

Heavy metal contamination in groundwater and surface water due to active Pb-Zn-Cu mine tails and water-rock interactions: A case study from the Küre mine area (Turkey)

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Abstract: This study aimed at elucidating the groundwater and surface water pollution resulting from water-rock interaction, mine tailings, and mining activities at Küre (Kastamonu) sulfidic Pb-Zn-Cu mine area and its vicinity. The study area has a surface area of approximately 2990 km². The Küre River drainage site covering the study area is approximately 440 km². The concentrations of SO₄, Al, As, Ba, Mn, Ni, Sb, and Pb in some groundwater (K10, K20, K21, K27, K28, K29, K30), and surface water (KR3) exceed the maximum limit values with respect to the Turkish Standards for Water Intended For Human Consumption and World Health Organization Standards. The most polluted waters were K10, K27, and KR3. The K10 well was drilled for observation at the edge of the liquid mine tailing pond of the Küre Pb-Zn-Cu mine area. The K27 well was opened in alluvium outside of the study area and it cuts the clastic units and Mesozoic ophiolites. The KR3 measurement point is located on the Ersizler River, which drains the Küre Pb-Zn-Cu mining site and its dumps. The SO₄, Al, As, Pb, and Sb concentrations of the K10, K27, and KR3 waters were 29.3, 0.8, and 15.1 meq/L; 1135, 1112, and 1186 ppb; 284, 255, and 271 ppb; 19.1, 19, and 18.5 ppb; and 18.7, 17.4, and 19.3 ppb, respectively, in the dry period. As revealed by the analysis, the study area had dual pollution source natural pollution caused by water-rock interactions (K27 and others) and anthropogenic pollution (K10 and KR3) caused by the mine tailings. Furthermore, the K10 water had high tritium (³H)-high electrical conductivity (EC) values that likely indicated anthropogenic contamination. The K27 water had low ³H-high EC values, presumably referring to geogenic contamination. The current study also demonstrated that there was leakage from the liquid mine tailing pond into the groundwater (K10), possibly implying discharge of the liquid mine tailings into the river (KR3).

Keywords: Water pollution, mineral-water interaction, Pb-Zn-Cu mine areas, mine tailings, Küre (Kastamonu)

1. Introduction

There are numerous pollution problems associated with water sources in Turkey due to geogenic interactions and/or anthropogenic impacts (Balçı et al., 2012; Keskin and Toptaş, 2012; Baba and Gündüz, 2017; Balçı and Demirel, 2018; Yücel and Baba, 2018). The dominant geological units, in which water sources are in contact, typically determine the physicochemical quality of the waters. Geogenic factors become as important as anthropogenic pollution sources, severely impacting and dictating the quality of water. Anthropogenic pollution sources, such as mining activities, frequently accelerate negative effects of geology on the water quality (Baba and Gündüz, 2017; Balçı et al., 2017). Turkey hosts numerous active and abandoned massive sulfide mines that are now characterized by large piles of mine spoil, and acidic and metal-rich water. The extensive mining of Pb-Zn-Cu mines in the country has resulted in significant changes in the chemical composition

of groundwater and surface water (Keskin and Toptaş, 2012; Yücel and Baba, 2018).

The study area has an active Pb-Zn-Cu mine area and mining activity and, as shown in Figure 1, it is located north of Kastamonu in the western Black Sea region. There are solid mine piles/tailings and a liquid mine tailing pond in the study area. The Pb-Zn-Cu mine areas were operated by the Genoese, Byzantines, and the Ottoman Empire (400–1000 years ago) (Bailey et al. 1966; Güner 1980; Balçı and Demirel, 2018). The areas were assigned to the Mineral Research and Exploration Institute (MTA) in 1939. Since 1998, the mine areas have continued its operations under Eti Bakır Co. The areas were customized in 2004. Before the areas were privatized, mining and production were conducted at depths up to 140 m. Recently, new reserves were found below 140 m and a new underground system, descending to 960 m, was constructed. Today, the Eti Bakır A.Ş. Küre plant produces 1,000,000 tons of raw copper

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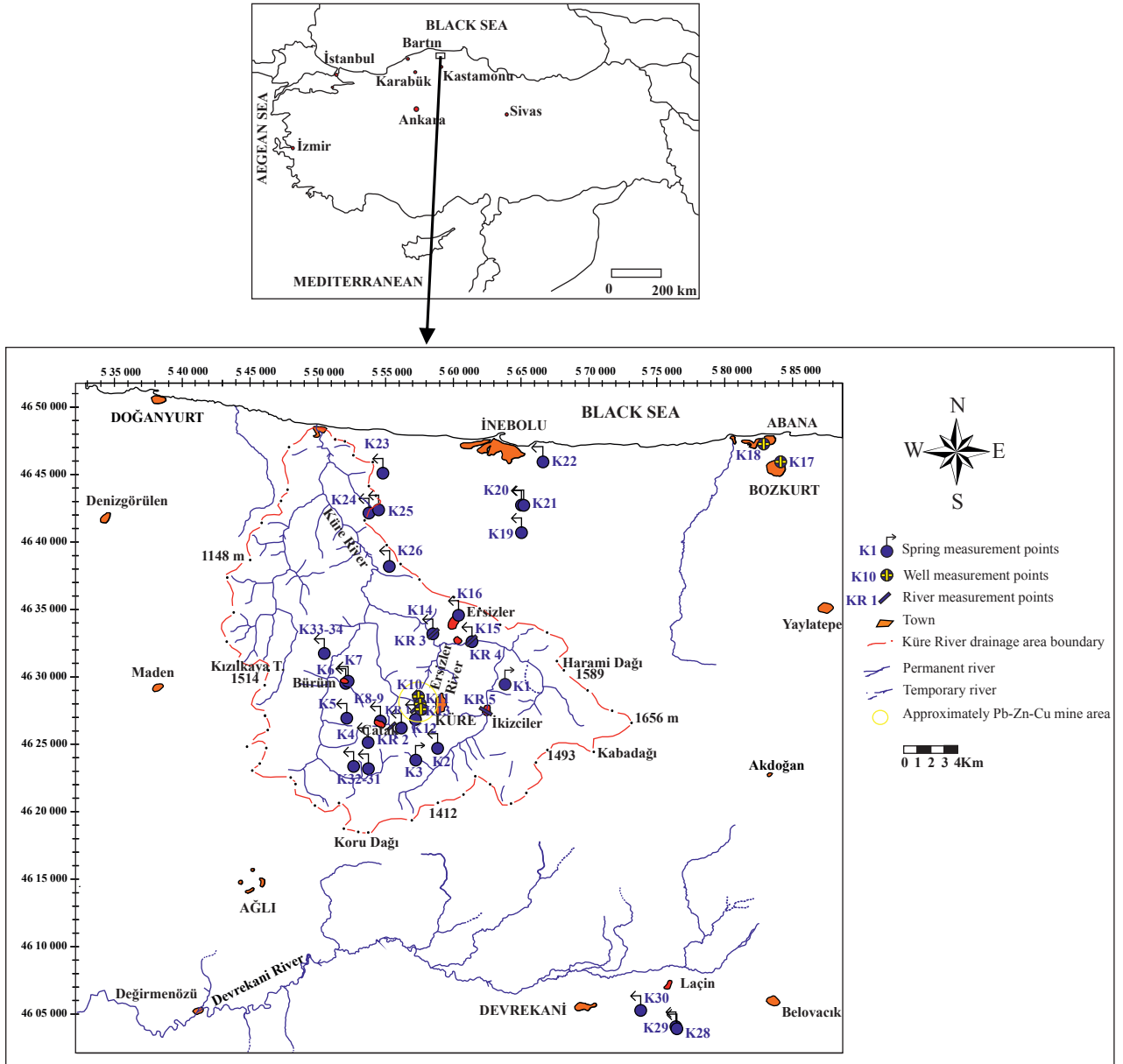


Figure 1. Location of the study region.

ore, 90,000 tons of copper concentrate, and 400,000 tons of pyrite concentrate every year through underground mining¹.

Mine tailings are usually enriched in various toxic metals (Edwards et al., 1996; Hudson and Edwards, 2005). In many areas, the spoil is uncontrolled, causing water and soil pollution (Hudson and Edwards, 2005). Sulfidic mine tailings are among the largest mining tailings in the natural environment, causing acid mine drainage (AMD). Thus these tailings have great potential to contaminate water sources, both groundwater and surface water, via a

series of complex mineral dissolution reactions (Lapakko, 2002; Balcı et al., 2007; Balcı et al., 2012; Balcı and Demirel, 2018). Dold (2014) rigorously defined the processes that occur in a typical tailing pond. According to Dold (2014), these environments have some problems, such as high sulfate concentrations from the dissolution of some minerals and/or enriched elements, such as Mo and As, which are emitted from primary ferric hydroxides during the alkaline flotation process. The K10 well in the mining activity area had lower pH values (6.45) than the other waters in the study area. Furthermore, the K10 well, which

¹ Eti Bakır A.Ş. (2020). Küre İşletmesi [online]. Website <http://etibakir.com.tr/tesisler/kure-isletmesi> [accessed 16 March 2020].

was drilled near the liquid mine tailing pond of the Küre Pb-Zn-Cu mine area, had a very high SO_4 concentration (29.27 meq/L) and some trace elements, such as Al, As, Ba, Mn, Ni, Se, Sb, and Pb. This information suggested that AMD might occur in the near future if the mine areas were abandoned without proper rehabilitation/removal methods.

Balcı and Demirel (2018) studied the waste rocks and lithological units of the Küre mine region to evaluate AMD generation by determining the acid base accounting, net acid generation, acid production potential, and neutralization potential of various lithological as well as mine tailing piles. Additionally, the authors demonstrated that sulfur minerals in the tailings dominantly contained pyrite and chalcopyrite along with gangue minerals consisted of calcite, dolomite, feldspar, muscovite, quartz, chloride, albite, kaolinite, illite, olivine, and gypsum. The authors revealed that acid drainage may have occurred over a long periods of interaction between the waste rocks and water. They also showed that the waste rocks were significant source of contaminants (e.g., Cu, Pb, Co, As, Ni, Cd), despite the presence of carbonate minerals acting as neutralization agents in the region.

This study discusses the concentrations and distribution patterns of trace and major elements/ions in the groundwater and surface water in the close vicinity of the Küre Pb-Zn-Cu mine region. Additionally, hydrogeological, hydrochemical, and isotopic characteristics of the waters were determined with the aim of understanding water sources as well as hydrological cycles. As revealed by previous studies, numerous water sources were contaminated with SO_4 , Al, As, Ba, Mn, Ni, Se, Sb, and Pb, mainly due to water-rock interactions, mine tailings, and mining activities in the study area. It was revealed that, while the natural pollution largely resulted from water-rock interactions, particularly from altered volcanic-volcanoclastic rocks enriched in Pb-Zn-Cu ores, and ophiolites, the antropogenic pollution dominantly originated from liquid mine tailing leaks.

2. Geological background

As shown in Figure 2, the basement rocks of the study area comprise Paleozoic shale, the Ballıdağ Formation, consisting of quartzites, Karadon Formation, consisting of clastics with a coal vein, Mesozoic ophiolites, and the Daday Group. The Triassic Akgöl Formation, consisting of altered volcanic-volcanoclastic rocks (sandstone-shale alternations, andesite, basalt lavas, and limestone), covers the Ballıdağ Formation unconformably. Moreover, the Akgöl Formation has massive sulfide mines (Altun et al., 1990; Uğuz and Sevin, 2007; Uğuz and Sevin, 2010). The Dogger Kastamonu Granitoid cuts all of these old units. Members of the Yarılgöz Group comprise Upper Jurassic

clastic and carbonate levels, and these members overlay the Pre-Lias units as angular unconformity. The group also tectonically covers the Akgöl Formation and Kastamonu Granitoid, and exhibits a transitive character with the Gökçeğaç Formation. The Akveren Formation, consisting of marl and limestone, covers the Gökçeğaç Formation. The Gökçeğaç Formation consists of Paleocene and Eocene carbonate and clastic rocks. Alluvium constitutes most of the modern deposits (Figures 2 and 3) (Altun et al., 1990; Uğuz and Sevin, 2007; Uğuz and Sevin, 2010).

3. Materials and methods

During the field sampling periods, conducted between September 2014 and May 2015, water samples from 28 springs (K1, K2, K3, K4, K5, K6, K7, K8, K9, K12, K14, K15, K16, K19, K20, K21, K22, K23, K24, K25, K26, K28, K29, K30, K31, K32, K33, K34), 6 wells (K10, K11, K13, K17, K18, K27), and 5 surface waters (KR1, KR2, KR3, KR4, KR5) were collected. While most of the sampled waters are used for drinking and/or domestic purposes, the K10, K11, and K13 wells are used to monitor the Küre Pb-Zn-Cu liquid mine tailing pond (Figures 1–4). The physicochemical characteristics of the samples, such as electrical conductivity (EC), total dissolved solids (TDS), temperature (T), pH, oxidation-reduction potential (ORP) (Eh), along with discharge (Q) values were measured in situ with a multiparameter probe (YSI-256 Instrument). The pH meter was calibrated against pH 4, 7, and 10 buffer solutions. ORP measurements were taken with a platinum electrode calibrated with a Zobell reference, and the ORP values were converted to the Eh equation provided in the manufacturer's catalog (YSI-256 catalog). Polyethylene bottles were used for water samples collected for chemical and isotopic analysis. Upon collection, the water samples were acidified with ultrapure nitric acid (HNO_3 , Merck KGaA, Darmstadt, Germany) for the trace element analysis. The high-performance ion chromatography system and inductively coupled plasma-mass spectroscopy at Hacettepe University were used for the major ion and trace element analyses, respectively. ^3H and oxygen-18-deuterium isotopes analyses were conducted at the Environmental Tritium Laboratory and International Karst Water Resources Application and Research Center of Geological Engineering Department at Hacettepe University, respectively.

4. Results and discussion

4.1. Hydrogeology

The field measurement data of all of the water samples are provided in Table 1, and Figures 1 and 2. The primary aquifers of the study area are the İnaltı Limestones, comprising of limestone, and the Akgöl Formation, consisting of altered volcanic-volcanoclastic rocks

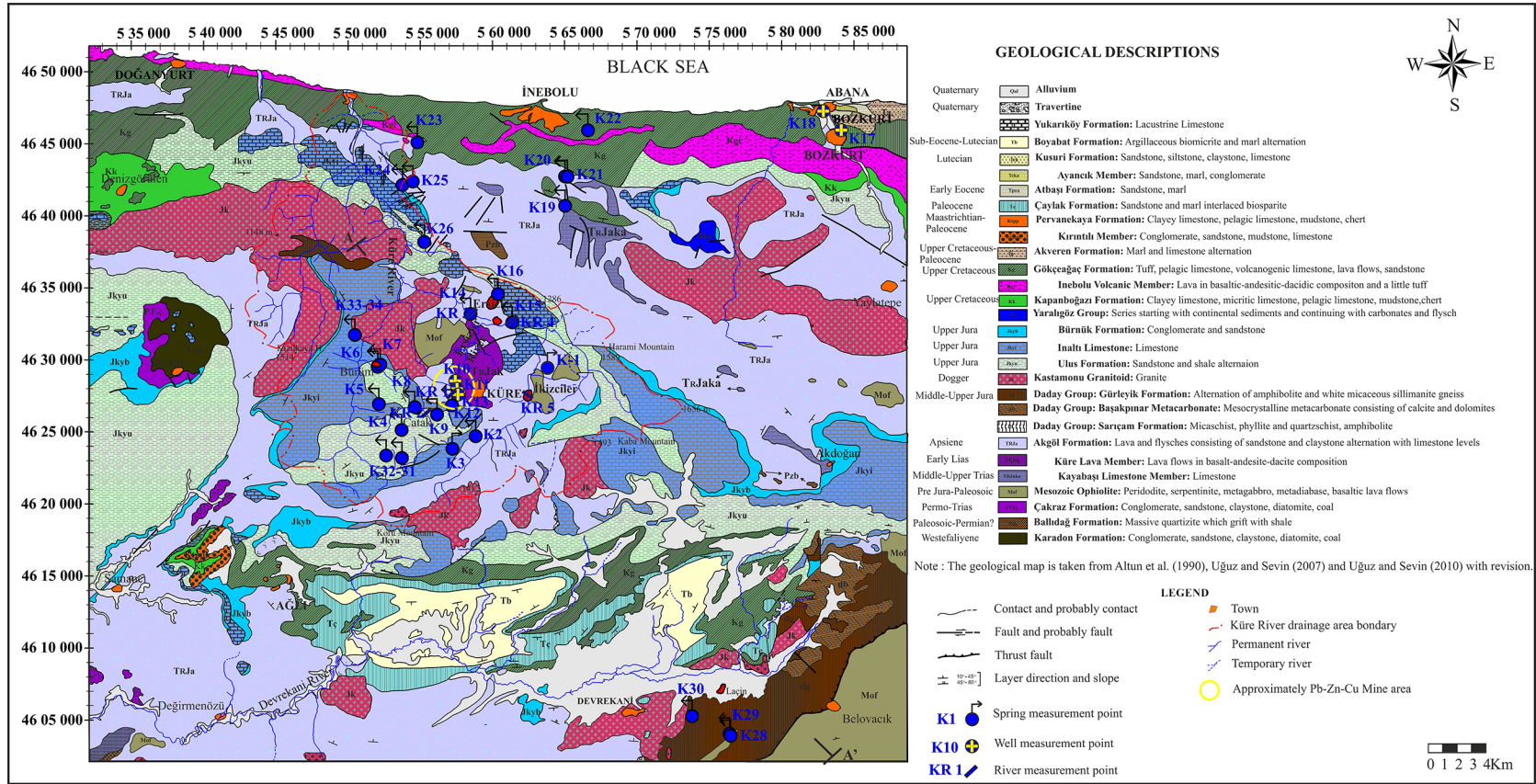


Figure 2. Geological map of the study region [geological maps were taken from Altun et al. (1990), Uğuz and Sevin (2007) and Uğuz and Sevin (2010), with revisions].

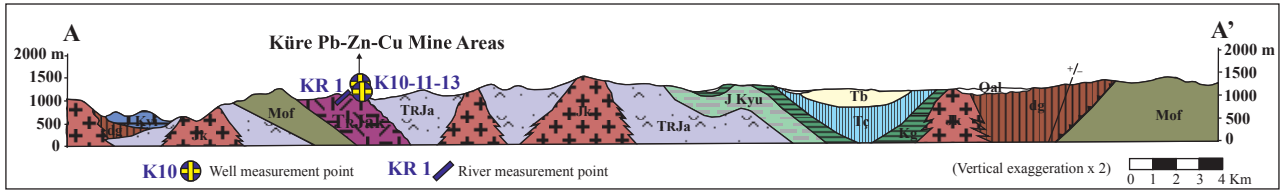


Figure 3. Cross-section of the study region.

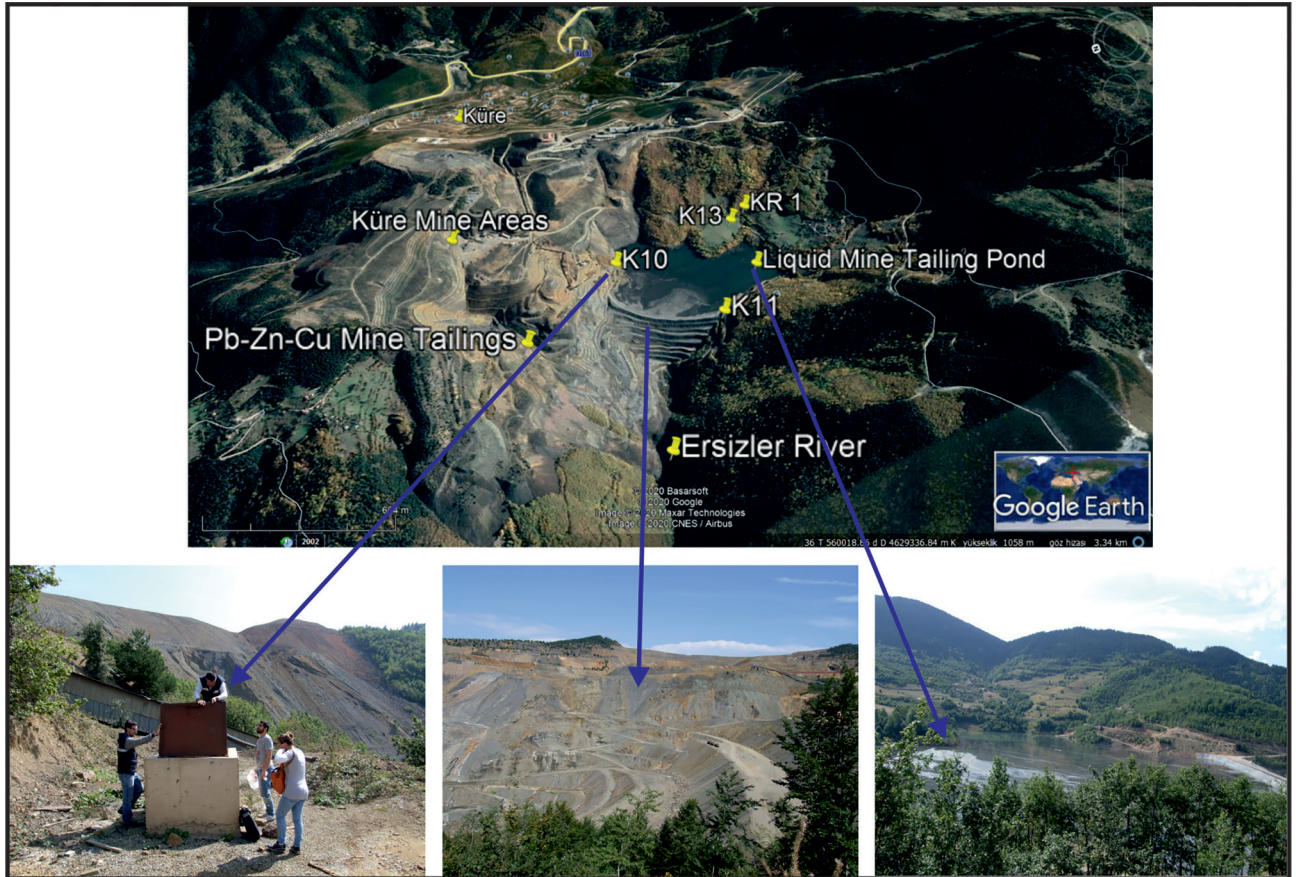


Figure 4. Pb-Zn-Cu mine tailings and observation wells at the edge of the liquid mine tailing pond.

(sandstone-shale alternations, andesite, basalt lavas, and limestone). Moreover, partial Ulus formations, and the Gökçeğaç Formation, consisting of sandstone-conglomerate-claystone, limestone and Mesozoic ophiolites with the fractured-cracked levels demonstrate the primary aquifer characteristics. While the sandstone-conglomerate levels show grained aquifer properties, limestone, andesite, and basalts, and the ophiolites exhibit fractured-cracked aquifer characteristics. Pb-Cu-Zn ores are located in the Küre Lava member of the Akgöl Formation².

During the dry period (September 2014), the EC, pH, and ORP (Eh) values of the waters ranged between

² Keskin TE (2017). Küre (Kastamonu) Pb-Zn-Cu maden alanı çevresinin hidrojeokimyasal özelliklerinin ve su-kayaç etkileşiminin incelemesi. TÜBİTAK Project No: 114Y031 (in Turkish).

305 and 2785 $\mu\text{S}/\text{cm}$, 6.12 and 8.26, and 217 and 854 mV, respectively. During the rainy period (May 2015), the values ranged between 276 and 2836 $\mu\text{S}/\text{cm}$, 6.31 and 8.24, and 237 and 401 mV, respectively. The EC value of most of the freshwaters ranged from 10 to 1000 $\mu\text{S}/\text{cm}$, but may have exceeded 1000 $\mu\text{S}/\text{cm}$, especially in the contaminated waters (Chapman and Kimstach, 1996; Yücel and Baba, 2018). The variation in the EC values of the groundwater may likely have originated from geogenic interaction, different groundwater residence times, and the mine tailings in the study area. There are various rocks types such as limestone, conglomerate, sandstone, basalt, and ophiolites in the study area. These rocks had different

Table 1. Field measurement data and chemical analysis results (meq/L) of the waters in the study area and Turkish Standards for Water Intended for Human Consumption.

No.	Date	EC	TDS	pH	Eh	Temp.	Discharge	Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	CO ₃ ⁻⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ⁻⁻	NO ₃ ⁻	F ⁻	EB
K1	15.09.2014	305	198	7.66	431	9.8	(-)	0.19	0.01	0.76	2.40	0.00	2.88	0.04	0.19	0.00	0.003	3.8
"	12.05.2015	280	182	7.40	283	8.83	0.1	0.18	0.005	0.96	2.45	0.00	3.20	0.047	0.18	0.00	0.003	2.3
K2	15.09.2014	435	283	7.19	439	10.6	0.4	0.07	0.01	0.47	4.15	0.00	4.30	0.05	0.10	0.01	0.003	2.6
K3	15.09.2014	537	349	7.15	450	14.7	1.3	0.27	0.02	0.96	4.51	0.00	5.18	0.06	0.19	0.03	0.006	2.6
K4	15.09.2014	489	318	7.21	356	8.5	0.2	0.14	0.02	0.28	4.83	0.00	4.59	0.07	0.13	0.01	0.006	4.6
K5	15.09.2014	523	340	7.41	454	13.1	0.3	0.12	0.01	0.25	5.29	0.00	5.18	0.06	0.11	0.01	0.003	2.8
"	12.05.2015	494	321	7.44	305	7.59	1.2	0.125	0.014	0.246	5.534	0.00	5.437	0.051	0.10	0.00	0.004	2.8
K6	15.09.2014	472	307	7.18	495	12.5	0.5	0.18	0.02	0.42	4.55	0.00	4.59	0.04	0.11	0.03	0.008	3.9
"	12.05.2015	503	327	7.36	310	9.43	0.6	0.147	0.020	0.428	5.782	0.00	5.631	0.047	0.09	0.00	0.009	4.9
K7	15.09.2014	468	304	7.24	484	16.2	0.3	0.15	0.02	0.47	4.60	0.00	4.59	0.04	0.12	0.01	0.008	4.7
"	12.05.2015	496	322	7.39	311	11.71	0.4	0.146	0.018	0.403	5.308	0.00	5.340	0.034	0.07	0.00	0.006	3.8
K8	15.09.2014	434	282	7.78	551	16.8	0.2	0.14	0.02	0.33	4.90	0.00	4.98	0.05	0.13	0.00	0.004	2.1
"	12.05.2015	379	246	7.75	303	10.23	(-)	0.137	0.018	0.280	4.253	0.00	4.175	0.052	0.13	0.00	0.004	3.7
K9	15.09.2014	570	372	7.15	482	17.7	(-)	0.28	0.03	0.75	5.76	0.00	6.15	0.13	0.20	0.01	0.009	2.4
K10	16.09.2014	2714	1765	6.45	217	14.3	(-)	1.79	0.09	16.54	20.36	0.00	6.24	0.36	29.27	0.01	0.009	3.9
K11	16.09.2014	492	320	6.96	438	10.6	(-)	0.23	0.05	2.90	2.91	0.00	4.78	0.07	0.78	0.01	0.015	3.7
K12	16.09.2014	521	338	7.4	459	8.3	2.7	0.14	0.02	0.46	5.63	0.00	5.46	0.06	0.16	0.02	0.002	4.6
"	12.05.2015	529	344	7.61	296	8.13	~20	0.094	0.016	0.353	5.607	0.00	5.437	0.058	0.22	0.00	0.004	3.0
K13	16.09.2014	591	384	7.12	399	10.8	(-)	0.36	0.05	0.85	5.69	0.00	5.85	0.05	0.56	0.01	0.006	3.5
K14	17.09.2014	461	300	7.62	467	18.9	0.1	0.51	0.02	1.61	2.87	0.00	3.41	0.35	1.03	0.05	0.008	1.6
"	11.05.2015	441	287	7.74	334	14.17	0.1	0.522	0.023	1.732	3.033	0.00	3.398	0.349	1.05	0.00	0.009	5.0
K15	17.09.2014	360	234	7.66	435	9.98	1.2	0.08	0.01	0.40	3.59	0.00	3.71	0.06	0.12	0.01	0.002	2.2
"	11.05.2015	359	233	7.714	237	9.90	~15	0.074	0.012	0.379	3.764	0.00	3.883	0.053	0.12	0.00	0.002	2.0
K16	17.09.2014	386	252	7.4	439	9.8	2.5	0.12	0.01	0.56	3.76	0.00	3.90	0.05	0.15	0.00	0.002	4.1
"	11.05.2015	412	268	7.73	248	9.9	(-)	0.112	0.010	0.642	4.123	0.00	4.369	0.074	0.16	0.00	0.001	3.0
K17	17.09.2014	447	291	7.25	854	15.6	7.4	0.43	0.04	0.84	3.88	0.00	4.10	0.16	0.61	0.03	0.006	2.8
K18	17.09.2014	487	317	7.3	572	14.9	15	0.41	0.04	0.77	4.13	0.00	4.49	0.16	0.58	0.05	0.006	0.6
K19	18.09.2014	343	223	7.55	485	9.7	25	0.15	0.02	0.74	3.09	0.00	3.51	0.06	0.15	0.01	0.003	3.5
"	11.05.2015	276	179	7.92	270	8.99	~93	0.158	0.017	0.580	2.614	0.00	3.010	0.057	0.14	0.00	0.004	2.5
K20	18.09.2014	539	350	7.19	495	15.6	7.5	0.90	0.04	1.10	4.02	0.00	4.78	0.54	0.25	0.01	0.009	4.0
"	11.05.2015	406	264	7.58	244	12.62	~25	0.441	0.020	0.786	3.520	0.00	3.981	0.245	0.18	0.00	0.005	3.9

Table 1. (Continued).

K21	18.09.2014	800	520	7.19	492	23.9	0.5	2.23	0.06	1.75	4.66	0.00	6.44	1.36	0.43	0.00	0.020	2.7
“	11.05.2015	793	515	7.18	264	23.89	1.1	2.327	0.052	1.977	4.553	0.00	6.408	1.322	0.50	0.00	0.016	3.8
K22	18.09.2014	476	309	7.54	532	13.9	1.1	0.30	0.02	0.26	4.89	0.00	4.98	0.09	0.07	0.00	0.008	3.0
K23	18.09.2014	580	377	7.53	458	15.0	0.6	0.11	0.02	3.29	3.56	0.00	6.15	0.10	0.25	0.01	0.005	3.4
K24	18.09.2014	488	317	6.93	476	17.0	1.8	0.26	0.02	0.26	5.03	0.00	4.98	0.11	0.08	0.01	0.003	3.6
K25	18.09.2014	694	451	7.27	473	15.2	0.15	0.31	0.05	1.84	5.89	0.00	7.32	0.20	0.16	0.02	0.010	2.4
K26	18.09.2014	442	288	7.29	493	14.3	1.1	0.15	0.01	0.50	4.33	0.00	4.49	0.06	0.13	0.01	0.003	3.1
K27	19.09.2014	2785	1808	6.12	542	12.8	0.05	8.22	0.24	14.04	15.71	0.00	33.59	1.16	0.80	0.02	0.025	3.5
“	12.05.2015	2836	1842	6.31	333	12.5	0.1	8.471	0.248	13.966	13.583	0.00	32.233	1.049	0.99	0.00	0.020	2.8
K28	19.09.2014	532	346	8.01	530	13.2	0.3	0.09	0.01	5.23	1.06	0.00	5.76	0.05	0.28	0.04	0.007	2.0
“	13.05.2015	481	313	7.99	401	9.55	0.4	0.068	0.013	5.142	0.966	0.777	4.563	0.043	0.30	0.00	0.003	4.2
K29	19.09.2014	465	302	8.26	528	11.2	0.3	0.07	0.03	4.98	0.77	0.00	5.27	0.04	0.09	0.02	0.007	3.8
“	13.05.2015	462	300	8.24	395	10.35	0.9	0.077	0.029	5.115	0.803	0.777	4.563	0.043	0.09	0.00	0.002	4.8
K30	19.09.2014	666	433	7.69	522	17.3	(-)	0.10	0.03	6.26	0.83	0.00	6.45	0.08	0.10	0.00	0.008	4.2
“	13.05.2015	638	414	8.03	376	10.66	(-)	0.132	0.035	7.091	1.026	0.777	6.796	0.077	0.12	0.00	0.010	3.1
K31	19.09.2014	621	404	6.98	509	12.2	1.0	0.13	0.01	0.75	6.55	0.00	6.83	0.06	0.09	0.01	0.004	3.1
“	12.05.2015	606	394	7.66	306	9.11	1.3	0.084	0.013	0.604	6.764	0.00	6.893	0.058	0.11	0.00	0.003	2.8
K32	19.09.2014	658	428	7.31	513	15.9	0.3	0.24	0.03	0.58	7.13	0.00	7.22	0.11	0.14	0.01	0.006	3.2
“	12.05.2015	645	419	7.63	324	9.10	0.5	0.247	0.031	0.587	7.127	0.00	7.184	0.108	0.14	0.00	0.007	3.6
K33	19.09.2014	385	250	7.43	311	18.6	0.2	0.17	0.02	0.42	3.92	0.00	4.10	0.04	0.20	0.00	0.003	2.1
K34	19.09.2014	538	350	7.35	517	13.9	0.4	0.12	0.02	0.27	5.27	0.00	5.27	0.09	0.06	0.01	0.004	2.2
KR1	16.09.2014	338	220	8.49	414	14.4	0.5	0.26	0.04	0.75	2.83	0.00	3.12	0.07	0.47	0.00	0.010	2.8
KR2	16.09.2014	298	194	8.15	435	9.9	(-)	0.13	0.04	0.26	3.02	0.00	3.02	0.04	0.11	0.00	0.006	4.1
“	12.05.2015	361	235	8.06	303	12.95	(-)	0.114	0.030	0.297	3.797	0.388	3.495	0.047	0.10	0.00	0.005	2.5
KR3	17.09.2014	1306	857	8.2	472	16.6	(-)	0.88	0.24	5.45	10.87	0.00	2.54	0.21	15.08	0.07	0.007	-1.3
“	11.05.2015	823	534	8.26	326	11.1	(-)	0.392	0.091	3.865	6.194	0.583	2.816	0.142	7.35	0.005	0.008	-1.7
KR4	17.09.2014	345	224	8.29	449	14.2	(-)	0.18	0.03	0.42	3.25	0.00	3.32	0.06	0.21	0.01	0.003	3.7
“	11.05.2015	348	226	8.37	249	10.3	(-)	0.182	0.028	0.469	3.629	0.583	3.107	0.072	0.20	0.00	0.005	4.1
KR5	12.05.2015	340	221	8.21	262	8.95	(-)	0.24	0.039	0.58	3.25	0.78	2.72	0.08	0.26	0.00	0.005	3.3
RTMH (2013)															5.2	0.81	0.08	

EC ($\mu\text{S}/\text{cm}$), TDS (mg/L), Eh (mV), temperature ($^{\circ}\text{C}$), discharge (L/s).

EB: Electric balance (%).

dissolution trends and permeability values, most likely regulating ion concentrations in the region. Consistently, the EC value of the Ersizler River was 4-fold higher after mixing with the liquid mine tailings. The pH values of the groundwater fluctuated with water-rock interaction and leakage from the tailing pond, further emphasizing the influence of geological factors on water chemistry³.

In the study area, discharge in the springs ranged from 0.1 to 25 L/s in the dry period and from 0.1 to 93 L/s in the rainy period. Springs with high discharges were observed in the karstic limestone and coarse-grained clastic. During the dry period, 6 springs with flow rates between 0.2 L/s and 2.7 L/s discharged from the İnalıtı Limestone. There were also 8 springs, with flow rates between 0.2 L/s and 1.8 L/s, which discharged from where the İnalıtı Limestone came into contact with other formations. In the sandstone levels of the Akgöl Formation, 6 springs, with flow rates between 0.1 L/s and 7.5 L/s, were observed, and there was also 1 spring, with a flow rate of 25 L/s (in the dry period), that discharged from the limestone level of the Akgöl Formation. For observation, 3 wells were drilled in the Küre Pb-Zn-Cu mine area on the Küre Lava Member of the Akgöl Formation (Figures 3 and 4). The ore content of the member and mining activities negatively affected the physicochemical parameters of the groundwater in the Küre region. There were 3 springs, with flow rates between 0.2 L/s and 1 L/s, that discharged from the sandstone and limestone level of the Ulus Formation. The clay levels in the formation reduced the permeability of the unit. There were 2 springs, with flow rates between 0.1 L/s and 1.1 L/s, which discharged from the Gökçeğaç Formation, consisting of limestone with clay-sandy, sandstone, and pyroclastic rocks. There were 2 springs (0.3 L/s) that discharged from especially fractured-cracked volcanic Mesozoic ophiolites. Much of the measured water in the study area was used for drinking, domestic, and/or irrigation purposes.

While the EC and pH values of the waters (K3, K12, K15, K16, K33, K34) that discharged from the İnalıtı Formation ranged from 360 to 538 $\mu\text{S}/\text{cm}$ and 7.15 to 7.66, respectively, in the dry period, these values of the waters (K2, K15 K6, K7, K8, K9, K24, K26) that discharged from where the İnalıtı Limestone came into contact with other formations ranged between 434 and 570 $\mu\text{S}/\text{cm}$, and 6.93 and 7.78, respectively (Table 1). The EC and pH values of the waters (K4, K31, K32) that discharged from the the Ulus Formation, comprising sedimentary rocks, ranged between 489 and 684 $\mu\text{S}/\text{cm}$, and 6.98 and 7.31, respectively. The EC values of the K10, K11, and K13 wells, drilled around the liquid mine tailing pond of the Küre Cu-Pb-Zn mine area, located in the Küre Lava Member of Akgöl Formation, were quite variable and

ranged between 492 and 2714 $\mu\text{S}/\text{cm}$. The pH values of the wells ranged between 6.45 and 7.12. The K10 well had the highest EC and lowest pH values. It is located downstream of the tailing pond and represents the deepest well drilled around the pool (985 m). The K10 well was effected by the liquid mine tailing pond due to leakage to groundwater and the increased EC values implied this mixing (Table 1). Moreover, an elevated SO_4 concentration (29.27 meq/L) and slightly acidic characterization (6.45) of the well reflected pyrite oxidation as a source in the well.

4.2. Water chemistry and pollution

In most countries, groundwater and surface water are at a serious risk in terms of major pollution due to mine tailings, mining activity, and abandoned mine areas, as well as the natural washing of rocks and hydrolysis of ores (Balçı et al., 2012; Keskin and Toptaş, 2012; Baba and Gündüz, 2017). The main necessary characteristics in drinking water meet the standards of drinking water, such as not being harmful to health and being pleasant to drink. The health suitability of water depends on the chemical and bacteriological properties of the water (Doğan, 1991). The amount of heavy metal in drinking water is very important. Some metals can have an adverse effect on human health, even in very small amounts (He et al., 2005). Certain chemical and biochemical processes, such as dissolution-precipitation, absorption-desorption, complexation-decomposition, and oxidation-reduction reactions control the concentration and motility of trace elements (He et al., 2005; Balçı, 2010; Keskin, 2010). Different metals have different mobility under various geochemical conditions. Under oxidizing and aqueous environmental conditions, sulfides are rapidly oxidized and Fe, Cu, Zn, and Pb are released from sulfides and incorporated into the groundwater and surface water (He et al., 2005).

There are different geological units, Pb-Zn-Cu ores, mine tailings, and mining activities in the study area. Therefore, the groundwater geochemistry in the study area offered great difference in terms of the physical and chemical properties, and the groundwater had Al, As, Ba, Mn, Ni, Se, Sb, and Pb pollution. The trace element concentrations of the water samples are presented in Table 2. The Al concentration in the groundwater varied between <0.001 and 1135 ppb in the dry and rainy period, respectively. The Al values in the K10 and K27 wells exceeded the upper limit value of the Turkish Drinking Water Standards (200 ppb). If Al accumulates in the body, bone disorders, anemia (Akpolat and Dilek, 2001), and Alzheimer's disease (Onur, 1997) might occur. In addition, Al leads to DNA alteration and epigenetic effects, increasing possibility of breast cancer (Darbre, 2005). The Sb values

³ Keskin TE (2017). Küre (Kastamonu) Pb-Zn-Cu maden alanı çevresinin hidrojeokimyasal özelliklerinin ve su-kayaç etkileşiminin incelemesi. TÜBİTAK Project No: 114Y031 (in Turkish).

Table 2. Trace element results of the waters in the study area (ppb) and Turkish Standards for Water Intended for Human Consumption.

No.	Date	Al	As	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Se	U
K1	15.09.2014	21.75	4.504	7.033	0.075	0.575	–	–	0.041	0.149	0.637	0.13	–	0.082
“	12.05.2015	23.55	–	12.8	–	–	–	125.1	4.49	–	3.091	0.051	–	–
K2	15.09.2014	19.41	1.574	15.53	0.07	0.036	–	–	0.32	0.059	0.654	0.003	–	0.179
K3	15.09.2014	19.65	1.036	27.05	0.061	–	–	–	0.11	0.615	0.775	0.002	–	0.44
K4	15.09.2014	20.74	0.346	28.4	0.062	–	–	–	0.237	0.44	0.816	–	–	0.48
K5	15.09.2014	19.3	0.497	51.52	0.115	–	–	–	0.029	0.595	0.953	0.008	–	0.371
“	12.05.2015	21.83	–	76.96	–	–	–	–	0.145	5.764	3.396	0.075	–	–
K6	15.09.2014	18.67	0.168	34.5	0.088	–	–	–	0.053	–	0.548	0.017	–	0.3
“	12.05.2015	14.24	–	63.96	–	–	–	–	0.235	4.484	21.08	0.148	–	–
K7	15.09.2014	21.94	–	29.82	0.081	–	–	–	–	–	0.624	–	–	0.285
“	12.05.2015	19.93	–	49.8	–	–	–	–	0.241	4.997	2.905	–	–	0.125
K8	15.09.2014	21.53	0.121	55.84	0.055	0.021	–	–	0.215	–	0.856	–	–	0.354
“	12.05.2015	17.94	–	51.63	–	–	–	–	–	1.782	3.761	–	–	–
K9	15.09.2014	15.71	0.059	44.07	0.09	–	13.44	–	0.143	0.543	1.96	0.005	–	0.32
K10	16.09.2014	1135	284.1	1161	0.538	12.17	–	9.579	13.66	15.1	19.07	18.71	4.519	0.375
K11	16.09.2014	20.43	4.402	61.98	0.074	0.374	–	8.336	2.143	–	2.922	0.14	–	0.105
K12	16.09.2014	16.43	0.951	23.69	0.023	–	2.029	–	–	–	1.2	0.012	–	0.299
“	12.05.2015	13.44	–	34.5	–	–	–	59.8	0.982	4.818	3.555	–	–	0.074
K13	16.09.2014	20.48	0.704	73.92	0.042	–	–	–	0.523	0.112	0.505	0.518	0.138	0.851
K14	17.09.2014	15.5	5.053	40.43	0.042	0.167	–	4.324	4.517	0.112	0.669	–	0.309	0.013
“	11.05.2015	11.84	–	86.46	0.03	–	–	–	0.064	–	2.622	–	–	–
K15	17.09.2014	14.61	1.701	12.55	0.069	0.079	–	–	0.015	–	0.493	0.003	–	0.178
“	11.05.2015	10.32	–	19.93	–	–	–	–	–	1.078	3.081	0.043	–	–
K16	17.09.2014	18.45	1.101	20.27	0.077	0.05	–	–	0.145	0.591	0.604	0.066	–	0.363
“	11.05.2015	9.855	–	32.04	–	–	–	–	–	1.369	2.049	0.072	–	0.049
No.	Date	Al	As	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Se	U
K17	17.09.2014	17.76	0.879	78.39	0.054	0.136	–	–	0.107	–	0.446	0.071	0.159	0.91
K18	17.09.2014	17.13	0.506	94.28	0.064	0.038	–	–	0.019	–	0.673	0.035	0.0095	0.923
K19	18.09.2014	18.15	0.722	14.05	0.038	0.033	–	–	0.144	–	0.643	0.059	–	0.363
“	11.05.2015	18.04	–	18.27	–	–	–	–	–	–	2.752	–	0.222	–
K20	18.09.2014	20.51	26.6	53.89	0.089	–	–	–	0.017	–	0.791	0.135	–	1.034
“	11.05.2015	14.94	10.27	53.2	–	–	–	–	0.229	1.719	2.72	0.105	–	0.254

Table 2. (Continued).

K21	18.09.2014	15.62	90.27	104.2	0.058	-	-	-	2.809	-	0.599	0.36	0.152	1.825
"	12.05.2015	10.62	107.5	171.1	-	-	-	-	1.617	1.546	2.916	0.419	0.228	1.053
K22	18.09.2014	18.36	0.337	22.08	0.069	-	-	-	0.166	-	0.996	0.018	-	0.319
K23	18.09.2014	18.72	-	140.4	0.044	-	-	-	0.151	-	0.609	0.112	-	0.273
K24	18.09.2014	16.86	0.475	161.8	0.058	-	-	-	0.031	0.007	0.586	0.024	0.067	0.517
K25	18.09.2014	16.37	1.19	155.4	0.077	-	48.25	-	1.778	-	3.197	0.142	-	0.409
K26	18.09.2014	17.73	0.074	22.61	0.089	0.153	-	-	0.022	-	0.735	-	-	0.153
K27	19.09.2014	1112	255.4	1226	0.455	15.97	-	14.62	123.1	22	19.04	17.44	5.699	14.76
"	13.05.2015	798.4	43.69	1244	-	-	-	-	141.6	22.5	41.17	13.03	4.813	6.654
K28	19.09.2014	15.38	22.88	6.238	0.048	2.063	-	13.85	0.055	3.941	0.515	0.177	-	2.372
"	13.05.2015	9.626	19.82	9.275	-	0.534	-	-	-	2.863	1.62	0.204	-	0.852
K29	19.09.2014	20.85	25.11	8.417	0.043	2.604	-	18.61	-	-	0.592	0.205	-	0.195
"	13.05.2015	8.519	25.82	13.32	-	1.397	-	-	-	-	2.562	0.22	-	-
K30	19.09.2014	20.84	15.57	12.96	0.086	0.572	-	37.67	0.251	5.597	0.586	0.124	-	0.445
"	12.05.2015	9.606	18.23	19.45	-	-	-	-	0.13	4.985	2.62	0.148	-	0.265
K31	19.09.2014	14.25	0.488	34.15	0.048	0.102	-	-	3.111	-	0.587	0.005	-	0.366
"	12.05.2015	10.42	-	49.95	0.025	-	-	-	3.318	4.694	2.964	-	-	0.169
K32	19.09.2014	14.77	0.204	66.68	0.026	-	-	-	-	-	0.59	-	-	0.841
"	12.05.2015	9.689	-	105.2	-	-	-	-	-	4.128	2.018	-	-	0.303
No.	Date	Al	As	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Se	U
K33	19.09.2014	19.05	3.058	62.73	0.044	-	-	-	-	-	0.532	0.06	-	2.491
K34	19.09.2014	-	0.071	21.81	0.035	0.253	-	-	-	0.081	3.421	0.048	-	0.466
KR1	16.09.2014	22.78	2.116	22.28	0.018	0.076	0.667	-	0.193	0.246	0.611	0.044	-	0.323
KR2	16.09.2014	21.43	1.529	25.15	0.027	-	-	-	0.099	-	0.561	0.062	-	0.371
"	12.05.2015	12.7	-	49.07	-	-	-	-	0.296	1.287	3.721	-	-	0.124
KR3	17.09.2014	1186	271.4	1185	0.308	27.75	3.461	-	497.9	29.9	18.51	19.27	5.572	0.069
"	11.05.2015	379.2	-	54.65	0.861	0.936	87.45	135.1	2272	23.7	4.287	0.374	1.931	0.166
KR4	17.09.2014	18.47	1.296	33.82	0.095	-	-	-	0.166	0.173	0.75	0.05	-	0.266
"	11.05.2015	12.02	-	52.01	-	-	-	-	0.156	-	2.678	0.042	-	0.216
KR5	12.05.2015	14.0	-	39.0	-	-	-	-	0.519	0.368	1.942	0.035	-	-
RTMH (2013)		200	10		5	50	2000		50	20	10	5	10	

Bold numbers indicate values that exceeded the drinking water standards.

–: Under the detection limit (0.001).

varied between <0.001 and 18.71 ppb, and the values for the K10 and K27 wells exceeded the 5 ppb upper limit value. The As values varied between <0.001 and 284 ppb and the As concentrations in the K10, K20, K21, K27, K28, K29, and K30 wells even exceed several times the standard limit value (10 ppb). Moreover, the As concentrations in the K1, K11, and K14 groundwater in the dry period did not exceed the standards, but were close to the limit value. This water mostly discharged from the Akgöl Formation, consisting of altered volcanic-volcanoclastic rocks, which contains Pb-Zn-Cu ores, and Mesozoic ophiolites.

Total As pollution can be seen in 2 forms, as natural and anthropological. Pliocene sediments/alluvial layer, mining sites, volcanic/magmatic rocks, geothermal systems, and black shales are natural pollutant sources (Rowland et al., 2011; Baba and Sözbilir, 2012; Şimşek, 2013; Gündüz et al., 2016; Baba and Gündüz, 2017). Geological structure is very important for As. For example, more than half of all total As might be found in quartz, feldspar, aluminosilicates, and iron ore minerals (Onishi and Sandell, 1955). The most polluted groundwaters in terms of As were the K10 and K27 wells. The results of the chemical and ^3H analyses, evaluations, and observations revealed that the K10 well had antropogenic pollution due to leakage from the liquid mine tailing pond to groundwater, while the K27 well and other groundwater had natural pollutions as a result of water-rock interactions (Figure 5). The ^3H results were consistent with this determination. The K10, K11, and K13 wells drilled for observation around the liquid mine tailing pond showed that these waters had a shallow underground residence time, as suggested by the ^3H analysis (7.17, 8.98, and 8.51 TU, respectively). Although the K10 and K11 wells were drilled downstream of the liquid mine tailing pond, the K13 well is located upstream of the pond, and the K13 well did not have any pollution. While the K10 well is the deepest (985 m), K11 is a shallow well. The K11 well was not affect by the tailing, since it is a shallow well. The K27 well was drilled in alluvium outside of the study area. The well has a depth of 95 m, pressurized features, and deep underground residence, as evidenced by the ^3H analysis (0.37 TU). Although the well was opened in alluvium, it cuts the clastic units and Mesozoic ophiolites.

The Ba concentrations of the groundwater ranged between 7.03 and 1226 ppb, and the concentrations in the K10 and K27 wells exceeded the limit values of 700 ppb in the World Health Organization Standard. The Ni concentrations varied between <0.001 and 22.5 ppb, and the values in the K10 and K27 wells exceeded the maximum limit values (20 ppb) of the standards. The Se values ranged between <0.001 and 5.699 ppb, and the K10 and K27 wells had values close to the limit value (10 ppb). The Pb values

of the waters varied between 0.446 and 41.17 ppb. The Pb values in the K10 and K27 wells exceed the limit values of the drinking water standards (10 ppb). Pb, which has a significant toxic effect, enters the red blood cells in the body, dispels the Fe out of the cells, and causes anemia due to Fe deficiency (Peker, 1970; Atabey, 2005; Keskin, 2010). Pb accumulated in bones can cause kidney infections, and abnormal brain and nervous system functions, and an increased amount of Pb in the blood can lead to a decrease in IQ levels in children (Kahvecioğlu et al., 2003; Keskin, 2010). The Mn values ranged from <0.001 to 141.6 ppb. The Mn concentration in the K27 well exceeded the limit of 50 ppb in the Turkish Drinking Water Standards. Mn is one of the main elements in human and animal nutrition (McNeely et al., 1979; WHO, 1984). While Mn deficiency causes slow growth, nervous system disorders, anemia, and bone disorders in children, it leads to Alzheimer's disease and bacterial growth if it exceeds the limit value.

In general, the concentrations of many trace elements and major ions decreased due to the dilution of water in the rainy period. However, the Ba, Co, Ni, Pb, Sr, Al, As, Fe, Mn, Sb, Se, and Zn concentrations in some waters were generally high due to the dissolution of the rocks in the environment with the effect of acidic rainwater according to the pH and Eh balance (Table 2). It was thought that there were 2 causes of the pollution of these trace elements in the water in the study area. The first was the water-rock interactions due to the natural washing of the rocks (especially from the Akgöl Formation, consisting of altered volcanic-volcanoclastic rocks and Mesozoic ophiolites), and the second was antropogenic pollution due to leakage from the liquid mine tailing pond. There was no risk of contamination in terms of other elements such as Co, Sr, Fe, Zn, F, U, and NO_3 according to the determined data of the waters in the study area. For example, Zn dissolution is known to be very low in calcareous, clay, and high pH environments due to its coprecipitation with the carbonates (Lisbeth et al., 2009; Kaya and Uygur, 2019). Hence, it is reasonable to assume that carbonated rocks and alkaline aqueous environments prevailing in the study area prevented the dissolution of elements, such as Zn in the waters.

The SO_4 , Al, Sb, As, Ba, Mn, Ni, and Pb concentrations in the KR3 sampling point exceeded the upper limit values of the drinking water standards (Table 2). KR3 is located on the Ersizler River, which drains the Küre Pb-Zn-Cu mining site and its tailings and therefore, the KR3 water was highly contaminated. Furthermore, the KR3 water was the only contaminated surface water, as suggested by the data obtained from the study area⁴.

⁴ Keskin TE (2017). Küre (Kastamonu) Pb-Zn-Cu maden alanı çevresinin hidrojeokimyasal özelliklerinin ve su-kayaç etkileşiminin incelemesi. TÜBİTAK Project No: 114Y031 (in Turkish).

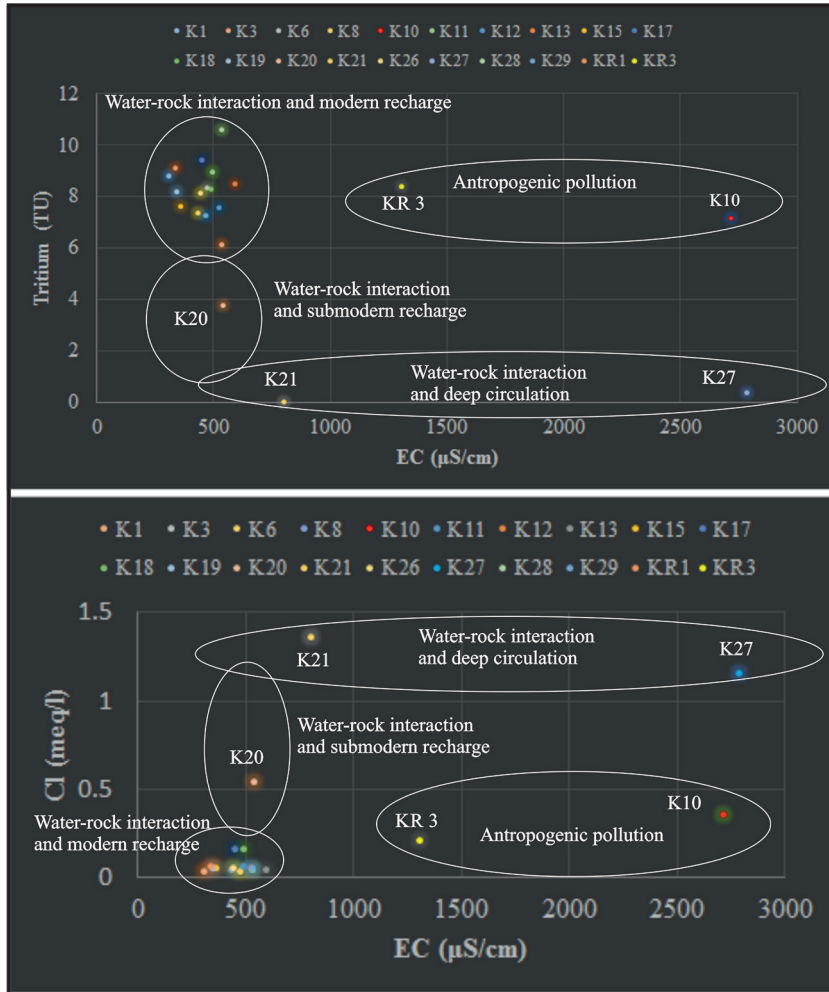


Figure 5. Relationship graphics of the EC-³H and EC-Cl.

Balcı and Demirel (2018) reported that the SiO₂, Fe₂O₃, Al₂O₃, CaO, and Fe values of the waste rocks of their study area ranged between 0.09% and 5.3%, 9.9% and 52.2%, 0.16% and 25.9%, and 0.5% and 25.8%, respectively and these values of the lithological units in their study area ranged between 0.3% and 21.8%, 0.07% and 18.9%, 0.02% and 23.6%, 3.0% and 27.5%, and 0.0005% and 13.2%, respectively. In addition to that, the Cu, Zn, Co, Ni, Ti, Mn, Cr, Pb, Cd, and As values of the waste rocks ranged between 70 and 44,010 ppm, 30 and 27,430 ppm, 31 and 1561 ppm, 4 and 191 ppm, 56 and 5120 ppm, 1 and 1200 ppm, 5 and 316 ppm, 15 and 385 ppm, 16 and 52 ppm, and 6 and 613 ppm, respectively, and the values of the lithological units ranged between 10 and 950 ppm, 65 and 490 ppm, 7 and 126 ppm, 1 and 921 ppm, 807 and 4812 ppm, 20 and 24,380 ppm, 18 and 341 ppm, 16 and 163 ppm, 0.1 and 24 ppm, and 1.7 and 60 ppm, respectively. The Fe₂O₃, Al₂O₃, CaO, and some trace elements, such as As, values were high in both the waste rocks and lithological units.

This information represented results compatible with As, Al, and other heavy metal pollution observed in the waters of the study area.

4.3. Geochemical evaluation

Figure 5 shows the relationship of the EC-³H, and EC-Cl. As shown in Figure 5, low ³H-high EC values indicated contamination caused by deep circulating water rock interactions (K21, K27), while high ³H-high EC values indicated anthropogenic contamination caused by liquid mine tailings (K10, KR3). High ³H-low EC values represented water-rock interactions. In addition to that, low chloride-high EC values indicated anthropogenic contamination caused by liquid mine tailings (K10, KR3), while high chloride-high EC values indicated contamination caused by deep circulating water rock interactions (K21, K27). Moreover, low chloride-low EC values represented water-rock interactions.

Considering the Piper diagram (Piper, 1944) (Figures 6 and 7), which was drawn according to the percentages of

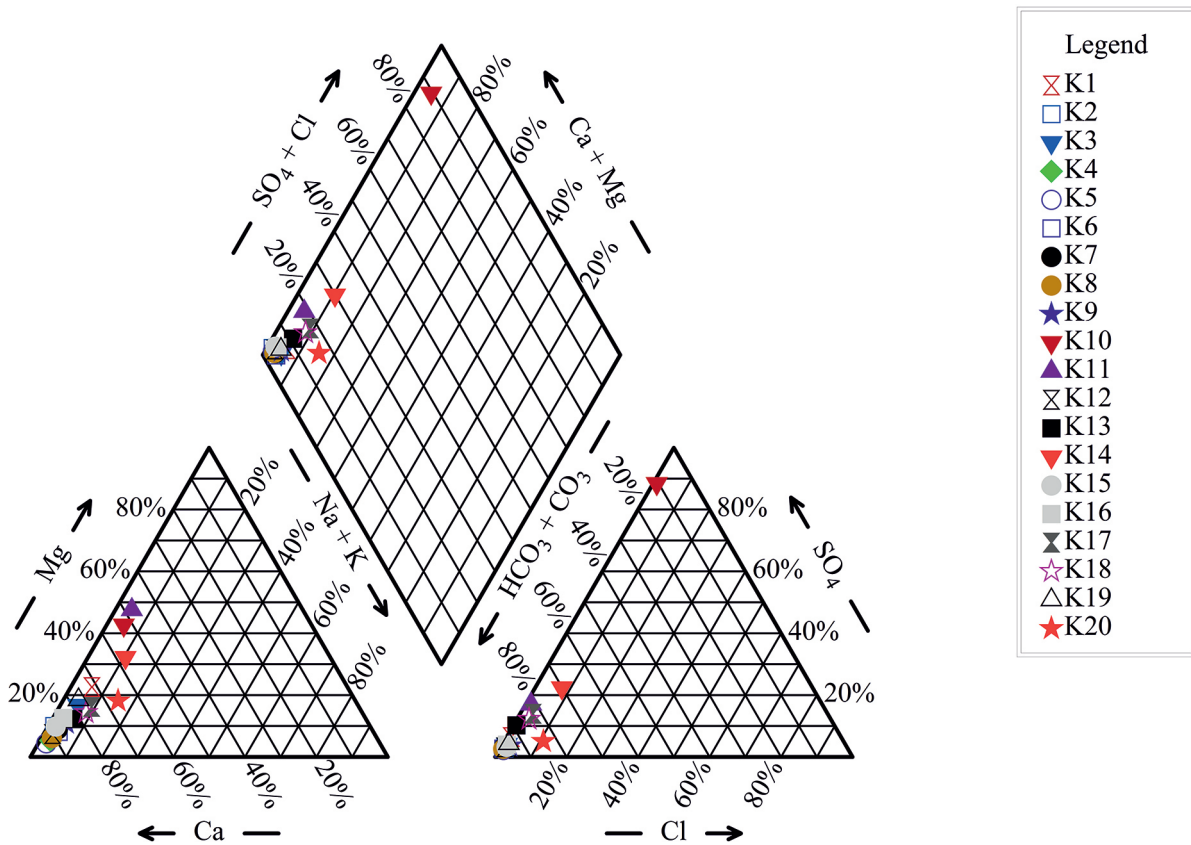


Figure 6. Piper diagram of the groundwaters in the study area (dry period).

major anions and cations, the facies differences according to IAH (1979) of the waters are clearly seen. As seen in Figures 6 and 7, especially the K10, KR3 waters, which were exposed to artificial pollution, had different facies in terms of anions, and they had Ca-Mg-SO₄-type facies. In addition to that, the K21, K27 waters, which had deep circulation, had mix facies in terms of cations, and the K28, K29, and K30 springs that discharged from ophiolitic rocks had Mg-HCO₃ facies. Moreover, these waters generally contained trace element pollution. The other waters in the study area had Ca-HCO₃ facies. No facies changes were observed in the rainy period in general.

Although the K10, K11, and K13 wells were opened around the liquid mine tailing pond, these wells had different facies. While the K10 and K11 wells were opened downstream of the tailing pond, the K13 well was drilled upstream of the pond. The K10 well is the deepest well, with a depth of 935 m, while K11 is a shallow well. The K10 well had Ca-Mg-SO₄ facies, K11 well had Ca-Mg-HCO₃ facies, and the K13 well had Ca-HCO₃ facies. It was thought that these differences may have depend on 3 reasons: 1) the K10 well was affected by the mining liquid tailing pond, 2) the K10 well had a lower pH value and higher SO₄ value due to the oxidation of pyrite, and

3) the K11 well was shallow enough not to be affected by liquid pond leaks. Moreover, these differences were clearly seen in the trace element content. In addition to that, the K14 spring had Ca-Mg-HCO₃ facies and the SO₄ concentrations were slightly higher than those of the other waters. It was thought that the spring, which discharged from the coast of the Ersizlerdere River, was affected by the liquid mine tailings.

According to the Turkish Inland Water Quality Regulations (2015, 2016), while the KR1, KR2, KR4, and KR5 river measurement points have been classified as class I in terms of the EC, pH, NO₃, Al, As, Cu, Ba, Fe, F, Pb, Mn, Ni, and Se, the KR3 river measurement point, which was contaminated by the liquid mine tailings, has been classified as class IV in terms of the Al, As, as class III for the EC, Cu, Ba, and Mn, and as class II for the NO₃, Pb, and Ni. Class I refers to clean waters suitable for drinking purposes and class II indicates slightly contaminated waters suitable for domestic usage after treatment and irrigation purposes. Class III expresses contaminated water suitable for industrial water after treatment. Class IV includes heavily contaminated water that is not suitable for any purpose at all (Turkish Inland Water Quality Regulations 2015, 2016; Yücel and Baba, 2018).

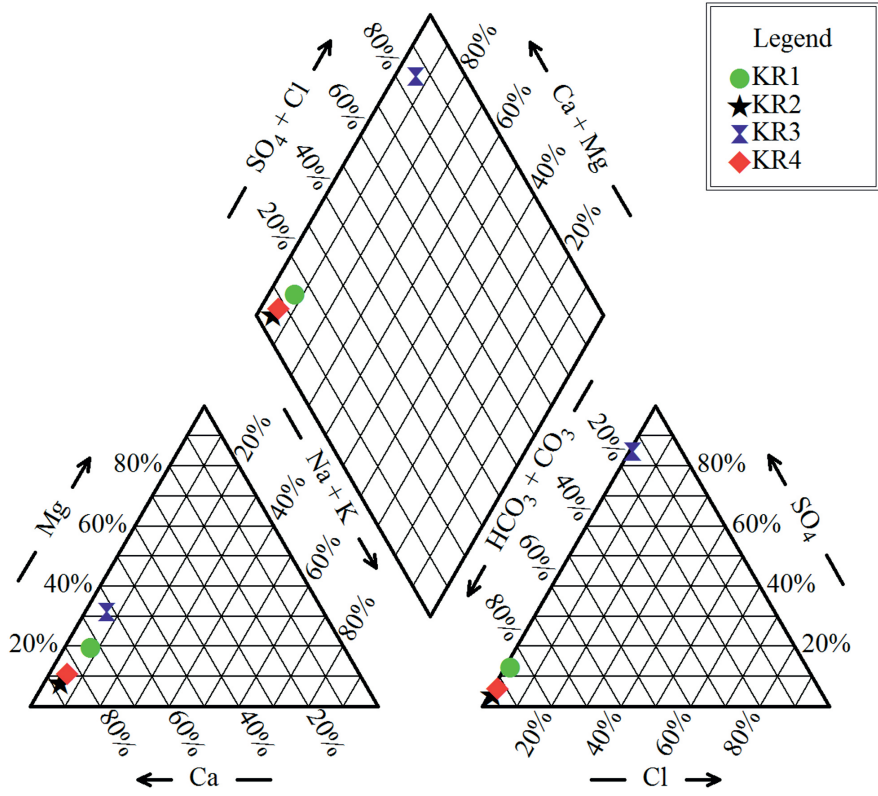


Figure 7. Piper diagram of the surface waters in the study area (dry period).

4.4. Isotope chemistry

The isotope analysis results of waters with a large discharge and around the ore deposits, according to study aim, are seen in Table 3. The $\delta^{18}\text{O}$, $\delta^2\text{H}$, and ^3H analyses were conducted to determine the origins and underground residence times of the groundwaters. The $\delta^{18}\text{O}$, $\delta^2\text{H}$, and ^3H isotope values for the waters ranged between -12.81% and -9.87% , -95.99% and -69.02% , and 0.00 and 10.60 TU, respectively.

Figure 8 provides the ^{18}O - ^2H graph is used to determine the origins of the waters. The waters were generally located between Yozgat (Şimşek, 1993; Kurttaş, 1997) and the Mediterranean meteoric line (MWL) (Payne and Dinçer, 1965; Sayın and Eyüpoğlu, 2005). These locations suggested a meteoric origin for the water samples. On the other hand, K27, which had a deep underground residence time, as suggested by the ^3H results, fell into a different area than the rest of the water samples in Figure 8. It was thought that the water was affected by the earlier cold climatic conditions and was recharged from higher elevations when compared to the other water samples, due to its higher negative values relative to the other waters.

Water in the study area was determined to be a modern recharge according to the results presented in Table 4 (Clark and Fritz, 1997). In other words, this water was recharged from the rainfalls over the previous few years. While K20, which is one of the springs that supplies the drinking and domestic water needs of the Inebolu district, was classified as a mixture between submodern and recent recharge in the dry period (3.75 TU), while the spring was classified as a modern recharge in the rainy period (7.41 TU) depending on the fresh rain water intake. The K21 and K27 waters had values of 0.00 and 0.37 TU, respectively, and were classified as submodern-recharged prior to 1952. This situation led to an increase in the contact time of the rocks with the water and thus, these waters may have higher element contents and EC values than the other waters. No significant change was observed in the other waters in the rainy period⁵.

5. Conclusions

This study aimed to determine the water pollution and hydrogeological properties of the Küre mine area and its vicinity. The concentrations of Al, As, Ba, Mn, Ni, Sb, and

⁵ Keskin TE (2017). Küre (Kastamonu) Pb-Zn-Cu maden alanı çevresinin hidrojeokimyasal özelliklerinin ve su-kayaç etkileşiminin incelemesi. TÜBİTAK Project No: 114Y031 (in Turkish).

Table 3. Isotope analysis results of some of the waters in the study area.

No.	Date	Tritium (TU)	Oxygen-18 (VSMOW ‰) (± 0.15)	Deuterium (VSMOW ‰) (± 2)
K1	15.09.2014	8.80 \pm 0.55	-12.41 \pm 0.11	-76.29 \pm 0.59
K3	15.09.2014	6.12 \pm 0.49	-12.78 \pm 0.16	-80.98 \pm 1.06
K6	15.09.2014	8.34 \pm 0.53	-11.45 \pm 0.14	-77.36 \pm 0.63
K8	15.09.2014	7.36 \pm 0.52	-12.40 \pm 0.09	-83.81 \pm 0.60
K10	16.09.2014	7.17 \pm 0.52	-11.79 \pm 0.11	-76.99 \pm 0.83
K11	16.09.2014	8.98 \pm 0.55	-12.25 \pm 0.12	-77.32 \pm 0.47
K12	16.09.2014	7.57 \pm 0.53	-12.10 \pm 0.13	-79.70 \pm 0.27
K13	16.09.2014	8.51 \pm 0.56	-11.55 \pm 0.08	-74.41 \pm 0.01
K15	17.09.2014	7.63 \pm 0.54	-11.98 \pm 0.13	-78.35 \pm 0.76
K17	17.09.2014	9.43 \pm 0.54	-11.10 \pm 0.06	-72.52 \pm 0.67
K18	17.09.2014	8.31 \pm 0.57	-11.19 \pm 0.04	-71.29 \pm 0.39
K19	18.09.2014	8.17 \pm 0.55	-11.34 \pm 0.06	-69.60 \pm 0.59
“	11.05.2015	7.34 \pm 0.50		
K20	18.09.2014	3.75 \pm 0.47	-10.17 \pm 0.06	-69.02 \pm 1.16
“	11.05.2015	7.41 \pm 0.50		
K21	18.09.2014	0.0 \pm 0.41	-10.73 \pm 0.11	-70.86 \pm 0.56
“	11.05.2015	0.0 \pm 0.36		
K26	18.09.2014	8.15 \pm 0.56	-10.95 \pm 0.17	-71.69 \pm 0.88
K27	19.09.2014	0.37 \pm 0.42	-12.81 \pm 0.10	-95.99 \pm 0.30
“	13.05.2015	0.83 \pm 0.38		
K28	19.09.2014	10.60 \pm 0.60	-9.87 \pm 0.06	-69.54 \pm 0.21
K29	19.09.2014	7.29 \pm 0.55	-11.25 \pm 0.11	-74.67 \pm 1.37
KR1	16.09.2014	9.11 \pm 0.55	-11.32 \pm 0.04	-72.68 \pm 1.10
KR3	17.09.2014	8.37 \pm 0.54	-10.95 \pm 0.13	-71.85 \pm 1.00

Pb, and SO₄ ions in the water samples exceeded the Turkish and WHO drinking water standards. The natural pollution originating from water-altered volcanic-volcanoclastic rocks containing Pb-Zn-Cu ore, and ophiolite, and the antropogenic pollution originating from liquid mine tailing leaks are effective processes that have resulted in water pollution in the area. The Al, Sb, Ba, Ni, and Pb concentrations in the groundwater varied between <0.001 and 1135 ppb, <0.001 and 18.71 ppb, 7.03 and 1226 ppb, <0.001 and 22.5 ppb, and 0.446 and 41.17 ppb, respectively, and these element concentrations in the K10 and K27 wells exceeded the upper limit of Turkish and World Drinking Water Standards. Mn values ranged between <0.001 and 141.6 ppb and exceeded the limit value of the Turkish Drinking Water Standards in the K27 well. The Al, Sb, Ba, Ni, and Pb concentrations of the K10 and K27 wells were 1135 and 1112 ppb; 18.7 and 17.4 ppb; 1161 and 1226 ppb; 15.1 and 22 ppb; and 19.1 and 19 ppb, respectively, in the dry period.

As pollution is considered to be an especially severe problem for the area, since the As values varied between <0.001 and 284 ppb, and in the K10, K20, K21, K27, K28, K29, and K30 groundwaters, it exceed several times the standard limit value. Furthermore, the As concentrations in the K1, K11, and K14 groundwaters did not exceed the standards, but were close to the limit values in the dry period. The most polluted waters in terms of As were K10 and K27. The As concentration of the K10 and K27 wells were 284 ppb and 255 in the dry period, respectively. The K10, K11 and K13 waters are located around the liquid mine tailing pond of the Küre Pb-Zn-Cu mine area and they had shallow underground residence times, as the ³H analysis indicated. Although the K10 and K11 wells were opened downstream of the liquid mine tailing pond, K13 is located upstream of the pond, and it did not have any element pollution. The K10 well had high ³H-high EC values that indicated anthropogenic contamination caused by liquid mine tailings. The K27 well had low ³H-high EC values that indicated

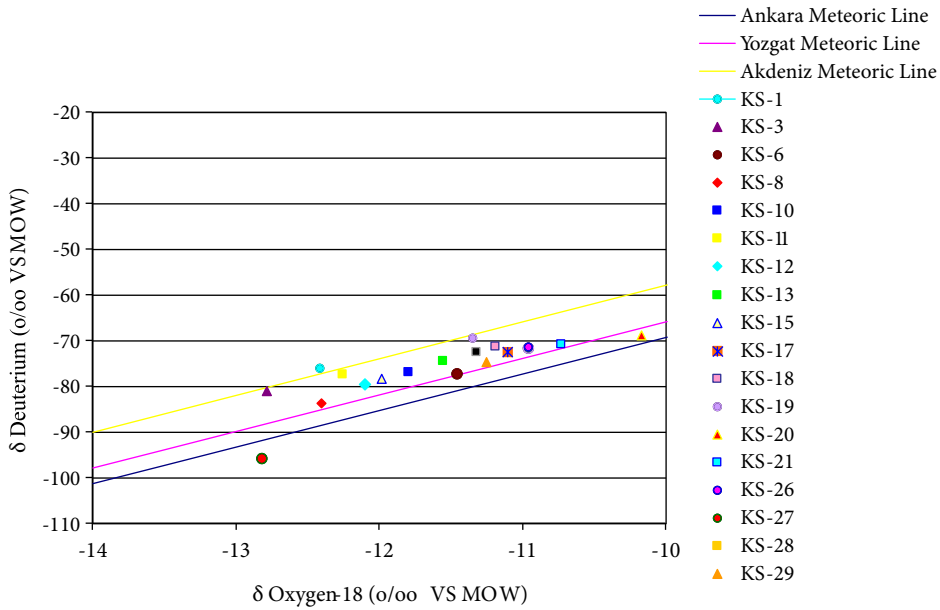


Figure 8. $\delta^{18}\text{O}$ – $\delta^2\text{H}$ graphs of some important waters [Mediterranean meteoric water line (MWL) from Payne and Dinçer (1965); Yozgat MWL from Şimşek (1993) and Kurttaş (1997); Ankara MWL from Sayın and Eyüpoğlu (2005)].

Table 4. Qualitative dating of the groundwaters in the continental regions (Clark and Fritz 1997).

Tritium value (TU)	Dating
<0.8 TU	Submodern-recharged prior to 1952
0.8–~4 TU	Mixture between submodern and recent recharge
5–15 TU	Modern (<5 to10 years)
15–30 TU	Some bomb ^3H present
>30 TU	Considerable component of recharge from the 1960s or 1970s
>50 TU	Dominantly the recharge from the 1960s

contamination caused by water-rock interactions with deep circulation. Moreover, the other waters had high ^3H -low EC values, which generally represented water-rock interactions.

The isotope analysis showed that the waters had a generally meteoric origin and modern recharge. However, it is likely that the K27 well was affected by the earlier cold climatic conditions and was recharged from higher elevations, as revealed by its higher negative $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values relative to the rest of the water samples. Moreover, the K27 well was classified as submodern-recharged prior to 1952. Thus, these waters may have had higher element contents and EC values than the other waters.

The SO_4 , Al, Sb, As, Ba, Mn, Ni, and Pb concentrations at the KR3 (Ersizler River) measurement point exceed the upper limit values of the drinking water standards. The KR3 is located on the Ersizler River, which drains the Küre

Pb-Zn-Cu mining site and its tailings. The SO_4 , Al, As, Pb, and Sb concentrations of the KR3 measurement point were 15.1 meq/L, 1186 ppb, 271 ppb, 18.5 ppb, and 19.3 ppb, respectively, in the dry period. Moreover, the EC value of the Ersizler River increased by approximately 4 times, from 298 to 1306 $\mu\text{S}/\text{cm}$, after mixing with the liquid mine tailings. Therefore, the results of this study suggested that liquid mine tailings are one of the pollution sources once they are discharged into the river. There was no pollution at the other river measurement points located upstream.

The investigation herein showed that weathering, dissolution, and oxidation influenced the physicochemical processes in the groundwaters. It is expected that if these processes continue over the long-term, they may have the potential to produce AMD in the region. It is also clear that these pollutants will accumulate underground

and gradually contaminate the groundwater and surface water. Therefore, long-term monitoring studies should be performed in the study area to predict the physicochemical controls on trace element concentrations in drainage from future mine tailings.

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