Heavy metal pollution and acid drainage from the abandoned Balya Pb-Zn sulfide Mine, NW Anatolia, Turkey

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Abstract This study was conducted to determine the effects of the waste-rock dump (WRD) of the underground polymetallic Balya Mine on the Kocacay River and eventually on Lake Manyas in Turkey. Data presented in this paper include geochemical characteristics of various kinds of water (mine, surface and groundwater) and of suspended-particle samples in the vicinity of Balya. The more polluted mine waters have low pH and high conductivity, while high concentrations of Zn, Cd, Mn tend to be found in the dry and wet seasons. High concentrations of Pb, As, Cr, Cu and S appear only in the wet season. The sources of the heavy metal concentration within the Kocacay River are leached waste, surface run off, and overflow from the spillway of the WRD. To minimize the formation of acids and dissolved metal, and for the remediation of the harmful effects of extreme contamination conditions, it is recommended that lime or alkali materials and organic carbon be added to simulate the action of sulfate-reducing bacteria.

Keywords Balya Mine · Waste rock dump (WRD) · Heavy metals · Suspended particles · Acid mine drainage (AMD)

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Introduction

Base metal mining and smelting activities have been frequent sources of heavy metal contamination in the environment, resulting in considerable water contamination (Benvenuti and others 1995; Banks and others 1997; Boulet and Larocque 1998; Rösner 1998; Lottermosser and others 1999; Lee and others 2000; Marques and others 2001). For example, following the cessation of mining activity in sulfide-ore mines, drainage from waste rock dumps (WRD) carries harmful dissolved and particulate products to the environment. Such drainage waters, which have a low pH because of the various microbiological and chemical reactions during weathering, often have high dissolved metal concentrations as well as sulfide ore particles. The discharge of significant amounts of metals can continue for a long time after a sulfide mining operation has discontinued (Merrington and Alloway 1994; Routh and Ikramuddin 1996; Rösner 1998; Parsons and others 2001).

In addition to dissolved metal ions and colloidal complexes, the suspended particles coming from a WRD also have harmful effects on aquatic environments (Hart and Hines 1995). This study of bulk suspended sediment from the Kocacay River, which receives the discharge from a large WRD at Balya, shows elevated levels of heavy metals. Furthermore, water discharge from the WRD contains elevated concentrations of dissolved metals, especially Zn, Pb, and As. Metal loading, resulting from the dissolution of minerals in a WRD formed during the dry season, is especially high after a rainfall period.

Up until now, there has been no detailed study of the characteristics of the WRD of the Balya Mine and heavy metal loads of the Kocacay River, which connects the WRD of Balya to Lake Manyas. Previous investigators have studied geological and geochemical aspects of the Balya Mine area (Kovenko 1940; Aygen 1956; Gjelsvik 1958) and its ore potential (Akyol 1982). The only data on the water quality of the historical mining district of Balya was published as an abstract by Aykol and others (2002).

The present study documents the distribution of heavy metals in aquatic ecosystems of the Balya Mine region. The incentive for this study comes from: (1) assessing the effect of WRD leachate on the ecologically significant Lake

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Manyas and the bird sanctuary in the eastern part of the lake, (2) understanding the environmental impact of heavily contaminated water and the stream sediments of the Kocacay River, which spreads toxic material to tens of villages along the stream between WRD of the Balya mine and Lake Manyas, and (3) evaluating the consequences of construction of the Manyas Dam midway between Balya and Lake Manyas, which will be used for the irrigation of the land downstream.

There is a clear need to restore these habitats affected by harmful impacts of the WRD products. The results of this study on the hazardous effects of WRD of the Balya Mine will provide a basis for appraisal of the environmental costs of cleaning up the adjoining aquatic ecosystems, such as the Kocacay River and Lake Manyas.

Geology and field description

The Balya Pb-Zn-Ag deposit and associated mine tailings are located in Northwest Anatolia, in Balya, near Balikesir, Turkey. It is the largest Pb-Zn mine in the region. This deposit is part of the geotectonic unit of the Western Pontides, an island-arc system that became attached to the Anatolian plate during the Late Cretaceous and Tertiary. The local geology consists of Permian, fossil-rich massive limestones and Triassic sedimentary rocks (a series of dark pelitic shale, sandstone, and calcareous conglomerate) which were folded during the Hercynian orogeny. Overlying Tertiary calc-alkaline volcanic rocks are related to Cenozoic rifting. The volcanic rocks are part of a rhyolite–dacite–andesite–basalt sequence of regional extent (Agdemir and others 1994). The main structural feature of the Balya area is the Balya Thrust fault, along which the Permian limestones are displaced over the Triassic series (Aygen 1956). The complicated structural pattern possibly resulted from recumbent folding during the Hercynian and Alpine orogenies (Gjelsvik 1958).

The type of ore deposit is contact metasomatic and the mine is set in an area of mountainous geomorphology, with rounded rolling hills and narrow short valleys that form a dendritic-type drainage network. Ore minerals are pyrite, marcasite, sphalerite, galena, chalcopyrite, and arsenopyrite. The reserves in Balya, estimated by (Akyol 1982), are 4.4 million tons, with 2.7% Pb, 7.2% Zn, and 0.3% Cu. The ore contains 7.2% Zn, 2.7% Pb, and 0.3% Cu (Akyol 1982). Minor components are pyrrhotite, marcasite, bismuth, sulfosalts, arsenopyrite, tetrahedrite-tennantite, bornite, argentite, heyrovskite, hematite, magnetite, pyrolusite, orpiment-realgar, and native tellurium. The primary cations in the galena fraction from the Balya deposit (Table 1) consist of 97.96% Pb, 0.11% Sn, 0.01% Bi, 0.54% Cu, 0.03% Fe, 0.004% Ni, and 0.01% As (Kovenko 1940).

The Balya Pb-Zn deposit was exploited from the early 1880s to the late 1940s. Although there are no reliable data about the amount of the concentrated ore produced, judging from the size of the tailings, which are composed of flotation tailings and a small amount of jig wastes, plus considerable amount of slag left over from the smelter in Balya, the amount of the concentrated ore appears to be significant. The total amount of WRD is approximately 2 million tons. The waste rock dumps are downstream from the smelter and ore dressing plant. At the first dump area, the waste material was drained into a primitive dam with a wall thickness of 90 cm. The second dump is just beneath the ore processing plant, where the waste material is directly drained into the stream. The WRDs of the Balya Mine are major sources of heavy metals in the stream. The Kocacay River carries the waste drainage into Lake Manyas, approximately 40 km downstream from the mining area. The sources of atmospheric dispersal of harmful material from the Balya mine area can be grouped into two classes: first, the dispersion from the old, dilapidated smelter stack which is no longer operative, and second, the dispersion originating from the old tailings. Galena, sphalerite, and pyrite are present in the atmospheric dispersal.

The total length of the section of the Kocacay River studied is more than 40 km, and the approximate average slope of the riverbed is 2%. At the head of the Kocacay River Valley, rainfall reaches 680 mm/year. The morphology of the stream is similar at all sites sampled, with an average depth range from 30–190 cm at different times of the year. The width of the river varies from 5–15 m, and the riverbed is covered predominantly with pebble- to cobble-sized detrital sediments. The riparian vegetation of Kocacay River is well conserved; the maximum width of the riparian strip is over 10 m near Lake Manyas, but it shows certain irregularities in various sections studied. An important ecosystem for wild birds is the Lake Manyas Bird Sanctuary, which is at the end of the Kocacay River and east to southeast of Lake Manyas, south of the Marmara Sea near the town of Bandirma. This lake, with

Table 1
Heavy metal loads of different WRD samples

Element	The chemical composition of ore deposits (%)[a]	The primary cations in the galena fraction % Ag g/t[a]	WRD				
			1	2	3	4	5
Pb %	2.7	97.76	5.47	13.31	5.30	5.35	5.40
Zn %	7.2	NA	4.18	5.27	5.54	2.43	2.26
Fe %		0.13	8.17	16.59	7.17	12.9	13.52
Cu %	0.3	0.54	0.172	0.330	0.225	0.199	0.194
Mn %		NA	0.13	1.19	0.25	0.13	0.12
As %		0.01	0.30	0.44	0.27	0.34	0.33
Cd %		NA	0.028	0.038	0.034	0.015	0.014

[a]Akyol (1982), WRD 2 is metallurgical waste

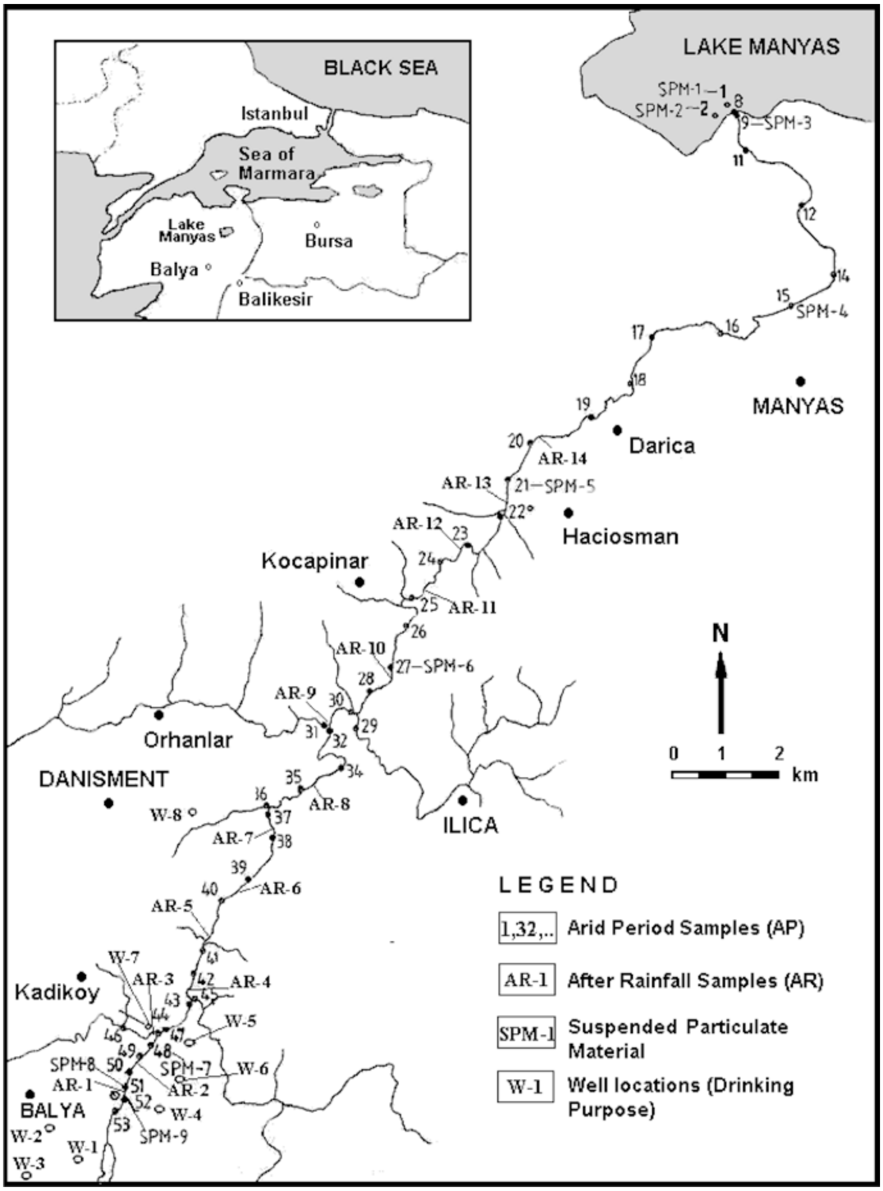

Fig. 1
Location of the Balya Mine (*inset*) and a detailed map showing sampling sites

an area of just 64 ha, is home to more species of birds than anywhere else in Turkey. More than 60 species of birds breed here every year. A sand/gravel type dam spanning the Kocacay River has been under construction since 1993, with the intent to provide energy, irrigation, and flood control to the area.

Sampling and analytical methods

Sampling at Lake Manyas and along the Kocacay River, and at the WRD of the Balya Mine, was carried out during the dry season or arid period (AP) at the end of July 2001. Sixty-six locations along 40 km of Kocacay River and five locations within the WRD of the Balya Mine were selected. Ten days after the AP sampling, 14 samples were taken within 2–3 h after a heavy rainfall (AR). AP water samples were collected from 53 locations and were designated as AP-1 to AP-53. AR water samples were collected at the locations from AR-1 to AR-14, which were considered to be the best locations to assess the impact of the WRD on the Kocacay River and Lake Manyas. The analysis of the sample from site AP-53, in the Kocacay River above the mining area of influence, represents the regional geochemical background. Well samples (W-1 to W-8), are within 10 km of the WRD. They are used to investigate harmful effects of the Kocacay River contaminants on groundwater quality. Suspended particle samples (SPM-1 to SPM-9) were also taken from the same parts of the river from the WRD to Lake Manyas area during the dry season. All sampling locations were reached by boat or car, and sample coordinates have been determined by the global positioning system (GPS) (Fig. 1).
Properties of the water samples, such as pH, temperature (T; °C), electrical conductivity (EC; μS/cm), were immediately measured in situ with portable devices (WTW instruments calibrated using standard solutions). Field

observations and personal communications were recorded on cards suitable as a keypunch source.
The water samples were stored in 0.5- and 20-l polyethylene containers. All samples were refrigerated (at 4 °C) for transport to the laboratory. Special care was taken to avoid contaminating the samples throughout the whole process. The water samples were analyzed by means of separation into two fractions to determine the contents of dissolved metals and suspended sediments (particles >0.45 μm).
Upon returning to the laboratory, each 20-l aliquot was filtered through pre-weighed a Sartorius nitrate cellulose membrane (pore diameter 0.45 μm) under nitrogen pressure (to prevent sample oxidation) to determine heavy metal loads in the suspended particles. The filters were first air-dried in the laboratory, and then oven-dried at about 80 °C for 24 h, and finally weighed to determine suspended-particles concentrations.
All water analyses were made by ICP-MS (Tables 2, 3, 4), while suspended particles and WRD samples were determined by ICP-ES (Tables 1, 5). Each measurement was carried out in duplicate to avoid analytical errors. Specific metals were selected for the following reasons: (1) Zn and Pb were selected because these were the metals mined and they are present in the WRD; (2) Fe, Mn, and Cu were selected because they were the most abundant metals in the WRD (especially Cu and Fe are relatively abundant and can easily be correlated with the mineralogy of the sulfide ores; i.e., chalcopyrite, pyrite); (3) As, Cd, and Cr were chosen for their potential toxicity, even though only traces of these were found; and (4) sulfur was chosen because it is the characteristic anionic element in acid-mine-drainage (AMD) systems.
Spatial distribution of geochemical parameters was graphically displayed using the Kriging method (Matheron 1982). The impacts of anthropogenic sources on the elemental concentration, distribution /migration pattern, and total dump mass affected by each element have been deciphered using these contour maps (The SURFER, Golden Software Inc., version 6.05). Universal Kriging is a procedure that can be used to estimate values of a surface at the nodes of a regular grid from irregularly spaced data points.

Results and discussion

Origin of acid water and dissolved metals

Tailings are considered an environmental problem, and therefore measures should be taken to reduce their environmental impact. However, waste rock has not been identified as an environmental problem and therefore it can be used for various purposes, such as road fill. Waste rock poses a threat to the environment because it can contain high amounts of sulfide minerals (Ledin and Pederson 1996).
Based on XRD analyses, metallurgical wastes (WRD-2) of the Balya Mine include the following metal sulfides, in decreasing abundance: pyrite>galena>sphalerite>chalcopyrite. In addition to these major metal sulfides, there is quartz, metal sulfates (anglesite and zinkite), and metal carbonates (siderite, cerrusite and smithsonite). Other waste dumps (WRD-1, 3, 4, 5) contain the same metal sulfides, metal sulfates, and metal carbonates, but in addition, they contain quartz, calcite, and gypsum. The sulfide minerals are readily oxidized and they form soluble metal sulfates in the waste dumps. Heavy metal loads of WRD samples, especially of Pb and Zn, are very high when compared to the heavy metal loads of the ore deposit (Table 1).
In open dumps of waste rock, the heat of oxidation activates air circulation that draws in fresh air from the bottom of the dumps, usually producing steam vents near the tops of the WRDs (Schafer 1992). This is also seen in the WRD of the Balya Mine.
Oxidation reactions may be acid-producing, neutral, or base-producing reactions, depending on other elements present in a sulfide mineral (Castro and Moore 2000).
Sulfate, generated by oxidation of monosulfides and pyrite, is the dominant anion in most AMD water (Nordstrom and Alpers 1997). The acidic, metal-rich waters that flow from abandoned mines can contaminate streams and rivers far downstream from the drainage source, and can have toxic effects on biota.
Oxidation of disulfide (S_2^{2-}), the anion in pyrite and marcasite, is responsible for acid in the AMD of Balya Mine. It is well known that oxidation of the sulfide ion (S_2^{2-}) is not enough to produce acid water. Other acid-producing reactions are: oxidation of iron (II) (under most pH conditions), followed by the hydrolysis of Fe^{3+}; and hydration of arsenic (III and V), followed by the oxidation of arsenic-bearing minerals and hydrolysis of transition-metal anions at near-neutral pH.
The oxidation of iron and sulfur in pyrite is increased by the activity of bacteria of the Thiobacillus and Ferrobacillus genera (Tuttle and others 1968), which are acidophilic. Some species, e.g., T. *ferrooxidans*, are very active at pH values between 2 and 3.5 (Tate 1995). Thus, inorganic pyrite oxidation may progress slowly for some time until it produces enough acid to arouse Thiobacillus. At that moment, the rate of oxidation and acid output can accelerate by up to three orders of magnitude (Nordstrom and Alpers 1997).
Results are given for each metal (As, Cr, Cd, Cu, Fe, Mn, Zn, and Pb) and for each sampling period for both solutions (river and well water) and suspended particles (Tables 2, 3, 4, 5). WRDs of the Balya Mine are characterized as acid generating, based on the ratio of neutralizing potential to acid production potential (NP/AP).
The lowest pH value for surface water (AR) measured in the river that is influenced by WRD is 2.22 (Table 3).
In the vicinity of Balya, where mining and smelting activities have occurred, some heavy metals such as Pb, Zn, As, and Cd, constitute an important environmental concern. Data presented in this paper prove that heavy metals and acid leachate are entering the Kocacay River via runoff from WRDs. The high amounts of metals and metalloids in the WRD of the Balya Mine are key contributors to the development of acid-sulfate water in the

Table 2
Heavy metal contents of Kocacay River water, arid period (AP)

ID	Heavy Metals (units are µg l^{-1})											pH	EC
	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Pb	Ni	Zn		µS cm^{-1}
Kocadere River water samples (summer period)													
AP-1	17	–	0.03	3.6	1.3	–	0.11	1.4	–	0.7	–	9.2	367
AP-2	20	–	0.06	5.3	1.8	14	0.42	1.2	–	0.7	0.7	8.98	377
AP-8	13	–	0.03	5.2	1.3	46	0.62	1.2	–	0.7	1	8.74	375
AP-11	15	–	–	13.2	0.5	69	0.26	1.8	–	–	–	7.26	674
AP-14	15	–	–	11.6	0.6	29	–	1.5	–	–	–	7.85	605
AP-15	15	–	–	12.9	0.6	–	–	1.6	–	–	–	7.65	631
AP-16	19	–	–	13.3	0.5	–	–	1.5	–	–	–	7.72	656
AP-17	8	–	–	13.1	1.4	27	–	1.8	–	0.2	–	7.93	572
AP-19	11	–	–	12.7	0.6	21	–	2.1	–	–	–	7.84	578
AP-20	3	–	0.02	2.8	22.7	–	–	1.2	–	0.2	4,365.8	7.85	543
AP-22	10	–	–	13.8	0.9	82	0.07	2.3	–	0.3	64.5	7.75	546
AP-24	10	–	–	10.6	0.7	25	0.38	1.7	–	–	7.5	7.45	498
AP-26	10	–	–	10.5	0.6	14	–	1.5	–	0.3	19.3	7.92	488
AP-28	11	–	–	11	1.6	51	–	1.2	–	0.2	4.8	7.75	494
AP-30	10	–	–	10.7	0.5	26	–	1	–	–	1.9	7.55	499
AP-31	31	–	–	15.9	0.4	28	0.19	3.5	–	–	0.9	7.22	1,049
AP-32	13	–	–	13	0.7	17	–	1	–	0.6	6.4	7.55	473
AP-34	12	–	–	11.9	1.9	23	–	1	–	–	4.6	7.75	459
AP-35	12	–	–	11.8	0.9	15	–	1	–	–	7.2	7.65	465
AP-38	14	–	–	11.1	0.8	18	–	1.1	–	0.2	4.5	8.02	439
AP-40	5	–	0.04	3.8	11.9	–	–	0.6	–	0.2	3,604.7	7.82	479
AP-42	10	–	–	12.2	0.8	29	–	0.7	–	0.4	77.6	7.55	493
AP-43	6	0.26	–	11.9	0.5	54	–	0.2	2	0.5	131.2	7.53	511
AP-44	6	–	–	11.6	0.6	–	–	0.2	–	–	19.8	7.41	412
AP-45	17	–	0.03	11.7	0.4	49	–	1.4	–	–	3.4	7.91	406
AP-46	5	–	–	11.3	0.8	23	–	0.1	–	–	–	7.66	374
AP-47	–	80.11	1.02	9.3	0.7	79	748.57	0.1	–	9.5	2,841.1	6.93	1,900
AP-48	–	118.11	5.1	8.4	0.4	–	2,857.04	0.2	–	10.2	5,983.2	7.12	2,100
AP-49	–	200.6	23.6	4.8	0.4	–	9,465.28	0.4	–	27.5	20,066.8	7.02	2,900
AP-50	–	160.47	8.06	10.7	1	–	5,684.47	0.5	–	15.8	2,384.1	7.04	2,700
AP-51	–	207.57	8.35	12.1	0.3	159	6,276.76	0.5	–	21.7	1,278.6	7.09	2,800
AP-52	2	28.5	5.63	15.8	0.5	–	3,490.83	0.6	–	19.8	1,153.8	7.4	2,200
AP-53	107	–	0.19	33.3	1.6	357	18.9	1	–	3	17.2	7.55	1,200
Determination limits													
	>1	>.05	>.02	>1	>.01	>10	>.05	>.01	>2	>.2	>.5		
Min	2	0.26	0.03	3.6	0.3	14	0.07	0.1	–	–	0.9	6.93	367
Max	107	207.57	23.6	33.3	22.7	357	9,465.28	3.5	2	27.5	20,066.8	9.2	2,900
Average	15.25	113.66	4.01	11.24	1.82	54.57	2,038.85	1.12	2.00	5.64	1,682.02	7.69	886

Table 3
Heavy metals, sulphur content, and physical parameters of Kocacay River water, after rainfall (AR)

ID	Heavy metals (units are μg l^{-1})											S	pH	EC
	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Pb	Ni	Zn	(ppm)		μS cm^{-1}
AR-1	13	65.07	4.6	11.9	15.7	152	2,049.93	1.5	–	12.1	3,686.3	81.0	6.54	1,071
AR-2	–	2,712	18.62	0.6	5,260.3	893	11,444.2	0.2	4,885	45.7	330,863.6	224.4	3.72	1,845
AR-3	1,174	4,231.5	26.81	9.8	5,464.1	87,474	12,046.4	0.5	2,348	67	203,517.7	374.3	2.57	3,560
AR-4	8	153.97	7.22	9.2	24.8	743	2,789.96	1.4	16	10.3	11,021	95.1	6.20	1,140
AR-5	7,186	805.76	20.28	28	3,164.4	464,974	3,630.29	1.6	56	42.9	61,496.7	507.2	2.22	4,570
AR-6	30	64.07	6.02	5.2	42.8	2,282	1,773.05	1.6	219	7.7	5,390.1	51.7	5.71	640
AR-7	15	79.6	6.48	3.5	27.8	530	2,079.37	1.2	139	7.5	6,276.3	73.8	5.99	780
AR-8	16	72.49	6.38	3.5	31.4	348	1,979.16	1.2	125	9.3	6,455.6	80.5	6.10	770
AR-9	36	0.22	0.68	9.2	6.1	2,546	27.13	1.4	5	3.6	20	4.2	6.70	250
AR-10	30	0.18	0.61	9.7	7.8	2,372	23.22	1.2	10	3.6	23.5	5.4	6.80	230
AR-11	29	–	0.74	11.7	13.3	3,078	27.84	1.5	13	5.1	36.1	8.7	6.74	250
AR-12	–	310.71	25.49	9.6	8.3	311	9,387.42	1.5	4	30.9	16,721.3	233.0	6.48	2,090
AR-13	2	197.61	12.2	10.9	10.3	295	5,001.72	1.3	24	18.5	6,904.1	183.5	6.61	1,730
AR-14	–	307.45	32.51	8.7	10.4	117	10,602.8	1.8	–	33.4	17,972.1	228.2	6.53	2,060
Determination limits														
	>1	>.05	>.02	>1	>.01	>10	>.05	>.01	>2	>.2	>.5	>1		
Min	2	0.18	0.61	0.6	6.1	117	23.22	0.2	4	3.6	20	4.2	2.22	640
Max	7,186	4,231.5	32.51	11.9	5,464.1	464,974	12,046.4	1.8	4,885	45.7	330,863.6	507.2	6.80	4,570
Average	776.27	692.36	12.05	9.39	1,006.25	40,436.79	4,490.18	1.28	653.67	21.26	47,884.60	153.6	5.63	1,499

Kocacay River. The underground sulfide ores in the region generally do not contribute acidity to the river and groundwater. This is because for rocks below the water table, the availability of oxygen is limited and rate of the oxidation is very slow for production of acid-sulfide water. While sulfide minerals other than pyrite and marcasite are not major sources of acids, they are an essential source of dissolved metals in the Kocacay River and in domestic drinking-water wells. Carbonates, oxyhydroxides, and silicates are other metal sources, which include minerals that react with the acid in WRD. The heavy metals contained in these metal-rich waters are considered serious pollutants, with a high enrichment factor and slow removal rate.

Although sulfates, dissolved metals, and metalloids are considered to be the primary water quality problems in Kocacay River, the presence of the acidic water can also pose serious problems. The concentration of heavy metals (Zn, Pb, Fe, Mn, Cu, Cr, Cd, and As) are tens to hundreds of times higher in the mine water and Kocacay River surface samples (AR) (Table 3) than in the less polluted parts of the Kocacay River (AP) (Table 2) and domestic drinking water well samples (Table 4). The heavy metal pollution rapidly reaches Lake Manyas through the dense surface drainage network. However, the up stream side of Kocacay River, especially in the WRD region, is badly affected by its soluble metal content, when compared with the mouth of the river (Lake Manyas).

Essential nutrient metals, such as iron, copper, manganese, zinc, and cobalt, as well as nonessential elements, such as lead, cadmium and arsenic, after-rain (AR) samples from the Kocacay River can easily exceed concentrations safe for aquatic life or domestic, industrial, or agricultural use. According to the US Environmental Protection Agency (USEPA), Maximum Contaminant Level Goal (MCLG) for Cd has been set at 5 parts per billion (ppb), because the EPA believes this level of protection would not cause any of the potential health problems described below. In the study area, some river water and domestic well-water samples contained arsenic and cadmium concentrations from several hundred to thousand micrograms per liter (Table 4).

The river waters have high As (2–107 μg/g) and Cd (0.26–207 μg/g) concentrations. Arsenic and cadmium are quite soluble at neutral or alkaline pH and are toxic to humans and wildlife at concentrations well below 1 mg/l (Castro and Moore 2000). According to Nordstrom and Alpers (1997), hydrolysis of transition metals, such as iron (II), copper, and zinc can also in some cases serve to buffer pH near 7.

The USEPA determined the maximum contaminant level for arsenic in drinking water to be 50 mg/l (USEPA 1998), while according to the World Health Organization (WHO) the maximum contaminant level in drinking water is 3 mg/l (WHO 1996). While the pH of the Kocacay River is likely to be near seven, it contains high concentrations of arsenic (max. 107 and min. 0 mg/l), an especially troublesome contaminant. This requires urgent precautions be taken.

While As and Cr have a regular distribution between WRD and Lake Manyas in AP samples, Cd, Co, and Mn clearly

Table 4
Heavy metal content of domestic wells in the study area

ID	Heavy Metals (units are µg l^{-1})											pH	EC
	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Pb	Ni	Zn		µS cm^{-1}
Drinking water samples from different wells													
W-1	5	–	–	17.6	0.4	–	4.82	0.1	–	–	–	6.91	527
W-2	4	–	–	17.5	0.6	–	2.51	0.1	5	0.2	9.8	6.98	417
W-3	4	–	–	20.2	0.4	–	0.18	0.3	–	0.2	0.5	7.55	413
W-4	116	–	–	18.9	0.3	–	0.41	0.1	–	–	4.3	7.26	489
W-5	3	–	–	18.6	0.8	57	0.12	0.6	–	–	3.6	7.37	520
W-6	29	–	–	16.1	0.4	48	–	0.1	–	–	5.1	7.42	456
W-7	4	–	–	15.3	3	–	0.07	0.6	–	–	3.3	7.70	414
W-8	4	–	–	8.5	1	13	0.11	0.4	–	–	326	7.65	272
Determination limits													
	>1	>.05	>.02	>1	>.01	>10	>.05	>.01	>2	>.2	>.5		
Guidelines µg l^{-1}													
WHO	10[a]	3	NA	50[a]	2,000[a]	NA	500[a]	70	10[b]	20[a]	NA	NA	NA
DWS	50	5	NA	100	1,000	NA	NA	NA	50	140	5,000	5–9	NA
HBGL	50	3.5	NA	100	1,300	300	700	NA	5	140	1,400	NA	NA

NA No standard available; ¯ indicates values below the determination limit. *DWS* domestic water source standard (ADEQ 1995); *HBGL* health-based guidance levels (ADEQ 1992)
[a]Provisional guideline value. For substances that are considered to be carcinogenic, the guideline value is the concentration in drinking water associated with an excess lifetime cancer risk of 10^{-5} (one additional cancer per 100,000 of the population ingesting drinking water containing the substance at the guideline value for 70 years).
[b]It is recognized that not all water will meet the guideline value immediately; meanwhile, all other recommended measures to reduce the total exposure to lead should be implemented. WHO (1996)

Table 5
Heavy metal contain of suspended particulate material (SPM) in Kocacay River

ID	Heavy Metals (units are µg l^{-1})										
	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Pb	Ni	Zn
SPM-1	14.6	0.6	4.6	22.3	18.4	8.4	307	0.7	63.5	15.3	2,830
SPM-2	19.3	1.5	2.6	21.3	19	4.6	153	0.6	58.6	21.3	2,742
SPM-3	6.6	0.2	3.3	28	16.6	2.6	33.3	0.8	27.6	34	3,424
SPM-4	1.5	0.2	0.08	0.8	1.1	0.1	34.4	0.01	11.4	1.9	490
SPM-5	0.3	0.02	0.1	0.6	0.7	0.1	29.5	0.01	1.8	0.9	120
SPM-6	0.6	0.09	0.1	0.5	0.6	0.09	67.7	0.01	3.1	0.5	229
SPM-7	13.6	2.5	2.5	0.6	6.9	0.4	10	0.01	157.4	0.6	2,269
SPM-8	53.9	49.3	0.4	1.5	24.1	6.5	67	0.04	236.5	2.4	8,260
SPM-9	28,221	15.4	2,021	0.2	706	31.6	172	4.2	2.2	155.6	288
Determination limits											
	>1	>0.05	>0.02	>1	>0.01	>10	>0.05	>0.01	>2	>0.2	>0.5

point to WRD as the source (Fig. 2a). The Cu and Mo distribution diagrams (Fig. 2b) show that the WRD is not the only source of these elements. On the other hand, distribution of Zn and Fe is characteristics with more than one source areas additional effect of WRD (Fig. 2b).

At the distance of 8 km from the WRD, AR samples of the Kocacay River have become neutralized (after sampling point AR-6) as a result of being diluted from drainage originating in forested areas and in farmlands. Therefore, in the absence of continued acid input from mining waste, the river starts to exhibit natural, and mildly eutrophic conditions in this part. Similarly, during the arid period, in the absence of continued acid drainage from waste piles, the acidic river water would also be neutralized.

On the other hand, elevated concentrations of As (max 116 µg/l) have been detected in domestic well W-4 around the WRD impoundment (Table 4). Waste sites and domestic wells are located over the volcanic host rocks. Volcanic rocks may not neutralize some or all of the acid produced by oxidation of pyrite and other minerals. In this case, near-neutral well water seems to be affected by acid mine drainage. While the pH values of the water samples from the wells around the WRD of Balya vary between 6.91–7.70, still anomalous concentrations of Zn, As, and Cr were detected (Table 4). The presence of more than one adversely affected well near the WRD indicates that the occurrence of arsenic in groundwater probably can be attributed to the anthropogenic activities in Balya Mine. The primary source of arsenic in these wells is WRD and arsenic-bearing sulfide minerals of Balya Mine. The highest concentrations of arsenic in groundwater are from wells drilled into the top of the volcanic rocks

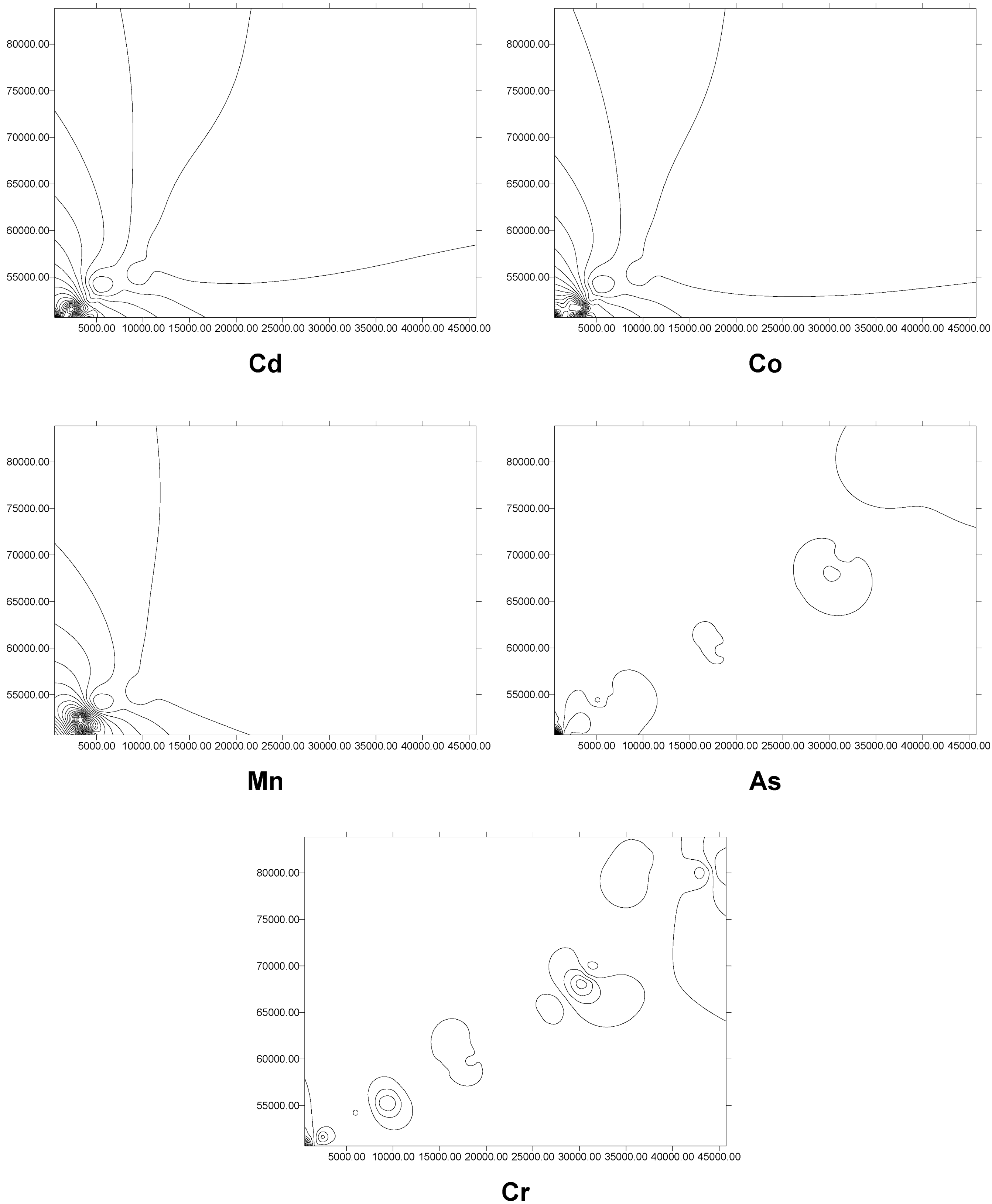

Fig. 2
a Cd, Co, Mn, As, and Cr distribution in Kocacay River between WRD (*lower left*) and Lake Manyas. **b** Cu, Zn, Mo, and Fe distribution in Kocacay River between WRD (*lower left*) and Lake Manyas

(rhyolite-dacite-andasite-basalt). In these wells, the static water level likely intersects the mineralized zone in the rock. This suggests that important mechanisms for arsenic release to groundwater are the introduction of oxygen at the borehole and the subsequent oxidation of arsenic-bearing

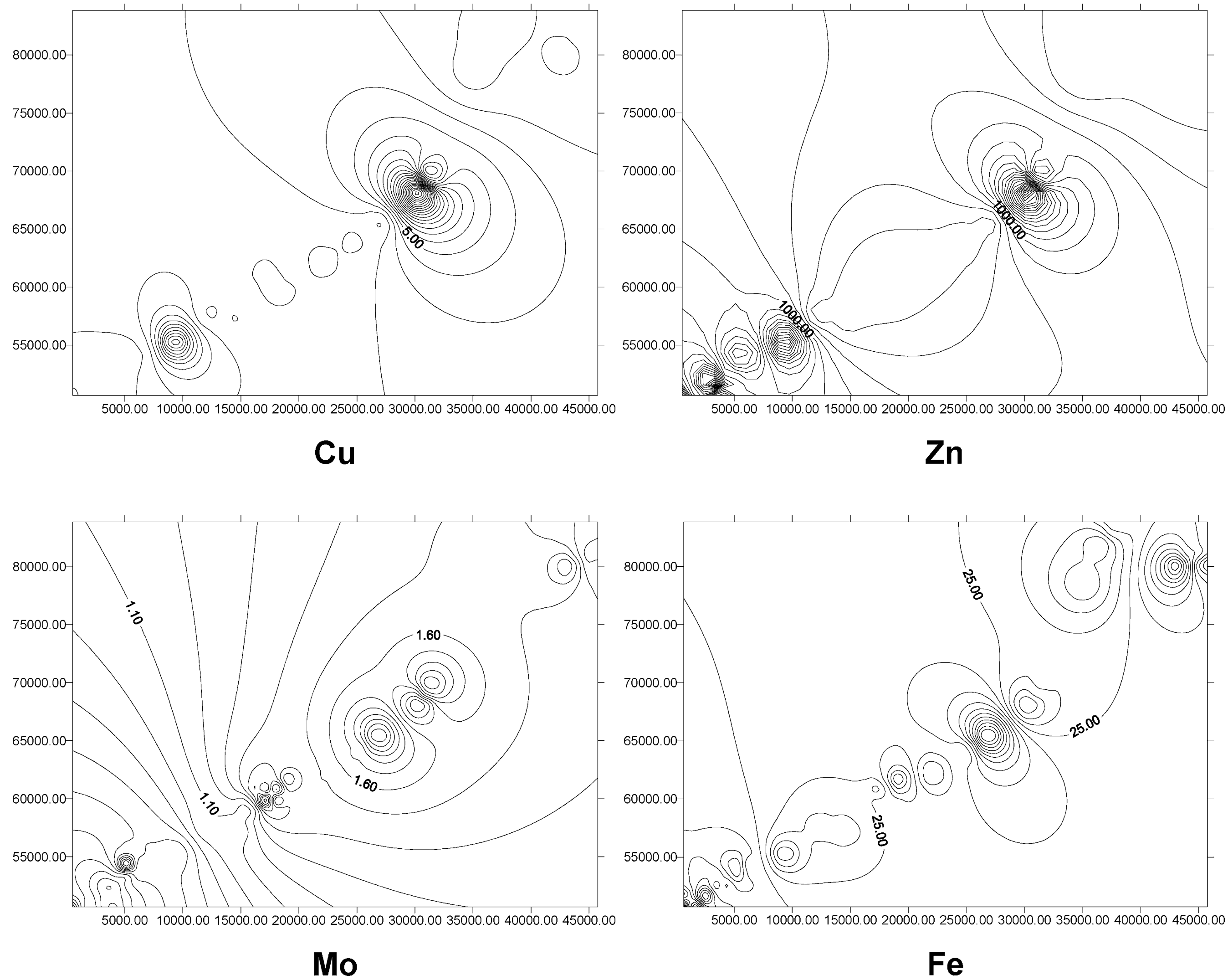

Fig. 2 a
(Contd.)

sulfide minerals: these results in mobilization of contaminants over a long period of time and in migration of As from the mining upstream.

The total heavy metal concentrations in the suspended particles are much higher than normal, especially for Zn, As, Cd, and Cr. SPM analyses showed that acid-soluble suspended heavy metals were consistently transported in the <45 μm fraction along Kocacay River in the arid period. The effect of WRD of Balya Mine on the Kocacay River is characterized by high heavy metal loads (Table 5) between the sample locations SPM-9 and SPM-7. However, the effect of a dense drainage network is very typical in causing lower heavy metal loads of the river between sample locations SPM-5 and SPM-6 (Fig. 1). The samples that were taken at Lake Manyas delta bank (SPM-1 and SPM-2) have a high Zn content, while their Cr content shows a relative increase independent of WRD of Balya Mine. However, there is no clear difference between the upstream and the downstream of Kocacay River, insofar as the heavy metal loads of suspended particulate matter is concerned.

The material in WRD of Balya Mine is well suited for such an acid-producing process. The low pH values and high sulfur/iron content of the after-rain (AR) samples of the Kocacay River show that these pyrite-rich mine tailings can act as a source of acid sulfate, especially when compared to their characteristics with arid period (AP) samples.

Controls on acidity and improvement of mine drainage water quality

Poor water quality in the Kocacay River is the result of one or more of the following conditions: high pyrite availability from WRD, low carbonate availability, and/or low inputs of organic matter and inorganic nutrients. It is necessary to take substantial preventive or remedial work for the rehabilitation of this condition.

The metal-attenuation mechanisms operative in small streams include co-precipitation, sorption, and, on rare occasions, dilution (Kwong and others 1997). The wastes and water from tailings, as well as mine drainage waters, can be treated using methods described by Ledin and Pedersen (1996). Conventionally, the mine drainage, as well as the waste itself, can be treated with alkalies to increase the pH and to precipitate metals. The main drawback of this method is that it has to be continuously repeated to be fully effective. The process may also have a negative effect on beneficial microorganisms. Several other treatment methods have been developed to stop weathering processes, thereby reducing the environmental impact of mine wastes. One approach has been to reduce the transfer of oxygen and water to the waste. This can be achieved by covering the waste or by placing the waste under water. A plant cover will probably also decrease the transfer of oxygen and water, and will give the area a more aesthetic appearance.

The other approach to reducing the environmental impact of mine wastes is to treat the drainage water. Various methods aim at using microorganisms for this in natural or engineered systems. Sulfate-reducing bacteria, metal-transforming bacteria, and metal-accumulating microorganisms are some examples. Often, some kind of reactor design is needed to effectively control these processes. Recently, much interest has been focused on the use of natural or artificial wetlands for treatment, as this is generally a low-cost and low-maintenance method. Bacterial sulfate reduction and microbial metal accumulation are processes desired in such systems. Few studies have dealt with long-term effects of wetland systems, but there are some indications that the wetland material has to be replaced for effective treatment. Furthermore, bacterial iron reduction may take place instead of sulfate reduction in some wetlands.

In general, the activity of microorganisms is neglected in the design of mine waste treatment systems, and the treatments are created merely from a technical point of view. This can result in situations where unexpected microbial processes take over, and, in the worst scenario, the overall effect is opposite to the desired effect.

According to Castro and Moore (2000), one possible approach would be to adjust the pH to six, by adding limestone or another base. This would precipitate many of the transition metals as hydroxides or oxides, and simultaneously provide optimum pH conditions for sulfate reduction bacteria (SRB). There would then be a strong probability that the addition of organic waste would start the sulfate reduction process. This process is useful for pit lakes, whereas the WRD of Balya needs a different process. It is necessary to grade the site and cover up of the Balya WRD with impermeable clay caps, as much of the acid in Kocacay River originates as runoff from its waste piles. The regional climate is arid and semiarid all year long, and there is little chance of establishing a ground cover of plants. However, preventing water from running over and through waste may go a long way toward slowing or stopping the formation of acids.

Before all of these long-term studies can be conducted, contaminated domestic wells have to be closed immediately, or a combination of the granule-activated carbon and carbon steel wool (Compos 2002) must be used in highly contaminated wells to remove As from the drinking water.

The main conclusion to be drawn from this study is that the risk of water contamination after a rainfall event is high, with low pH values and significant transport of metals by water leaching the tailings and waste rocks. A corollary of this is that the Manyas Reservoir will be filled with high metal loads of the Kocacay River's floodwater if there is not a proper and effective rehabilitation process carried out at WRD of Balya Mine. And a high As and Cd content of neutral or near-neutral water in the lake would have a serious and adverse affect on agriculture and livestock farming in the region.

Conclusions

Previously, there have not been any significant data related to the early mining activity waste remains (which are strongly enriched with Pb, Zn, Fe, Cu, Mn, As, and Cd), by the affect of different weathering processes on WRD of Balya Mine, and the metal loads and acidity of Kocacay River water. The results of different chemical and in-situ analyses on AP and AR samples in the Kocacay River system demonstrate that the nature and distribution of heavy metals leached from related lead /zinc mining wastes are controlled by a complex set of physicochemical and biological factors. The acidity of the mine water is buffered to a greater or lesser degree by dilution from the dendritic-type drainage network of the Kocacay River, yet the water still contains considerable amounts of metals, which can lead to catastrophic changes in the aquatic ecosystem. Low pH and high concentrations of sulfur and EC in these environments appear to be the most significant factors controlling the pyrite-oxidation process. The higher amounts of As in some well samples are attributed to the migration of As from the mining upstream, which has resulted in mobilization of contaminants over a long period of time. According to personal communications, commonly seen cancer cases in residents of Balya town and its vicinity are probably related to the content of As and heavy metals in the groundwater. Some heavy metals (Cu, Zn, Mo, Fe, Cr, and As) have different hot spots or source areas along the Kocacay River, while some of them (Cd, Co, and Mn) clearly indicate single a point source of contamination at and near the WRD of Balya Mine. When the Manyas Dam is completed, the Kocacay River (as a main drainage network of the area) will start filling the reservoir with contaminated As and Cd rich-water which ultimately will affect agriculture and livestock farming in the region.

References

Agdemir N, Kirikoglu S, Lehmann B, Tietze J (1994) Petrology and alteration geochemistry of the epithermal Balya Pb-Zn-Ag deposits, NW Turkey. Miner Deposita 29:366–371

Arizona Department of Environmental Quality (ADEQ) (1992) Human health-based guidance levels for the ingestion of contaminants in drinking water and soil. ADEQ, Phoenix, Arizona

Arizona Department of Environmental Quality (ADEQ) (1995) Arizona Administrative Code (AAC)—water quality boundaries and standards. ADEQ, Phoenix, Arizona, Title 18, Chapter 11, pp 1–39
Akyol Z (1982) Geology, mineralogy and ore potential of the Balikesir-Balya region (in Turkish). Earth Sci Rev 3(1–2):168–169
Aygen T (1956) Geology of Balya region (in Turkish). Bull Miner Res Expl Inst Turkey D/11
Aykol A, Orgun Y, Budakoglu M, Turhan M, Gultekin AH, Yavuz F, Esenli V, Kumral M (2002) Heavy metal pollution in Kocadere River Balya Balikesir, Turkey (in Turkish). 55th Geological Congress of Turkey, pp 30–31
Banks D, Younger PL, Arnesen RT, Iversen ER, Banks SB (1997) Mine water chemistry: the good, the bad and the ugly. Environ Geol 32:157–173
Benvenuti M, Mascaro I, Corsini F, Lattanzi P, Parrini P, Tanelli G (1995) Mine waste dumps and heavy metal pollution in abandoned mining district of Boccheggiano southern Tuscany, Italy. Environ Geol 30:238–243
Boulet MP, Larocque ACL (1998) A comparative mineralogical and geochemical study of sulfide mine tailings at two sites in New Mexico, USA. Environ Geol 33:130–142
Campos V (2002) The effect of carbon steel wool in removal of arsenic from drinking water. Environ Geol 42:81–82
Castro JM, Moore JN (2000) Pit lakes: their characteristics and the potential for their remediation. Environ Geol 39:1254–1260
Gjelsvik T (1958) Notes on the geology of Balya Mine. Bull Miner Res Expl Inst Turkey 51:19–25
Hart BT, Hines T (1995) Trace elements in rivers. In: Salbu B, Steinnes E (eds) Trace elements in natural waters. CRC, Boca Raton
Kovenko V (1940) Balya lead mines (Turkey). Bull Miner Res Expl Inst Turkey 4/21:587–594
Kwong YTJ, Roots CF, Roach P, Kettley W (1997) Post-mine metal transport and attenuation in the Keno Hill mining district, central Yukon, Canada. Environ Geol 30:98–107
Lee CH, Lee HK, Lee JC (2000) Hydrogeochemistry of mine, surface and groundwaters from the Sanggok Mine creek in upper Chungju Lake, Republic of Korea. Environ Geol 40:482–494
Ledin M, Pedersen K (1996) The environmental impact of mine wastes—roles of microorganisms and their significance in treatment of mine wastes. Earth Sci Rev 41:67–108
Lottermoser BG, Ashley PM, Lawie DC (1999) Environmental geochemistry of the Gulf Creek copper mine area, northeastern New South Wales, Australia. Environ Geol 39:61–74
Marques MJ, Martinez-Conde E, Rovira JV (2001) Heavy metals pollution of aquatic ecosystems in the vicinity of a recently closed underground lead-zinc mine (Basque Country, Spain). Environ Geol 40:1125–1137
Merrington G, Alloway BJ (1994) The transfer and fate of Cd, Cu and Zn from two historic metalliferous mine sites in the UK. Appl Geochem 9:677–687
Matheron G (1982) Image analysis and mathematical morphology, vol 1. Academic Press, London
Nordstrom DK, Alpers CN (1997) Geochemistry of acid mine waters. In: Plumlee GS, Logsdon MJ (eds) The environmental geochemistry of mineral deposits, Part A. Processes, techniques, and health issues, vol 7A. Soc Econ Geol, Littleton, Colorado, pp 1–28
Parsons MB, Bird DK, Einaudi MT, Alpers CN (2001) Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California. Appl Geochem 16:1567–1593
Routh J, Ikramuddin M (1996) Trace-element geochemistry of Onion Creek near Van Stone lead-zinc mine (Washington, USA). Chemical analysis and geochemical modeling. Chem Geol 133:221–224
Rösner U (1998) Effects of historical mining activities on surface water and groundwater—an example from northwest Arizona. Environ Geol 33:224–230
Schafer WM (1992) Acid-forming mine waste: prediction, control, and treatment. Randol Gold Forum 1992,Vancouver, BC Randol International, Golden, CO, pp 345–353
Tate RL III (1995) Soil microbiology. Wiley, New York
Tuttle JH, Randles CI, Dugan PR (1968) Activity of microorganisms in acid mine water. Influence of acid water on aerobic heterotrophs of a normal stream. J Bacteriol 95:1495–1503
US Environmental Protection Agency (1998) Water quality standards, code of federal regulations, Title 40, Part 131, Section 36 (b)(2)(7-1-98 edition)
WHO guidelines for drinking water quality (1996) vol 2, 2nd edn. Health criteria and other supporting information, pp 940–949