Turkish Journal of Earth Sciences

http://journals.tubitak.gov.tr/earth/

Research Article

Turkish J Earth Sci
(2014) 23: 129-146
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doi:10.3906/yer-1212-3

Comparative geochemical study of soils developed on characteristic black and yellow polymetallic massive sulfide deposits in Eastern Pontides (NE Turkey)

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Received: 05.12.2012 • **Accepted:** 20.07.2013 • **Published Online:** 18.01.2014 • **Printed:** 17.02.2014

Abstract: The Harşit-Köprübaşı (Tirebolu) and Killik (Espiye) volcanogenic massive sulfide (VMS) deposits occur in the Eastern Pontide tectonic belt, one of the major tectonic units comprising Anatolia. They are hosted by Late Cretaceous dacitic to rhyolitic rocks overlain by thin layers of pelitic sediments. The region is considered as a metallogenic province since it is a host to numerous VMS deposits, mainly of the Kuroko type, with varying sizes and reserves and with fairly similar geochemical and mineralogical characteristics. In this study, 489 soil samples were systematically collected from both known mineralized sites and remote areas that have no indication of ore mineralization or alteration to investigate the relationship of Zn, Cu, and Pb concentration distributions on 2 completely delineated ore deposits that are treated as natural physical models and on unmineralized distant areas in order to determine regional backgrounds, local thresholds, and anomalous values that are characteristic to the Eastern Pontide metallogenic province to use in exploration programs as a cost-effective prospecting method. Applicability of proposed geochemical modeling based on the results during surficial geochemical prospecting to potential hydrothermally altered areas occurring in the region and elsewhere in the world is discussed. The results were found to be highly convincing if sampling campaigns and data evaluations are cautiously conducted.

Key words: Soil geochemistry, exploration, copper, zinc, lead, volcanogenic massive sulfide, Killik, Köprübaşı, Eastern Pontides

1. Introduction

The study area (Figure 1) occurs in the Eastern Pontides, one of the major tectonic units of Turkey (Ketin 1966; Ketin & Canitez 1972). This belt is about 500 km long and 100 km wide at most and has a very complex volcanic island arc structure that evolved during Kimmeridgian-Alpine orogeny. Lithologic units of the region are products of subduction-related magmatism, which developed in 4 stages: (i) tholeiitic episode representing primitive arc stage during Early Liassic to Kimmeridgian; (ii) calc-alkaline episode representing normal arc stage during Upper Cretaceous; (iii) calc-alkaline episode representing mature arc stage during Eocene; (iv) Neogene volcanic episode representing postcollisional stage. The Eastern Pontides, a paleosubduction zone within the Northern Tethys Subduction Zone, is considered a polymetallogenic province in which numerous volcanogenic massive sulfide (VMS) mineralizations occur in association with Late Cretaceous felsic marine successions of inner-arc basins (Tokel 1972, 1977; Adamia *et al.* 1981; Khain 1984; Tokel 1995; Ciftci 2000). Moreover, the number of the VMS deposits, across about 300 km of the Black Sea coast, makes the region one of the most significant ore districts in the world (Pejatovic 1979). The VMS deposits of the region are considered to be Kuroko-type in a broad sense (Hamamcıoğlu & Sawa 1971; Aslaner 1977; Çağatay & Boyle 1977; Leitch 1981; Aslaner & Gedikoğlu 1984; Akıncı 1985; Schneider *et al.* 1988; Leitch 1990; Van 1990; Çağatay 1993; Özgür 1993; Kolaylı 1994; Aslaner *et al.* 1995; Tüysüz 1995; Akçay *et al.* 1998; Ciftci 2000; Çiftçi *et al.* 2005).

This province has been a major source for the base metal production in Turkey for about the past 40 years. The majority of this production came from the VMS deposits of the region. The Killik and Harşit-Köprübaşı deposits, which are treated as natural physical models, are among about 25 massive sulfide occurrences in this region. Stratigraphically, all of these deposits are hosted by felsic volcanics of Late Cretaceous age (Ciftci 2000).

The Kuroko-type VMS deposits show distinct alteration patterns in different size as reviewed by Franklin (1986) and Lydon (1988). A few comprehensive investigations

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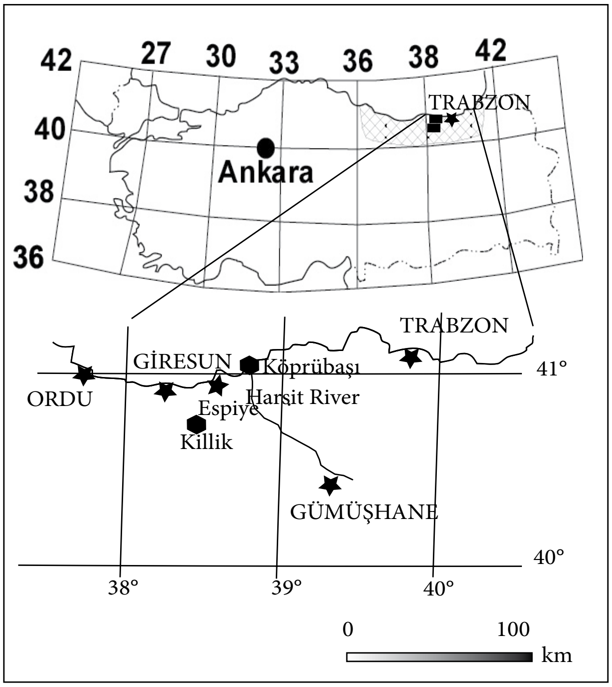

Figure 1. Location map of the subject deposits.

were carried out on the alteration characteristics of the region's VMS deposits, including those of Schneider *et al.* (1988), Özgür and Palacios (1990), Çağatay (1993), Özgür (1993), Kolaylı (1994), Tüysüz (1995), and Karakaya (2012).

The soil geochemistry is frequently employed in mineral exploration programs in the region. However, since most of the terrain is very steep, humid, and covered with dense vegetation, with background values for all base metals are very high, earlier attempts ended in varying levels of success (Köprübaşı 1992; Çiftçi 1993; Cordan 1993; Çiftçi *et al.* 2005). Besides the soil geochemistry, biogeochemistry was also used for the VMS explorations in the area (Akçay *et al.* 1998).

This study attempts to apply the known geochemical methods with a special emphasis on data handling and sampling to 2 completely delineated ore deposits with contrasting characteristics, the first being a yellow semi-black ore and the other being a dominating black ore, but both are in the same province. These sites are deliberately selected from areas where only underground mining activities were practiced, no slugs from earlier mining activities were piled, and no indication of soil contamination or transport was noticed. Soils developed on these deposits were studied to determine the background, threshold, and anomaly values to compare the geochemical distribution patterns.

2. Geology of the study area

Although the region's tectonic evolution is somewhat disputed, there is general consensus on the petrogenetic characteristics of the region's rocks. The geology of the Eastern Pontides (NE Turkey) is the consequence of long-lived subduction, accretion, and collision events that took place in association with the closure of the Tethyan Ocean (Okay & Şahintürk 1997 and references therein). The Eastern Pontides rest generally on pre-Liassic composite basement rocks consisting of (i) high-temperature, low-pressure metamorphic units intruded by Lower Carboniferous high-K I-type granitoids (Okay 1996; Topuz & Altherr 2004; Topuz *et al.* 2004b, 2007, 2010); (ii) Permo–Triassic low-temperature, high-pressure metamorphic units (e.g., Okay & Goncuoğlu 2004; Topuz *et al.* 2004a); and (iii) molassic sedimentary rocks of Permo–Carboniferous age (Okay & Leven 1996; Capkınoğlu 2003). This composite basement is overlain transgressively by Liassic volcanics and volcaniclastics that deposited in an extensional arc environment. The volcanic members of this sequence are represented by calc-alkaline to tholeiitic basaltic to andesitic rocks (e.g., Şen 2007; Kandemir & Yılmaz 2009). The Liassic volcanics and volcaniclastics grade into Malm–lower Cretaceous carbonates. The Late Cretaceous era is represented by a volcano-sedimentary rock succession more than 2 km thick in the north and by flyschoid sedimentary rocks with limestone olistoliths in the south (Okay & Şahintürk 1997 and references therein).

Late Cretaceous volcanics compositionally range from basalt to rhyolite (e.g., Eğin & Hirst 1979; Manetti *et al.* 1983; Çamur *et al.* 1996; Arslan *et al.* 1997; Okay & Şahintürk 1997; Boztuğ & Harlavan 2008). The Kuroko-type VMS deposits have a region-wide occurrence and are essentially associated with Late Cretaceous felsic volcanics (Ciftci *et al.* 2005 and references therein). The Late Cretaceous magmatism occurred as a result of northward subduction of the İzmir-Ankara-Erzincan Neotethys Ocean (e.g., Şengor & Yılmaz 1981; Okay & Şahintürk 1997; Yılmaz *et al.* 1997). The collision between the Eastern Pontides and the Tauride-Anatolide block to the south is constrained to have occurred in the Paleocene to early Eocene (e.g., Okay & Şahintürk 1997; Okay & Tüysüz 1999). Postcollisional Eocene volcanic and volcaniclastics unconformably overlie the older units and locally seal the İzmir-Ankara-Erzincan suture (Altherr *et al.* 2008). As a result of a long-lived subduction and collisional events, ages of the granitoids in the Eastern Pontides range from Early Carboniferous to Late Eocene (e.g., Boztuğ *et al.* 2004; Topuz *et al.* 2005, 2010; Arslan & Aslan 2006; Karslı *et al.* 2007; Kaygusuz *et al.* 2008; Kaygusuz & Aydınçakır 2009).

Both of the subject deposits are hosted by highly altered dacitic tuffs of Late Cretaceous age. A thin layer of tuff, tuffite, and limestone succession partially overlies the ore bodies. These thin sequences are overlain by barren felsic to intermediate volcanics of Late Cretaceous age (Figure 2).

3. Description of the area

3.1. Geographic background and main sources of pollution

The study area occurs in the E-W trending Eastern Black Sea Mountains with 2 branches both running parallel to the Black Sea coast. The elevation in the study area ranges

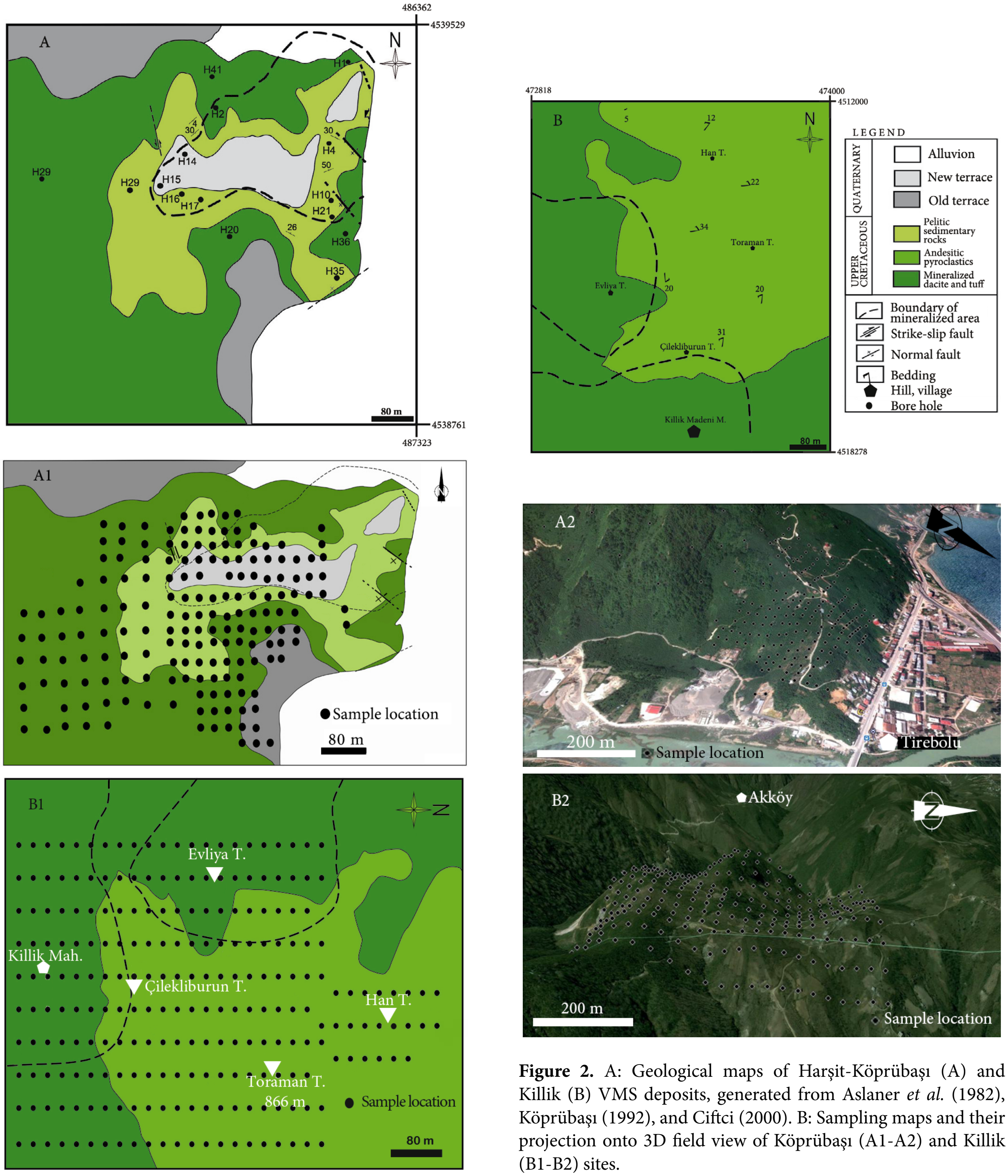

Figure 2. A: Geological maps of Harşit-Köprübaşı (A) and Killik (B) VMS deposits, generated from Aslaner *et al.* (1982), Köprübaşı (1992), and Ciftci (2000). B: Sampling maps and their projection onto 3D field view of Köprübaşı (A1-A2) and Killik (B1-B2) sites.

from 120 m to 1300 m. The coastal part of the region experiences a mild but very humid climate with rainy and very occasionally snowy winters during December–February and hot summers during June–August. The average annual temperature in the coastal cities is about 15 °C. However, inner parts of the region receive less rainfall but more snow. This in turn brings diversity in vegetation. The coastal line is densely vegetated, mainly with hazelnut trees and tea bushes; the inner parts are, however, covered by chestnut, pine, and fir trees until elevations as high as 2700 m (Ciftci *et al.* 2005).

The mining history in the region goes back to as early as Byzantine times, but the major mining activities recorded are from the late 1700s and onward (Ciftci *et al.* 2005). Mine dumps, and particularly massive amounts of slags from these activities, are the major source of pollution in the region. Discharge of such sites to the drainage system in the region along with already high average metal contents of the region's soils developed on the felsic volcanics and the granitoids are the main sources of pollution. Number and coverage of such sites are not well documented and recorded. Thus, it threatens all geochemical exploration programs in the region and has to be taken into consideration.

3.2. Soils

During this investigation soil profiles developed on the felsic volcanic rocks were of interest. Soil profiles vary greatly in thickness throughout the region from a few centimeters to over a meter as a result of topography and altitude. Soils generally have well-developed A/B/C zones with a marked zone A along the coastal line (can be considered as Podzols), changing character towards the inner mountainous region to azonal soils, where A organic horizons directly rest over the rock (A/C profile) (can be considered as Entisols). Particularly in depressed areas, the zone A may reach about 1 m in thickness. In the study area, soils can be considered acidic due to the common presence of acid-producing pyrite.

3.3. Mineralizations

The VMS deposits of the Eastern Pontides could be grouped into 3 major categories: (i) Cu-pyrite type (Au) (e.g., Murgul – Artvin; Kutlular – Sürmene – Trabzon), (ii) Pb-Zn (Ag) type (e.g., Harşit-Köprübaşı - Giresun), and (iii) Zn-Cu type (e.g., Killik – Espiye – Giresun; Madenköy – Çayeli – Rize; Cerattepe – Artvin).

Harşit-Köprübaşı and Killik VMS deposits in the region are the sites of our baseline study. Although these deposits were mined in 1990s, both are now subject to new drillings to develop new reserves. Harşit-Köprübaşı was mined mainly for zinc and lead, and Killik for zinc and copper.

The Köprübaşı VMS deposit is located in the western portion of the Pontide tectonic belt, 2 km from the town of Tirebolu to east, at the entrance to the Harşit Valley from the Black Sea coast. The deposit is hosted predominantly by the felsic volcanic complex that grades into andesitic breccia at its base. The felsic complex is formed chiefly by dacitic tuffs that are highly altered. Kaolinitic alteration is somewhat widespread but silicic alteration is also very common. Disseminated pyrite is present in these rocks throughout the district. The host rocks are overlain by the volcano-sedimentary unit consisting of intercalated tuffs, chert, marl, limestone, and sandstone. The measured thickness of this unit is about 50 m. This intercalated character of this unit indicates that the district experienced sequential depositional conditions from deep sea to terrestrial to yield those sequential facies. The tuffs of the unit are neutral to basic in character with a smaller amount of felsic tuff. Limestones in the unit contain microfossils such as foraminifer species, mainly *Globigerina* and *Gumbelina*. The fossils are Campanian-Maastrichtian in age. The unit is cut by basalt-dolerite dykes.

The deposit can be considered to be stratiform and flat-lying. It is composed of a mixture of massive, disseminated, and stockwork mineralizations, which are irregularly distributed within a single mineralized zone. However, it appears that the stockwork ore is more commonly associated with breccia, and it most probably corresponds to the central portion of sulfide of the chimney mound, whereas the massive ore is on the flanks of the chimney or between 2 chimneys. It can hardly be considered to represent sulfide pods because of the inconsistent thickness and continuation of the massive zones. The disseminated ore exists irregularly almost everywhere, but particularly at the bottom and the top of the deposit. The mineralization grades into low-grade ore zones, and then it terminates into pyrite disseminated felsic tuffs. The general outline of the deposit is comparable with the common architecture of the VMS deposits. Although there are sections that could be as thick as 100 m, the average thickness for the ore body is about 40 m. The disseminated ore is represented mainly by euhedral to subhedral pyrite crystals; galena and sphalerite also occur in disseminated form. This statement is also valid for the stockwork ore. In the massive ore horizons, it appears that the black ore dominates along with significant tetrahedrite-tennantite (mainly tetrahedrite) series minerals and pyrite. Presence of yellow ore is limited to rare chalcopyrite and bornite. Pyrite is always abundant in all of the zones. The Harşit-Köprübaşı deposit can be considered as the "Pb-Zn (Ag) type" according to Solomon's (1976) classification with about 12% composite tenor (6% Zn and 6% Pb) and had about 6,000,000 t of reserve (Acar 1972). Köprübaşı (1992) reported 4% Zn and 4% Pb during his dissertation study. Analysis of an ore boulder produced similar results for the base metals (9% Pb, 8% Zn, 0.5% Cu, 220 ppm Ag) (Ciftci 2000). Sphalerite accounts for zinc, galena for lead, and tetrahedrite for silver and antimony. The deposit has an ore mineral paragenesis of pyrite – sphalerite – tetrahedrite – galena. Dissemination and replacement micro-ore textures are very common (Ciftci 2000).

The Killik deposit can be considered as the "Zn-Cu type" according to Solomon's (1976) classification with about 8.2% composite tenor (5% Zn, 2.5% Cu, 0.7% Pb) and had about 100,000 t of reserve (Çakır & Çelik 1982; Hokelekli & Boynukalın 1982). Analysis of an ore boulder recovered during the initial stage of this investigation produced similar results for the base metals (4.32% Zn, 1.97% Cu, 0.05% Pb). This deposit has an ore mineral paragenesis of pyrite – chalcopyrite (I) – sphalerite – galena – tetrahedrite / tennantite – chalcopyrite (II) (Ciftci 2000). The deposit is essentially stratabound with characteristics of the Zn-Cu type of the stratiform, Kuroko-type VMS deposits. The deposit comprised 2 contiguous lenticular sulfide bodies, which dip about 20° towards the south and have a size of about 120 m × 20 m. The deposit is about 60 m below the surface and has been mined from underground.

In general, alteration styles developed around the VMS deposits are similar to those of the hydrothermal mineralizations described by Meyer and Hemley (1967). Quartz and sericite predominate in the zones enveloping disseminated and massive ore zones. Kaolinite and illite also occur in varying proportions. A montmorillonite-rich layer of clay blanket is considered a marker layer defining the outermost boundary of the VMS ore bodies in the region.

4. Sampling and analytical methods

Both ore bodies are lens-like in shape and their projections onto the topographic map are circles with about diameters of about 400–500 m. The square grid sampling method is preferred due to its obvious advantage in better coverage of the surface and for generating data that are more suitable for better graphical evaluation and data presentation. Sampling intervals are also selected accordingly so as not to overlook any significant anomalies within which at least 4 samples should be taken (Rose *et al.* 1981). Samples were collected from an area of about 3 km^2 combined and the samples were taken at equal intervals, every 40 m along evenly spaced lines of a square grid on a 1:2000 scale map. A total of 250 samples from the Killik and 239 samples from the Köprübaşı site were collected to carry out this research (Figs. 2b).

The samples were taken from zone B. Due to the intense vegetation and rough topography, remarkable zonal variations in the soil profiles were observed throughout the study area during the orientation survey. Average sampling depth was about 20 cm in the region (Zone B could reach up to 1.5 m of depth in places). Cu, Zn, and Pb variations throughout the zone are found to be fairly uniform. About 200–250 g of soil samples was collected, from which splits of 20–50 g were prepared for the X-ray fluorescence (XRF) analyses. Samples were heated at 105 °C for 24 h, crushed to powder, and screened using an 80-mesh sieve to acquire 177-µm particle size, which is considered to be ideal for soil samples (Rose *et al.* 1981; Thomson 1986). Pressed powder pellets with 40-mm diameters were prepared from about 6 g of sample mixed with a PVA binding agent, backed by about 5 g of boric acid powder under 300 kg/cm^2 pressure for XRF measurements (Schroeder *et al.* 1980). XRF was chosen because of its superiority in sample preparation considering the number of samples being analyzed. The XRF measurements were carried out at the Geological Engineering Department of Karadeniz Technical University (Trabzon, Turkey) using a JEOL SX2 XRF analyzer employing an Rh X-ray tube and LIF 200 crystal. Analyses were tested using a PerkinElmer AAS randomly. Total metal values were measured with ±3% precision. Averages of 3 readings were taken for each element. The spectrometer was calibrated using US Geological Survey and Geostandards recommendations.

5. Assessment of background and threshold values

Normal abundance of any element in unmineralized and uncultivated soils (or earth surface) is considered to be natural background in a broad sense. It may vary depending on the soil type and associated conditions. Threshold, on the other hand, is the upper limit of the background populations in the simplest term. It is a boundary value over which anomalous values and under which background values are located. In some complicated cases, more than one threshold value could be considered. Setting this value right is highly critical since the fate of exploration programs is reliant on it. If it is set higher, some meaningful populations would be overlooked, and if set lower, some meaningless populations would be overrated. Consequently, such unsuccessful practices will cost time and capital.

The following were considered in setting threshold values and distinguishing anomalous populations from background populations: extent of the data and their statistical and graphical assessment, objective of the study, and nature of the region's soils (e.g., higher base metal contents). Since the log concentration is generally the best approach in studying the distribution frequency of elements, the same procedure was applied in this study. Local threshold values for the region were then determined through a combination of histograms of the element distribution frequencies and adding multiple folds of standard deviations to the local background values (Shaw 1961), which were the arithmetic means of whole analyses. Calculated values are then evaluated first with the histograms and then with the anomaly maps.

In geochemical prospecting, the process of distinguishing anomalous values from background values and determining threshold values in log-normalized distribution frequencies of concentrations is shown in Figure 3. As can be seen, both background and anomalous populations show distinct peaks. The intercept is taken as the regional threshold. Sampling from remote sites (in nearby areas) away from the mineralized areas for setting background values still yielded much higher values in comparison to the world average soil values. This itself is a significant outcome of the study, because world average values for uncultivated soils are 36 ppm for zinc, 12 ppm for copper, and 17 ppm for lead (Rose *et al.* 1981) (Table 1). Regional background values determined during orientation study were 70–125 ppm for zinc (2- to 3-fold the world average), 32–79 ppm for copper (3- to 6-fold the world average), and 141–158 ppm for lead (8- to 9-fold the world average) (Table 2). Tables 3 and 4 list sample location-based analysis for all 3 elements in the soils at both the Harşit-Köprübaşı and Espiye-Killik sites.

Figures 4A and 4B show the log-normal distribution histogram of Zn concentrations and distribution of these values in soils over the Köprübaşı-Harşit deposit. In these soils, regional background for zinc is 70 ppm, arithmetic mean (x) is 102 ppm, and standard deviation (s) is 27 ppm. Calculated local thresholds based on these values are 129 ppm (x + s), 156 ppm (x + 2s), and 183 ppm (x + 3s).

Log-normal distribution histogram and distribution of Cu concentrations in the same soils are shown in Figures 5A and 5B. In these soils, regional background for copper is 35 ppm, arithmetic mean (x) is 41 ppm, and standard deviation (s) is 14 ppm. Calculated local thresholds based on these values are 55 ppm (x + s), 69 ppm (x + 2s), and 83 ppm (x + 3s). Main sources of copper in the VMS deposits of the region are mainly Cu-bearing sulfides and sulfosalts, and, to a lesser extent, pyrite, which are all relatively low or nil in the ore mineral paragenesis (excluding pyrite). This is the main reason why copper is comparatively low in these soils.

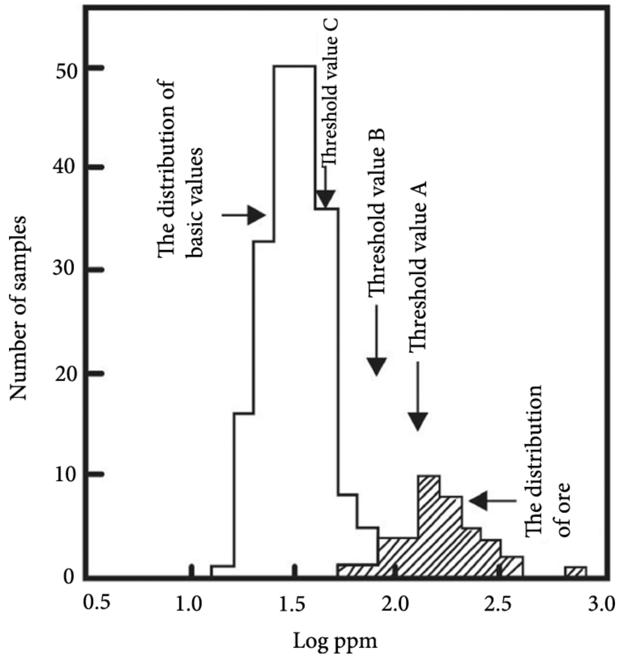

Figure 3. Distribution of the background, threshold, and anomaly values (Rose *et al.* 1981).

Table 1. World average values of Zn, Cu, and Pb in soils, felsic rocks, and earth crust in parts per million (ppm).

	Zn	Cu	Pb
Clark	130	70	16
Felsic volcanics	60	30	48
Top soils	36 (10–300)	12 (2–100)	17 (2–2000)

Distribution of Pb concentrations in the same soils is somewhat different due to the lower mobility of lead and higher initial lead content of dacitic source rocks. The Pb log-normal distribution histogram and its concentration distribution are shown in Figures 6A and 6B. Regional background for lead is 158 ppm, arithmetic mean (x) is 184 ppm, and standard deviation (s) is 53 ppm. Calculated local thresholds are 237 ppm (x + s), 290 ppm (x +2s), 343 ppm (x + 3s), 396 ppm (x + 4s), and 449 ppm (x + 5s).

In the Killik (Espiye) prospect, source rocks are essentially comparable. However, ore mineral paragenesis is different than that of Harşit in that chalcopyrite (main source for Cu) and sphalerite (main source for Zn) predominate and galena becomes minor to trace. This is in turn attributed to the distribution of the elements concentrations in the soils. The log-normal distribution histogram and the concentration distribution of Zn are shown in Figures 7A and 7B. Its regional background is 125 ppm, arithmetic mean (x) is 127 ppm, and standard deviation (s) is 38 ppm. Calculated local thresholds are 165 ppm (x + s), 203 ppm (x + 2s), and 241 ppm (x + 3s).

A histogram for log-normal distribution of Cu and its concentration distribution are shown in Figures 8A and 8B. Regional background for Cu is 79 ppm, arithmetic mean (x) is 107 ppm, and standard deviation (s) is 30 ppm. Calculated local thresholds are 137 ppm (x + s), 167 ppm (x + 2s), and 197 ppm (x + 3s).

Log-normal distribution histogram for Pb and its concentration distribution are shown in Figures 9A and 9B. Regional background for Pb is 141 ppm, arithmetic mean (x) is 170 ppm, and standard deviation (s) is 51 ppm. Calculated local thresholds are 221 ppm (x + s), 272 ppm (x + 2s), 323 ppm (x + 3s), 374 ppm (x + 4s), and 425 ppm (x + 5s).

Table 2. Regional background, local thresholds, and anomaly values for the elements of interest in the soils developed over Harşit (Köprübaşı) and Killik (Espiye) ore deposits.

Location	Element	Regional background	Local thresholds	Average anomalous values
Harşit-Köprübaşı	Zn	70	129–156–183	316
	Cu	32	55–69–83	200
	Pb	158	237–290–343–396–449	1000
Killik-Espiye	Zn	125	165–203–241	630
	Cu	79	137–167–197	562
	Pb	141	221–272–323–374–425	1995

Table 3. Concentrations (ppm) of Zn, Cu, and Pb in the Köprübaşı-Harşit soils analyzed, which were used to construct the concentration contour maps.

Pb (ppm)									Cu (ppm)									Zn (ppm)								
215	139	97	95	1090	270	159	125	100	82	13	40	71	232	59	11	128	17	153	110	91	102	370	158	87	79	68
200	108	157	78	575	270	253	85	95	10	12	11	66	181	59	50	110	16	84	101	138	126	253	123	114	79	79
78	93	215	225	291	172	267	10	85	95	43	56	77	100	142	11	46	14	230	79	82	92	341	92	89	74	71
180	63	125	255	575	400	242	55	115	82	10	55	70	115	50	16	48	11	94	107	76	131	175	125	68	71	74
360	40	79	245	155	360	159	157	175	91	24	52	64	154	65	17	47	14	153	78	107	125	91	115	80	102	76
355	48	108	635	159	430	200	85	160	110	29	57	64	73	385	13	48	16	156	61	80	120	82	189	82	102	71
360	82	62	255	255	475	185	188	267	128	11	11	48	58	47	90	45	12	196	114	82	114	136	141	113	405	76
650	82	32	200	165	263	188	155	70	111	23	129	10	109	95	16	38	25	175	79	113	102	140	114	89	98	83
3770	60	161	215	194	232	270	270	175	201	10	55	70	99	59	13	33	37	241	89	75	105	115	142	106	74	81
6579	95	157	255	145	240	200	155	185	279	23	118	67	68	141	13	37	31	405	91	73	142	82	128	116	71	77
140	81	110	225	125	330	191	188	115	75	26	115	46	133	203	9	34	38	209	65	88	103	83	92	69	91	102
616	97	135	575	145	330	175	113	125	100	11	95	49	106	66	7	32	37	263	63	70	90	84	102	102	120	71
93	108	516	178	175	2264	139	108	125	56	17	11	40	103	83	12	33	32	79	79	326	84	57	207	92	220	71
125	170	77	129	140	450	125	147	160	59	25	12	44	51	51	11	35	40	83	123	136	83	57	146	79	82	89
145	223	245	225	125	287	294	300	125	96	32	42	68	116	66	35	37	32	131	138	92	126	82	128	125	470	79
172	173	285	240	110	226	225	85	115	58	29	48	72	115	56	19	34	35	89	122	103	170	125	116	79	96	88
160	124	1225	270	110	267	100	140	115	41	23	123	61	98	56	18	18	30	131	104	128	68	82	141	79	75	89
220	194	400	215	127	320	85	225	140	58	17	73	73	73	42	73	15	30	115	67	115	153	64	113	79	71	155
141	242	100	215	500	141	125	115	140	80	10	56	100	84	59	85	14	36	72	134	92	140	183	89	102	79	71
90	186	550	48	745	412	110	81	114	47	27	108	145	114	51	22	16	37	71	79	126	94	218	206	65	102	95
1510	175	345	215	890	287	91	67	65	126	10	80	145	57	54	23	17	23	65	159	99	91	164	48	68	77	126
141	212	130	226	157	255	100	63	315	51	10	79	81	112	51	23	13	28	68	216	93	98	140	97	62	68	160
200	207	860	200	300	225	127	115	95	57	16	109	58	82	10	45	16	28	72	155	128	115	128	88	64	61	77
141	415	1440	62	255	255	172	115	160	11	10	146	82	131	32	41	15	20	137	307	128	99	123	88	64	68	77
108	194	145	77	172	294	125	112	291	10	34	72	63	73	11	125	18	29	77	91	91	99	91	89	64	68	67
178	127	226	191	1100	291	139	78	287	43	13	69	69	88	13	54	14	20	61	68	106	91	354	91	69	61	68
275	150	215	194	430	251	147	270	330	13	42	75	75	85	10	130	12	16	57	91	92	175	169	83	71	71	102
140	285	115	155	135	127				26	13	15	13	15	15				68	64	68	65	64	60			

Table 4. Concentrations (ppm) of Zn, Cu, and Pb in the Espiye-Killik soils analyzed, which were used to construct the concentration contour maps.

Pb (ppm)									Cu (ppm)									Zn (ppm)								
67	126	471	122	67	92	126	94	194	113	96	95	83	119	70	69	192	97	147	48	246	587	196	49	127	45	94
220	157	3646	122	522	65	157	100	129	58	67	94	108	112	80	100	324	69	96	176	63	168	309	3096	41	217	64
100	126	2923	1008	300	129	94	33	129	162	68	67	134	90	68	431	7	157	73	36	251	124	117	86	412	139	74
126	94	238	92	291	133	94	100	226	61	85	126	209	281	90	406	233	102	261	91	446	172	247	43	148	78	109
126	63	1163	122	9415	97	61	100	97	87	113	101	55	102	127	17	111	74	63	130	170	108	124	206	78	100	139
100	153	922	126	97	162	61	67	129	145	90	111	70	74	967	210	181	132	254	618	177	350	439	70	12	176	159
251	503	1873	92	194	162	122	67	129	68	55	74	97	68	119	89	157	912	134	294	65	127	32	44	376	160	129
409	153	178	67	97	346	64	133	162	60	64	81	61	90	320	97	152	111	198	1084	124	451	160	157	108	89	88
251	157	268	324	97	346	92	67	162	112	71	79	59	867	98	307	147	73	263	23	155	147	156	134	89	258	99
126	660	208	129	97	189	31	63	226	82	58	84	241	333	119	112	406	91	157	323	43	57	271	342	93	98	58
157	597	208	162	129	1634	167	94	324	59	73	112	112	81	196	65	198	162	23	31	47	61	5	108	299	91	285
126	597	297	129	129	4023	67	97	194	57	175	76	80	140	164	359	71	116	192	157	298	5	309	289	70	116	778
94	346	157	97	2043	3453	283	67	200	45	230	95	81	59	80	149	98	93	89	103	76	76	85	66	68	48	139
1320	367	189	162	9334	194	283	67	233	365	185	86	79	85	359	77	75	195	92	221	22	515	165	87	89	1007	154
251	519	157	97	1509	97	126	65	100	75	195	186	119	75	399	67	678	184	111	156	94	116	230	72	229	72	184
346	458	126	129	200	97	126	97	194	83	177	57	75	79	75	95	87	52	80	146	309	161	95	77	172	132	195
126	92	94	129	251	712	126	97	251	103	75	78	122	71	121	79	79	140	265	40	134	194	179	206	107	150	108
183	126	251	32	167	189	126	150	194	59	71	80	73	68	109	102	114	82	179	605	119	103	378	170	103	149	150
122	126	126	100	283	157	63	833	251	74	68	62	68	472	101	60	60	59	54	112	260	87	175	92	112	54	144
244	94	122	129	67	911	126	194	194	60	81	59	129	161	90	88	73	1034	283	132	111	49	103	150	172	95	185
283	346	94	67	153	5469	63	200	324	64	53	136	63	168	68	87	54	82	72	139	114	172	77	195	127	183	99
244	122	126	65	67	133	126	226	259	49	53	63	76	99	69	151	131	342	62	103	44	103	120	93	67	216	21
59	183	122	97	122	100	167	67	162	85	88	143	100	61	102	85	165	261	194	119	172	279	83	234	113	92	151
149	122	367	97	100	133	200	233	129	71	107	86	107	63	457	60	121	80	91	172	164	291	650	129	221	99	82
61	122	183	97	61	300	94	100	129	70	96	119	97	95	63	73	226	181	22	151	182	83	175	103	88	206	282
31	63	183	97	129	67	126	133	133	186	177	311	219	484	75	60	212	104	240	85	376	251	103	84	136	48	194
446	126	122	97	214	157				550	107	71	98	66	61				130	1545	123	23	95	119			

6. Assessment of anomalous values

When the distribution of Zn concentrations in the subject areas was considered, anomalous values cover rather larger areas. Most of these areas superimpose on the primary ore deposition sites.

For the Köprübaşı deposit, when the lowest reported Zn content, 4% à 40,000 ppm, is taken and considering that host rocks contain about 80 ppm Zn (Köprübaşı 1992), the concentration ratio for Zn is 40,000:80 ppm = 500. However, in the overlying soils, the average of anomalous values is 316 ppm and the regional background is 80 ppm. Thus, the Zn contrast is 316:80 ppm = 4. The ratio of these 2 contrasts is 4:500 = 1/125. This means that the Zn content of overlying soils is 1/125 of the primary ore mineralization.

The Cu content is 0.5% (5000 ppm) and host rocks contain about 45 ppm Cu (Köprübaşı 1992). Thus, the concentration ratio for Cu is 5000:45 ppm = 111. In the overlying soils, the average of anomalous values is 200 ppm and the regional background is 32 ppm. Hence, Cu contrast is 6. The ratio of the contrasts is 1/19. This means that the Cu content of overlying soils is 1/19 of the primary ore mineralization.

As for Pb, the lowest reported content is 4% (40,000 ppm). Host rocks contain about 50 ppm (Köprübaşı 1992). The concentration ratio for Pb is 800. In the overlying soils, the average of anomalous values for Pb is 794 ppm and the regional background is 158 ppm. As a result, Pb contrast is 5. The ratio of the contrasts is 1/160. This indicates that the Pb content of overlying soils is 1/160 of the underlying source deposit.

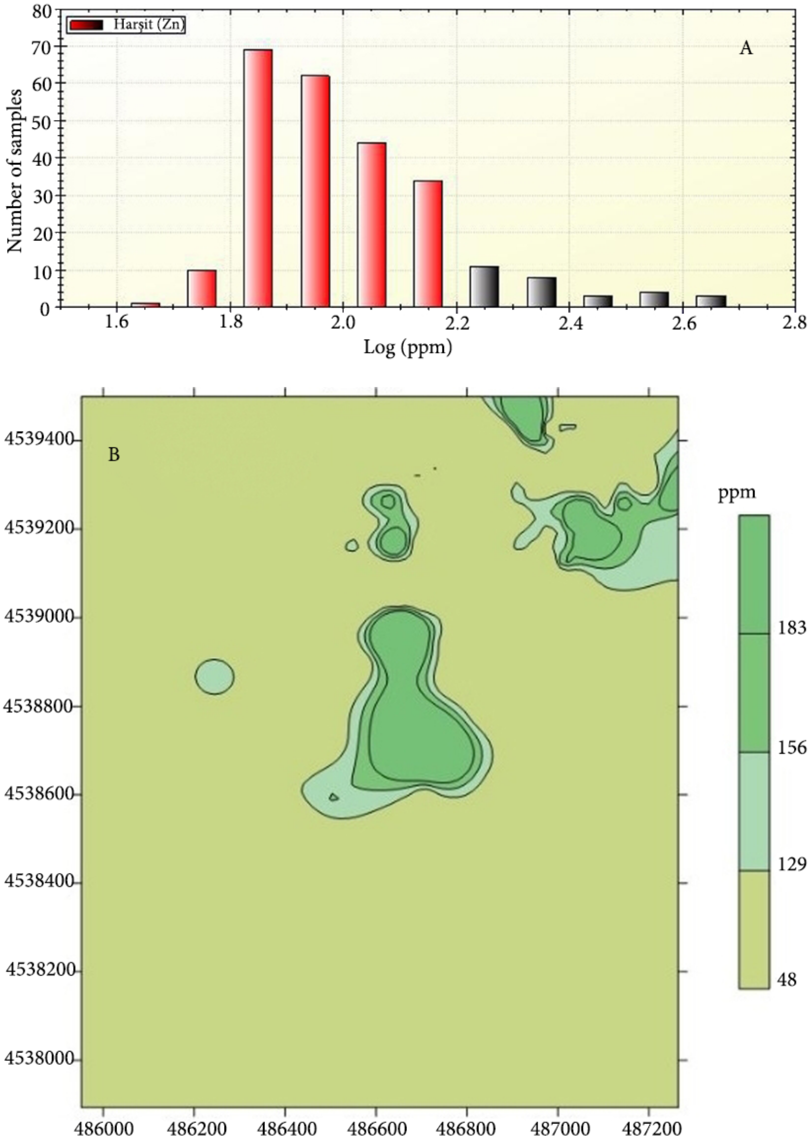

Figure 4. (A) Histogram of frequency distribution of Zn and (B) contour map of its concentrations in soils developed over the Harşit-Köprübaşı VMS deposit.

Soils developed over the Killik deposit, on the other hand, are essentially similar in acidity and field appearance. However, base metal contents are a bit different because of the nature of underlying ore mineralization. When the lowest reported content of Zn (5% à 50,000 ppm) is taken and host rocks contain about 80 ppm (Çakır & Çelik 1982; Hokelekli & Boynukalın 1982), the concentration ratio for Zn is 50,000:80 ppm = 625. However, in the overlying soils, the average of the anomalous values is 630 ppm and the regional background is 125 ppm. Thus, Zn contrast is 5. The ratio of the contrasts is 1/125.

Reported Cu content is 2.5% (25,000 ppm) and host rocks contain about 45 ppm Cu (Köprübaşı 1992). Thus, the concentration ratio for Cu is then 555. In the overlying soils, the average of the anomalous values is 562 ppm and the regional background is 79 ppm. Consequently, Cu contrast is 7. The ratio of the contrasts is 1/79.

The lowest reported content for Pb is 0.7% (7000 ppm). Dacitic host rocks contain about 50 ppm Pb on average (Köprübaşı 1992). Thus, contrast for Pb is 140. In the overlying soils, the average of the anomalous values for Pb is 1995 ppm and the regional background is 141 ppm. Therefore, Pb contrast is 14. The ratio of the contrasts is 1/10.

7. Discussion

A total of 489 samples were collected from zone B of the soil profiles developed over the Harşit-Köprübaşı and Espiye-Killik deposits to investigate Cu, Zn, and Pb

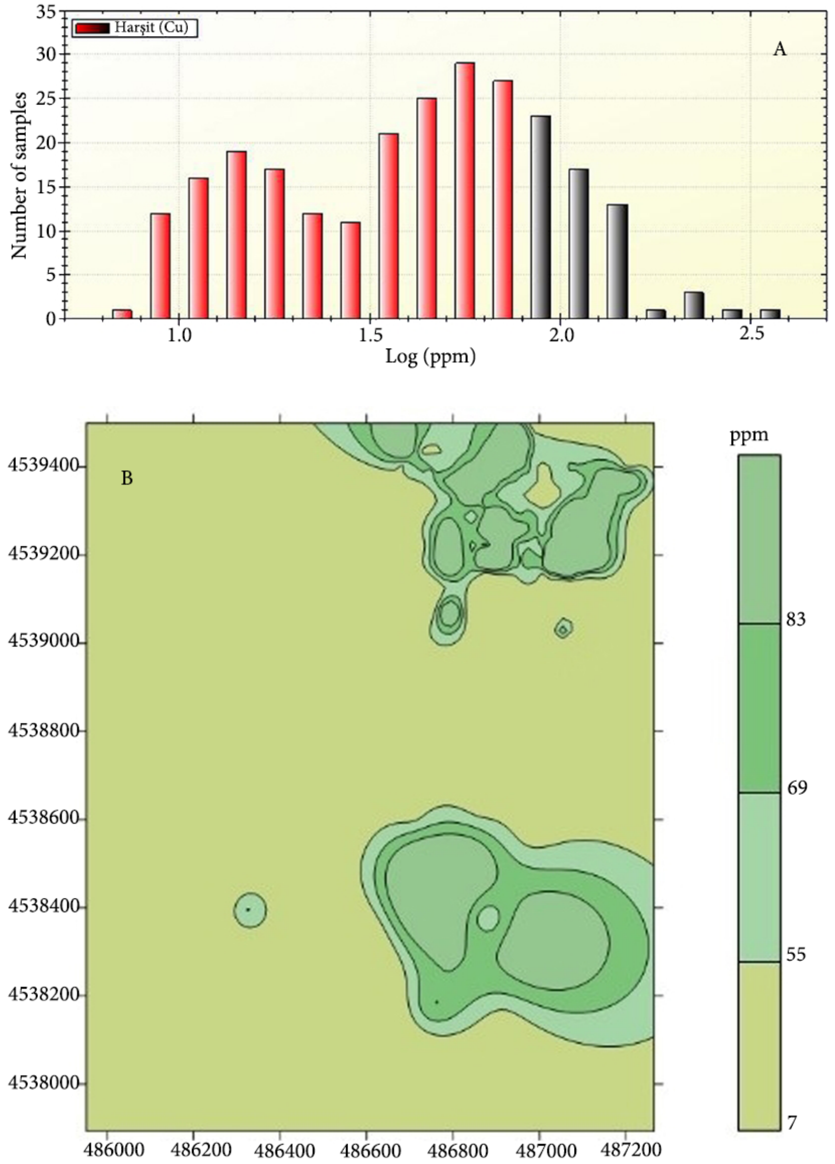

Figure 5. (A) Histogram of frequency distribution of Cu and (B) contour map of its concentrations in soils developed over the Harşit-Köprübaşı VMS deposit.

concentrations and their distribution patterns to relate all these to the underlying polymetallic massive sulfide bodies. These elements occur in major quantities in these ore bodies, mainly in the form of sulfide minerals. Since the study area is within a volcanic arc environment in a world-class metallogenic belt (Çiftçi *et al.* 2005), soil values were comparatively evaluated and found to be much higher than those values (Table 2).

The most significant outcome of the study was to acquire explicit data to be useful in locating drillings in such areas in that ore bodies occur as buried and are overlain by a thick soil cover. Thus, any successful outcome would mitigate the exploration costs compared to drilling and subsurface activities. Zn, Cu, and Pb were therefore used as indicator elements to investigate the relationship of their concentrations and distribution patterns to a 2 completely delineated ore deposits in an orientation survey in that they served as natural physical models. Contour maps of concentrations for the elements were constructed.

These elements revealed high contrasts and overlapped each other at the location of the ore deposits due to enhancement of the anomalies by hydromorphic dispersion, which is an indication that soil samples would produce reliable and repeatable results. The successful

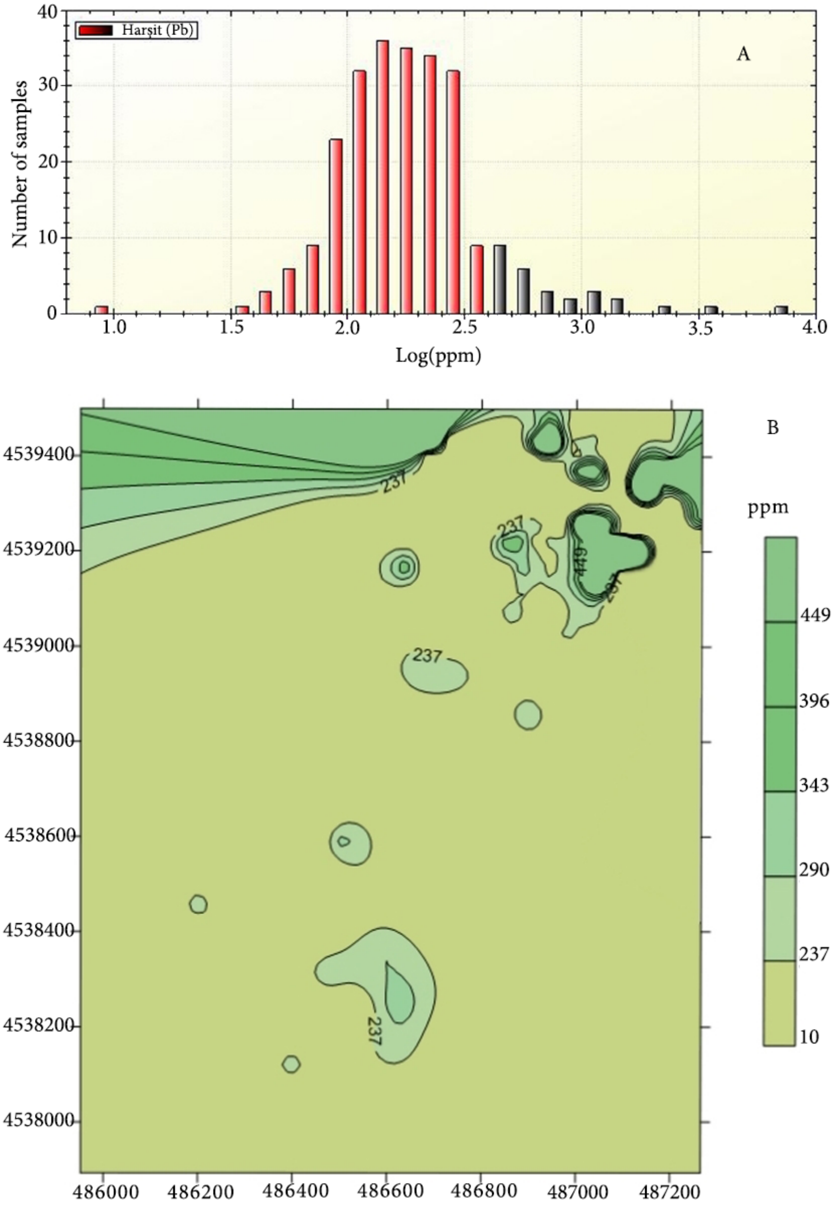

Figure 6. (A) Histogram of frequency distribution of Pb and (B) contour map of Pb concentrations in the soils developed over the Harşit-Köprübaşı VMS deposit.

delineation of the deposits is remarkable considering the rough topography and the climatic limitations.

Success of such efforts is governed by sampling strategies, analyses, and data evaluation in order to find representative regional backgrounds, to set proper threshold values, and to find realistic anomalous areas (Thomson 1986).

Outcomes of the study were tested on 2 sites with essentially similar soil characteristics but developed over 2 ore bodies with dissimilar element contents. Although zinc is of common share in both deposits, while copper is the major element in the Killik deposit, it is minor to trace in the Köprübaşı deposit. On the other hand, lead is just the opposite of copper, major in the Harşit deposit and minor in the Killik. Thus, their distribution patterns and concentration contrasts indicate the behavioral difference for copper and lead under similar geochemical conditions. Since anomalous areas overlapped underlying delineated ore bodies fairly well in both sites, this method could be used in this region or other areas having similar characteristics with a high level of confidence.

Calculated contrast ratios for the elements are in good agreement with the element contents of the deposits (Table 5). Zn behaves basically identically since it is a major

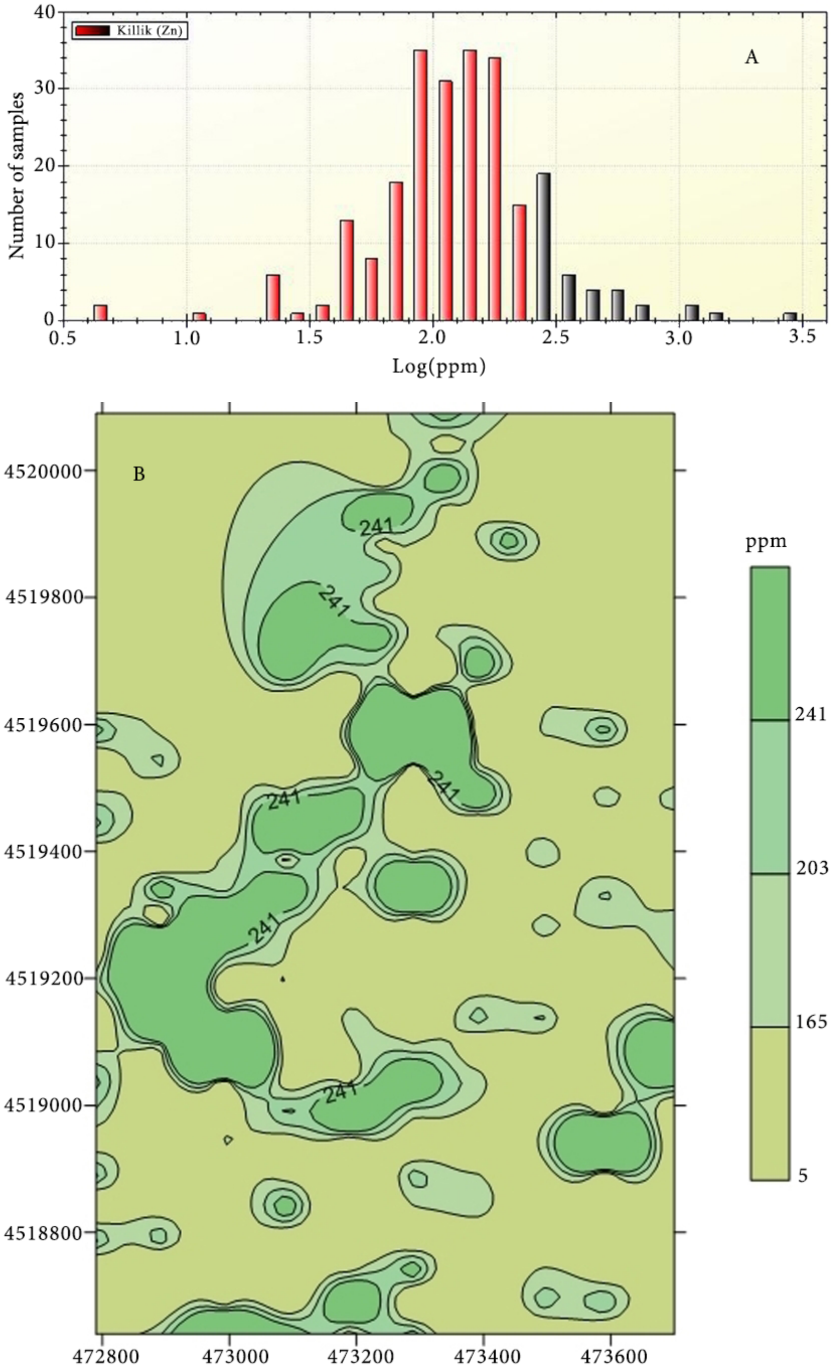

Figure 7. (A) Histogram of frequency distribution of Zn and (B) contour map of Zn concentrations in the soils developed over the Killik-Espiye VMS deposit.

component of both ore bodies. Moreover, soils are very similar in terms of Eh and pH conditions. However, Cu in the Killik soils and Pb in the Köprübaşı soils set the major differences as inherited from the underlying ore bodies. Since Cu is the major component of the Killik ore body, soils overlying the deposit are about 4 times higher than that of Köprübaşı soils in terms of the contrast ratios. Correspondingly, the Pb is about 16 times higher than that of Killik soils in terms of the contrast ratios.

Both ore deposits were mined out through underground mining methods. Since the surface was not contaminated, the topography is suitable and the presences of a soil cover

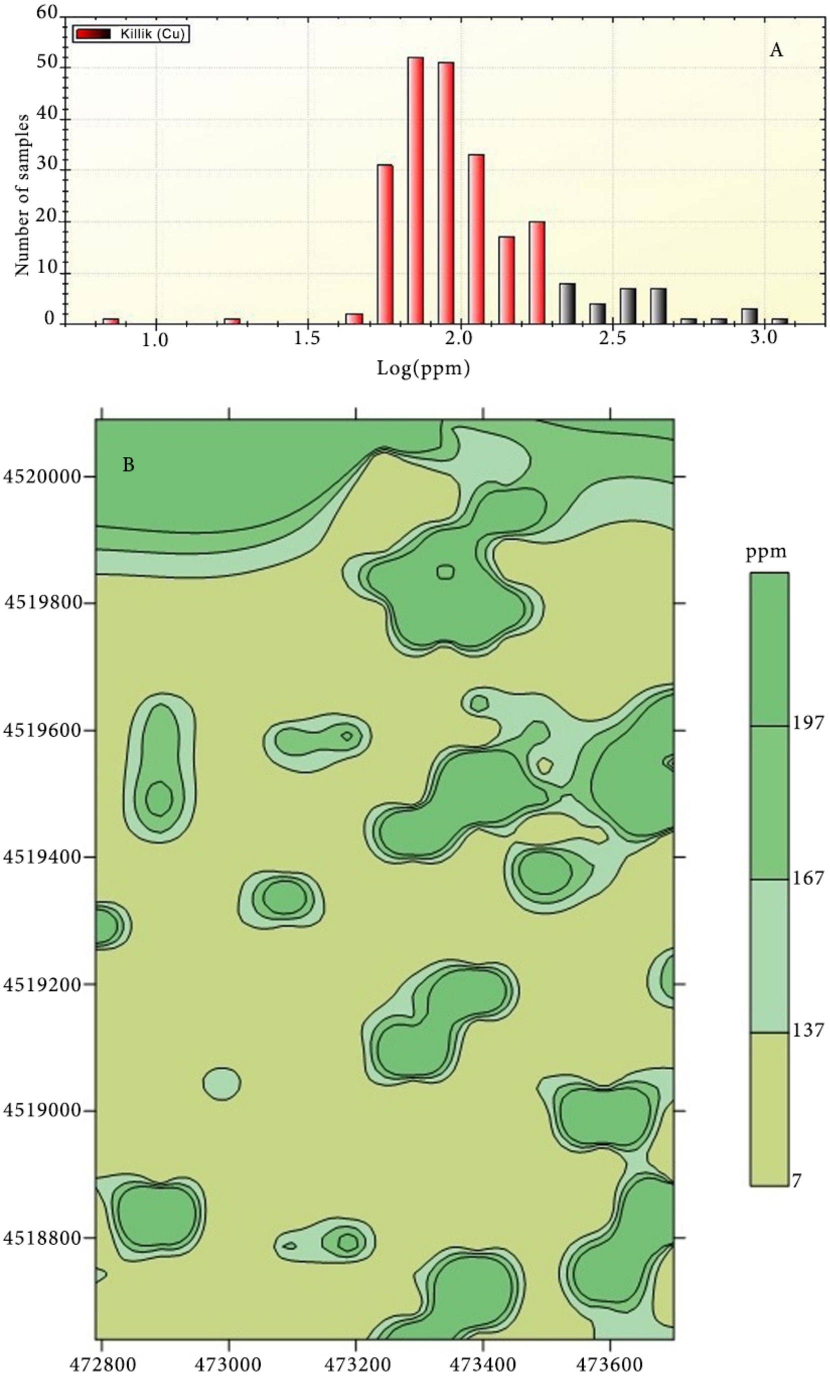

Figure 8. (A) Frequency distribution histogram of Cu and (B) contour map of Cu concentrations in the soils developed over the Espiye-Killik VMS deposit.

3–5 m thick and clastic and hydromorphic dispersion from the buried ore mineralizations were expected.

Zinc occurs as a trace constituent in many common minerals and rocks. However, its most important primary mineral is the zinc sulfide, sphalerite or zincblende (ZnS), and wurtzite, a low-temperature and low-pressure diform of zinc sulfide. Oxide, sulfate, carbonate, and hydroxide forms of the zinc minerals are also abundant in nature, occurring mostly as weathering products of sphalerite in environments with high Eh potentials. In igneous rocks, it is contained mostly in pyroxenes, amphiboles, micas, garnets, and magnetite. Modes of presence of zinc in a

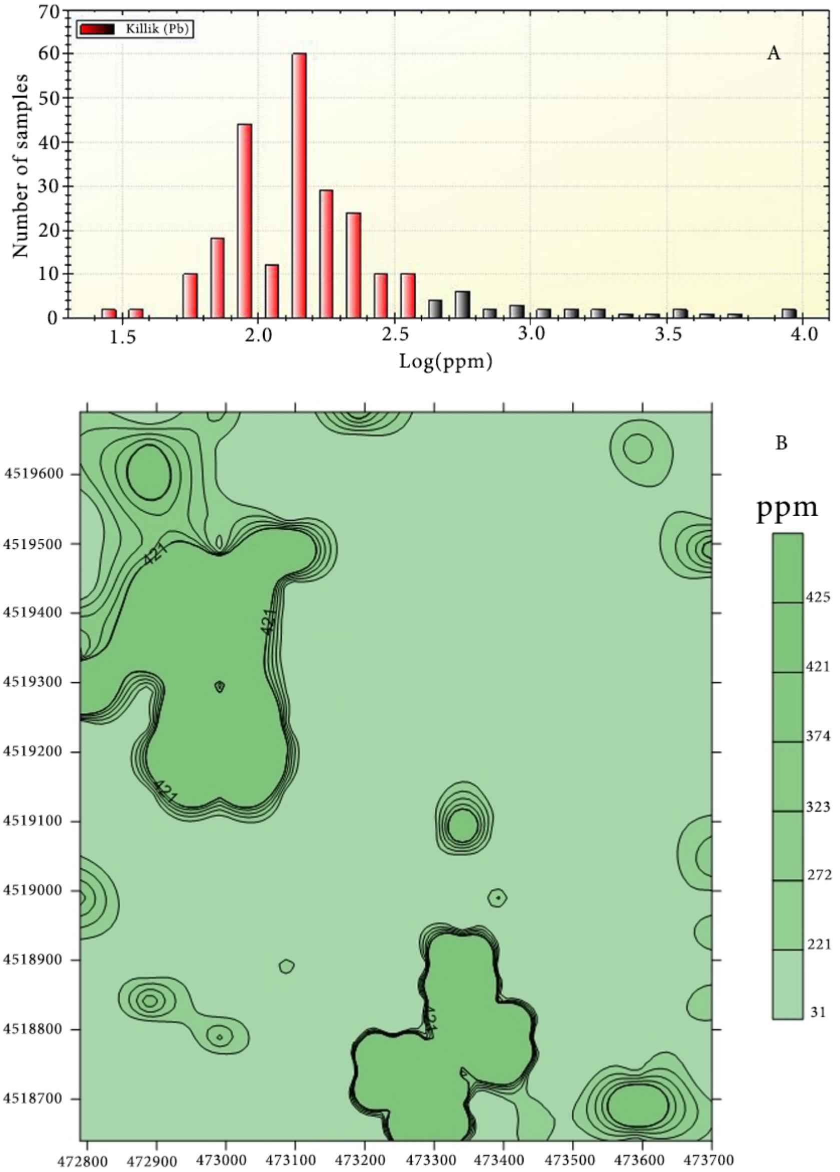

Figure 9. (A) Histogram of frequency distribution of Pb and (B) contour map of Pb concentrations in the soils developed over the Killik-Espiye VMS deposit.

region's rocks are expected as zinc sulfide. In soils, zinc mobility is controlled mainly by pH and Eh conditions. Under acidic and oxidizing conditions, its mobility is high (Levinson 1980; Riemann & Caritat 1998). Consequently, larger areal coverage of anomalous values in the soils and the lower contrasts are the consequences of these geochemical behaviors. It occurs as adsorbed onto clays, Fe-Mn oxides, and organic matter.

The most widespread primary copper mineral in the earth's crust is the copper iron sulfide, chalcopyrite ($CuFeS_2$). Other sulfides (e.g., bornite, covellite), oxide (cuprite and tenorite), and sulfate and carbonate-hydroxy-carbonate (e.g., azurite, malachite) forms of the copper minerals are also common in nature. Copper also occurs in metallic form. However, copper also occurs in rock-forming minerals, e.g., biotite, pyroxenes, amphiboles, and magnetite. Felsic volcanics normally contain less copper compared to mafic rocks. The highly pyritized nature of the region's felsic volcanics accounts for their high copper content; that is, copper is present either in the pyrite structure or as chalcopyrite or oxidized copper species, due mainly to its paragenetic association with pyrite. In soils, the mobility of copper is controlled essentially by pH and Eh. Under acidic conditions, it is highly mobile

Table 5. Contrast ratios of the elements of interest calculated for the 2 deposits.

	Harşit-Köprübaşı	Espiye-Killik
Zn	1/125	1/125
Cu	1/19	1/79
Pb	1/160	1/10

(Levinson 1980). In environments with high Eh potential, its mobility is moderate. In neutral to alkaline conditions, the mobility of copper is more like that of zinc (Riemann & Caritat 1998) and its occurrence in the environment resembles that of zinc. Thus, in the soils of the study area, the mobility of copper would be expected to be moderate to high. As a result, the copper enrichment in the soils was not as high as that of the parent rocks. Thus, the larger areal coverage of anomalous values in the soils and lower contrasts are the consequence of the geochemical behavior of Cu in such acidic environments.

Lead in natural environments essentially occurs as galena (sulfide form) and cerussite (carbonate form). Sulfate and oxide forms are relatively rare. It is also found as a trace constituent of many rock-forming minerals. Lead tends to be higher in felsic rocks compared to both copper and zinc. In soils, lead that migrates through the organic-rich upper layers, either in the dissolved or colloidal form, is likely to be removed from the solution by adsorption or exchange reactions with the clays, metal oxides, and organic matter that accumulate in the lower horizon B. In natural environments, the solubility of lead is affected by reactions precipitating solid compounds, adsorption and ion exchange reactions with solid particles, and the formation of aqueous complexes. The first 2 processes remove lead from solution, immobilizing it. Lead is known to be highly immobile under both reducing and oxidizing conditions and it bonds strongly to adsorbents (e.g., organic matter); thus, it does not readily migrate. In both acidic and alkaline conditions, mobility of lead is low (Riemann & Caritat 1998) and it occurs as adsorbed onto organics and phases with unbalanced surfaces. As a result, the constricted areal coverage of anomalous values in the soils and the higher contrasts are the consequence of the geochemical behavior of Pb in surface environments.

In soil analyses, the arithmetic mean and the median values of all 3 elements are quite different, requiring a log-normal distribution due to high anomaly contrast. The elements have highly skewed data, suggesting a log-normal distribution. All elements have skewness constants larger than 4. This conclusion is also supported by the chi-square tests on the data sets.

8. Conclusions

The following conclusions can be drawn based on the results acquired from soil analyses carried out for the Harşit-Köprübaşı and the Espiye-Killik sites.

- Soil sampling gives highly reliable and repeatable results in locating ore deposits.
- Zn shows larger concentration distributions in both sites due mainly to its high mobility in acidic environments. However, it showed low contrast in both sites.
- Cu behaves like Zn due to high mobility in the surficial environments resulting in extensive areal coverage. However, it showed low contrast in the Killik area and high contrast in the Köprübaşı area.
- Pb gave localized anomalies overlapping the ore bodies due essentially to its lower mobility. However, it showed high contrast in the Killik area and low contrast in the Köprübaşı area.
- Concentration contrasts appear to be directly controlled by the source from which clastic and hydromorphic dispersion originated rather than the rocks from which the soils were developed.
- In local threshold calculations, local background values in combination with histograms were used to set optimal values for the study area.
- Multiple folds of standard deviations were added to the mean values to narrow the areal coverage down to much more meaningful levels.
- In comparison to the usual extensive anomalies produced by Zn and Cu, Pb gave better results and could therefore be used as an exploration guide in regional surveys to narrow down the anomalous areas.

Acknowledgment

The authors thank Prof Dr Selçuk Tokel for his contribution and constructive criticism during the field work and preparation of the manuscript.

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