

Environmental Impact and Drainage Geochemistry in the Vicinity of the Harput Pb-Zn-Cu Veins, Elazığ, SE Turkey

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Abstract: The aim of this study was to examine the environmental impact of major, minor and rare-earth elements (REE) in spring waters and major and minor elements in stream sediments proximal to known vein-type Pb-Zn-Cu ores. Accordingly, a total of 21 water samples were collected from natural springs in the Köprücük, Çolaklı, Kabakçılar and Ekinli areas where ore-bearing rocks are widely exposed. Stream-sediment samples were taken from the Kurt, Kızıldağ and Karacalar and Billurik streams, and a total of 57 samples were sieved to three different size fractions (-80 +140, -140 +200 and -200 mesh) and analyzed by ICP-MS and IE methods. The concentrations of Al, Ba, Br, Fe, K, Mn, Na, Pb, SO₄, U and F in the spring waters are higher than the values recommended as the maximum allowable levels in drinking waters. In the stream-sediment samples, the -200 mesh fraction yielded Mo, Pb, Zn, As, U and Ca contents higher than the world average crustal composition; moreover, metal contents were found to be generally elevated in this stream-sediment size fraction. As values, in particular, are several times higher than the mean values for granitic rocks of the region. In correlation coefficient studies of the spring waters, it was observed that the REE are inversely related to pH and significantly positively related to SO₄, Fe and Al. Consequently, it is concluded that the concentrations of several major and minor elements and REE in the spring waters, and the distribution of elements in the different size fractions of the stream sediments, can be utilized both in geochemical prospecting and in identifying high risk areas for metal pollution.

Key Words: drainage geochemistry, REE, stream sediments, spring water, Elazığ, Turkey

GD Türkiye Harput (Elazığ) Civarı Pb-Zn-Cu Damarlarının Drenaj Jeokimyası ve Çevresel Etkileri

Özet: Çalışmanın amacı, cevherleşmelerin jeokimyasal prospeksiyon çalışmalarına katkısını ve çevresel etkisini incelemektir. Bu nedenle kaynak sularında ana, iz ve nadir toprak elementleri (NTE), dere kumlarında ise ana ve iz element derişimleri incelenmiştir. Bu amaçla, ceherleşmelere yakın, Köprücük, Çolaklı, Kabakçılar ve Ekinli civarından toplam 21 kaynak suyu örneği alındı. Kızıldağ, Kurt, Karacalar ve Billurik Dereden toplam 57 örnek üç farklı tane boyu (-80 +140, -140 +200 and -200 mesh) ICP-MS (inductively coupled plasma-mass spectroscopy) ve IE (ion electrode) yöntemi ile analiz edildi. Kaynak suları, element içerikleri tavsiye edilebilir içme suyu standartları ile karşılaştırılmış ve Al, Ba, Br, Fe, K, Mn, Na, Pb, SO₄, U ve F içeriklerinin, dere kumu örneklerinde ise Mo, Pb, Zn, As, U ve Ca medyan değerleri kıtasal kabuktaki ortalama element içeriklerinden yüksek olduğu, As, değerinin ise bölgedeki granitik kayalardaki ortalama değerden birkaç kat daha yüksek olduğu belirlenmiştir. Bunun yanında dere kumlarındaki element içeriklerinin ince taneli (-200 mesh) boyutta zenginleştiği saptanmıştır. Korelasyon katsayısı incelemelerinde NTE ile pH arasında ters, SO₄, Fe, Al arasında anlamlı pozitif ilişki gözlemlendi. Sonuç olarak gerek kaynak sularındaki element derişimleri ve gerekse dere kumlarının farklı tane boyu fraksiyonlarındaki element dağılımlarının jeokimyasal incelemelerinde ve bu bölgelerde metal kirliliğinin belirlenmesinde yararlı olabileceği düşünülmektedir.

Anahtar Sözcükler: drenaj jeokimyası, NTE, dere kumu, kaynak sular, Elazığ, Türkiye

Introduction

The study area is located in the eastern part of the Taurus Orogenic Belt where a variety of mineralization types occur. The Pb-Zn-Cu vein mineralization of the study area is associated with granitic, dioritic and basic volcanic rocks of the Coniacian–Campanian Elazığ Magmatites. Besides the Elazığ Magmatites, there are two different

units in the study area: the Middle Eocene–Oligocene Kırkgeçit Formation, and the Upper Miocene–Pliocene Karabakır Formation (Figure 1).

Environmental geochemical studies in the area were begun by Özdemir & Sağıroğlu (2000). They investigated Cu and other metals contaminations in soils, waters and plants in and around Maden Creek and identified indicator

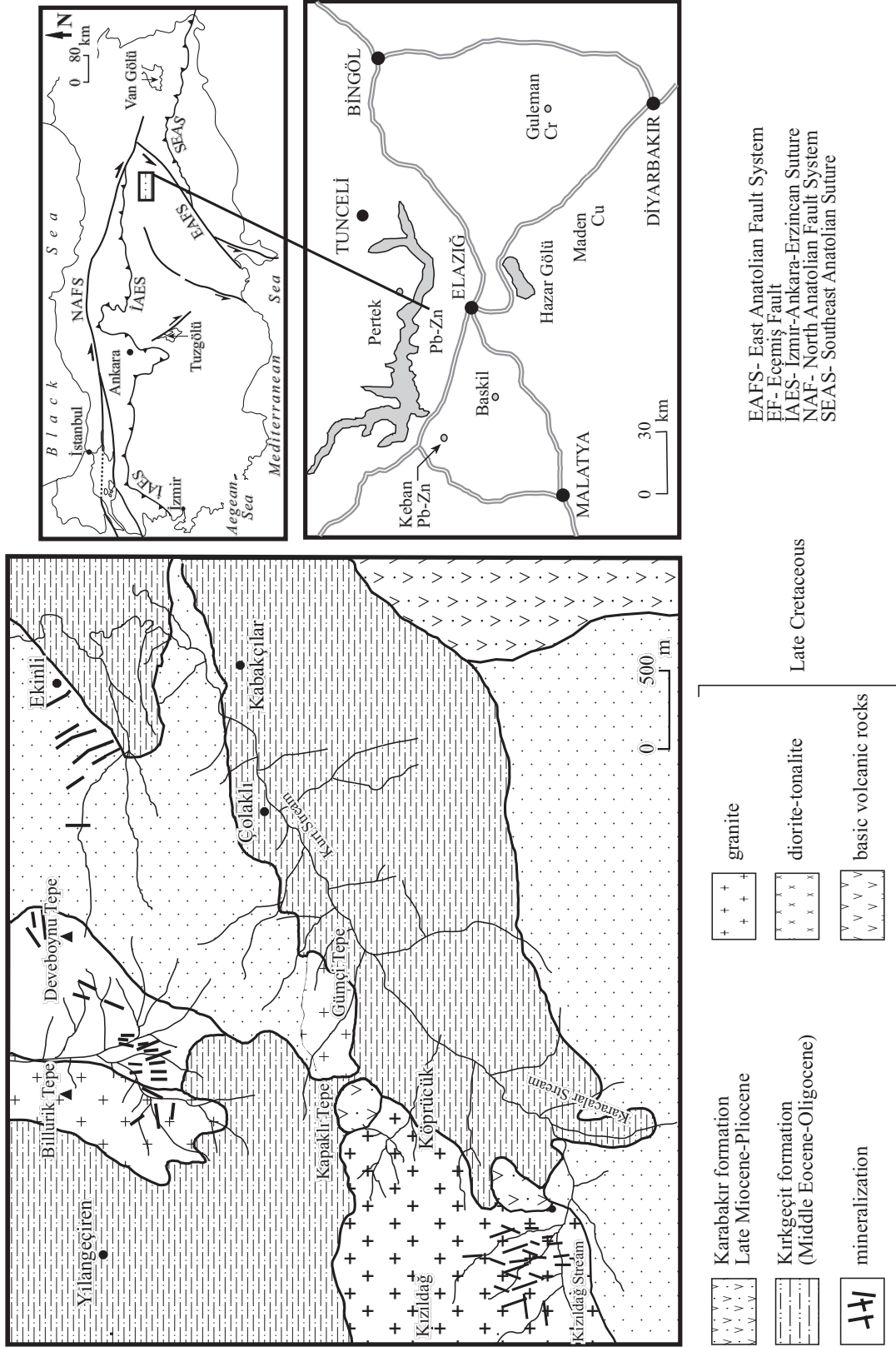


Figure 1. Location map and geology in the vicinity of Pb-Zn-Cu veins, modified from Sağiroğlu & Şaşmaz (2004).

plant types for copper. Kalender & Bölücek (2004) studied the impacts of Ag-Pb-Zn deposits on groundwater, stream sediments and plants (moss and algae) in the Euphrates River area. There have been several other key studies on pollution of spring waters and stream sediments in Turkey and elsewhere in the world: the lateral distribution of heavy metals around the Murgul mine and their environmental impacts (Akçay & Tüysüz 1997); heavy-metal pollution in sediments of the Pasvik River drainage (Dauvalter & Rognerud 2001); fluoride levels in the groundwater of the south-eastern part of the Ranga Reddy district (Sujatha 2003); hydrological and geochemical controls governing the distribution of trace metals in a mine-impacted lake (Martin & Calvert 2003); the geochemistry of some rare-earth elements in groundwater (Janssen & Verweij 2003); heavy-metal partitioning in river sediments severely polluted by acid mine drainage (Galan *et al.* 2003); and uranium contamination in ground and stream waters (Wine & Walt 2004).

As is well known, a number of ore minerals are altered by water and, consequently, display hydromorphic anomalies around ore deposits or in spring waters. River beds in the vicinity of mineral deposits also typically contain river sands that may yield various element anomalies. Therefore, the present study focuses on the drainage geochemistry and environmental impact of vein-type Pb-Zn-Cu ores exposed in the north-eastern part of the Harput (Elazığ) area. In this study, some of the element distributions in spring water and stream sediments of different size fractions (-80 +140, -140 +200, -200 mesh) were examined, as were the chemical behaviours of those elements and the relationship between high element concentrations and pH (Table 2 & Figure 4). The major- and trace-element concentrations of the water samples were compared with the values of the United States Environmental Protection Agency (USEPA) and some other drinking water standards and, as a result, potential threats to human health were determined. The element distributions in the stream-sediment and spring-water samples also were studied with respect to their contribution to geochemical prospecting studies.

Sampling and Analytical Methods

Water samples were collected from natural springs proximal to Pb-Zn veins situated in an area of magmatic

rocks near the villages of Köprücük, Çolaklı, Kabakçılar and Ekinli; (Figure 1, 21 samples [CL 1 to CL 22]; Figures 2 & 3). Sediment samples were collected from four areas: Kızıldağ, Karacalar and Kurt streams and Billurik Creek (19 samples – CS 1 to CS 19). Sampling was conducted in September 2003 (dry season), the month in which precipitation in the region is lowest (4.4 mm). The average temperature is 20.25 °C in September. The average temperature was 15.21°C between 1992 and 2001, and the average annual rainfall during that period was 372 mm (data were taken from reports of the Elazığ Meteorology Department). Water samples were taken using a hand pump and water sampler and filtered using 0.5-µm membrane filter paper (4.5 cm diameter); subsequently, 5 ml of prepared 65% concentrated HNO₃ solution were added to 250 ml of each water sample and the samples were stored in the laboratory at 4 °C until analysed. Spring-water samples were analysed for major, minor and rare-earth elements and SO₄ by ICP-MS and for F by specific IE (ion electrode) analysis. Detection limits were 20 ppb for SO₄ and 0.1 ppm for F. Other detection limits and the results of the analyses of the spring-water samples are given in Table 1. Temperature and pH measurements were conducted using a Thermo Orion Model 250 instrument at the sampling sites (Figures 2 & 3). The results of the pH measurements are given in Figure 4.

Each 2–3 kg sample of fine-grained sediment dug from a depth of about 10 cm was sieved using a 2 mm (BS10 mesh) stainless steel screen. The samples were then stored in polyethylene sample bags. Prior to analysis, the samples were dried in the laboratory and sifted using steel sieves to mesh sizes -80 +140 +200 (CS 1-CS 19; Figures 2 & 3). All sediment samples were analysed by ICP-MS (inductively coupled plasma-mass spectroscopy). 15 gr of each sediment sample was leached with 90 ml 2-2-2 HCl-HNO₃-H₂O at 95 °C for one hour, diluted to 300 ml, and then analysed by ICP-MS. Standard DS5 was used in the sediment analyses. Detection limits and the results of the sediment-sample analyses are given in Table 4.

Results and Discussion

Chemistry of the Spring-water Samples

The results of the analyses and summaries of statistical values for the spring-water samples are given in Table 1.

ENVIRONMENTAL IMPACT OF PB-ZN-CU ORES

Table 1. Element concentrations of the spring-water samples (in mg/L); SD: standard deviation; element contents of natural groundwater (in mg/L; Rose *et al.* 1979); *= Janssen & Verweij 2003); a– Ley 18284 (1969) Codigo Alimentario Argentino; Modificaciones (1988) and (1994); b– USEPA 1980, 2000.

Element	Mean	Median	SD	Max. value	Min. value	Ground-water	Max. allowed values	Detection Limits
Al	226	84.5	474	2274	38	10	50b	1
As	6.45	2.6	9.74	44.5	1.4	2	50a	0.5
B	42.55	40	13.27	69	20	10	-	20
Ba	48.39	38.07	26.72	102.05	5.2	20	50b	0.05
Br	131.41	123	37.03	194	85	20	10b	5
Ca	112849	79405	69513	265931	37118	50000	-	50
Cd	0.17	0.1	0.12	0.38	0.1	0.03	5b	0.05
Ce	1.71	0.35	6.06	28.84	0.2	-	-	0.01
Cl	6136	5000	37100	18000	3000	20000	4000b	1000
Co	0.62	0.16	1.6	7.6	0.03	0.1	-	0.02
Cr	2.47	2.1	1.56	8.3	1.2	1	50a	0.5
Cs	0.09	0.04	0	0.43	0.01	0.02	-	0.01
Cu	23	15	20	88	11.2	3	1000a.b	0.1
Fe	1046	59	2647	8917	10	100	300a.b	10
K	3827	557	4280	19107	557	3000	12000b	50
Li	6.20	5.5	5	18.2	0.6	3	-	0.1
Mg	14611	13284	7762	30115	4143	7000	50000b	50
Mn	115	8	263	954	3	15	50b	0.05
Mo	4.80	3.50	1.30	29.00	0.50	1.50	-	0.10
Na	18180	17735	6870	31801	6958	30000	20000b	50
P	1084	136	3858	16886	35	20	-	20
Pb	15.54	5.20	11.10	55.10	5.20	3	15b	10
Rb	3.18	0.57	2.40	7.48	0.57	1	-	0.01
S	44954	15000	14947	232000	4000	30000	-	1000
SO ₄	147706	49285	14947	762285	13142	-	250000b	100
Sb	0.57	0.43	0.50	2.21	0.25	2.00	6b	0.05
Se	0.78	0.70	0.34	1.80	0.70	0.40	50b	0.50
Si	19593	10646	6096	28618	10646	7466	-	1
Sn	0.85	0.46	0.90	2.57	0.40	0.10	-	0.05
Sr	390	353	234	944	112	400	-	0.01
U	31.29	15.89	39.79	135.22	0.92	1	30b	0.02
Zn	45.68	41.70	25.20	111.30	18.80	20	5000a.b	0.50
F	1787	925	1599	5360	200	100	1500b	20.00
Dy	0.1	0.03	0.59	1.9	0.01	-	-	< 0.01
Er	0.2	0.02	0.35	1.1	0.01	-	-	< 0.01
Eu	0.1	0.01	0.13	0.4	0.01	0.08*	-	< 0.01
Gd	0.3	0.03	0.59	1.9	0.01	-	-	< 0.01
Ge	0.1	0.05	0.02	0.1	0.02	-	-	1.17
La	2.6	0.32	6.07	19.6	0.11	0.28*	-	< 0.01
Lu	0.01	0.01	0.05	0.2	0.10	-	-	< 0.01
Nd	1.4	0.20	3.26	10.5	0.07	0.08*	-	< 0.01
Y	0.2	0.16	0.19	0.7	0.05	0.06*	-	< 0.01
Yb	0.1	0.01	0.33	1.1	0.01	-	-	< 0.01
Pr	0.4	0.06	0.94	3.1	0.02	0.06*	-	< 0.01
Sm	0.2	0.03	0.54	1.7	0.02	0.06*	-	< 0.02
Tm	0.1	0.01	0.19	0.6	0.01	-	-	< 0.01
Tb	0.01	0.01	0.08	0.3	0.01	-	-	< 0.01
Ho	0.01	0.10	0.09	0.4	0.01	-	-	< 0.02
pH	7.73	7.79	0.12	8.35	6.62			

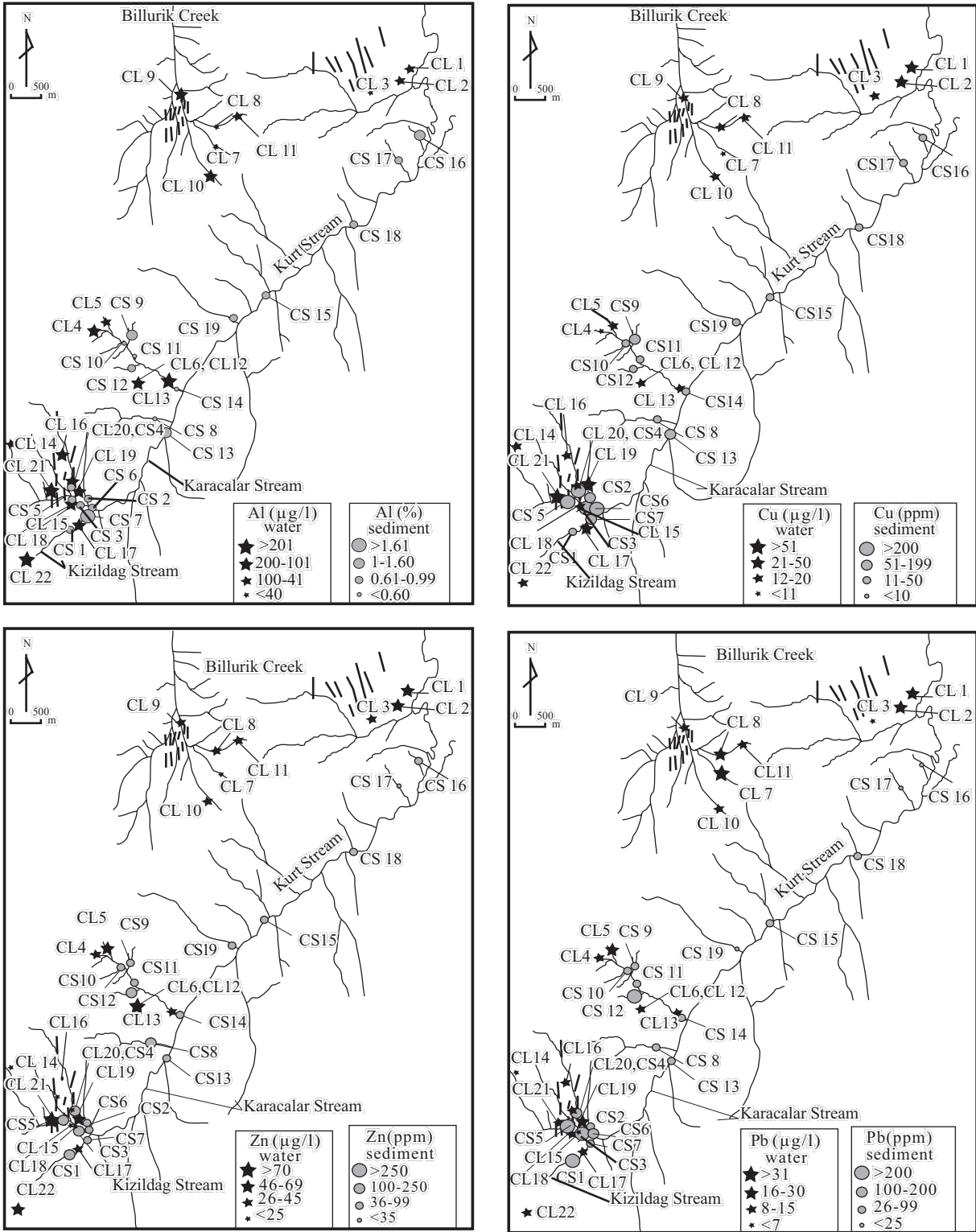


Figure 2. Sample locations and distributions of Cu, Pb, Zn and Al. CL– spring-water samples; CS– stream-sediment samples.

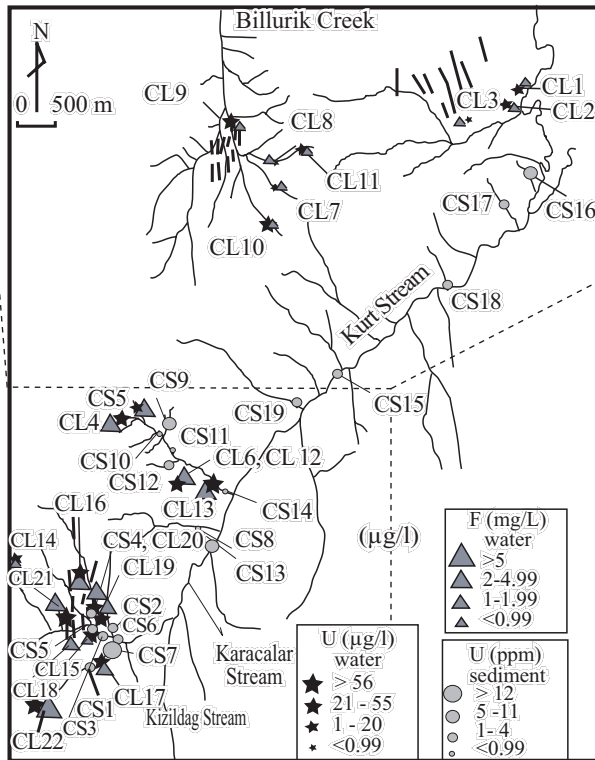
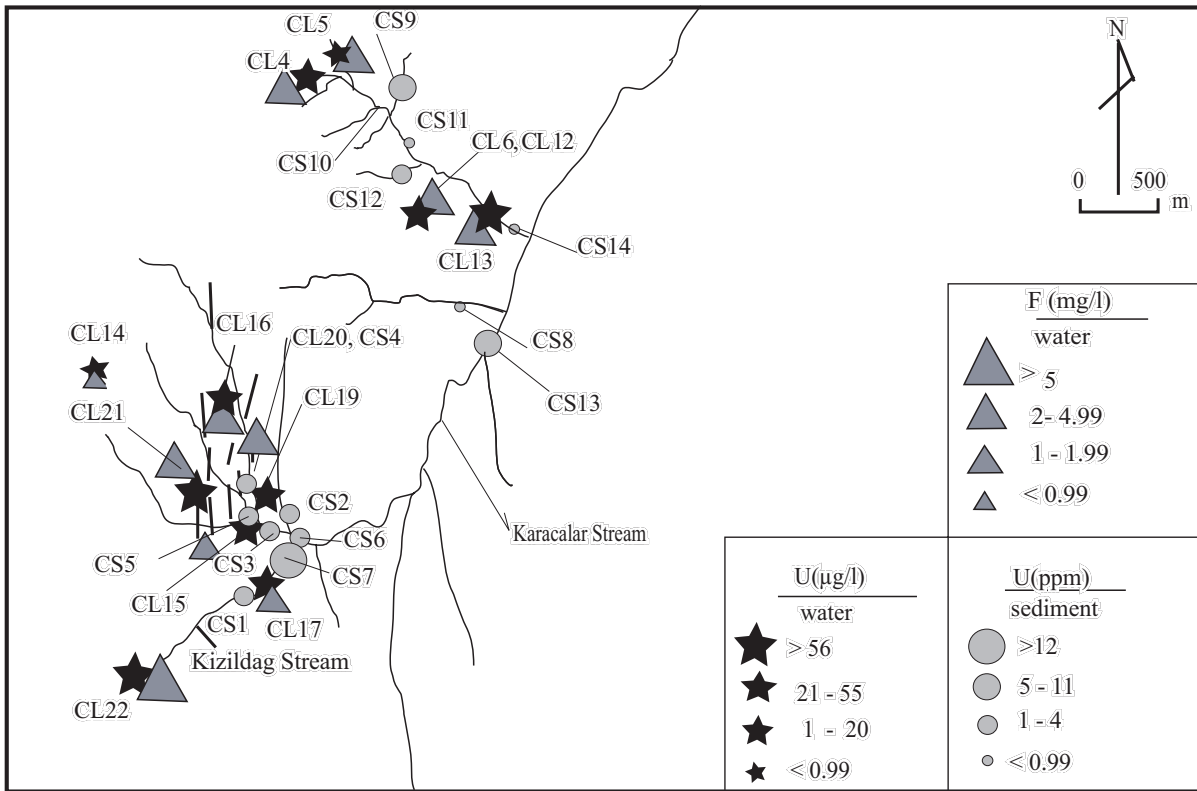


Figure 3. Sample locations and distributions of U and F. CL– spring-water samples; CS– stream-sediment samples.

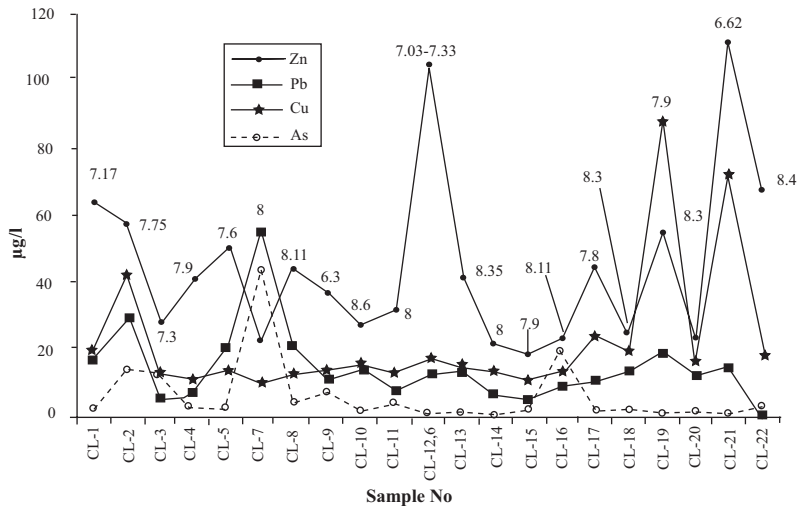


Figure 4. Plot showing element contents and pH values of the spring waters.

When the median values of the element concentrations were compared with element contents of groundwaters (Rose *et al.* 1979), it was found that the concentrations of Al, As, B, Br, Ca, Cd, Ce, Co, Cs, Cu, Li, Mg, Mo, P, Pb, SO₄, Sb, Se, Si, Sn, U, Zn and F in the spring waters are higher than the reported values for groundwaters. Also, the maximum values of these elements were compared with the maximum recommended contaminant levels of drinking waters as reported by the USEPA (1980, 1984, 2000), Ley 18284 (1969), and the Codigo Alimentario Argentino, Modificaciones (1988, 1994) (Table 1). As a result, it was determined that Al, Ba, Br, Fe, K, Mn, Na, Pb, SO₄, U and F concentrations in these spring waters are enriched by factors of ~ 1.5 to 29 with respect to these standard levels (Table 1). Similarly, the spring-water samples were observed to be relatively enriched with respect to Eu, La, Nd, Y, Pr and Sm as compared to the other groundwater samples (Table 1). Because the number of samples with logarithmic distributions was less than 30, Spearman correlation coefficients were computed in order to obtain more meaningful results and to elucidate the chemical behaviour of elements in the spring waters (Table 2). Negative correlations were detected between Cu-pH ($r = -0.28$, $p = 0.22$), Zn-pH ($r = 0.22$, $p = 0.35$), Pb-pH ($r = -0.11$, $p = 0.65$), Br-pH ($r = -0.16$, $p = 0.49$), As-pH ($r = -0.23$, $p = 0.32$) and Cu-Sb ($r = -0.39$, $p = 0.08$) in the spring waters. In all the water samples, positive correlation was observed between U

and F ($r = 0.39$, $p = 0.08$), and also a slight correlation between F and pH ($r = 0.22$, $p = 0.35$). U anomalies in samples CL 5, CL 12, CL 13 and CL 15 are accompanied by high F contents (Figure 3). The distribution of pH values and elements at different sample locations is shown in Figure 4. At locations CL 7 and CL 16, there are notably high pH values of 8 and 8.11, respectively, as well as anomalous values for Pb and As.

Eu, Lu, Tm, Tb and Ho were detectable in sample CL 21, and the values of La, Nd, Y, Pr, Sm, Ge and Gd were above detection limits in all of the spring-water samples. The highest total REE value was 42.6 µg/L in sample CL-21 (Figures 2 & 3). All REE have quite similar chemical and physical properties, as reflected in the high positive correlations shown in Table 2. Positive correlation was indicated among Yb, La, Pr and Sm, and between these REE and Ca, Fe, Mn and S. The spring waters are clearly enriched in the normalised REE diagram (Figure 5).

Chemistry of the Stream-sediment Samples

Two major problems are addressed in this paper: (1) the chemical compositions of spring waters and stream sediments sampled from locations proximal to the Harput Pb-Zn-Cu veins; (2) the effects of element distributions on geochemical prospecting and pollution. Therefore, elements occurring in both of the sampled media (i.e., spring-water and stream-sediment samples) were

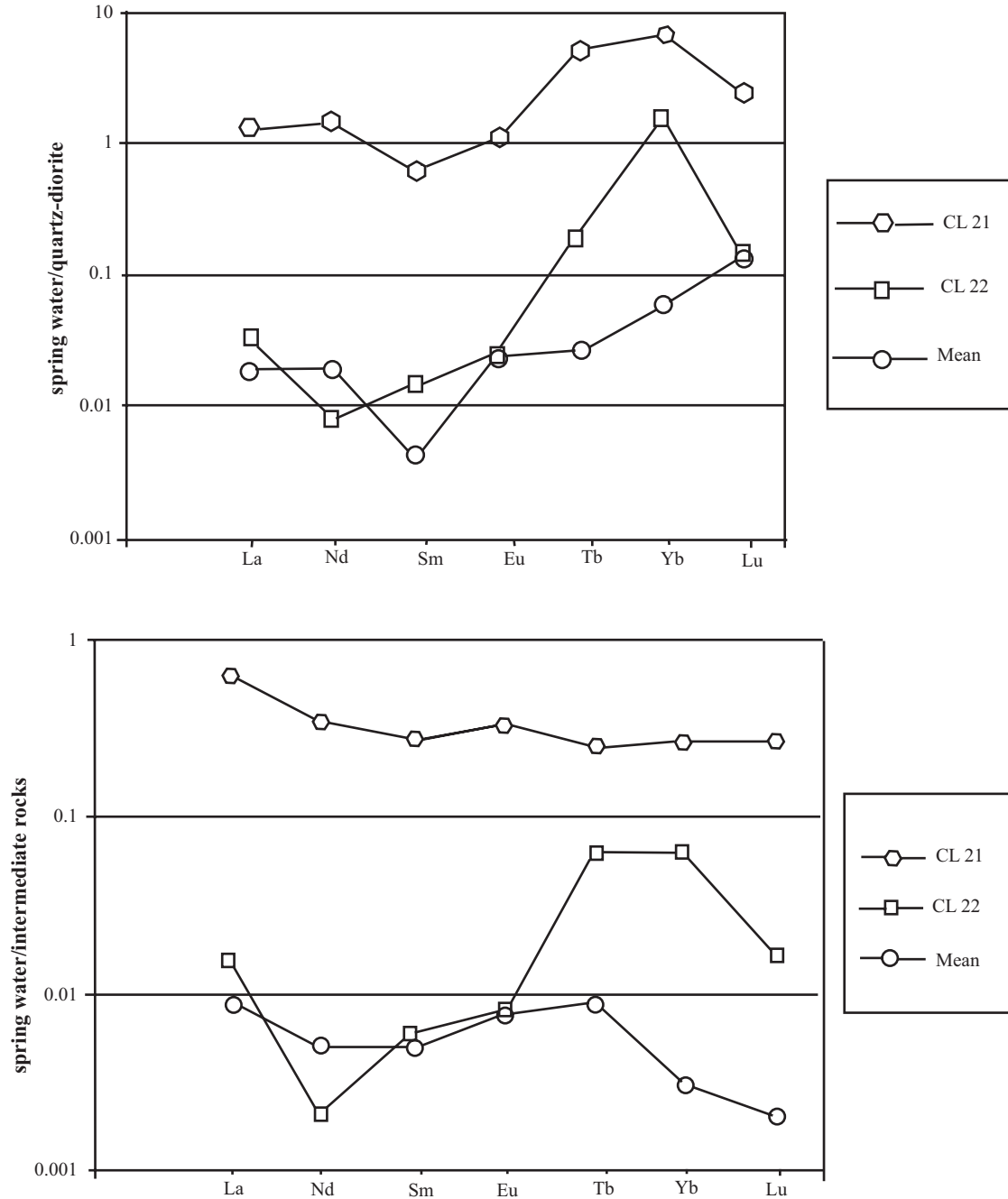


Figure 5. Normalized diagrams of rare-earth elements in the spring waters (values for quartz diorite and intermediate rocks from Wedepohl 1978).

compared (Figures 2 & 3). Summary statistical data (median, maximum, minimum values and geometric means) and the elemental contents of the different size fractions (-80, -140, -200 mesh) of the stream sediment samples are given in Table 3, in which the compositions

of the different size fractions are not only compared with the average crustal composition, but anomalous values and their chemical features are also determined.

In the stream sediment samples, the highest median values for As, Mo, Cu, Pb, Zn, Ni, Co, Au, Th, Sr, Cd, Sb,

Table 3. Summary of some statistical values for bulk samples and element contents (-80 +140; -140 +200; -200 mesh) of the different size fractions, with world average crustal composition from Faure (1998), mean granitic-rock composition from Sağiroğlu & Şaşmaz (2003); n= 57 (in ppm).

Element	Median	-80 Max	Min	Mesh G. M.	Median	-140 Max	Min	Mesh G. M.	Median	-200 Max	Min	Mesh G. M.	Crustal Average	Granitic Rocks
Mo	1.7	13.1	0.1	1.76	2.3	13.4	0.2	1.96	2.9	11.4	0.2	2.14	1	-
Cu	32	456.3	9.4	45.44	31	567	11.8	49.29	41.9	595.9	15.2	55.94	75	-
Pb	42.7	205.4	11.7	54.48	50.9	251.5	12.6	57.37	65	278.3	16.6	62.6	8	<100
Zn	58	187	21	63.66	61	206	26	68.33	72	289	36	81.56	80	27.5
Ag	0.1	0.4	0.1	0.13	0.1	0.4	0.1	0.14	0.1	0.5	0.1	0.13	-	-
Ni	11	60.5	1.4	9.5	14.1	43.7	1.8	11.28	19.8	52.9	2.9	15.81	-	-
Co	10.3	20.2	2.8	9.2	9.9	26.1	2.8	9.42	10.5	23.6	3.1	9.83	29	-
Mn	775	1960	367	809.72	702	2459	453	850.86	775	3363	457	920.05	1400	100
Fe%	2.8	5.21	0.95	2.45	2.59	5.73	1.15	2.58	2.69	4.52	1.54	2.68	7.06	5
As	16.6	51.8	10.8	21.41	17.9	63.8	10.5	22.49	22.6	78.4	9.2	25.1	1	11.66
U	3.1	8.7	0.6	2.79	3.9	9.9	0.5	3.18	4.4	28.9	0.7	3.96	0.91	-
Au	0.6	9.1	0.5	1.03	1	28.5	0.5	1.49	1.2	20.4	0.5	1.88	-	-
Th	11.2	37.4	1.7	9.74	11.7	43.3	1.5	10.4	13.5	38	1.8	11.42	-	-
Sr	52	569	8	58.36	89	654	11	74.16	106	607	19	92.79	260	-
Cd	0.2	0.9	0.1	0.25	0.2	1.2	0.1	0.25	0.3	2.2	0.1	0.29	0.98	<10
Sb	0.9	5.3	0.3	1.17	1	6.3	0.3	1.22	1.1	5.8	0.3	1.25	-	18
Ca%	4.2	19.42	0.81	4.1	5.17	23.49	1.17	5.07	7.68	21.5	1.26	6.24	53	-
P%	0.025	0.177	0.005	0.02	0.029	0.189	0.007	0.03	0.035	0.117	0.01	0.03	-	-
La	19	47	4	16.69	23	57	4	18.97	23	68	5	22.79	16	24.5
Cr	11.6	51.5	1.4	10.29	14.7	48.9	1.4	11.95	18	53	3.1	16.15	185	-
Mg%	0.53	1.28	0.04	0.4	0.57	1.41	0.05	0.46	0.64	1.54	0.08	0.52	32	-
Ba	84	148	22	64.59	91	179	24	76.85	115	193	27	92.28	250	868
Ti%	0.011	0.025	0.002	0.01	0.012	0.078	0.002	0.01	0.012	0.067	0.003	0.01	-	-
B	3	6	1	2.54	3	6	1	2.64	3	6	1	3.2	-	-
Al%	0.69	1.65	0.34	0.65	0.79	1.67	0.37	0.74	0.98	1.63	0.45	0.96	84	-
Na%	0.01	0.091	0.003	0.01	0.012	0.097	0.003	0.01	0.016	0.087	0.005	0.02	23	-
K%	0.08	0.17	0.05	0.09	0.08	0.17	0.05	0.09	0.11	0.21	0.06	0.11	9	-
W	0.3	3.1	0.1	0.32	0.4	3.5	0.1	0.33	0.3	2.9	0.1	0.31	-	-
Hg	0.01	0.09	0.01	0.02	0.01	0.14	0.01	0.02	0.01	0.15	0.01	0.02	-	-
Sc	3	5.8	0.4	2.4	3.2	5.4	0.5	2.77	3.8	5.9	0.7	3.37	30	-
Tl	0.1	0.2	0.1	0.11	0.1	0.3	0.1	0.13	0.1	0.3	0.1	0.13	0.36	-
S%	0.05	0.44	0.05	0.07	0.07	0.32	0.05	0.08	0.05	0.3	0.05	0.07	-	-

Ca, P, La, Cr, Mg, Ba, Ti, B, Al, Na, K, Sc, U and Tl were observed in the -200 mesh size (Table 3). Mo, Pb, Zn, As, U and La in the stream-sediment samples are higher than in the world average crustal composition, and the median values for Pb, Zn, As and Mn in the stream-sediment samples are higher than their values in local granitic rocks (Table 3). Contrasting element values were calculated and plotted (Figure 6), and these values show that Mo, Pb, Zn, Fe, Cu, Al, Ca and Ba are enriched in the -80 mesh fraction; S, K, Sb, Cd and As are enriched in the -200 mesh fraction. Consequently, we know that the background values of these elements are high.

Positive correlation was observed between Mo-Pb, Cd-Cu, Cd-Mg, Cd-Mn, Cd-F, S-Cd, S-Cu, S-Fe, S-Mg, S-Mn, S-Pb, S-Mo, Pb-Ba, Pb-Cu and Zn-Cu. U and Al, while negative correlation was found between U and Ca ($r = -0.59$, $p = 0.01$) (Table 4).

During weathering and movement into spring waters, fractionation among nuclides of different chemical elements are largely controlled by differences in the chemical properties of these elements in solution (Bourdon *et al.* 2003). The tendency of an ion to precipitate as a hydroxide can then be related, at least theoretically, to ionic potential, defined as the quotient of the positive charge on a sample ion divided by its radius (Krauskopf 1989). According to Krauskopf (1989), any positive ion in water is somewhat attracted to the negative ends of polar water molecules in its vicinity. The high Ba, Fe, Na and K contents of the spring waters are probably the main sources of increased concentration due to low ionic potential values (interval 1 – 3) of these elements, and they are dissolved as cations in the water. Al has a high ionic potential (interval 3 – 8) and may be dissolved as oxide and/or hydroxide in water. The high Fe contents of the spring waters (average 1046 $\mu\text{g/l}$) may indicate the presence of some inorganic compounds, such as C and S (Freeze & Cherry 1979). Dissolved anion complexes may occur in water because S has the highest ionic potential (>10); the high SO_4^{2-} values confirm this. Low pH values (e.g., 6.62) are found in spring waters that are in contact with oxidizing pyrite and specularite. High (e.g., 8.35) pH values are considered to result from the presence of organic materials, carbonate and clay minerals in the area, as pointed out by Tüysüz *et al.* (1997). Therefore, it is believed that the high clay mineral content of sample CL7 played an important role in the alkalinity of spring waters. Negative correlation

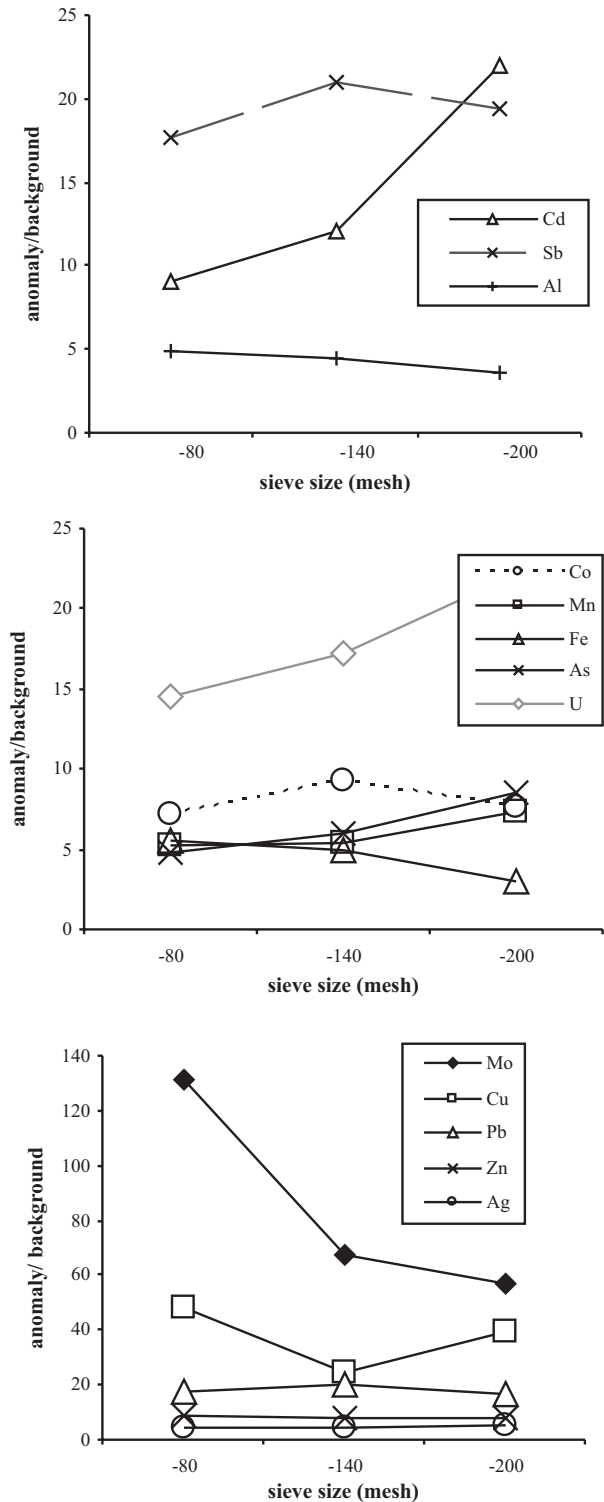


Figure 6. Distributions of contrasting compositional values in the different size fractions.

Table 4. Element contents and correlation coefficients for the stream-sediment samples (n=19). *0.05 significant level (p); ** 0.01 significant level (p).

	Mo	Cu	Pb	Zn	Fe%	As	U	Sb	Ca%	Ba	Al%	K%	S%
Mean	3.4	102.2	85.7	85.1	2.7	26.9	4.7	1.8	7.5	89.8	0.8	0.1	0.1
SD	3.5	147.2	77.2	56.5	0.9	15.9	4.6	1.8	5.9	45.6	0.3	0	0.1
Max.	13.4	595.9	278.3	289	5.7	78.4	28.9	6.3	23.5	193	1.7	0.2	0.4
Min.	0.4	9.4	11.7	21	1	9.2	<0.5	0.3	1	22	0.3	0	0.1
Det. Lim.	0.01	0.1	0.1	1	0.01	0.5	0.1	0.1	0.01	1	0.01	0.01	0.05

Mo	1.00																	
p=	0.00	Cu																
Cu	0.607**	1.00																
p=	0.00	0.00	Pb															
Pb	0.319*	0.253	1.00															
p=	0.015	0.057	0.00	Zn														
Zn	0.557**	0.462**	0.474**	1.00														
p=	0.00	0.00	0.00	0.00	Fe													
Fe	0.242	0.454**	-0.079	0.143	1.00													
p=	0.07	0.00	0.561	0.288	0.00	As												
As	0.123	0.131	0.222	0.276*	-0.241	1.00												
p=	0.364	0.33	0.097	0.038	0.071	0.00	U											
U	0.236	0.092	-0.011	-0.097	0.105	0.029	1.00											
p=	0.078	0.497	0.937	0.471	0.438	0.831	0.00	Cd										
Cd	0.374**	0.374**	0.313*	0.814**	0.078	0.242	-0.222	1.00										
p=	0.004	0.004	0.018	0.00	0.566	0.069	0.097	0.00	Sb									
Sb	0.597**	0.438**	0.341**	0.648**	0.295*	-0.066	0.204	0.466**	1.00									
p=	0.00	0.001	0.009	0.00	0.026	0.625	0.128	0.00	0.00	Ca								
Ca	-0.241	-0.124	-0.097	-0.119	-0.119	0.071	-0.586	0.158	0.00	1.00								
p=	0.071	0.356	0.472	0.378	0.037	0.601	0.01	0.241	0.005	0.00	Ba							
Ba	0.184	0.352**	-0.149	0.037	0.452**	-0.002	-0.229	0.168	0.171	0.26	1.00							
p=	0.17	0.007	0.268	0.784	0.00	0.986	0.087	0.211	0.204	0.051	0.00	Al						
Al	-0.011	0.394**	-0.055	0.06	0.527**	-0.065	0.316	0.105	-0.04	0.249	0.663**	1.00						
p=	0.933	0.002	0.685	0.657	0.00	0.63	0.017	0.438	0.768	0.062	0.00	0.00	K					
K	0.466**	0.498**	-0.025	0.371**	0.461**	0.211	0.197	0.335*	0.537**	-0.17	0.684**	0.385**	1.00					
p=	0.00	0.00	0.854	0.004	0.00	0.115	0.142	0.011	0.00	0.192	0.00	0.003	0.00	S				
S	0.340*	0.157	0.229	0.236	-0.094	0.501**	0.082	0.111	0.188	-0.06	0.01	-0.212	0.159	1.00				
p=	0.014	0.267	0.102	0.092	0.508	0.00	0.565	0.432	0.182	0.653	0.941	0.131	0.26	0.00				

between Pb-As and pH is related to the solubility of pyrite and specularite, and Pb in highly acidic waters may be concentrated in solution via dissolution of galena. According to Dauvalter & Rognerud (2001), Pb behaves differently from the other heavy metals. However, Pb and As increase with high pH values at two locations (CL

7 & CL16) due to enrichment in altered carbonate and clay minerals. Some sedimentary grains exhibit clay (e.g., kaolinite) coatings with occluded pyrite and specularite.

There is negative correlation between Cu and Sb. Dorransoro *et al.* (2002) pointed out that Sb and Cu have low or moderate solubility but Sb is more soluble than Cu

in high pH solutions. Martin & Calvert (2003) reported that dry-season concentrations of total Zn, Cu and Pb in a mine-impacted lake averaged 41, 4.4 and 0.24 µg/L, respectively; in the present work it is observed that the spring waters averaged 45.68, 23, 15.54 µg/L, respectively. The high correlation between U and F is believed to originate from polarization of F^- ($r = 1.25 \text{ \AA}$ radius ion) by U^{4+} ($r = 1.08 \text{ \AA}$ radius ion). Solubility of U^{4+} increases at low pH in the presence of fluoride by formation of uranous fluoride complexes, and above pH 7-8 by complexing of U^{4+} with hydroxyl ions (Bourdon *et al.* 2003). Sujatha (2003) determined that fluoride is inversely related to Ca^{2+} , but the present study shows that fluoride positively correlates at the 0.05 level ($r = 0.46$ $p=0.03$). Also in this study, positive correlation between Cl and S ($r = 0.438$ $p = 0.047$), and between Cl and pH ($r = 0.407$ $p = 0.067$) was recognized; negative or poor correlation between REE and pH – Cl and also high positive correlation between REE and Al – S was observed. In contrast to Janssen & Verweij (2003), the concentration of dissolved REE is not considered to be controlled by pH but, rather, may be dependent on adsorption-desorption processes of $Fe^{3+}(OH)_3$ and/or $Al(OH)_3$ minerals. As might be expected, SO_4 also contributed significantly. As shown in Table 1, SO_4^{2-} concentrations are about three times higher than the maximum allowed values, indicating that the REE are derived from S-rich, ore-forming hydrothermal solutions. According to Gosselin *et al.* (1992), chlorite and, to some extent, sulfate preferentially complex with REE in acidic conditions, but Marcos (2002) noted that with increasing pH (above 6.8), carbonate species became predominant; chloride and sulfate complexes remain as the dominant players in REE speciation even at pHs of about 8. This observation may be explained by a higher solubility or a lower sorption of the REE.

The relative proportions of various crystalline phases are closely related to grain-size distribution in stream sediments. Galan *et al.* (2003) reported that most of the metals are bonded to ion exchange sites (especially in clay minerals), and that the highest concentrations of such potentially toxic elements (such as As, Mo, Cu, Pb, U and La; -200 mesh; Table 3) are found at the heads of rivers near the mining/pollution sources and in the fine sediments of the estuary. According to contrast anomaly values, there are increases in the amounts of Fe, Zn, Pb, Cu and Mo in the -80 +140 mesh size. The size fraction (-80 +140 mesh) may be operationally defined as the

residual phase, and Cu, Cr, Fe, Mg and Zn are enriched in this phase (pyrite, sphalerite, chalcopyrite and silicate minerals). High concentrations of Sb, Cd, As, Mo and U in the fine-grained sediments may be due to the fact that these elements increase in alkaline waters and by adsorption of these elements onto clay minerals and Al-Mn-Fe oxy-hydroxides; some elements have low ionic potentials (e.g., La, U, and Mo) and thus may be transported in solution over long distances.

The distribution of Al, Cu, Zn, Pb and U in the stream sediments and spring waters are shown in Figures 2 and 3. While these elements are enriched in spring waters proximal to the mineralized veins, they may be by adsorbed on to Al-Fe oxy-hydroxides and clay minerals in fine-grained sediments far from the mineralized areas. At our sample locations, U and F are seen to increase in parallel fashion; this indicates that U is concentrated in the presence of fluoride by formation of uranous fluoride complexes in spring waters.

Kalender & Bölücek (2004) determined that average U concentrations in spring waters and stream sediments were 17.7 µg/l and <5 ppb, respectively, near the skarn-associated Ag-Pb-Zn deposits of the Keban (Elazığ) area, while U concentrations in spring waters and stream sediments around the Harput vein-type Pb-Zn deposits are 31.29 µg/l and 4.7 ppm, respectively. Although there are Pb-Zn deposits in both places, the different deposit types, wall-rock compositions, hydrothermal solutions and temperatures are thought to have affected the concentration of these radioactive elements. According to Kalender & Hanelçi (2004), the Keban Pb-Zn deposits are associated with low-Na potassic alteration types in a low sulfide belt; this could be the reason for the low concentrations of radioactive elements in that area. It is well known that high concentrations of uranium occur in salt crusts which form on the surfaces of floodplain sediments in slightly elevated positions (micro-relief). Such crusts form when capillary-ascending groundwater evaporates and dissolves sulfates – which mainly originate from pyrite oxidation and sulphuric-acid leaching – typically precipitating as gypsum, epsomite or gossarite (Wine & Walt 2004).

Conclusions

In the study area, the highest major- and trace-element concentrations are observed around the Kızıldağ Pb-Zn mineralization. Al, Ba, Br, Fe, K, Mn, Na, Pb, SO_4 , U and

F are higher than maximum allowed contaminant levels for drinking water and quite high enough to be dangerous to agriculture and stock raising and, thus, to human health.

In spring waters proximal to the Harput-area deposits, a negative correlation between pH (6.5–8.5) and high element concentrations is notable. The pH of the spring waters (pH= 8) are considered to have been affected by the clayey limestones of the Kıkgeçit formation and by the alteration minerals (especially kaolinite) in the magmatic rocks. Since the concentration of dissolved REE is not directly controlled by pH, their behaviour may be controlled by the dissolution of pyrite and other sulphide minerals. Because this solution dissolved REE-rich granitic (source) rocks, it took up significant SO₄, Fe, and Al. Furthermore, the sample location (CL 21) nearest to the most mineralized area yielded the highest total REE value, indicating that hydrothermal ore-forming solutions must have been contaminated by continental crust (Shou *et al.* 2002) insofar as the composition of the source rock is the factor having the greatest effect on REE contents. This study

has shown that the REE may be useful as geochemical tracers in spring waters. As, U and La in the stream sediment and spring water samples are also higher than the world average crustal composition.

The present study has demonstrated that the distribution and behaviour of these elements in stream sediments and in flowing waters proximal to the Harput mineralized areas may be helpful in guiding geochemical prospecting studies and particularly in identifying high-risk metal pollution areas.

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