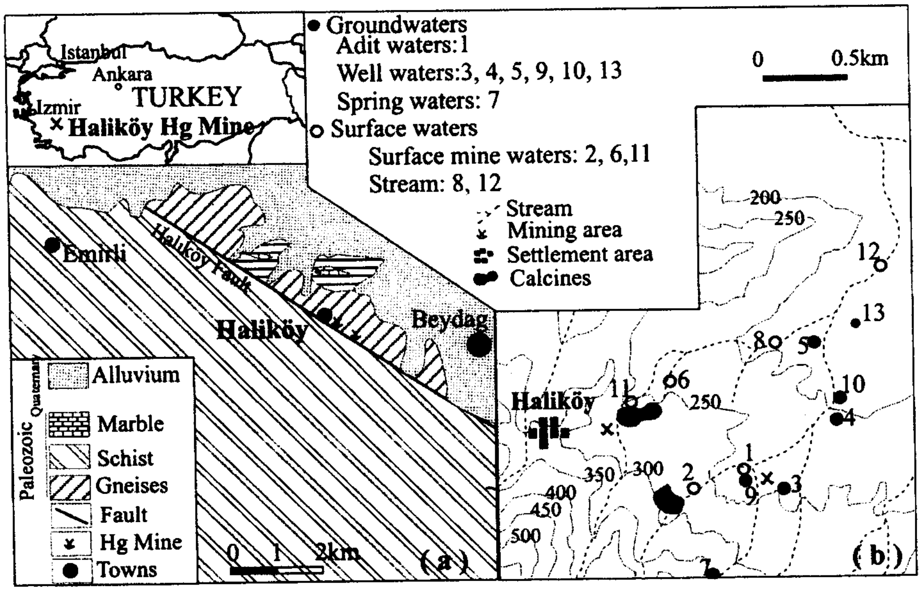

Figure 1. Simplified geological map of the study area (after Dora et al. 1995) (a) and the locations of the water samples from the Halıköy Hg mine area (b)

contents and the other was unacidified for anion analyses. Electrical conductivity, pH and temperature values were measured in the field. The major cations and trace elements in the water samples were analyzed in the Acme Analytical Laboratories (Vancouver-Canada) by ICP-MS. Cl and HCO_3 were determined volumetrically and SO_4 by gravimetry in Dokuz Eylül University laboratory (Table 1).

RESULTS AND DISCUSSION

Metamorphic rocks of Menderes Massif, which are of high to low grade metamorphics (gneiss, mica schists, phyllites, quartz schists, marbles) form the basement of Halıköy Hg mine area (Fig. 1a). Chlorite-quartz schist is located at lower part and quartzite and biotite-muscovite-quartz schists in the upper parts of the metamorphic succession (Gökçe and Spiro 1995). The Halıköy Hg deposits consist of formations in terms of vein and veinlets. Mineralized veins containing cinnabar (HgS) are found along the Halıköy Fault which is relatively linear, strikes 110-140° and dips 45-65°NE. Cinnabar was deposited along the main fault under epithermal conditions. Near the Halıköy mine the Halıköy Fault forms a 35m wide clay alteration zone between augen gneiss and schists. Wider alteration around the deposits is found expressed as kaolinite in gneiss and sericite in schists (Akçay et al 1996). Cinnabar, metacinnabar, pyrite, marcasite, chalcopyrite, arsenopyrite, quartz and calcite are common mineral assemblages (Gökçe and Spiro 1995).

Mine water samples, surface waters and groundwater samples with the exception of sample 9 near the mine area are characterized by dominantly Mg and Ca cations. Mg and Ca concentrations vary from 4.0 to 400 mg/L and 12 to 250 mg/L,

Table 1. Chemical properties of the water samples.

		1	2	3	4	5	6	7	8	9	10	11	12	13	TSE
		adit	mine	well	well	well	mine	spring	stream	well	well	mine	stream	well	1997
pH		4.9	6.5	6.5	4.5	6.3	4.0	6.6	4.9	7.8	3.7	5.2	4.0	6.1	6.5-9.2
EC	(µS/cm)	4300		260	1800	2600	1250		530	550	250	410	1260	1850	2000
Ca	mg/L	250	79.9	17	150	250	170	12	30	32	55	27	73	200	200
Mg	mg/L	400	123	9	152	210	215	4.0	13	14	60	12	90	140	50
Na	mg/L	44	12	15	26	58	20	8.0	14	77	12	13	17	28	175
K	mg/L	16	5.8	1.3	2.7	5.6	3.8	1.6	3.7	10	3.5	2.9	4.4	1.1	
Cl	mg/L	30	4.0	7.0	11	21	9.0	5.0	10	5.0	6.0	7.0	8.0	14	600
SO_4	mg/L	3000	780	52	1080	1500	2250	45	250	50	475	253	720	1100	250
HCO_3	mg/L	60	30	83	30	235	5	65	15	350	10	40	50	80	
Ag	µg/L	0.53	0.59	0.13	0.28	0.67	0.27	0.83	0.65	0.59	0.55	0.74	0.47	0.3	
Al	mg/L	1.68	0.92	0.81	3.35	0.65	259.50	0.52	19.35	0.38	4.99	17.90	9.50	0.35	0.2
Fe	mg/L	500.2	0.28	2.05	0.40	0.156	9.95	0.15	38.0	0.46	0.39	38.1	66.5	0.22	200
Mn	mg/L	13.0	0.55	0.43	3.50	0.40	14.90	0.010	1.05	0.028	2.60	0.95	2.90	4.0	500
Si	mg/L	29.9	19.3	18.5	24.4	15.25	37.4	1.85	11.4	39.8	25.9	8.4	13.7	16.5	
As	µg/L	300	5.0	1.0	< 1	< 1	124	1.0	15	7.0	1.0	10	18	1.0	50
B	µg/L	125	790	< 20	22	37	290	< 20	< 20	41	53	< 20	30	< 20	2000
Cd	µg/L	0.75	1.1	0.2	0.9	0.3	7.6	0.1	0.5	< .05	0.7	0.5	0.5	0.2	5
Co	µg/L	20	15	1.2	33	2.5	540	0.4	34	0.1	40	30	27	0.1	
Cr	µg/L	< .5	0.5	0.6	< .5	0.7	7.4	< .5	2.7	< .5	0.8	2.3	1.5	< .5	50
Cu	µg/L	7.0	7.1	3	14	4.0	6.0	2.0	25	0.5	30	22	14	2.2	3000
Hg	µg/L	< .1	< .1	< .1	< .1	< .1	< .1	< .1	0.5	< .1	< .1	0.3	< .1	< .1	1
Ni	µg/L	60	60	1.6	102	27	960	1,8	69	< .2	66	61	54	4.4	50
Pb	µg/L	6.2	1.5	3.0	2.0	1.8	8.0	1.8	2.0	2.0	2.8	2.0	2.0	2.2	50
Zn	µg/L	230	170	18	140	40	3400	2.0	220	5.0	150	200	160	35	5000

respectively. The mine and groundwater samples collected downstream were significantly enriched in SO_4 (reaching to 3000 mg/L). However, HCO_3 dominates for samples 3, 7 and 9 that were collected located upstream of the mining area. The pH of surface, mine and groundwaters of Halıköy Hg mine varies from 3.7 and 7.8. The pH of mine waters is between 4 and 5.2. The source of acidity is caused by the oxidation of iron sulfide phases, mainly pyrite. Acidity increases downstream due to the advancing of pyrite oxidation. Groundwater samples located in lower parts of the mine area have pH values of 3.7 and 6.1. Precipitation of iron and aluminum oxyhydroxides remove hydroxide from water and cause the pH to decrease (Gal 2000), which could explain the decline in pH to the downstream as observed in sample 12. The distribution of pH in water samples are presented in Fig. 2a. The highest electrical conductivity value was observed in sample 1 (adit water) of 4300 μS/cm. The other mine and groundwater samples have variable EC values of 250 and 2600 μS/cm depending on circulating conditions, lithological properties of the basement rocks and dilution. The mining works (open pit mine, exploitation galleries, calcines) expose substantial quantities of sulphides to air that accelerate the oxidation processes and causes acid-mine drainage (Milu et al. 2002). The following reaction describes the overall processes (Banks et al. 1997).

$$4FeS_2 + 14H_2O + 15O_2 = 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+_{(aq)}$$

Aluminosilicates in the basement rocks around the study area release Si, Al, Mg, Ca and K into the water as a result of dissolution. Si concentrations of water samples are high with an average value of 20 mg/L. Sample 7, which is suggested as uncontaminated groundwater since it is located upstream of the mine area, has the lowest Si concentration of 1.8 mg/L. Waters draining the mining area have much higher values reaching to 40 mg/L. Since solubility of Al increase in acid water, Al contents of ground and mine water samples in Halıköy Hg mine reaches to remarkable values of 260 mg/l as in sample 6 which is a mine water draining the calcines (Fig.2c). Additionally, widely distributed kaolinite in and around the mine area are considered as one of the main sources of high Al and Si concentrations in water samples. Figure 2e shows the Fe distribution of water samples. The highest Fe value (500 mg/L) was observed in adit water (Sample 1). After discharging from the adit, Fe concentrations decrease downstream (Fig. 2e). Increasing oxygen contents in groundwater downstream causes the dissolved iron to precipitate as hydroxide. Red colored precipitations were observed in the creek. Sample 1, adit discharge water sample, and sample 6, mine water draining the calcine, have the highest Mn values of 13 mg/L and 15 mg/L, respectively (Table 1). There is an inverse relation between pH and element concentrations of water samples(Table 2). Decrease of pH causes an increase in metal and SO_4 contents. SO_4 has high correlations with major ions with the exception of HCO_3. This indicates that oxidation of sulfide minerals, which controls the SO_4 content, also controls the concentrations of the other major cations. High positive correlations of SO_4 with Mn (r=0.83), Fe (r=0.68) and As (r=0.85) show that they are related to the oxidation of the sulfide minerals. The clay alteration zone show enrichment in As (500-2000 mg/kg), Cu (50-500 mg/kg) and Pb (50-300 mg/kg) (Akçay et al, 1996).

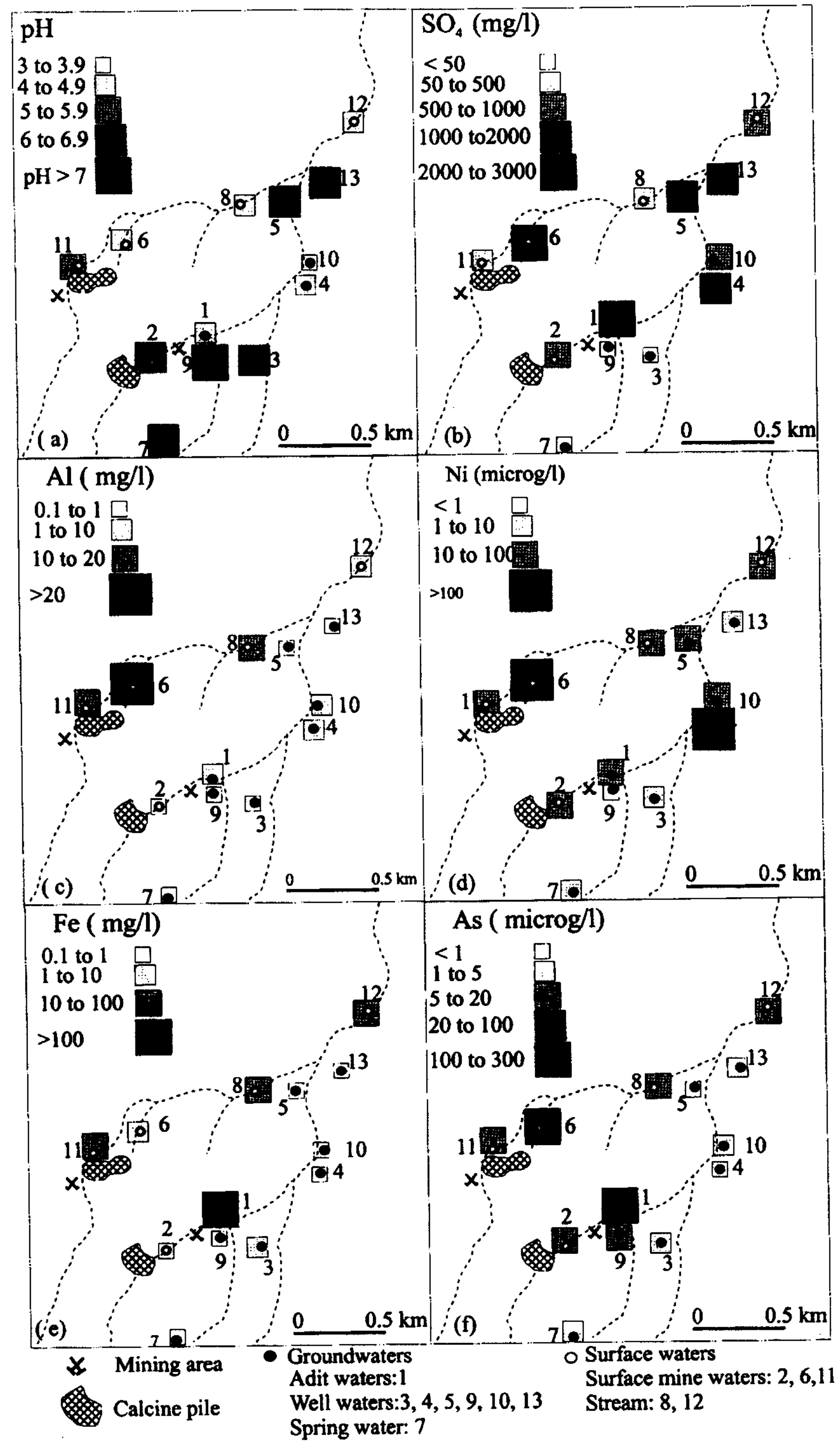

Figure 2. Distribution of pH (a), SO_4 (b), Al (c), Ni (d), Fe (e) and As (f) in water.

Table 2. Correlation of major ions and some selected metals for water samples

	pH	K	Mg	Ca	Na	Cl	SO_4	HCO_3	Mn	Fe	Cu	Ni	Al	As
pH	1.0	0.08	-0.28	-0.18	0.46	-0.04	-0.37	0.72	-0.55	-0.20	-.067	-0.46	-0.39	-0.31
K		1.0	0.64	0.40	0.61	0.59	0.58	0.34	0.47	0.82	-0.15	-0.09	-0.09	0.78
Mg			1.0	0.89	0.31	0.81	0.97	-0.09	0.73	0.72	-0.26	0.27	0.23	0.92
Ca				1.0	0.42	0.81	0.87	0.06	0.51	0.45	-0.32	0.22	0.19	0.76
Na					1.0	0.44	0.25	0.88	0.03	0.21	-0.43	-0.15	-0.13	0.30
Cl						1.0	0.76	0.10	0.43	0.71	-0.19	-0.04	-0.05	0.85
SO_4							1.0	-0.16	0.83	0.68	-0.22	0.46	0.42	0.91
HCO_3								1.0	-0.33	-0.11	-0.49	-0.29	-0.26	-0.14
Mn									1.0	0.59	-0.05	0.75	0.71	0.85
Fe										1.0	-0.04	-0.07	-0.09	0.92
Cu											1.0	-0.10	-0.08	-.016
Ni												1.0	0.99	0.30
Al													1.0	0.27
As														1.0

This explains the high As contents in some water samples and the high positive correlation coefficient between As and major cations and SO_4. The relationship between metal contents and pH for waters are presented in Fig. 3. Samples 4, 8, 10, 11, 12, 13, and 1 plot on as acid low metal waters. Samples 2, 3, 5, 7 and 9 are located as near neutral low metal content water. Sample 6 that is a mine water sample passing though to the calcine pile plot on as acid, high metal water. Waters from the mining area are of acidic character and their heavy metal contents are generally higher than those of the near neutral waters. This indicates that the source of heavy metal downstream the mine area is by the leaching by acid water of calcine piles, altered basement rocks and mineralized rocks. Some trace elements were analyzed to identify the contaminants in water samples and evaluate their distributions in the study area (Table 1). The sample 7 was collected from a spring where there are no known upstream Hg deposits, thus this sample represents an uncontaminated baseline in the study area. Sample 7 does not show any significant enrichment in major ion and heavy metal contents. The concentrations of most metals (As, Ba, Cd, Ce, Co, Cr, Cu, Fe, Hg, Mn, Ni) are below the Turkish drinking water standards (TSE, 1997) for sample 7, with the exception of a naturally increased Al content of 520 µg/L (Table 1). Chemical analyses of the other water samples indicate that waters around the mine area are enriched in a number of elements. The highest concentrations of major ions and metals are encountered in sample 1 and 6. SO_4 is the dominant anion for mine waters and a majority of the ground water samples reach concentrations up to 3000 mg/L. All of the mine waters and ground waters with the exception of samples 3, 7 and 9 exceed the drinking water standards, 250 mg/L (TSE 1997). Fig. 2b shows the distribution of the SO_4 in the mine area. Sample 1 and 6 have the highest SO_4 values and in the downstream SO_4 values decrease in the downstream in surface and groundwater samples. Al contents of water samples presented in Fig. 2c are also high especially in sample 6 (260 mg/L). Al concentrations decrease in ground and surface waters due to the dilution and precipitation of Al oxyhydroxides. Al concentrations of the water samples are above the drinking water standards, 200 mg/L (TSE 1997, WHO 1993). Fe concentrations of only two samples (5 and 7) are below the safe level

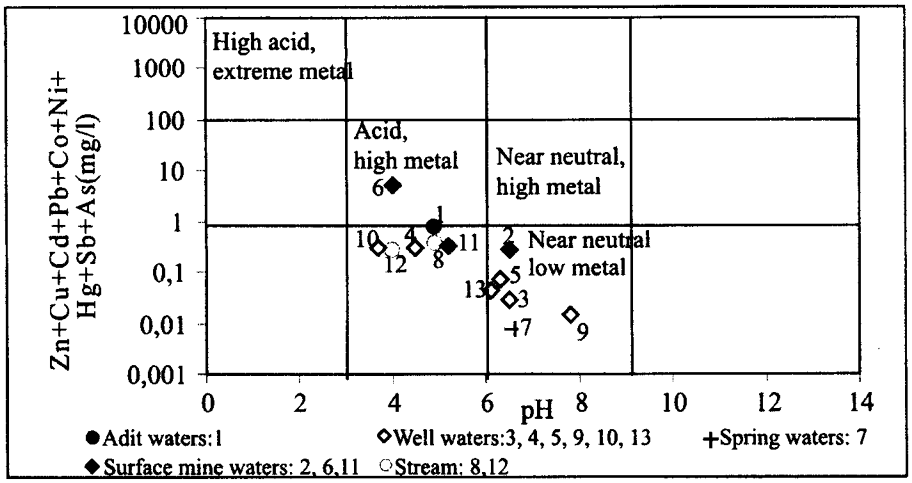

Figure 3. Scatter diagram of the metal concentrations versus Ph (modified from Gray et al., 2000)

for drinking water. The rest have higher values reaching to 500 mg/L. Mn values that are between 4.0 and 15000 µg/L have also remarkable high similar to Fe (Table 1 and Fig 2). Only groundwater samples 7, 9 and 13 have lower values than drinking standards for Mn. Arsenic concentrations of water samples range between 1 and 300 µg/L. As concentrations of samples 1, 6, 8,11 and 12 that are all mine and surface waters exceed the drinking water standard, 10 µg/L (TSE 1997 and WHO 1993). The groundwater samples have As concentrations less than 10 µg/L. Ni contents of water samples vary between 0.2 and 960 µg/L (Table 1; Fig. 2d). Groundwater samples 4, 5 and 10, and all mine and surface waters were enriched in Ni content that exceed the Turkish potable water standard of 50 µg/L Ni. Zn concentrations are between 1.4 and 3400µg/L. The highest Zn content was observed in sample 6 draining the calcines. Cd was only enriched above the standards in sample 6. Although heavy metal concentrations of mine and ground waters are high, Hg concentrations are below 0.1 µg/L with the exception of samples 11 and 8. Hg concentrations of samples 11 and 8 that are surface waters draining the calcine are 0.5 and 0.3 µg/L, respectively, and are below the drinking water standards of 1 µg/L WHO (1993) and TSE (1997). However they are above the 0.012µg/L Hg standards recommended by EPA (1992) for aquatic life. The low Hg concentrations in groundwater samples is due to the highly resistance nature of cinnabar to chemical and physical weathering and its solubility in water (Gray et al. 2000). It has been also known that cinnabar oxidizes more slowly than other sulphides (Plouffe, 1997). The concentrations of the other metals presented in Table 1 are below the drinking water standards. Generally none of the mine waters and surface waters samples are suitable for drinking water. Among the ground waters, sample 7 is uncontaminated and sample 3 is slightly contaminated since they are located upstream of the mine area. Sample 7 which is spring water has low trace metals and SO_4 concentrations with a near-neutral pH of 6.6. Acid leachates and acid-mine drainage give rise a decrease in pH and an increase of dissolved Fe, Al, SO_4 and trace metals. Oxidation and buffering of pH by aluminosilicates caused the coprecipitation of Al and Fe compounds resulting in the decrease of metals in the groundwater through to the flow direction. Since the host rocks are dominantly weathered gneiss and mica schists, and there are no carbonates, aluminosilicates are the main minerals that control the acid neutralization. However acid neutralization capacity of these minerals is lower than that of carbonate minerals. Therefore acid production is faster than neutralization resulting in the drainage water to have acidic character. The distribution of the elements shown in Fig. 2 indicates that the main sources of the pollutants in the study area are derived from calcines and adit discharge.

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