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Determining water and sediment quality related to lead-zinc mining activity

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Abstract: This study focuses on the Koru and Tesbihdere Pb-Zn mining districts, located at the upstream areas of the Umurbey dam basin. Mining activities in Koru, one of the longest operated mines in NW Turkey, date back to the beginning of the 1900s. The purpose of the study is to (1) determine the hydrochemical properties of the water resources and to assess the potential environmental consequences of mining activities in the Koru and Tesbihdere mining districts, and (2) investigate the effects caused by mining activities on the water resources and sediment quality in the Umurbey dam basin. Concentrations of As, Cd, Cu, Fe, Mn, Pb, and Zn in river sediments downstream of the Tesbihdere and Koru mining district, and in the Umurbey dam sediments were higher than the world average for river sediments. The geoaccumulation index and enrichment factor revealed that sediments were strongly polluted with Pb and Zn, moderately to strongly polluted with Cd and moderately polluted with Cu. The chemical analyses of water resources revealed that the maximum Fe, Zn, Pb, Mn, and Cu concentrations reached 2890 µg/l, 1785 µg/l, 1180 µg/l, 984 µg/l, and 419 µg/l, respectively. The Koru River is classified as polluted water according to Turkish inland water quality regulations. The environmental contamination problems in the local drainage system are caused by leakage from past and current tailing ponds into the Koru River.

Introduction

Water contamination from mining activities is one of the most serious environmental problems in many countries, including Turkey (e.g. Baba and Gungor 2002, Gemici 2008, Karakaya and Celik Karakaya 2014, Sanliyuksel Yucel and Baba 2013, 2016, Sanliyuksel Yucel et al. 2014, 2016, Yolcubal et al. 2016, Sanliyuksel Yucel and Yucel 2017). Base metal mining activities have repeatedly caused heavy metal contamination in the environment, resulting in high levels of water contamination (Benvenuti et al. 1995, Banks et al. 1997, Boulet and Larocque 1998, Rösner 1998, Lottermoser et al. 1999, Lee et al. 2000, Marques et al. 2001, Aykol et al. 2003, Tchounwou et al. 2014). Lead-zinc mining activities are some of the primary sources of heavy metal pollution in the environment (Horvath and Gruiz 1996, Yang et al. 2003, Li et al. 2007, Zhang et al. 2012). Under certain conditions, heavy metals released by Pb-Zn mining may activate, migrate, and accumulate in various target media that may directly or indirectly impact plants, animals, and humans (Wang et al. 1994, Chiaradia et al. 1997, Grattan et al. 2002, Liu et al. 2005, Pusapukdepob et al. 2009, Bai and Yan 2008, Kim et al. 2008, Zhang et al. 2012).

The Tethyan Metallogenic Belt, extending from Europe through Anatolia to Iran, is one of the world's major metal producing belts (Yigit 2012). Mineral deposits in the Biga Peninsula in northwest Turkey typify, in many ways, the characteristics of mineral deposits found throughout the Tethyan Eurasian Metallogenic Belt (Yigit 2012). There are 205 known metallic mineral deposits in the Biga Peninsula and these are mainly lead and zinc (Engin et al. 2012). Tertiary volcanism covers extensive areas and has created numerous important metallic and industrial deposits in the Biga Peninsula (Yigit 2009). Koru and Tesbihdere mining districts are examples of the intermediate-sulfidation (IS) style epithermal systems, and are associated with Eocene-aged volcanic rocks in the northern Biga Peninsula (Yigit 2012). The Koru and Tesbihdere mining districts are aligned northwest to southwest, and located in the Lapseki County of the Biga Peninsula (Figure 1). The largest orebody in the Koru mining district is Tahtalikuyu was first operated between 1900 and 1912 by Greek and Italian mining companies (Yalcinkaya 2010). The ore from the Tahtalikuyu contains, on average, 30–40% Pb+Zn and 100 g/t Ag (Yalcinkaya 2010).

The lithological units in the study are: Middle Eocene-aged Akcaalan andesites (Siyako et al. 1989), Oligocene-aged Adadagi pyroclastics (Bozkaya 2001), Plio-Quaternary-aged Karaomerler basalt (Bozkaya 2001), and Quaternary-aged alluvium (Figure 2a). The lowermost unit in the study area is Akcaalan volcanic rocks, mainly consisting of andesite and basaltic andesite lava, andesitic tuff, rhyodacite and dacitic lava, and tuff. In the upper layers, as well as pyroclastic volcanic rocks, limestone bands are found (Bozkaya and Gokce 2009). This unit is unconformably overlain by Adadagi pyroclastics. Pyroclastic rocks contain agglomerates and tuffs of trachytic, trachyandesitic, dacitic, rhyolitic, and rhyodacitic composition, and andesitic and dacitic lavas containing agglomerates, lapilli stone, and ash tuffs with lava interlayers. Adadagi pyroclastics are exposed in a wide area around the Koru and Tesbihdere mining districts. The corresponding parts of the upper levels of this unit are in the form of layers, silica rich zones, as well as areas with Pb-Zn mineralization and alteration with common brecciation. Adadagi pyroclastics are heavily altered by hydrothermal fluids; silicification, kaolinization, alunitization, and chloritization are widespread (Bozkaya et al. 2007, Bozkaya and Gokce 2009). Cicek and Oyman (2016) reported that mineralization in Koru and Tesbihdere is commonly observed in the Adadagi pyroclastics, which includes rhyolitic lava-domes and tuffs (Figure 2b). Basalt is the youngest volcanic rock in the form of basaltic lavas and agglomerates, and is represented by the Karaomerler basalt. Karaomerler basalt is composed of basaltic lavas with a hypo-hyaline porphyritic texture, and agglomerate. The basalt unconformably overlies Akcaalan andesite and Adadagi pyroclastics in the northern part of the study area. Alluvium unconformably overlies all the earlier units and is composed of fragments of volcanic and volcano-sedimentary origin, of heterogeneous size, with no diagenesis. Alluvium is generally located along the Koru River.

The elevation in the study area has a range of 50–500 m. The Koru and Tesbihdere mining districts have an approximate elevation of 180 m and 370 m above mean sea level, respectively. The Koru and Tesbihdere underground operated mining districts are located at the upstream areas of the Koru River. The Koru River is a tributary of the Umurbey River, which flows across the Umurbey plain and eventually flows into the Sea of Marmara. Mining activities have caused changes in the hydrology, land cover and land use of mine site. The Koru River is one of the major sources of water for the Umurbey dam. The total length of the Umurbey River is 22 km, the average flow rate is 16.777 m^3/s, and the river basin area of the Umurbey dam is 279 km^2 (Sasi and Berber 2012). Using Pleiades satellite image in December 2016, the dam lake area was calculated to be 1.39 km^2. The Umurbey-Koru River confluence is at a height of 873 m. The Umurbey River has its source in the Dede and Kaplan mountains (Ilgar, 2015). The Umurbey dam is situated along the Umurbey River's flow path. Drinking water for several residential areas is supplied from wells drilled within the flood plain of the Umurbey River, including Umurbey village and Lapseki County. The Umurbey dam was established to increase the efficiency of intensive agriculture in the Umurbey plain area, and to meet the irrigation water requirements of the region. The Umurbey plain is one of the most important areas in Turkey for peach, nectarine, cherry, plum, and apple production. The high quality of the fruit produced provides a large business advantage for both domestic and foreign markets (Ilgar 2015). The water quality in the Umurbey dam and its tributaries is important for providing safe drinking water to the local residents. The aim of this study is to (1) determine the hydrochemical properties of the water resources (the Umurbey dam and its tributaries) and to assess the potential environmental consequences of the mining activities in the Koru and Tesbihdere mining districts and (2) investigate the effects caused by mining activities on the water resources and sediment quality in the Umurbey dam basin.

Materials and methods

Two water sampling campaigns were conducted (one in the dry season and one in the wet season) to observe seasonal variations. A total of 30 water sampling points from springs, surface water, groundwater, and tailing ponds were selected to determine hydrochemical composition (Figure 3). The discharge rates of springs and surface water were also measured during sampling. Static groundwater levels were measured using an electric sounding device (Eijkelkamp, 30 m) from wells. Groundwater samples were collected using a bailer sampler (Eijkelkamp, 250 ml). Values for pH, temperature and electrical conductivity were recorded by means of a portable multi-parameter field meter (WTW 340i multiparameter). All probes were calibrated at each sampling site before sampling using standard calibrating solutions. Water samples were filtered into polyethylene bottles

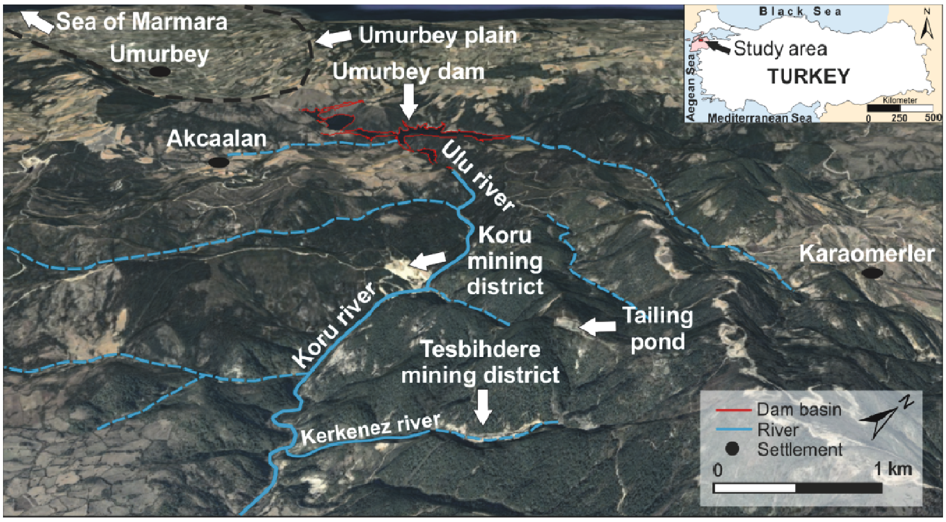


Fig. 1. Location map of Koru and Tesbihdere mine districts and Umurbey dam basin on Google Earth view (December, 2016)

(50 ml*2) using disposable cellulose acetate syringe filters of 0.45 µm. Water samples taken for measuring the dissolved phase of metal concentrations were acidified (nitric acid 65% Suprapure®, MERCK, Germany) to pH< 2 prior to analyses. Water samples were kept in refrigerator at 4°C until analyzed. Water samples were analyzed for major cations, anions, and metals. Major cations and metals were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500ce Octopole Reaction System) and major anions were analyzed using ion chromatography (IC-AES, Dionex GP50). The analyses were done at the Geothermal Energy Research and Application Centre in the Izmir Institute of Technology,

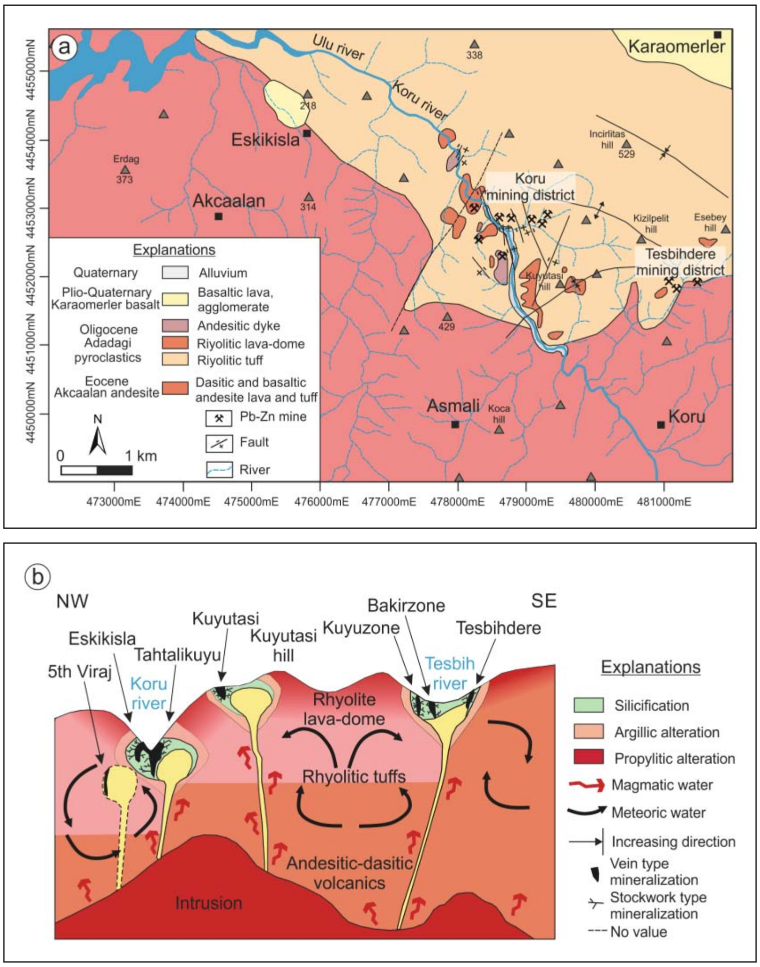


Fig. 2. (a) Geological map of the study area (modified from Bozkaya and Gokce 2001, Yalcinkaya 2010, Cicek and Oyman 2016) (b) NW to SE trending schematic cross section through Koru and Tesbihdere mining district (Cicek and Oyman 2016)

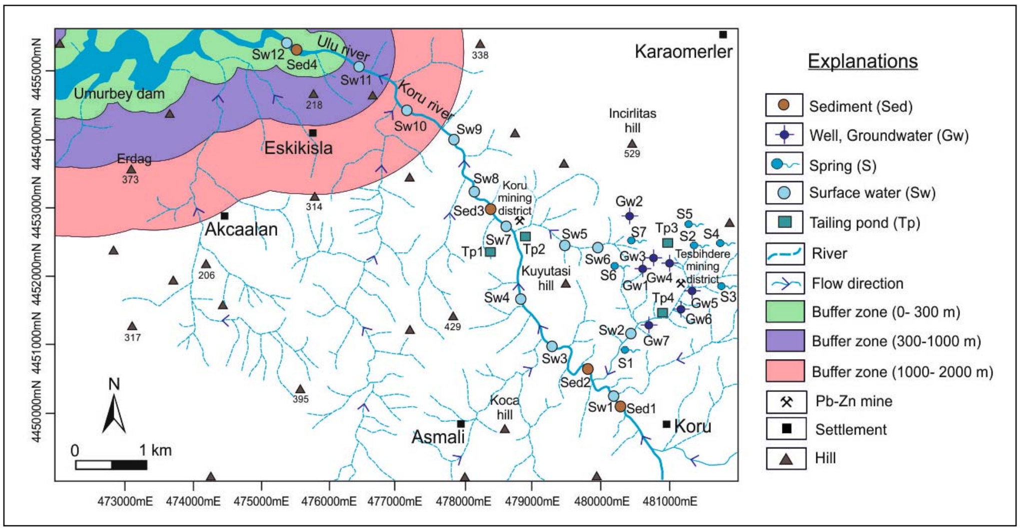


Fig. 3. Location map of the water and sediment sampling and protected zone of Umurbey dam according to Turkish water basin protection regulations

in Turkey. Bicarbonate content was measured by titration with 0.02 N H_2SO_4 using methyl orange as the indicator.

Four sediment samples from the Koru River and the Umurbey dam were collected to determine their mineralogical and geochemical characteristics. Composite river sediment samples were collected at a depth of 0 to 5 cm using a plastic scoop along a traverse across the river bed. About 1 kg of sediment was stored in doubled polyethylene bags. Sediment samples were analyzed using X-ray fluorescence (XRF, Spectro IQ II) for major oxides and metals at the Centre for Material Science in the Izmir Institute of Technology. Mineralogical analyses of sediment samples were performed using X-ray diffraction (XRD, Philips PW 3710/1830) at the General Directorate of Mineral Research and Exploration Analysis Laboratories. Analyses using scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometry (EDX), were carried out on all samples using a JSM 7100F (JEOL, USA) at the Centre for Material Science at the Canakkale Onsekiz Mart University, in Turkey.

Results and discussion

Sediment geochemistry

Sediments have been widely used as environmental indicators and determination of metal concentrations in sediments has been extensively used for purposes of pollution monitoring (Algan et al. 2004, Liu et al. 2006, Salah et al. 2012, Obaidy et al. 2014, Ali et al. 2016, Borowiak et al. 2016, Tokatli 2017). The pH and EC values of sediments (1:2 solid:solution ratio) were measured at the end of 24 hours. The pH and EC values of Umurbey dam sediment were 6.56 and 689 µS/cm, respectively. The pH values of Koru River sediments ranged from 7.29 to 7.50 and EC values ranged from 226 to 541 µS/cm. Sediment samples presented neutral to slightly alkaline character. According to geochemical data, the SiO_2 content of sediment samples ranged from 56.3 to 60.25%, Al_2O_3 from 19.75 to 21.34%, K_2O from 3.96 to 7.87% and Fe_2O_3 from 5.93 to 8.22%. Total sulphur concentration of sediments varied between 0.04 and 0.1%.

The As, Cd, Cu, Fe, Mn, Pb and Zn concentrations in sediments downstream of Tesbihdere and Koru mining district and in Umurbey dam sediments were higher than average values for world river sediments calculated by USEPA (1999). The maximum concentration of selected elements in sediments of the Koru River corresponded to the order: Al> Fe> Zn> Mn> Pb> Cu> As> Cd, with the following concentration values: Al (114300 mg/kg), Fe (57520 mg/kg), Zn (3096 mg/kg), Mn (1653 mg/kg), Pb (1013 mg/kg), Cu (153 mg/kg), As (31.2 mg/kg) and Cd (1.8 mg/kg), respectively (Table 1). The decreasing trend of total selected elements was observed in Umurbey dam sediment as Al> Fe> Zn> Mn> Pb> Cu> As> Cd, with the following concentration values: Al (118300 mg/kg), Fe (63710 mg/kg), Zn (2509 mg/kg), Mn (2637 mg/kg), Pb (596 mg/kg), Cu (116 mg/kg), As (25.7 mg/kg) and Cd (1.1 mg/kg), respectively.

The enrichment factor (EF) of metals is an indicator reflecting the magnitude of contaminants in the environment (Feng et al. 2004, Choi et al. 2012). The EF was calculated by a comparison of each tested metal concentration with that of a reference metal (Muller 1981, Gopal et al. 2016). Iron was used as a conservative tracer to differentiate natural from anthropogenic components (Tippie 1984, Obaidy et al. 2014). Enrichment factor was calculated using the method proposed by Sinex and Helz (1981) as follows:

$$EF = (Me/Fe)_{sample}/(Me/Fe)_{background}$$

where (Me/Fe) sample is the metal to Fe ratio in the sample of interest; (Me/Fe) background is the natural background value of metal to Fe ratio. World surface rock average proposed by Martin and Meybeck (1979) was considered as background concentration. Sutherland (2000) reported five contamination categories for the EF. As shown in Table 2, average EF values for selected elements had an order Pb> Zn> Cd> Cu> Mn> Al> As, suggested that sediment samples were significant enriched in Pb and Zn, moderate enriched Cd and Cu, while Al, As, and Mn exhibited minimal enrichment. The results obtained from the sediments showed a high degree of enrichment of Pb, Zn and Cd in river sediments downstream of the Tesbihdere and Koru mining district exceeded by several orders of magnitude the value of EF ≥ 1, which indicated that metals were anthropogenically induced. Highest EF values were calculated in Sed3 which was sampled at the downstream Pb-Zn mines and had continuously received a vast amount of tailing pond leakage for a long time. High EF values (e.g. 16.79 for Pb and 10.95 for Zn) were calculated at Umurbey dam sediment, which supplies irrigation water for Umurbey plain.

The second index for contamination assessment is geo-accumulation index (I_{geo}), described as enrichment of metal concentration above baseline concentration, and was calculated using the method proposed by Muller (1969). Geo-accumulation index is expressed as follows:

$$I_{geo} = \log_2 [C_n / (1.5 B_n)]$$

where C_n sample is the measured concentration of element in the sediment sample and B_n background is the geochemical

Table 1. Metal concentration of sediment samples (mg/kg)

Sampling location	Al	As	Cd	Cu	Fe	Mn	Pb	Zn
Sed1	109100	2.7	0.9	67	44490	558	65	635
Sed2	112600	18.9	1.2	102	57520	1275	302	1843
Sed3	114300	31.2	1.8	153	49650	1653	1013	3096
Sed4	118300	25.7	1.1	116	63710	2637	596	2509
Mean	113575	19.62	1.25	109.5	53842.5	1530.75	494	2020.75
World surface rock average*	69300	13	0.2	32	35900	720	20	129

* Martin and Meybeck (1979)

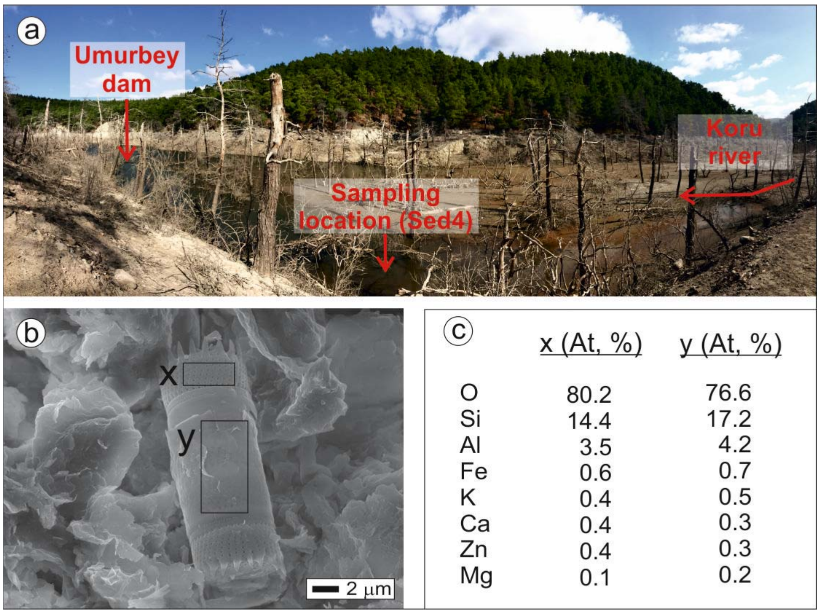
background value (world surface rock average calculated by Martin and Maybeck, 1979). The factor 1.5 is introduced to include possible variation of the background values due to lithogenic effect (Mmolawa et al. 2011, Salah et al. 2012). Muller (1969) proposed seven classes of geo-accumulation index. The calculated results of I_{geo} indicated that Pb and Zn exhibited strongly contaminated, Cd exhibited moderately to strongly contaminated and Cu exhibited moderately contaminated degree. I_{geo} values of Al and Mn showed uncontaminated to moderately, while As and Fe showed uncontaminated to contaminated degree. On the basis of the mean values of I_{geo}, Koru River and Umurbey dam sediments were enriched with metals in the following order: Pb> Zn> Cd> Cu> Mn> Al> Fe> As. The total geo-accumulation index (I_{tot}) of the entire study area for different metals was found to be positive and this suggested that concentration of most elements in Koru River and Umurbey dam sediments were higher than world surface rock average value. This data is consistent with the EF values.

According to the XRD analyses, dam sediments included quartz, feldspar group minerals, mixed layer clay minerals, kaolin group minerals, illite/mica group minerals and pyrite. Well-developed euhedral crystals of albite were shown in SEM images containing 69.9% O, 16.5% Si, 7.5% Na and 6.1% Al in EDX analysis. Koru River sediments consisted of quartz, feldspar group minerals, mixed layer clay minerals, illite/mica group minerals, kaolin group minerals, pyrite and zeolite group minerals. EDX analysis of river sediments were identified high Zn (0.3%), Mn (0.2%) and Cu (0.2%) concentrations, similar to XRF analysis.

Diatoms typically respond promptly to environmental changes because they have short generation times and rapidly reach a steady state with surrounding media (Dixit et al. 1992, Cattaneo et al. 2011). Cattaneo et al. (2011) reported that the response of benthic diatoms to metal contamination suggests some guidelines for the choice of different organisms to best monitor metal effects under various environmental conditions. Within lake sediments, diatoms have been particularly useful as bioindicators (Bellinger and Sigee 2015). Freshwater, lake and inflow, lower temperature diatom *Aulacoseira subarctica* (Müller 1906) and *Fragilaria* sp. (Lyngbye 1819) were determined in Umurbey dam sediment (Figure 4a and Figure 4b). On SEM images, the diameter of *Aulacoseira subarctica* was 4–8 µm, with mantle height varying from 8–14 µm. The EDX results showed that maximum Al, Fe and Zn concentration of diatoms are 4.2%, 0.7% and 0.4%, respectively (Figure 4c). It is suggested that diatoms are useful for biological monitoring of Umurbey dam basin.

Table 2. Degree of metal contamination in sediment sample

Sampling location	Assessment of metal contamination	Al	As	Cd	Cu	Fe	Mn	Pb	Zn
Sed 1	EF	1.27	0.29	3.63	1.68	–	0.62	2.62	3.97
Sed 2		1.01	0.91	3.74	1.98	–	1.1	9.42	8.91
Sed 3		1.19	1.73	6.51	3.45	–	1.66	36.62	17.35
Sed 4		0.96	1.11	3.09	2.04	–	2.06	16.79	10.95
Sed 1	I_{geo}	0.06	-2.05	1.58	0.48	-0.27	-0.95	1.11	1.71
Sed 2		0.11	-0.04	2.0	1.08	0.09	0.23	3.33	3.25
Sed 3		0.13	0.67	2.58	1.67	-0.11	0.61	5.07	4.0
Sed 4		0.18	0.39	1.87	1.27	0.24	1.28	4.31	3.69



	x (At, %)	y (At, %)
O	80.2	76.6
Si	14.4	17.2
Al	3.5	4.2
Fe	0.6	0.7
K	0.4	0.5
Ca	0.4	0.3
Zn	0.4	0.3
Mg	0.1	0.2

Fig. 4. (a) Snapshot from Umurbey dam in October 2016 (b) Morphology of *Aulacoseira subarctica* (Müller 1906) in dam sediment (c) EDX results of x and y sections

Hydrogeology

The study area is situated within a climatic transition between Black Sea and Mediterranean climate zones. The long-term (1928–2016) mean annual temperature is 15.01°C with a minimum of -11.5°C and a maximum of 39°C based on data collected at Canakkale Meteorological Station located approximately 30 km to the southwest of the study area. July is the hottest and January is the coldest month, with mean temperatures of 25 and 6.2°C, respectively. Precipitation is usually in the form of rain with the heaviest rainfall observed during the winter months. The average annual precipitation is 616.2 mm and the average monthly precipitation is 51.35 mm according to data from 1928 to 2016. Apart from during the winter months the amount of evaporation is greater than precipitation, with a yearly total evaporation of 1340 mm. The volcanic rocks are widely distributed across the study area and the hydrogeology of the study area is primarily controlled by volcanic rocks. The angles of fractures in silicified volcanic rocks range from 75º to 90º and demonstrate fractured aquifer characteristics in the study area. Dense argillic alteration, especially in Adadagi pyroclastics show impervious properties. These clay zones act as a barrier beneath the fractured aquifer. Cooling fractures of volcanic rocks provide a good avenue for deep penetration and circulation of groundwater. The flow rates of springs originating from Adadagi pyroclastics range between 0.08 and 0.2 l/s in wet season, 0.01 and 0.1 l/s in dry season. There are 7 wells opened to monitoring with 30 m depth around Tesbihdere mining district. The groundwater level in these wells varies from 1.87 to 19.35 m in the wet season and from 4.26 to 23.1 m in the dry season. The Kerkenez River is nearly 2 km long, has mean flow of 0.5 l/s in the winter and 0.2 l/s in the summer months. There is a currently inactive tailing pond belonging to Tesbihdere mining district on the Kerkenez River. The majority of the rivers practically dries up during the summer season and starts to flow again after autumn rains. The highest flows are observed during the spring months. The surface water flow in the wet season varies from 0.1 to 0.5 l/s while in the dry season it varies from 0.05 to 0.2 l/s. The alluvium is the most important aquifer which has high porosity and high permeability in the study area.

Hydrogeochemistry

pH is classed as one of the most important water quality parameters (Rahmanian et al. 2015) as it influences many biological and chemical processes within a water body. The minimum pH value was 5.71 with maximum pH of 10.75 for all water resources identified in the dry sampling period (Table 3). The median pH value of all water resources in the dry season was 6.8, reaching 7.28 in the wet season with mean pH value in the dry season of 6.92 and in the wet season of 7.30. The pH values of springs varied from 5.71 to 6.88 in the dry season and from 5.72 to 6.97 in the wet season. The water samples that were collected from the old gallery were acidic in character. The pH values of groundwater varied from 6.38 to 7.63 in the dry season and from 7.01 to 8.34 in the wet season. The pH of water resources surfacing in altered and mineralized zones of Adadagi pyroclastics generally exhibited slightly acidic to neutral character (Figure 5a). This indicated that waters leached acidic character from altered and mineralized basement rocks. Acid mine/rock drainage has limited effect on water resource quality. Acid-neutralization is mainly controlled by chemical weathering of carbonate and silicate minerals in the study area, these minerals release elevated levels of Ca and Mg. Due to the rapid rate of reaction and the common occurrence of calcite,

Table 3. Major ion, pH, conductivity and temperature results of water resources in different seasons

Parameter	Unit	Season	Groundwater (n = 7)	Spring (n = 7)	Surface water (n = 12)	Tailing pond (n = 4)
			(Min-Max)			
pH	–	Dry season	6.38–7.63	5.71–6.88	6.43–7.11	7.17–10.75
		Wet season	7.01–8.34	5.72–6.97	7.01–7.73	7.21–10.05
EC	µS/cm	Dry season	278–1794	218–528	349–1328	831–1489
		Wet season	305–1635	218–517	327–1087	936–1310
T	°C	Dry season	16.2–21	16.3–19.3	18.8–24.4	20.2–21.3
		Wet season	14.2–16.2	15.8–16.3	16.3–17.5	16.5–17.1
Na^+	mg/l	Dry season	11.51–59.8	9.54–24.89	11.45–22.86	32.71–60.73
		Wet season	14.93–63.2	10.62–25.81	13.46–22.45	31.7–54.5
K^+		Dry season	5.89–20.67	0.99–9.05	2.01–4.97	2.49–38.52
		Wet season	6.73–21.36	1.27–8.42	2.12–5.78	11.5–35.1
Ca^{2+}		Dry season	38.41–111.86	18.83–45.28	28.65–66.75	92.29–219.2
		Wet season	41–216.88	17.17–46.16	26.8–69.42	162.73–231.82
Mg^{2+}		Dry season	8.6–99.12	4.98–26.51	9.17–24.36	9.33–31.89
		Wet season	7.61–105.9	4.57–24.15	9.02–22.98	8.25–28.06
Cl^-		Dry season	7.1–22.79	7.0–27.9	8.79–27	15.85–27.96
		Wet season	6.35–22.1	6.82–26.83	8.71–13.4	10.97–23.26
HCO_3^-		Dry season	15.4–244.88	20.7–181.2	45.2–129.7	29.28–139
		Wet season	12.8–290	21.2–193.8	59.9–129.1	79.2–154
SO_4^{2-}		Dry season	69.8–642.9	10.76–186.8	59.5–232.8	296.7–628.5
		Wet season	59.21–608.45	9.17–172.3	54.5–191.6	420.8–663.4

and it is the most important neutralization agent (Gemici 2008). The highest pH value was measured from the Tp2 where flotation slurry was collected. The pH value measured in Umurbey dam was 7.12 in the dry season and 7.41 in the wet season. The pH value of surface waters varied from 6.43 to 7.11 in the dry season and from 7.01 to 7.73 in the wet season. The pH values of water resources in the Koru River fluctuated with atmospheric conditions and leakage from tailing ponds.

The EC value of most freshwaters ranges from 10 to 1000 µS/cm but may exceed 1000 µS/cm, especially in polluted waters (Chapman and Kimstach 1996). The EC values of groundwater varied from 278 to 1794 µS/cm in the dry season and from 305 to 1635 µS/cm in the wet season. The highest EC values were measured in Gw2 and Gw6 wells (Figure 5b). High EC value of groundwater is related to excessive water-rock interaction and deep water circulation. The EC values in springs were measured 218 to 528 µS/cm in the dry season and 218 to 517 µS/cm in the wet season, and the highest EC values were in adit water. The EC values measured in tailing ponds were between 831 and 1489 µS/cm. The EC measured in Umurbey dam was 349 µS/cm in the dry season and 327 µS/cm in the wet season. The EC values for surface waters in the dry season varied from 349 to 1328 µS/cm and from 327 to 1087 µS/cm in the wet season. Electrical conductivity values of the Koru River were increased after mixing with tailing pond leakage.

Among the external factors temperature is one of the most important factors which influence the aquatic ecology (Huet 1986, Kamal et al. 2007). Temperature values of water resources varied from 16.2 to 24.4°C in the dry season and 14.2 to 17.5°C in the wet season. Water resources had mean temperature of 19.95ºC in the dry season with median value

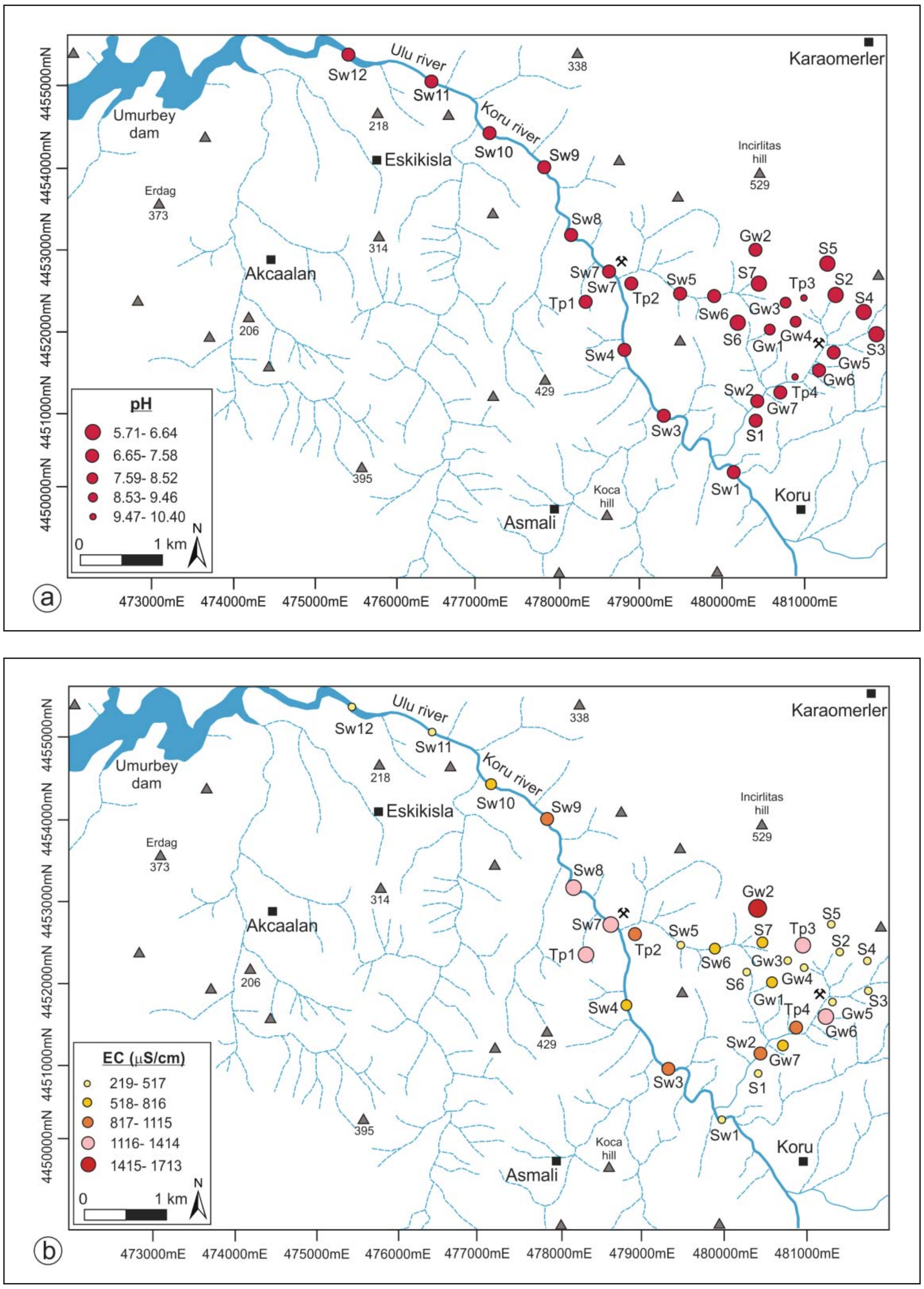


Fig. 5. pH and EC distribution of water resources (mean values for two seasons)

20.2ºC, while in the wet season mean temperature was 16.44ºC with median value of 16.4ºC.

The sequences of major cations and anions in water resources generally were as follows: Ca^{2+}> Na^{+}> Mg^{2+}> K^{+} and SO_4^{2-}> HCO_3^{-}> Cl^{-}, respectively. According to the water classification method of IAH (1979), springs were Ca-HCO_3 water type except for adit water, S7 (Figure 6). Adit water was Ca-Mg-SO_4 water type, SO_4^{2-} is the dominant anion and its concentration reached 186.8 mg/l in the dry season. The high SO_4^{2-} concentrations and elevated EC values in water resources indicated that sulphide oxidation occurs at the mining site. Turkish inland water quality regulations (2015) classify water resources into four classes (Table 4). Class I refers to clean waters suitable for drinking purposes and class II refers to slightly polluted waters suitable for domestic usage after treatment and irrigation purposes. Class III refers to polluted water suitable for industrial water after treatment. Class IV includes heavily polluted water that is not suitable for any purpose at all. Hydrochemistry of the Umurbey dam reservoir exhibited Ca-HCO_3 water type and Mn concentrations of water samples reached 584 µg/l. According to this value, the dam lake was classified as polluted water according to Turkish inland water quality regulations. The sequences of metal concentration in the dam lake were as follows: Mn> Fe> Zn> Al> Cu> Pb> As> Cd. Tailing ponds were Ca-SO_4 water type. The maximum Fe, Zn, Pb, Mn and Cu of tailing ponds were 2890, 1785, 1180, 984 and 152 µg/l, respectively. The Fe concentrations in the tailing ponds were much greater than the other sampled water resources. When tailing pond leaked into the Koru River, the dissolved Fe precipitated as a hydroxide because of increasing oxygen in the surface waters downstream. Yellow orange red-coloured sediments were observed in the Koru River bed. Groundwater was Ca-SO_4 water type, except for Gw3. Sulphate was the dominant anion, Mg and Ca were dominant cations in wells. The maximum SO_4^{2-} concentration of groundwater was measured as 642.9 mg/l in dry season. The maximum Zn, Mn, Cu, Pb and Cd concentrations of groundwater were 1685, 660, 419, 19.1 and 13.47 µg/l, respectively. Groundwater exhibited class III water quality for Cu, class II for Cd, Mn and Zn.

Manganese, Zn, Cu and Pb concentrations of adit water reached 315, 311, 34.1, and 19.85 µg/l, respectively in the dry season. According to the criteria of Turkish inland water quality regulation, adit water was classified as slightly polluted water. The water sample that was collected from the galleries was acidic in character, and metal contents were generally higher than spring water. This indicated that altered and mineralized volcanic rocks (containing iron sulphide) oxidize in contact with water, increasing the acidity of the water. The pH value of water resources is a major control on the solubility of most metal compounds (Smith 2007, Gemici 2008). The sequences of mean metal concentration in water resources generally were as follows: Zn> Fe> Mn> Pb> Al> Cu> Cd> As, respectively. The maximum total metal concentration (mean value of two sampling seasons) of water resources reached 4530 µg/l (Figure 7). Metal concentrations in water resources indicated seasonally varying levels. The mean concentration of Mn in water resources was observed as 216.24 and 164.73 µg/l during the dry and wet season, respectively. The Koru River upstream from the mine site (Sw1) was classified as class I for all chemical parameters investigated during two sampling terms. According to water quality regulations, Koru River was classified as polluted water for high Mn (360.1 µg/l), Zn (264 µg/l), Pb (36.5 µg/l), and Cu (29.14 µg/l) concentrations downstream of the mine site. Following the leakage of tailing ponds into the Koru River, EC value, SO_4^{2-} and metal concentrations of surface water showed a significant increase. Leakage from tailing ponds included significant amounts of metals and carried long distances to enrich metal concentration in water and sediment. Climate effects especially heavy rainfall events had a great impact on the dispersion of metal concentrations in surface waters. In the wet season, metal concentration of surface waters decreased because of the dilution effect resulting from increased discharge rate of the river.

The active production in Koru mining district continues in underground and the ore fraction is enriched in the flotation

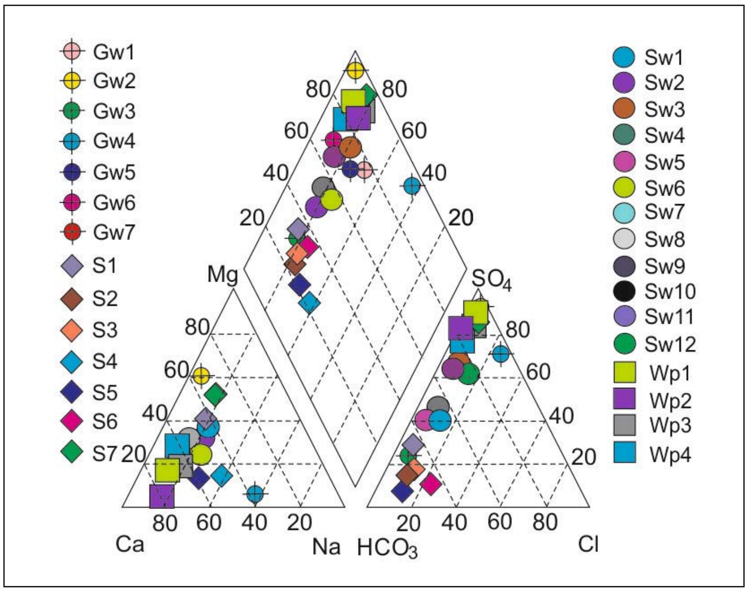


Fig. 6. Piper trilinear diagram of water resources (mean values for two seasons)

Table 4. Metal concentration of water resources in different seasons (μg/l)

Metal concentration			Groundwater	Spring	Surface water	Tailing pond	Turkish inland water quality regulations (2015)			
			n = 7	n = 7	n = 12	n = 4	Class I	Class II	Class III	Class IV
Al	Dry season	Min-Max	13.45–87.1	10.25–126.4	14.2–57.6	99.4–130.7	≤ 300	< 300	1000	> 1000
		Mean	41.63	35.2	33.59	119.66				
	Wet season	Min-Max	12.8–82.64	5.05–94.9	9.14–47.89	100–220.7				
		Mean	38.28	25.95	30.65	146.83				
As	Dry season	Min-Max	0.06–0.95	0.05–1.04	0.5–4.13	1.57–5.1	≤ 20	50	100	> 100
		Mean	0.32	0.4	2.81	3.2				
	Wet season	Min-Max	0.05–0.8	0.05–1.62	0.4–3.85	2.02–5.6				
		Mean	0.34	0.99	2.38	4.2				
Cd	Dry season	Min-Max	1.5–13.47	0.15–2.47	0.1–2.44	0.99–1.89	≤ 2	5	7	> 7
		Mean	4.84	0.99	1.07	1.37				
	Wet season	Min-Max	0.05–8.8	0.05–2.15	0.05–0.95	0.46–1.15				
		Mean	3.44	0.69	0.45	0.86				
Cu	Dry season	Min-Max	8.85–419	0.5–34.1	3.47–29.14	71.2–101	≤ 20	50	200	> 200
		Mean	102.28	6.51	8.71	86.73				
	Wet season	Min-Max	7.22–340	0.1–25.8	0.9–20.8	56–152				
		Mean	79.97	5.04	6.27	102.86				
Fe	Dry season	Min-Max	17.68–100.2	9.7–32.8	17.9–327.2	395–2890	≤ 300	1000	5000	> 5000
		Mean	53.76	18.93	139.49	1690.56				
	Wet season	Min-Max	14.9–81.2	9.51–37.1	14.3–158.9	650–2067				
		Mean	40.01	19.05	74.06	1240.03				
Mn	Dry season	Min-Max	13.5–660	0.95–315	79.1–584	156–984	≤ 100	500	3000	> 3000
		Mean	147.5	54.05	220.5	442.93				
	Wet season	Min-Max	26.78–552	1.14–283.5	76.7–360.1	91.2–589				
		Mean	129.92	47.99	190.07	290.96				
Pb	Dry season	Min-Max	1.85–19.1	0.4–19.85	1.2–36.5	200–1180	≤ 10	20	50	> 50
		Mean	8.21	5.97	10.15	497.13				
	Wet season	Min-Max	1.04–11.7	0.25–12.7	1.8–26.9	100–643				
		Mean	6.43	4.69	8.32	290.66				
Zn	Dry season	Min-Max	32.3–1685	10.3–311	18.1–264	297–1785	≤ 200	500	2000	> 2000
		Mean	479.07	58.43	101.54	1177.53				
	Wet season	Min-Max	28.9–1132	10.65–248.5	15.4–205	258–1589				
		Mean	385.58	48.02	85.85	952.16				

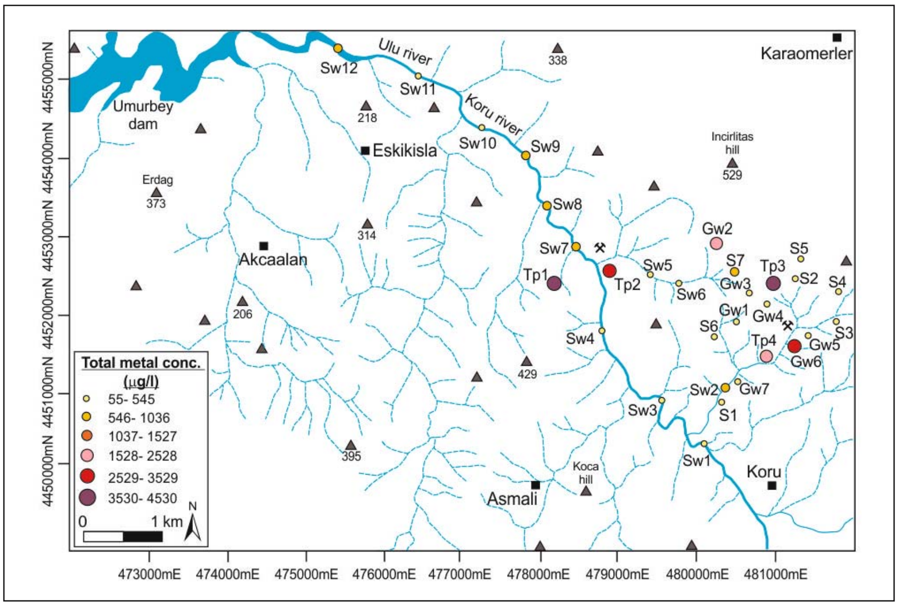


Fig. 7. Total metal concentration of water resources (mean values for two seasons)

plant and the waste is collected in tailing pond via pumps. Nowadays an old mine gallery is used as tailing pond on the Koru riverbed. The heavy metals Pb, Zn, and Cd represent a hazard to the environment and they are toxic to humans and other living organisms. The heavy metals stored in tailings at former metal mines can be dispersed to surrounding ecosystem such as streams and groundwater due to weathering and leaching processes. Similar environmental contamination problems were seen in Europe (Mighanetara et al. 2009, Byrne et al. 2010). It is also worth noting the difference between metal distributions of historically contaminated sediments in the depth of the profiles in old mining areas as in the previous studies (e.g. Aleksander-Kwaterczak and Helios-Rybicka 2009, Ciszewski et al. 2012). In this way, the most proper management strategy and treatment method can be determined for Umurbey dam basin.

Conclusions

This study is the first study to determine the environmental effects of IS epithermal style Koru and Tesbihdere Pb-Zn mining districts on quality of water resources. Water resources in Umurbey dam basin are the one of major components of environmental resources that is under threat from mining activities. The Koru River is the major river whose waters supply Umurbey dam. Leakage from past and current tailing ponds into the Koru River caused water contamination problem in local drainage system. The water contamination was observed intensely up to the confluence of the Koru River and Umurbey dam reservoir, and this was clearly seen in change of pH, EC, SO_4^{2-} and metal contents of the Koru River along flow direction toward Umurbey dam. The pH value of water resources surfacing in altered and mineralized zones of Adadagi pyroclastics generally has slightly acidic to neutral character. The carbonate and silicate minerals around the mine area affect the occurrence of the alkaline waters entering the system and this has a significant impact on the overall dynamic system. The Koru River was classified as polluted water for high Cu, Fe, Mn, Pb and Zn concentrations downstream of the mine site. The overall water pollution load was significantly higher in dry season than in wet season. Metal constituents in surface water decreased in the wet season because of dilution. A remarkable metal concentration increase was observed for Pb, Zn and Mn in the Koru River sediment. The geoaccumulation index and enrichment factor values for Pb and Zn revealed that Koru River sediments were strongly contaminated. It has been determined that the metal content of Umurbey dam and the Koru River sediment is higher than metal content of surface water. This is thought to be related to the precipitation of high molecular weight metals into sediment. This study recommended that continuous monitoring of metal quality in water resources, sediment and other aquatic biota of Umurbey dam basin should be directed to assess the risk of metals to save the ecology in the vicinity of this basin.

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