

# Evaluation of the water quality related to the acid mine drainage of an abandoned mercury mine (Alaşehir, Turkey)

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**Abstract** Mobility of metals in water, mine wastes, and stream sediments around the abandoned Alaşehir mercury mine was investigated to evaluate the environmental effects around the area. Mine waters are dominantly acidic with pH values of 2.55 in arid season and 2.70 in wet season and are sulfate rich. Acidity is caused mainly by the oxidation of sulfide minerals. Pyrite is the main acid-producing mineral in the Alaşehir area. Of the major ions,  $\text{SO}_4$  shows a notable increase reaching 3981 mg/l, which exceeds the WHO (*WHO guidelines for drinking water quality*, vol. 2. Health criteria and other supporting information, 1993) and TS (*Sular-İçme ve kullanma suları*. Ankara: Türk Standartları Enstitüsü, 1997) drinking water standard of 250 mg/L. Mine waters have As, Fe, Mn, Ni, and Al with concentrations higher than drinking water standards. Hg concentrations of adit water samples and surface waters draining the mine area are between 0.25 and 0.274  $\mu\text{g/L}$  and are below the WHO (*WHO guidelines for drinking water quality*, vol. 2. Health criteria and other supporting information, 1993) drinking water standard of 1.0  $\mu\text{g/L}$ . However, the concentrations are above the 0.012  $\mu\text{g/L}$  standard (EPA, *Water quality standards. Establishment of numeric criteria for*

*priority toxic pollutants, states' compliance, final rule*. Fed. Reg., 40 CFR, Part 131, 57/246, 60847–60916, 1992) used to protect aquatic life. Stream sediment samples have abnormally high values of especially Hg, As, Ni, and Cr metals. Geoaccumulation (Igeo) and pollution index (PI) values are significantly high and denote heavy contamination in stream sediments. The stream sediments derived from the mining area with the surface waters are potentially hazardous to the environment adjacent to the abandoned Hg mine and are in need of remediation.

**Keywords** Acid mine drainage · Hg mining · Water contamination

## Introduction

Cinnabar was mined in Turkey for use as paint in ancient times, and mercury metal was recovered in the Roman and possibly Greek eras. Modern production began early in the twentieth century but remained insignificant until the 1960s when rotary furnaces were installed. Until 1974, Turkey produced more than 12,000 flasks of mercury, which was about 5% of the world output. More than 50 known mercury deposits and occurrences are in the west half of Turkey (Yıldız and Bailey 1978). These mines were gradually abandoned until early 1990s due to the low prices, low demand, and environmental concerns of mercury (Gemici and Oyman 2003) (Gemici and Tarcan 2007).

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However, no environmental recreation studies have been done since their abandonment. The acid drainage and the mine wastes, which are potentially hazardous for surface and ground waters and soils, create potential environmental problems around these mines (Gemici 2004) (Çolak et al. 2003).

Alaşehir mercury mine, which is one of these abandoned mercury mines, is located approximately 120 km east of Izmir. The mercury mine area is positioned 3 km south of Alaşehir town, at an altitude of 550 m in the northern side of the Alaşehir Mountains that suddenly rise from the Alaşehir plains. The terrain of the mine site is rugged and highly inclined to the south. Elevation increases towards the west and finally reaches 400 m in height. The mine site is drained by a stream and its side streams that have a seasonal flow. The study area has arid sunny summers and wet cold winters. According to the meteorological data of the last 30 years, the annual temperature is 16.8°C. The average yearly rainfall is about 710 mm for the same period.

The mine was discovered in 1962 and produced mercury at a rate of about 25 flasks a month, working about 300 days a year. Its total recorded production in 1974 was 2,142 flasks of mercury (Bircan and Aydoğanlı 1969; Yıldız and Bailey 1978). The ore was obtained partly from open mines and galleries. Today, the production has been discontinued. Environmental recreation study has not been performed since the abandonment of the mine. Acidic mine drainage from the galleries and mine wastes are causing potential environmental problems near the Hg mines. The ephemeral stream draining the area is a tributary of the Gediz River. The Gediz graben has an important role in agriculture in Turkey. Almost 75% of grape production in Turkey takes place on this plain.

The present study aims at determining the extent of Hg and some heavy metal contamination related to past mercury mining in the Alaşehir area. In order to evaluate Hg release, a number of hydrogeochemical measurements were taken in samples of stream sediments, mine wastes, and surface and groundwater from the abandoned Alaşehir Hg mine and the mining area downstream.

### Geology and mining activities

The mine field is in the northern part of the Alaşehir Mountains, which is formed by Mesozoic limestones

that overlie sharply separated Paleozoic muscovite–biotite–garnet schists (Fig. 1). Silicified, carbonated rock lenses, chromite pieces that form on the surface, and serpentinite fragments exist in the minefield. It is thought that the rock is formed by the alteration of serpentine and it shows similarity with the silica-carbonate rocks that is found in Hg deposits in the California coast range. Another similarity with deposits in California is the formation of rocks near the glaucophane schists (Holzer 1953; Baykal 1954; Schuiling 1962; Yıldız 1978).

There are hot and mineral springs in the Alaşehir valley but none of them precipitate any Hg minerals (Yıldız and Bailey 1978). Ore bodies were seen mainly in two types of rocks:

- (1) Ore bodies in fissures of broken schists, which were exposed to hydrothermal alteration. They are found with pyrite and limonite, which are alteration products of pyrite.
- (2) Ore bodies in carbonated and silicified serpentines. They are found with silica. In some conditions, silica turns into limonite by alteration. Ore is more common in these parts.

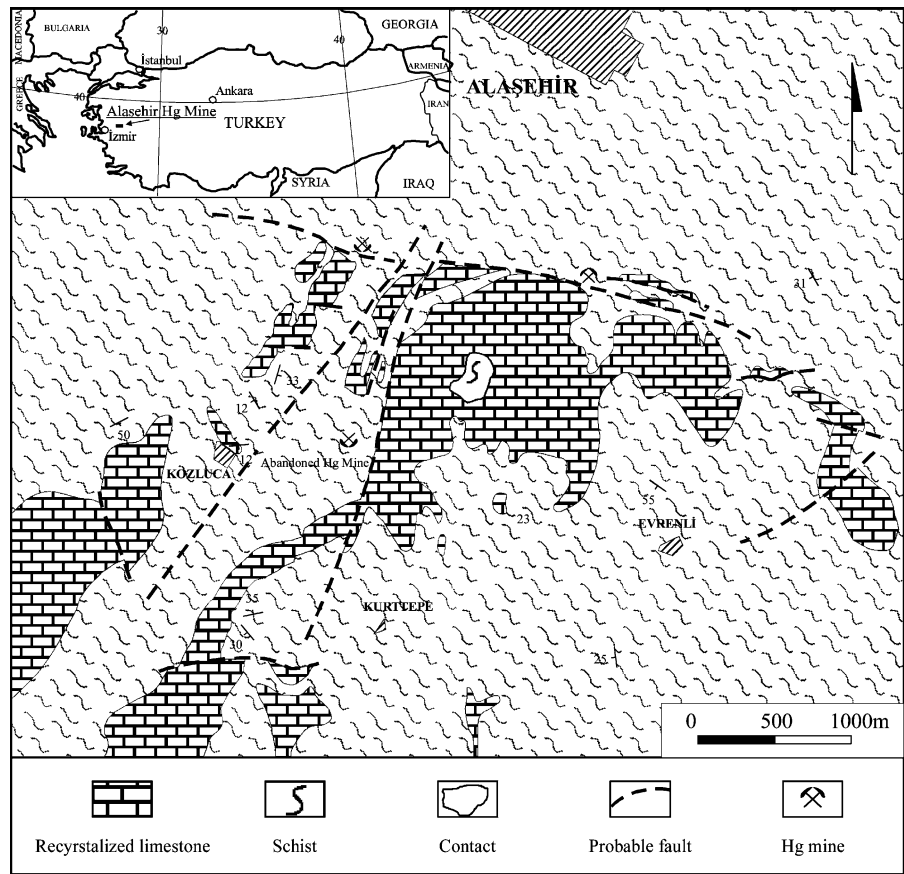
Economic Hg mineral is cinnabar. There is a close relationship between pyrite, marcasite (minerals of sulphur), and cinnabar. Quartz has close relations with the ore and it is the most-found gang mineral. Limonite that is formed by the alteration of pyrite is especially common. The existing minerals in the ore bed are cinnabar, pyrite, marcasite, and quartz. It is disseminated in 0.5 m-wide gouge zones with sugary quartz, and it forms scattered crystals and fracture coatings in silica-carbonate rock. Pyrite is common, and marcasite, less so (Yıldız 1978). Stibnite and realgar are found in small deposits nearby, but have not been identified in the mercury ores. Mining has been done in irregular pits up to 10 m wide and, to a much lesser extent blocking an adit that is about 80 m long. Both the small ore lenses and the larger gouge zones strike N50–60E and dip moderately to the southeast (Yıldız and Bailey 1978).

### Materials and methods

#### Surface water and ground water sampling

Samples were taken from the surface and ground waters in arid and rainy seasons to assess the environmental

**Fig. 1** Location and the geological map of the study area (Yıldız and Bailey 1978)



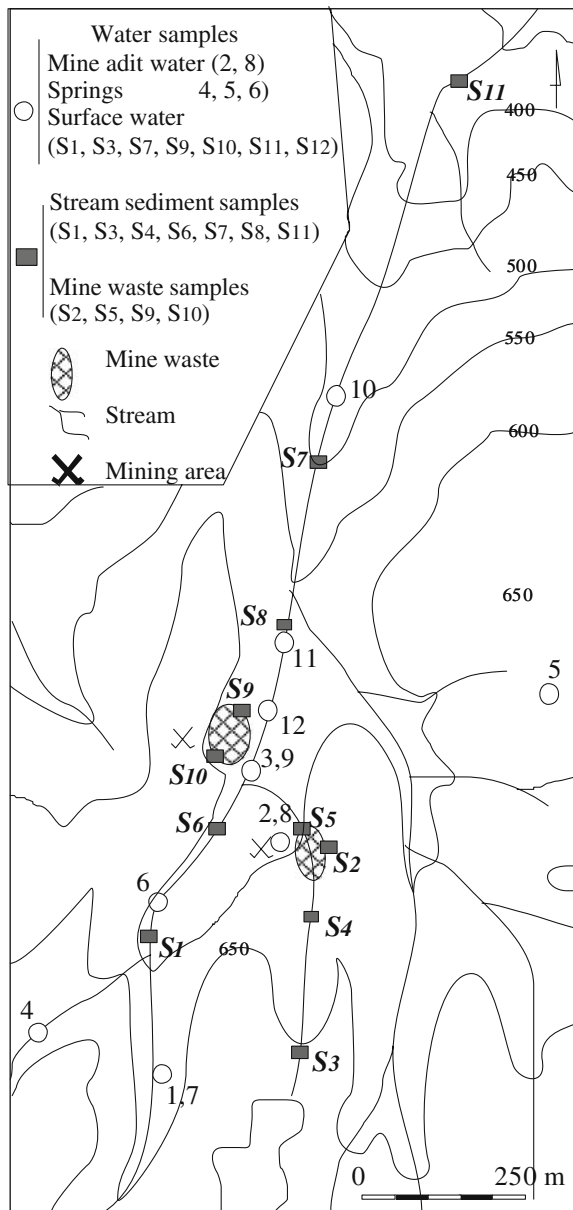
impact of the Alasehir mercury mine during the study of hydrogeological and hydrogeochemical features. Sample points were determined as springs, surface water, and mining drainage water (leaking water from galleries and wastes). Water samples were collected in June 2004 (samples 1–5) and December 2004 (samples 6–12) from the selected sample points (Fig. 2).

Samples 2 and 8 represent leaking water from the galleries; samples 9–12 represent surface water samples; samples 4–6 represent the springs found in higher elevations from the mining field. The streams are seasonal in the study area. The seasonal streams pass through the mining field and reach the Alaşehir plain. Acid mine drainage waters contribute to the surface waters that leachate the mine wastes, and they finally reaches the tributaries of the Gediz River in the rainy seasons.

Two samples were collected from each sampling location and stored in polyethylene bottles. One of the bottles was acidified with HNO<sub>3</sub> to decrease the pH

value to 2 and the other was unacidified for anion analyses. EC (electrical conductivity), pH, Eh, and temperature values were measured in the field at the time of sampling with handheld meters. All samples were subjected to multielemental analysis by ICP-MS at ACME Analytical Laboratories in Vancouver (Canada). Fifty cubic centimeter of water samples were collected in precleaned glass bottles and preserved with pure HNO<sub>3</sub> and potassium dichromate. They were sent to Activation Laboratories, Canada, for analyses by cold vapor atomic absorption spectrometry.

Anion constituents were analyzed in the Dokuz Eylul University, Geochemistry Laboratory. Cl and alkalinity (CO<sub>3</sub> and HCO<sub>3</sub>) were determined by titration with silver nitrate and hydrochloric acid, respectively. SO<sub>4</sub> was determined by visible spectrophotometer with barium ions. Aquachem (Calmbach 1997) and Phreeqc (Parkhurst and Appelo 1999) computer software programs were used while evaluating the characteristic of its hydrogeochemistry.



**Fig. 2** Distribution of water, mine wastes and stream sediments in and around Alasehir Hg mine

### Mine wastes and stream sediments

Samples from the mine wastes and stream sediments were collected in order to determine the dispersion of heavy metals and other pollutants derived from old mercury mines. Stream sediment samples (samples S1, S3, S4, S6, S7, and S11) were composited by collecting material from channel-bed alluvium. Sample 8 is a precipitation sample collected in the stream.

Mining wastes were also sampled from the study area. Mining wastes included calcines and waste rocks. Samples S2, S5, and S10 are the waste rocks and sample S9 is the calcine.

Approximately 3 kg of stream sediment was collected with a plastic scoop at sampling sites (Fig. 2). Following Herr and Gray (1995), samples were taken from old mercury mines in the vicinity of Alasehir and were sieved through a -10 mesh (2 mm sieve) in the field. In the laboratory, the sediment samples were air-dried and sieved through a -80 mesh (0.18 mm). A sample weighing 1.0 gram was leached with 6 ml 2-2-2 HCl-HNO<sub>3</sub>-H<sub>2</sub>O 95°C for 1 h and diluted to 20 ml.

Stream sediments and mine waste samples were analyzed by ICP-mass spectrometry in Acme Analytical Laboratories Ltd, Vancouver, Canada. Mercury was determined after aqua-regia digestion using cold vapor atomic absorption spectrometry.

## Results and discussions

### Water chemistry

The results of the chemical analyses of the water samples from the study area are presented in Table 1. Adit waters are acidic in character and their pH values are between 2.55 and 2.7 for arid and wet seasons, respectively. Their electrical conductivity values reach 5,600  $\mu$ S/cm.

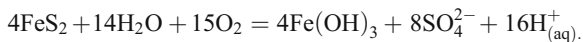
Spring waters and surface waters from the study area are alkaline in character with pH values ranging from 7.02 to 8.3. Sample 5 was collected from a spring where there are no known upstream Hg deposits. Thus this sample represents an uncontaminated baseline in the study area. Sample 5 did not show any significant enrichment in major ion and heavy metal contents. The dissolved solids for sample 5 were less than that of the samples taken from the lower elevations of the mine area. Its electrical conductivity was 138  $\mu$ S/cm. The electrical conductivity values ranged from 1,150 to 1,400  $\mu$ S/cm for other surface water samples and approximately 1,000  $\mu$ S/cm for ground water samples. Mg, Ca, and SO<sub>4</sub> are predominant ions according to the classification based on IAH (1979) in surface waters sampled in the wet season. This shows similarity with the samples taken in the arid season, but their values are higher (Table 1).

**Table 1** Chemical analyses of the water samples from the study area (in µg/L)

Samples	1	2	3	4	5	6	7	8	9	10	11	12
EC	1,250	5,060	1,400	970	138	1,007	862	4,640	1,155	1,416	1,278	1,265
pH	8.2	2.55	8.3	7.17	7.44	7.02	8.26	2.7	7.87	8.3	8.05	7.22
T (°C)	22.2	16	19	19	16	14	9	12	11	11	12	12
Eh (mV)	-77	235	-82	-20	-34	-15	-84	228	-62	-87	-74	-26
Na	12,852	10,737	16,801	13,580	5,434	15,758	17,126	10,720	17,217	18,042	17,579	17,578
K	3,586	6,291	5,222	2,908	1,793	3,458	3,127	4,929	4,078	5,186	4,985	4,790
Ca	63,133	376,778	133,394	82,266	15,177	79,523	56,886	349,351	82,933	120,915	99,278	92,635
Mg	82,607	154,193	130,233	80,815	6,104	78,046	73,898	126,570	102,201	117,124	108,817	106,592
SO <sub>4</sub>	51,000	3,981,000	438,000	45,000	18,000	63,000	63,000	3,354,000	204,000	573,000	414,000	327,000
Cl	18,000	14,000	22,000	17,000	2,000	21,000	58,000	54,000	68,000	36,000	152,000	116,000
HCO <sub>3</sub>	542,000	1,000	512,000	600,000	66,000	593,000	510,000	0	550,000	273,000	370,000	445,000
H <sub>3</sub> BO <sub>3</sub>	137.2	<20	134.5	<20	<20	165.7901	120.0549	142.9225	205.8084	297.2788	262.9774	188.6577
Ag	<0.05	<0.05	<0.05	<0.05	<0.05	1.27	1.71	3.48	3.25	1.83	1.82	1.54
Al	235	89,470	421	341	283	108	27	65,563	103	2,105	3,686	2,389
As	1.4	3,177.6	7.5	2.5	1.1	3.1	1.7	2,583.8	4.5	104.4	186	168.1
Ba	113.58	7.31	83.08	175.52	29.56	186.68	111.91	3.81	83.43	36.91	47.07	46.11
Bi	<0.05	0.06	0.23	<0.05	0.11	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Br	75	81	85	84	39	81	77	90	93	89	101	96
Cd	0.06	4.49	0.32	<0.05	<0.05	<0.05	<0.05	2.54	0.07	<0.05	<0.05	<0.05
Ce	0.32	57.74	0.51	0.24	0.3	0.09	0.08	43.9	0.15	0.66	1.17	0.64
Co	0.18	5,960.58	169.95	0.25	0.19	2.72	0.08	4,520.39	70.32	92.55	111.71	77.31
Cr	2.9	12,569.6	20.4	5.4	2	9.7	0.8	9,764.6	5.3	227.6	396.2	278.8
Cu	2.8	161	5.5	2.1	12.4	2.6	2.4	162.1	2.4	1.4	1.8	1.2
Fe	184	670,950	1,496	129	234	328	<10	649,273	742	13,896	21,891	15,133
Hg	0.025	0.12	0.03	<0.1	<0.1	0.035	0.039	0.173	0.038	0.116	0.21	0.274
Li	9.6	46.3	16.6	9.8	3.6	11.4	8.6	30.9	11.6	13.3	12.2	11
Mn	11.34	1,672.34	367.05	7.4	10.24	2.03	3.08	1,276.64	123.85	269.07	118.72	49.95
Mo	2	12.8	1.8	0.3	0.4	0.3	0.7	10.3	2.6	1.7	2	2.2
Ni	4.4	105,887	3,242.8	21.3	2.4	76.3	1.7	93,869.4	1,740.5	2,455.7	2,838.2	2,114
Pb	2.5	2.5	3.7	2.4	2.7	1	1	3.5	1.3	0.07	0.8	0.6
Sb	17.76	97.17	33.99	2.24	0.25	2.26	1.92	69.14	30.65	51.52	61.34	60.64
H <sub>2</sub> SiO <sub>3</sub>	23,512.151	125,439.84	21,107.278	19,845.068	23,620.579	23,075.66	23,197.989	116,829.56	20,601.282	23,526.052	26,517.548	25,235.875
Zn	16.4	1,675.4	650.7	523.8	282.5	16.7	3.4	1,285.6	12.8	18.2	25.5	19.5

SO<sub>4</sub> concentrations increased for samples 9–12 downstream. This is a result of the dissolution of sulfides along the stream and calcine piles. Because of this, facieses of the waters change gradationally downstream. Water samples from higher elevations of the mining area contain Mg, Ca, and HCO<sub>3</sub>; these are water types that reflect the carbonated aquifers (Gemici et al. 2004; Tarcan and Gemici 2005). Acidic mine waters turn into Ca, Mg, and SO<sub>4</sub> water type. The dominant anion is SO<sub>4</sub> and its concentration reaches 3,980 mg/L in acid mine waters. Mg and Ca are also dominant cations in surface waters. However, HCO<sub>3</sub> is dominant; SO<sub>4</sub> increases; and waters turn into Mg, Ca, SO<sub>4</sub>, and HCO<sub>3</sub> water type along the direction of the flow.

The source of acidity is caused by the oxidation of sulfide phases, especially pyrite (Gal 2000). The mining works (open pit mine, exploitation galleries, drillings, calcines) expose substantial quantities of sulphides to air that accelerate the oxidation processes and causes acid-mine drainage (Milu et al. 2002). Pyrite is common and found together with the zinover throughout the mining area (Holzer 1953; Baykal 1954; Schuiling 1962; Yıldız and Bailey 1978). The following reaction describes the overall processes (Banks et al. 1997):



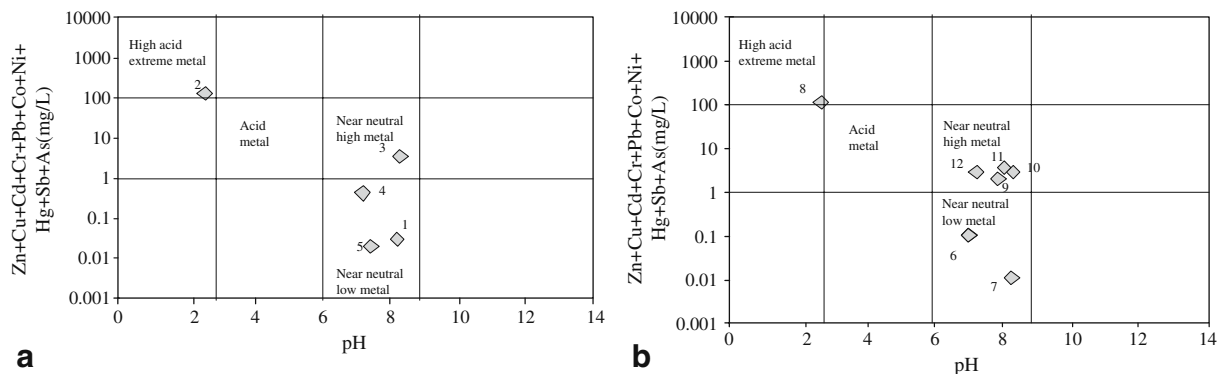
The high sulfate concentrations and elevated EC measurements indicate that sulfide oxidation occurs at the site. The EC continues to increase downstream suggesting that the stream is impacted by pyrite oxidation; however, acidity appears to be decreasing downstream (sample 10 – pH=8.3). Therefore, while the mine site has altered the stream chemistry with

increased metal and sulfate concentrations, the streams are not acidic. The limestones around the mine area affect the occurrence of the alkaline waters entering the system and this has a significant impact on the overall system.

pH directly affects the metal contents of the water samples. The relationship between heavy metal contents and pH of the water samples in the arid and wet seasons is shown in Fig. 3. The ground waters that are near neutral are low metal content waters. Adit and surface waters leaching the mine wastes are high metal content waters. The water samples that were collected from the galleries are acidic in character, and heavy metal contents are generally higher than in the neutral waters. This indicates that the source of heavy metals downstream in the mine area is adit waters and waters leached by acid water of calcine piles, altered basement rocks, and mineralized rocks.

The aluminosilicates, that occur in the basement rocks of the study area, increase silica, aluminum, magnesium, calcium, and potassium concentrations in waters because of dissolution. H<sub>2</sub>SiO<sub>3</sub> concentrations in the surface water and ground water samples are 23–125 mg/L in the summer season. H<sub>2</sub>SiO<sub>3</sub> concentrations in uncontaminated water samples 5 and 6, which occur in the upper part of the mine field, were approximately 23 mg/L. Aluminum concentrations of surface waters and mine waters reach very high values at 89.47 mg/L in the Alaşehir old Hg mine due to increase in the aluminum dissolution in the acidic waters that leachate the mine wastes (Table 1).

The Fe concentrations in the surface drainage waters are much greater than those of the ground waters. Acid mine drainage waters having very high Fe concentrations (about 670 mg/L in sample 2) dilute



**Fig. 3** Scatter diagram of the concentrations of the metals for **a** arid season and **b** wet season



with the stream water and Fe contents decrease to 0.7 mg/L in sample 9. However after passing the calcine piles Fe concentrations increase downstream gradationally. The dissolved iron precipitates as a hydroxide because of the increasing oxygen quantity in the surface waters downstream. Red-colored sediments were observed in the stream.

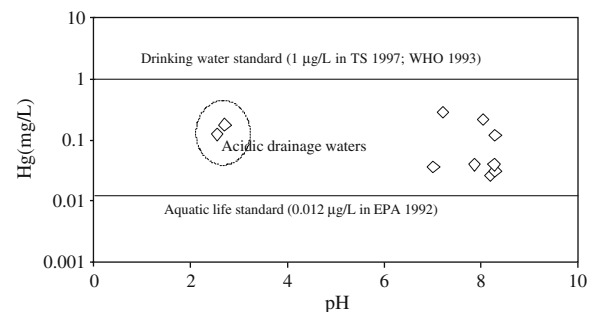
One of the most important pollutants in the study area is arsenic. As value in arid season is 3,177 µg/L in mine drainage water and it is remarkably above the drinking water standards (As: 10 µg/L, TS 1997 and WHO 1993). On the other hand, As value decreases, similar to the other constituents in the rainy season, due to dilution. Uncontaminated ground water samples (4 and 5) have lower As concentration values than the limit value, which is 10 µg/L. As values in stream water also decrease with the surface flow direction.

Chemical analysis of other water samples showed that waters around the mine site are enriched with heavy metals. The highest concentration of major ions and metals were observed in adit waters (Sample 2 and 8). SO<sub>4</sub>, which is a dominant anion for water from the study area, had concentrations of 3,981 mg/L and around 250 mg/L for adit and surface waters, respectively. SO<sub>4</sub> concentration exceeded that of drinking water standards (TS 1997). Sample 5 represents uncontaminated groundwater. The sample did not show an increase in either any major ion or heavy metal content. Thus, all of the parameters are below the Turkish Drinking Water Standards (TS 1997).

Sample 2 was of the adit water and had the highest Al content; it reached 89 mg/L. Due to dilution and precipitation of aluminum compounds, Al concentrations decreases to 2–3 mg/L in groundwater and surface waters downstream. One of the metals that reached to high concentrations in water samples taken from the area was Fe. Iron values reaching 670 mg/L are highly above that of drinking water standards (0.2 mg/L) in all the mine drainage waters. In rainy season samples, Fe concentrations were similar to the arid season in mine drainage waters. Ni concentrations were below 50 µg/L Turkish drinking water standard in ground water samples. But mine drainage waters exceeded drinking water standards. Zn concentrations were between 3, 4, and 1,375 µg/L. The highest Zn content was observed in (Samples 2 and 8) mine drainage water (Table 1).

Compared with sample 5 which was assumed as the uncontaminated ground water, Hg concentrations were remarkable enriched for acid mine waters around the mine area. For uncontaminated ground waters, Hg values were below the detection limit and could not be determined. Hg concentrations were around 0.12–0.173 µg/L for adit waters and 0.025–0.274 µg/L for surface waters draining the mine area. Hg contents of all of the water samples were less than the 1.0 µg/L Turkish drinking water standards and that recommended by the WHO (1993). However, they were above the 0.012 µg/L Hg standards recommended by EPA (1992) for aquatic life as, shown in Fig. 4.

The low Hg concentrations in ground water samples was due to the highly resistant nature of cinnabar to chemical and physical weathering and its solubility in water (Gray et al. 2000). Low concentrations of metals in ground water samples were possible due to the adsorption by iron hydroxide or precipitation and combination with sulfide (Pierce and Moore 1980; Lee et al. 2001). When the pH increases, the eventual precipitation of Al hydroxides will contribute to enhance metal adsorption (Cidu et al. 1997). Waste rocks, calcine piles, and acid mine drainage waters cause decrease in pH and increase in especially Fe, Al, As, SO<sub>4</sub>, and some trace metal around the mine area. Alteration of basement rocks controls the acid neutralization. Acid-neutralization is mainly controlled by chemical weathering of silicate minerals and carbonated rocks in the study area. These rocks release elevated levels of Ca and Mg. Minerals such as pyrite and marcasite in the area control the acidification processes. The chemical weathering rate of the primary silicate and aluminosilicate mineral is slow relative to the production rate of acid by pyrite oxidation (Deutsch 1997). Therefore weathering of the carbonated rocks that outcrops around the mining



**Fig. 4** Plots of Hg versus pH and reference values for drinking water and aquatic life standards

area mainly control the neutralization of the acidic mine waters. Since the rapid rate of reaction and the widely occurrence of calcite, it is the most important neutralization agent. Calcite neutralizes acid by dissolving and complexing with hydrogen ions to form bicarbonate and carbonic acid. These inorganic carbon species remove hydrogen from the solution that result in decrease of acidity (Deutsch 1997).

#### Saturation states and species

Saturation state of the minerals probably controls the chemical composition of waters in the study area. An equilibrium mass-balance model has been used to calculate the elemental aqueous speciation and the stability of solid phases with respect to the dissolved constituents. The chemical equilibrium modelings of the waters were carried out by using the PhreeqCi

computer code (Parkhurst and Appelo 1999) at outlet temperature and measured pH (Tarcan and Gemici 2003; Tarcan et al. 2005). The potential for mineral precipitation or dissolution may be assessed using the saturation index (SI). Oversaturation is indicated when the solubility product ( $Q$ ) values are higher than the solubility constant ( $K$ ) values ( $Q > K$ ) at a particular temperature and precipitation may be expected. When  $Q < K$ , the solution is theoretically undersaturated and dissolution might be possible. The acidic drainage waters from the adits were saturated with the quartz, chalcedony, cinnabar and Hg(l) minerals (Table 2). Saturation index values are negative for albite, chromite, gypsum, hematite, goethite, pyrite, FeSO<sub>4</sub>, and clay minerals such as montmorillonite, kaolinite, and illite. Saturation index values of calcite, dolomite, albite, clay minerals and some Fe bearing minerals such as goethite and

**Table 2** Saturation indices of some selected minerals and the speciation of arsenic and iron

Samples	1	2	5	10
Albite	0.44	-9.42	0.35	-1.50
Arsenolite	-17.66	-7.82	-15.01	-12.80
Arsenopyrite	-54.24	-39.47	-51.74	-47.46
Calcite	1.13		-1.06	0.89
Chromite	14.37	-8.13	11.19	18.64
Cinnabar	-7.66	3.21	-2.87	-4.44
Dolomite	3.77		-1.16	3.07
Fe(OH) <sub>2</sub>	-4.08	-11.82	-5.19	-2.48
Fe(OH) <sub>3</sub>	-1.96	-10.12	-3.15	-0.52
FeSO <sub>4</sub>	-12.8	-7.5	-12.50	-10.20
Gibbsite	1.96	-4.53	2.73	-0.62
Goethite	3.18	-4.89	2.08	4.79
Gypsum	-2.16	-0.12	-2.85	0.95
Hematite	7.34	-8.82	5.12	10.51
Hg(l)	9.63	4.74	9.28	10.41
Illite	5.92	-12.29	6.74	0.70
Kaolinite	5.05	-6.23	6.82	0.30
Montmor-Ca	4.78	-7.87	5.72	1.67
Orpiment	-81.50	-11.19	-71.87	-68.26
Pyrite	-42.49	-17.87	-39.14	-35.67
Realgar	-32.27	-21.81	-29.41	-28.38
Siderite	-0.21		-1.18	1.37
Quartz	0.22	1.09	0.37	0.47
	As(3) < 2.5% (HAsO <sub>2</sub> + As(OH) <sub>3</sub> + H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup> + H <sub>3</sub> AsO <sub>3</sub> )	As(3) > 99.9% (HAsO <sub>2</sub> + As(OH) <sub>3</sub> + H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup> + H <sub>3</sub> AsO <sub>3</sub> )	As(3) > 74.5% (HAsO <sub>2</sub> + As(OH) <sub>3</sub> + H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup> + H <sub>3</sub> AsO <sub>3</sub> )	As(3) < 9.5% (HAsO <sub>2</sub> + As(OH) <sub>3</sub> + H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup> + H <sub>3</sub> AsO <sub>3</sub> )
	As(5) > 96.5% (H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> + HAsO <sub>4</sub> <sup>-2</sup> + AsO <sub>4</sub> <sup>-3</sup> )	As(5) < 0.1% (H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> + HAsO <sub>4</sub> <sup>-2</sup> + AsO <sub>4</sub> <sup>-3</sup> )	As(5) < 25.5% (H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> + HAsO <sub>4</sub> <sup>-2</sup> + AsO <sub>4</sub> <sup>-3</sup> )	As(5) > 90.5% (H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> + HAsO <sub>4</sub> <sup>-2</sup> + AsO <sub>4</sub> <sup>-3</sup> )
	Fe (2) > 99.9%	Fe (2) > 99.9%	Fe (2) > 99.9%	Fe (2) > 99.9%



hematite are positive in surface waters. However cinnabar, gypsum,  $\text{FeOH}_2$ , pyrite and siderite have negative values. Saturation index values are all positive for albite, quartz, chalcedony, clay minerals, hematite goethite, chromite and  $\text{Hg}(\text{l})$  in spring waters. Precipitations of these minerals are expected. On the other hand, calcite, dolomite, cinnabar, pyrite,  $\text{FeSO}_4$  and gypsum give negative values for whole ground water samples. All of the waters from the study area are typically undersaturated with respect to main As-bearing minerals such as arsenolite, orpiment, realgar. They would be predicted to dissolve.

The mobility of arsenic under oxidizing conditions is primarily affected by the adsorption of As (V) onto metal oxyhydroxide surfaces. Arsenic generally occurs as arsenate (AsV) and arsenite (AsIII) in aqueous solutions (Dove and Rimstidt 1996). The reducing nature of ground water reduces As to As (III). Arsenic forms soluble arsenate (As(V)) under oxidizing conditions in combination with iron, lead, and manganese. Under reducing conditions, arsenic forms sulfide minerals such as orpiment (Deutsch 1997 and Gemici and Tarcan 2004). When plotted on an Eh–pH diagram it can be observed that waters are predicted to be dominated by  $\text{H}_3\text{AsO}_3$  species of arsenic (Fig. 5).

Depending on the Eh–pH characteristics, As (III) is the dominant arsenic species for waters from the study area. Arsenite (As III) species are more mobile than As (V) in ground water system since As (III) is less likely to become strongly sorbed to a mineral surface than a negatively charged As (V) complex (Ongley et al. 2001). The plotted data in Fig. 5 are located near the boundary of  $\text{H}_3\text{AsO}_3$  and  $\text{HAsO}_4^{2-}$ . For acid mine

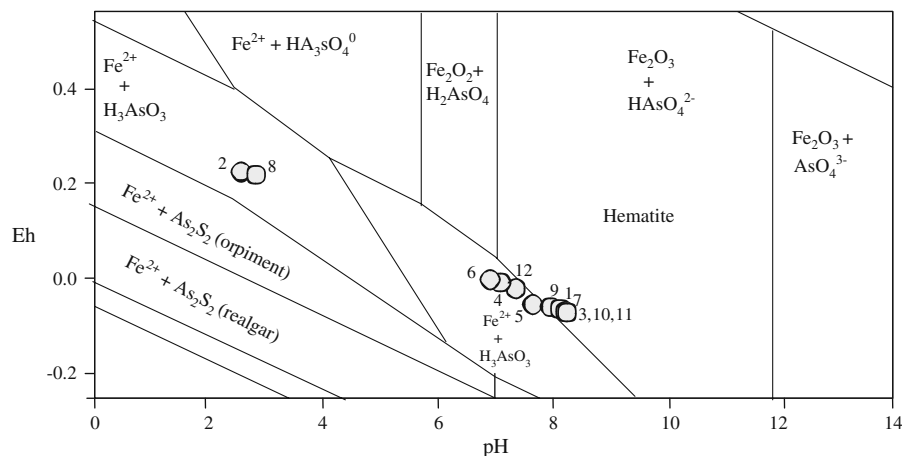
drainage waters and samples 6, 4, 12 and 5, As (3) is the dominant. These results coincide with the species calculations performed with the PhreqC for arsenic and iron (Table 2). Arsenic probably exist as As (5) in the surface waters located up and downstream of the mining area. Arsenite (AsIII) is the dominant arsenic species for spring and acid mine drainage waters (Table 2). Thermodynamic calculations showed that 90.5–96.5% of arsenic for samples 10 and 1 would be in equilibrium as  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$  and for samples 2 and 5 would be in equilibrium as  $\text{HAsO}_2$ ,  $\text{As}(\text{OH})_3 + \text{H}_2\text{AsO}_3^-$ ,  $\text{H}_3\text{AsO}_3$ . The iron concentrations in all the water samples suggested dominance of reduced form  $\text{Fe}^{2+}$  (Table 2). The reaction of mine water with atmospheric oxygen causes the oxidation of the dissolved ions (II) to iron (III) and precipitation of iron oxyhydroxide.

### Mine wastes and stream sediments

Stream sediments and mine wastes were sampled from the study area to evaluate the distribution of metals through the environment. Chemical analyses of the stream sediments and mine wastes are presented in Table 3.

Stream sediments are eroded downstream from waste rocks and calcine piles in the catchment area. Hg concentrations for calcine sample (S8) and sample S10 were above 100 ppm (Table 3). Other waste rock samples have 9.94–18.84 ppm Hg concentrations. Arsenic values were remarkably high for calcine sample with concentrations of 668 ppm. Arsenic values reached 1,164 ppm in waste rocks samples. Calcine piles are one of the main sources of

**Fig. 5** Distribution of water samples in Eh–pH diagram (modified form Vink 1996)



**Table 3** Chemical properties of mine wastes and stream sediments

		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
Mo	ppm	0.7	10.5	0.2	2.7	4.6	1.7	1.4	2.5	2.2	<0.1	1.2
Cu	ppm	16.3	250.1	16.2	3.9	3.8	21.9	27.4	23.7	4.6	1.7	24.5
Pb	ppm	7.1	8.4	8.3	5.9	6.8	6.8	11.8	3	<0.1	6.9	8.7
Zn	ppm	47	86	50	9	17	60	74	93	3	4	66
Ag	ppm	<0.1	0.1	<0.1	0.1	0.2	<0.1	<0.1	<0.1	<0.1	0.4	0.1
Ni	ppm	49.4	>10000	125	14.6	58.6	597.8	754.7	>10000	198.3	35.8	681.1
Co	ppm	18.3	629.4	17.5	9.7	26.9	70.2	68.6	365.6	23.8	8.7	59.3
Mn	ppm	434	23	312	<1	2	448	640	281	<1	<1	438
Fe	%	2.55	5.71	2.38	0.37	0.31	2.99	4.2	38.24	4.13	1.24	3.58
As	ppm	25.6	1,164.4	14.2	256.5	77.4	117.4	186.2	999.1	668.6	121.6	129.8
U	ppm	1.2	27.4	0.5	0.7	0.8	1.6	2.6	27.7	0.6	0.1	1.5
Au	ppb	2	24.2	2.9	232.1	76.5	12.6	7.8	28.3	10	625.9	6.1
Sr	ppm	27	7	20	1	1	18	30	79	36	1	30
Cd	ppm	0.1	0.3	0.1	<0.1	<0.1	0.1	0.2	0.1	0.5	<0.1	0.1
Sb	ppm	7.8	162	5.7	1,149.4	197.1	246.5	97	151.1	181.9	54.7	76.7
Ca	%	3.28	0.16	2.57	0.06	0.03	0.86	1.64	1.12	3.52	0.04	1.66
La	ppm	13	3	10	1	<1	11	11	3	<1	3	11
Cr	ppm	30	1,590.8	26.5	162.7	281.7	92.2	139.9	6170.1	132.9	120	127.6
Mg	%	1.88	0.25	0.27	0.02	0.02	0.44	0.46	0.32	0.01	0.01	0.62
Ba	ppm	73	3	79	64	14	67	86	86	35	59	94
Ti	%	0.03	0.001	0.002	<0.001	<0.001	0.021	0.01	0.002	0.006	<0.001	0.013
B	ppm	7	6	1	<1	<1	<1	4	12	<1	<1	2
Al	%	0.66	0.4	0.3	0.1	0.09	0.56	0.53	1.86	0.12	0.36	0.5
Na	%	0.008	0.019	0.005	0.003	0.002	0.006	0.007	0.01	0.019	0.011	0.006
K	%	0.28	0.14	0.14	0.08	0.09	0.22	0.2	0.04	0.11	0.27	0.19
Hg	ppm	1.77	9.94	0.37	76.94	18.84	3.82	11.66	33.76	>100	>100	8.52
S	%	<0.05	6.07	<0.05	<0.05	0.08	<0.05	<0.05	0.93	6.07	0.13	<0.05

contaminants. Ni and Cr are also important contaminants with high values in calcine and waste rocks. Ni and Cr values were between 58 and over 1,000 ppm and 120–1,590 ppm, respectively. In mining wastes, other metals have contents of 1.7–250.5 ppm for Cu; 3–86 ppm for Zn; 0.1–8.4 for Pb; 8.7–629 for Co; and 54.7–190 ppm for Sb. According to the Earth's crust

reference values (Shacklette and Boerngen 1984; Wang and Chen 1998) that are presented in Table 4 samples from calcine piles (S9) and rock wastes (S2, S5, and S10) have abnormally high values, especially for Hg, Ni, Fe, As, Cr, Co and Cu. The enrichment of the other metals (Zn, Pb, Sb) were small relative to the case of Hg, Ni, As (Tables 3 and 4).

**Table 4** The geoaccumulation (Igeo) of the stream sediment and mine waste samples from the study area

Samples	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	Earth crust reference*
Cu	0	3	0	0	0	0	0	0	0	0	0	25
Pb	0	0	0	0	0	0	0	0	0	0	0	19
Zn	0	0	0	0	0	0	0	0	0	0	0	60
Ni	1	6	3	0	1	5	5	6	3	1	5	19
Co	1	6	1	0	1	3	3	5	1	0	3	9.1
Mn	0	0	0	0	0	0	0	0	0	0	0	550
As	2	6	1	5	3	4	5	6	6	4	4	7.2
Cr	0	5	0	1	2	1	1	6	1	1	1	54
Hg	5	6	2	6	6	5	6	6	6	6	6	0.089

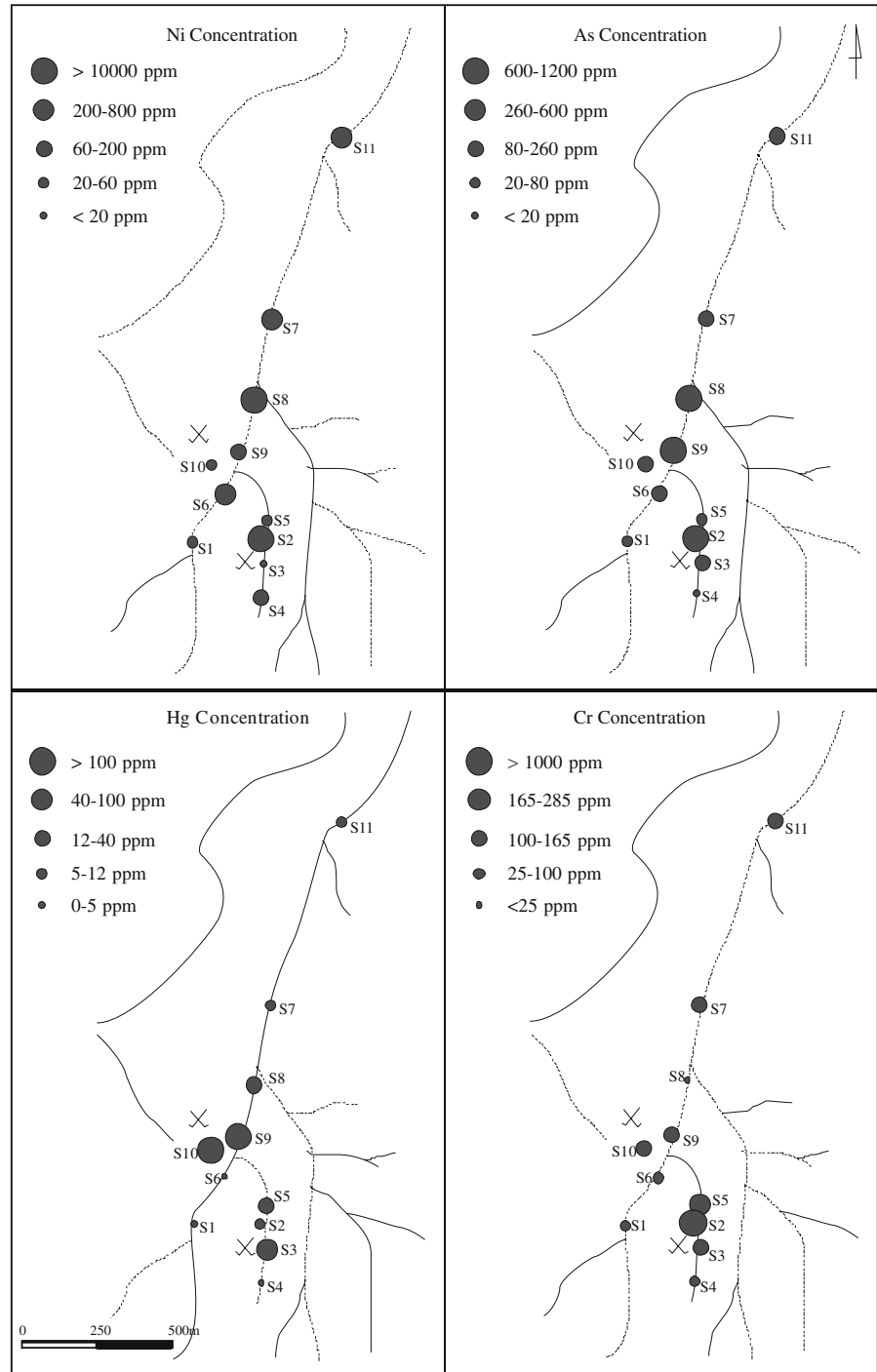
\* Means of trace contents in the lithosphere in ppm (Shacklette and Boerngen 1984; Wang and Chen 1998)

Metal contents in mine wastes and in nearby stream sediments are similar. Stream sediments also have high metal contents. A remarkable increase was observed especially in arsenic concentrations. Figure 6 shows

the variations of some selected metals from the mine area to downstream.

Low value of metals is found in upper parts of the mine area. High metal concentrations are observed in

**Fig. 6** Ni, As, Hg and Cr concentrations in stream sediments and mining wastes at Alasehir mine area



the samples close to the mine area. Metals move downstream during the rainy season and their concentrations decrease along the riverbed. Hg concentrations in the stream sediments varied between 0.37 and 76.94 ppm. Similarly, As values were lower in the upper parts of the mine area (sample S3, As; 14.2 ppm). As reached the greatest value in sample S8, which is a precipitate sample collected in the streambed. The others metals such as Ni, Cr, Hg, and Fe were high in the precipitate sample. This shows that most of the As in surface waters precipitate downstream (Table 2 and Fig. 6). Stream sediment sample S11 was the farthest sample to the mine. In this sample, As value decreased to 130.7 ppm and the Hg value decreased to 8.1 ppm.

Effects of mining activities on stream sediments were assessed using two indices: index of geoaccumulation (Igeo) and pollution index (PI). The indices of geoaccumulation enable the assessment of contamination by comparing current and preindustrial concentrations. Igeo was originally used with bottom sediments by Müller (1969). It is computed using the following equation:

$$I_{geo} = \log_2 C_n / 1.5 B_n$$

where  $C_n$  is the measured concentration of the element  $n$  and  $B_n$  is the geochemical background value of the element in fossil argillaceous sediment (average shale, Loska et al. 2004). However, a modified geoaccumulation index was used in the study as defined by Loska et al. (2004). The concentrations of the elements in the Earth's crust (Shacklette and Boerngen 1984; Wang and Chen 1998) were used as  $B_n$  value. The constant 1.5 is used because of the lithogenic effect (Salomos and Förstner 1984). The following descriptive classification is given for the index of accumulation by Müller (1969). <0 practically uncontaminated; 0–1 uncontaminated to moderately contaminated; 1–2 moderately contaminated; 2–3 moderately to heavily contaminated; 3–4 heavily contaminated; 4–5 heavily to extremely contaminated; >5 extremely contaminated.

The indices of the geoaccumulation are presented in Table 4. The Igeo results show that mine wastes (waste rocks and calcine piles) are uncontaminated with Cu, Pb, Zn, and Mn. However, they are enriched in Ni, Cr, Co, As, and Hg metals.

They are classified as heavily-to-extremely contaminated with the mentioned metals according to the

Igeo index. Stream sediment samples show similar results as mine wastes. Based on the accumulation index, stream sediment samples are uncontaminated with Cu, Pb, Zn, and Mn for same samples with Cr and Co. Average value of Hg in the Earth's crust is quite low (Hg=0.089 ppm; Shacklette and Boerngen 1984). However Igeo index for As and Hg metals in stream sediments from the study area are high and are classified as heavily and extremely contaminated. The Igeo values range from 2 to 6 for Hg and from 1 to 5 for As. In addition to As and Hg, Ni and Cr are the other important contaminants. Their Igeo values also reach 5 (Table 4).

The second index for contamination assessment is the pollution index value (PI), which was proposed by Nishida et al. (1982) to evaluate the contamination in soils and stream sediments. Many researches have used PI to estimate the degree of multiple metal contaminations (Nishida et al. 1982; Chon et al. 1996; Kim et al. 2001; Sponza and Karaoglu 2002). The pollution index is computed by averaging the ratios of the total concentrations of the heavy metals to tolerable levels (Kim et al. 2001). In this study, the PI value was calculated for nine elements.

$$PI = (As/20 + Cd/3 + Cu/100 + Hg/2 + Pb/100 + Sb/5 + Zn/300 + Ni/50 + Cr/100) / 9$$

Any element enrichment can be derived from anthropogenic inputs or natural geological resources (Nimick and Moore 1991). PI values above 1.0 indicate that the metal concentrations are higher than the permissible levels (Kim et al. 2001). PI values were high and varied between 0.6 and 31.5 for stream sediment samples. Samples from mine wastes had PI values reaching 34.9 (sample S2). Samples collected from the upper parts of the mine area were uncontaminated based on the pollution index values. PI value is 0.6 for sample S3. Around the calcine piles, PI values for stream sediments increased up to 31.5 and gradually decreased downstream to 4.6 (sample S11). PI values for the area downstream were found to be higher than the permissible level of 1.0. Mine wastes were the main source of contaminations in the stream sediments. The stream sediments derived from the mining area with the surface waters are potentially hazardous to the environment adjacent to the abandoned Hg mine and are in need of remediation.

## Conclusions

Adit waters are acidic and their pH values change between 2.55 and 2.7 with electrical conductivity value of  $5,060^{\circ}\mu\text{S}/\text{cm}$ .  $\text{SO}_4$  is the dominant anion with concentrations of 3,980 mg/L in acid mine waters. This is a result of the dissolution of sulfides along the stream and calcine piles. The source of acidity is caused by the oxidation of sulfide phases, especially pyrite.

pH directly affects the metal contents of the water samples. Some of the water samples sampled in the mine site are acidic and have high contents of heavy metal. Fe concentrations for adit waters reach 670 mg/L. The dissolved iron precipitates as hydroxide because of the increasing oxygen quantity in surface waters downstream. Red-colored sediments were observed in the stream. One of the most important pollutants in the study area is arsenic, reaching 3,177  $\mu\text{g}/\text{L}$  for mine drainage water in an arid climate. As values and other constituents decrease in the rainy season because of dilution. Hg concentrations are around 0.12–0.173  $\mu\text{g}/\text{L}$  for adit waters and 0.025–0.274  $\mu\text{g}/\text{L}$  for surface waters draining the mine area. Hg contents of all of the water samples are less than the 1.0  $\mu\text{g}/\text{L}$  Turkish drinking water standards and that recommended by the WHO (1993). Low Hg concentrations in groundwater samples are caused by the high resistance of cinnabar to chemical and physical weathering and its solubility in water. The adsorption by iron-hydroxide or precipitation and combination with sulfide also causes low levels of Hg concentrations.

The concentrations of the some major and secondary ions increase to downstream. Dissolutions of elements by water–rock interactions between surface waters and mine wastes and stream sediments give rise to an increase in total dissolved solids for surface waters. A remarkable increase is observed after passing the Hg mining area for Ca, Mg,  $\text{SO}_4$  and Fe. Similarly the values of other toxic elements such as As, Hg, Ni, Co and Cr also increase downwards. Alteration of basement rocks, pyrite, and marcasite minerals controls the acid neutralization. This indicates that the source of heavy metal downstream the mine area is adit waters, leaching of calcined piles with surface waters, and altered mineralized rocks.

Results of the geoaccumulation index (Igeo) showed that mine wastes are uncontaminated with Cu, Pb, Zn, and Mn. However, they are enriched in Ni, Cr, Co, As, and Hg metals. They are classified as

heavily to extremely contaminated with the above-mentioned metals according to the Igeo index. Based on the accumulation index, stream sediment samples are uncontaminated with Cu, Pb, Zn, Mn for same samples with Cr and Co. However, Igeo index for As and Hg metals in stream sediments from the study area are high and are classified as heavily and extremely contaminated. The Igeo values range from 2 to 6 for Hg and from 1 to 5 for As. In addition to As and Hg, Ni and Cr are other important contaminants. Their Igeo values also reach 5. Pollution index (PI) values are high and vary between 0.6 and 31.5 for stream sediment samples. Mine wastes pose a danger to the environment adjacent to the abandoned Hg mine and require urgent remediation. Distribution of the metals in the stream sediments show that metals from the mining area move downstream in the rainy season, giving rise to contamination in the areas adjacent to the mining area.

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