Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi

Afyon Kocatepe University Journal of Science and Engineering

AKÜ FEMÜBİD **23** (2023) 045803 (1056-1071) AKU J. Sci. Eng. **23** (2023) 045803 (1056-1071)

**DOI: 10.35414/akufemubid.1180088**

**Araştırma Makalesi / Research Article**

# Evulation Metal of Contamination by Natural Background and Average Earth's Crust Values in The Inci Stream Sediments Around Chromite Deposits in Guleman (Alacakaya-Elazığ), Turkey

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Geliş Tarihi: 25.09.2022 Kabul Tarihi: 03.08.2023

***Keywords***
Contaminant factor; Enrichment factor; Geoaccumulation index; Guleman chromite deposit; Stream sediments

**Abstract**

The total concentration of elements in the Inci stream sediments on the drainage network of chromite deposits was determined to evaluate the level of contamination by natural background, the average of ultramafic and mafic rocks in this study. The average concentration shows that toxic heavy metals originated from mineraliszing in the Inci stream sediments that have a controlling influence on accumulation and transportation both lithologically and anthropogenically. The metal enrichment factors of Pb, As, Ni, Sr, and Ba, and geoaccumulation factor values (Igeo) of Pb, As, Sr, Ba, and Rb indicated that these values are higher than background values and heavily contaminated. The highest metal concentrations and assessments of contaminants were obtained from ultramafic rock normalization. Enrichment factor (EF), contamination factor (CF), and Igeo values indicate that primary ore metals are represented by Pb, Cu, Mn, Ni, and Cr. Cr's enrichment factor (EF) is moderate contamination due to the high Cr concentration in the host rock. However, Cr is extremely contaminated according to the Earth's average in the stream sediments around the chromites deposit. The calculated Cu, Ni, and Cr threshold values are higher than the probable effect level (PEL) and threshold effect level (TEL). That is why these regions should be evaluated for relationships between human health and geochemistry in further multidisciplinary studies and considered important in terms of potential Cr, Cu, Mn, Ni, Pb and Zn mineralization.

# Guleman Kromit Yatağı Çevresindeki İnci Çayı Sedimentlerindeki Metal Kirliliğinin Temel Değer ve Ortalama Yerkabuğu Değerleri Tarafından Değerlendirilmesi (Alacakaya-Elazığ), Türkiye

***Anahtar kelimeler***
Kirletici faktör; Zenginleştirme faktörü; Jeobirikim indeksi; Guleman kromit yatağı; Dere sedimanları

**Öz**

Bu çalışmada, kromit yatağının drenaj ağı üzerindeki İnci Çayı çökellerindeki toplam element konsantrasyonu, temel değere göre, ultramafik ve mafik kayaçların ortalamasını göre kirlilik düzeyi değerlendirilmiştir. Ortalama konsantrasyon, zehirli ağır metallerin, hem litolojik hem de antropojenik olarak birikim ve taşıma üzerinde kontrol edici bir etkiye sahip olan İnci Çayı çökellerindeki mineralleşmeden kaynaklandığını göstermektedir. Pb, As, Ni, Sr ve Ba'nın metal zenginleştirme faktörü ve Pb, As, Sr, Ba ve Rb'nin jeoakümülasyon faktörü değerleri (Igeo), bu değerlerin temel değerlerden daha yüksek olduğunu ve yoğun şekilde kontamine olduğunu göstermiştir. En yüksek metal konsantrasyonları ve kirleticilerin değerlendirilmesi ultramafik kayaç normalizasyonundan elde edilmiştir. Zenginleştirme faktörü (EF), kirlilik faktörü (CF) ve Igeo değerleri, birincil cevher metallerinin Pb, Cu, Mn, Ni ve Cr ile temsil edildiğini göstermektedir. Cr'nin zenginleştirme faktörü (EF), ana kayadaki yüksek Cr konsantrasyonundan dolayı orta derecede kirletilmiştir. Ancak kromit yatağının etrafındaki akarsu çökellerinde Cr toprak ortalamasına göre aşırı derecede kirlenmiştir. Hesaplanan Cu, Ni ve Cr eşik değerleri olası etki seviyesinden (PEL) ve eşik etki seviyesinden (TEL) daha yüksektir. Bu nedenle bu bölgeler insan sağlığı ve jeokimya arasındaki ilişkiler açısından, daha ileri multidisipliner çalışmalarda değerlendirilmeli ve potansiyel Cr, Cu, Mn, Ni, Pb ve Zn mineralizasyonu açısından önemli kabul edilmelidir.



## 1. Introduction

This study includes an assessment of metal contamination in stream sediments of Alpin Type chromite deposit, which is the largest chromite deposit in Turkiye (Fig. 1). The chromite ores occurred in Upper Cretaceous Guleman Ophiolites in Alacakaya (Fig. 2). Guleman ophiolite consists of two main units, both tectonites and cumulates. Other components of the ophiolite include basic volcanites, cumulates including dunites, wehrlite, clinopyroxenite, gabbros, diabase dykes, and sheetdyke complex. Tectonites are composed of chromite- and dunite-bearing harzburgites. In the study area were determined 500 chromite mineralizations were conducted by different researchers who were a distance from one centimetre to hundred meters, such as lens shape (Helke 1962, Engin 1985, Üşümezsoy 1990, Çakır 1994). The chromite formation occurs either in tectonites or cumulates, but the $Cr_2O_3$ tenor in tectonites is higher than in cumulates. The chromite ores are observed as usually disseminated and lens shape. Another unit outcropping in the study area is the Maden Group (Fig. 2). Maden Complex consists of ophiolitic rocks, sedimentary rocks, and some volcanic rocks (Aktaş and Robertson 1984). Some researchers called Maden Complex the Maden Group (Yılmaz et al. 1987, Yiğitbaş et al. 1993). Ertürk et al. (2018) studied the Maden lithological units and observed, from bottom to top, pelagic limestone, mudstone within lower volcano-sedimentary units, and diabase, pyroclastic rocks, andesites, and basalt within upper volcanic units. Upper Maastrichtian-Middle Eocene Caspian Group and Lower Miocene Lice Formation are the other units in the surroundings of the study area (Özkan 1983).

There are a lot of stream sediment studies around mafic and ultramafic host rock environments. The studies reveal the behaviour of Cr and Ni etc., toxic metals and also calculated assessment index values show the contamination level with numerical values. Some of these studies are summarised below to explain the study's hypothesis. Also, why was such a stream sediment contamination assessment done next to the chromite deposit? The river bedload at the contaminated site contains sizable amounts of trace metals as well. However, the concentrations of Ni and Cr in the bedload are lower than those in the bed material. These trace elements are therefore largely stationary (Rhoads and Cahill 1999). Kalender (2012) studied waste and water contamination. Groundwater element content was correlated to the natural water content, and Al, Cd, Co, Cu, Mg, Nd, Fe, Ni, and Mn values are higher than the natural water chemical composition. The high metal concentration in samples indicated that the source of contamination should be due to surface weathering of the lithological units (harzburgite, dunite, pyroxenite, and alteration yield serpentinite) and by leaching of wastes. The study in waters has compelled research to detect metal content in the stream sediments and their environmental impact assessment.

Stream sediment contamination by trace elements is a significant issue on a global scale, mainly due to mineralization and mining activities. Moreover tailings and waste may have serious impacts on the environment for decades (Cook et al. 1990, Singh et al. 1997, Varol 2011, Kalender 2012, Romero et al. 2013). Chromite-bearing ultramafic rocks are caused by the toxic elements enrichment in the Munzur and Pülümür streams. Metal and metalloid concentrations were normalized to the upper crust average values were observed enrichments in Cr, Ni, Co, Cs, W, Pb, As, Sb, Au, Hg and Cr, Ni, Co, W for studied stream sediments. The calculated Igeo index values indicate Cr, Ni, As, Hg, Cd, and Cr, Ni, As in the Munzur and Pülümür streams due to the ultramafic host rocks and mineralization products (Çimen et al. 2015). In order to investigate the function of TOC in the distribution of heavy metal pollution and assessment of contamination levels, Bakshe and Jugade (2021) evaluated the spatial distribution of potentially toxic heavy metals (Ni, Co, Cr, Hg, Cd, Pb, Cu, and Zn) and pH. (total organic carbon). Ni is related to pH, and chromium behaves according to pH and TOC values.

The study focuses on the contamination index values, which will be estimated according to the background values content of elements in the stream sediments in the sampling locations. The results are compared with the calculated contamination index values using the average ultramafic and mafic rock values. Considering the lithological characteristics, the effect of natural lithological units on contamination index values will be explained.

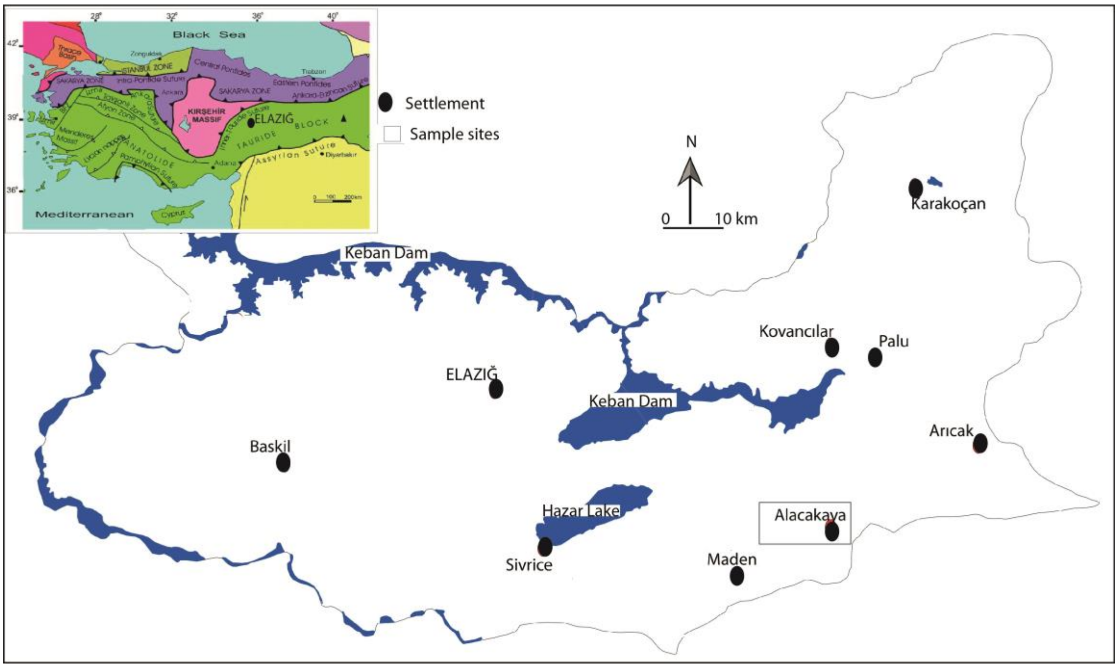


**Figure 1.** Location map of the study area.

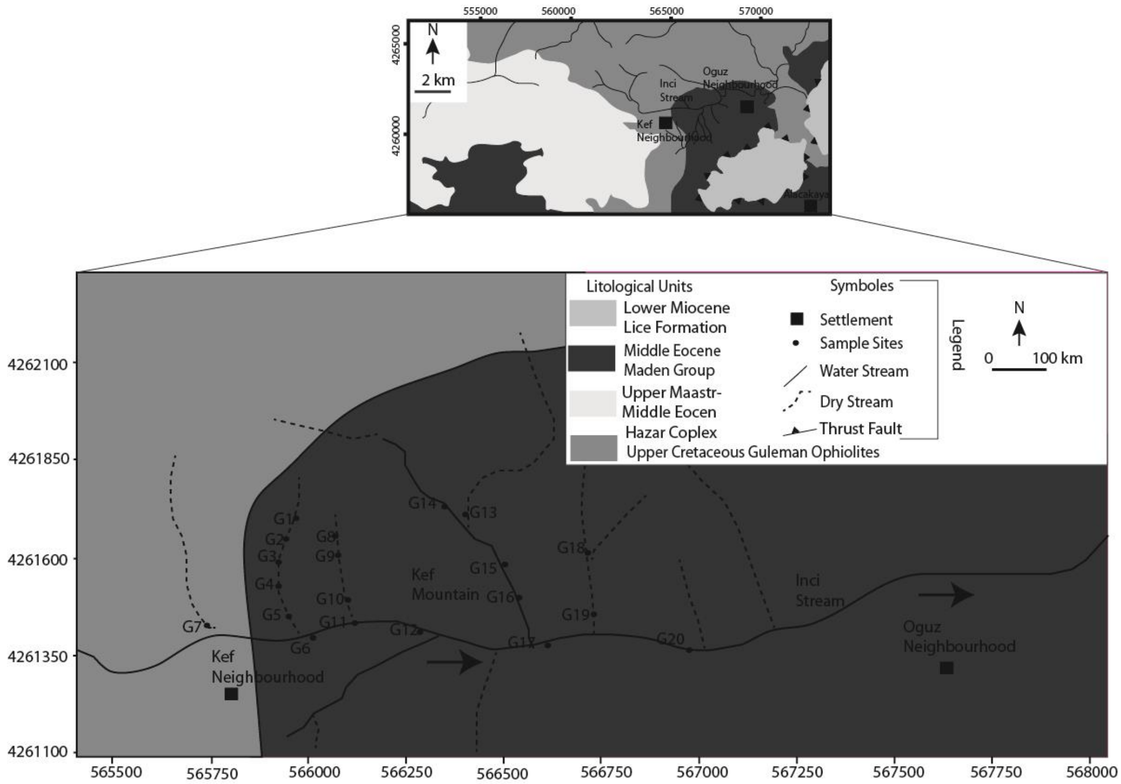


**Figure 2.** Sample sites on the geology map (Özkan 1983).

## 2. Material and Methods

### *2.1. Climatically*

Maximum flow occurs from February through April. However, the minimum flow occurs from August to October. The annual mean rainfall during that period was 372 mm. Moreover, air temperature varied between 15.21 $^0$C (Elazığ) and 34.00 $^0$C between 1992 and 2001 (Data were taken from reports of the Elazig Meteorology Department).

### *2.2. Sampling*

In this study, according to previous studies (Kalender and Bölücek 2004, 2007, Kalender 2012), 20 stream sediment samples (from G1 to G20) were collected from the Inci Stream sediments (Fig. 2). Sampling site locations are given in Table 1.

**Table 1.** UTM ED 50 coordinates of the Guleman stream sediment samples.

| Sample no | Y | X |
|---|---|---|
| G1 | 565965.63 | 4261695.84 |
| G2 | 565945.56 | 4261648.1 |
| G3 | 565923.9 | 4261596.16 |
| G4 | 565920.1 | 4261535.11 |
| G5 | 565947 | 4261447.85 |
| G6 | 566017.6 | 4261396.75 |
| G7 | 565936 | 4261379.27 |
| G8 | 566073.13 | 4261658.47 |
| G9 | 566074.28 | 4261605.59 |
| G10 | 566098.42 | 4261497.52 |
| G11 | 566111.98 | 4261431.54 |
| G12 | 566160.29 | 4261433.41 |
| G13 | 566399.81 | 4261719.96 |
| G14 | 566428.39 | 4261648.13 |
| G15 | 566501.97 | 4261579.14 |
| G16 | 566523.81 | 4261505.56 |
| G17 | 566611.41 | 4261373.13 |
| G18 | 566718.69 | 4261613.81 |
| G19 | 566734.97 | 4261453.06 |
| G20 | 566972.47 | 4261355.83 |

When the water flow rate was low in September, samples were taken. Samples were elemineted using a sieve with a 2 mm-diameter aperture (BS10 mesh). These stream sediments with a weight of 2 kg taken at 50-100 m intervals along the stream shore sediments were used in polyethylene bags. They were then given numbers and allowed to dry at room temperature. Kurutulduktan sonra analize uygun partikül boyutu fraksiyonlarının (35, - 35 + 80, - 80 + 140, - 140 + 200, - 200 meş) belirlenmesi için farklı elek boyutlarına elenmiştir. Fine sand (75 m), silt, and clay (20 m) grain sizes exhibit significant concentrations of heavy metals in investigations of heavy metal pollution in sediments (Ackerman 1980, Kalender and Bölücek 2004, 2007, Kalender 2012). The 75-m fraction in the current study was utilized to represent medium-fine sand to silt. Mechanical wet sifting was used to separate the bulk samples from the 75 m sediment fraction. Using 15 grams, each sample was freeze-dried for 8 to 9 hours. The sieved fraction was dried at room temperature.

### *2.3. Chemical analysis*

Acme Analytical Laboratories Ltd. (Canada) used ICP-OES to analyze the samples, which were collected at 0.5 gr. 0.5 gr samples were leached with 90 ml HCl- $HNO_3$- HF at 95 $^0$C for one hour, diluted 150 ml and then analyzed by ICP-OES. Standard DS5 was used in the sediment analyses. The results are given in Table 2.

**Table 2.** Chemical analysis results of the Inci stream sediments. *=%; the other values are given in ppm.

| Elements | G1 | G2 | G3 | G4 | G5 | G6 | G7 | G8 | G9 | G10 | G11 | G12 | G13 | G14 | G15 | G16 | G17 | G18 | G19 | G20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mo | 0.13 | 0.12 | 0.01 | 0.13 | 0.18 | 0.14 | 0.15 | 0.27 | 0.12 | 0.36 | 0.16 | 0.09 | 0.15 | 0.06 | 0.12 | 0.12 | 0.16 | 0.09 | 0.07 | 0.05 |
| Cu | 14.64 | 10.87 | 11.34 | 8.91 | 15.46 | 50.95 | 45.9 | 19.25 | 10.65 | 19.21 | 43.52 | 43.51 | 12.8 | 6.2 | 11 | 10.25 | 10.68 | 10.57 | 8.9 | 22.14 |
| Pb | 3.07 | 1.99 | 2.09 | 2.59 | 5.8 | 3.07 | 1.71 | 8.68 | 7.4 | 9.26 | 3.35 | 2.96 | 11.65 | 3.41 | 7.42 | 8.72 | 1.05 | 0.73 | 6.95 | 0.85 |
| Zn | 33.2 | 28.2 | 31.7 | 29.6 | 39.5 | 38 | 26.2 | 47 | 35 | 61.4 | 39.4 | 36.2 | 42.5 | 19.3 | 38.6 | 41.3 | 10.3 | 11 | 35.1 | 15.5 |
| Ni | 2358.8 | 2115.5 | 2156 | 1983.4 | 2393.3 | 383.3 | 931 | 1793.5 | 1581.5 | 2371 | 330.4 | 318.5 | 2218.5 | 2029 | 2268 | 2007.4 | 1347.6 | 1607.4 | 2099 | 836.6 |
| Mn | 1101 | 904 | 960 | 859 | 1190 | 690 | 651 | 1259 | 939 | 1464 | 852 | 809 | 1087 | 787 | 986 | 951 | 373 | 423 | 925 | 466 |
| Fe* | 6.79 | 6.27 | 6.31 | 6.04 | 7.24 | 5.14 | 5.82 | 6.97 | 6.28 | 8.5 | 4.56 | 4.47 | 6.4 | 5.47 | 6.43 | 6.04 | 2.55 | 2.7 | 6.05 | 2.9 |
| As | 1.5 | 0.7 | 1.7 | 1.1 | 1.6 | 2.7 | 1.5 | 2.9 | 1.4 | 2.7 | 3 | 2.3 | 1.8 | 1 | 1 | 2.5 | 1.2 | 1 | 2.7 | 1.3 |
| Th | 0.4 | 0.3 | 0.3 | 0.4 | 0.8 | 0.7 | 0.2 | 1.5 | 0.9 | 1.6 | 0.8 | 0.7 | 0.7 | 0.2 | 0.5 | 0.6 | 0.1 | 0.1 | 0.4 | 0.2 |
| Sr | 4.5 | 3.6 | 2 | 4.3 | 6.5 | 24.5 | 8.4 | 12.5 | 7.7 | 14 | 44.1 | 40.8 | 6.8 | 3.7 | 6.2 | 7.9 | 9.3 | 12.5 | 6.5 | 25.5 |
| Cr | 153.3 | 172.1 | 150.8 | 160.3 | 153.1 | 374.7 | 403 | 179.1 | 187.2 | 207.5 | 330 | 306.2 | 91.1 | 83.1 | 77.7 | 83.4 | 298.8 | 229.2 | 87.2 | 214.5 |
| Ba | 8.2 | 9.2 | 5.1 | 8.1 | 17.6 | 21.7 | 14.1 | 25.2 | 17.2 | 41.6 | 31.6 | 35.5 | 16.4 | 7.5 | 13.6 | 17.4 | 3.9 | 4.6 | 14.5 | 10.7 |
| Ti* | 0.005 | 0.004 | 0.005 | 0.004 | 0.005 | 0.061 | 0.01 | 0.011 | 0.011 | 0.014 | 0.049 | 0.04 | 0.006 | 0.003 | 0.01 | 0.007 | 0.006 | 0.005 | 0.006 | 0.016 |
| Ga | 0.9 | 0.8 | 0.8 | 0.9 | 1.4 | 5.7 | 2.7 | 2.8 | 1.9 | 3 | 7.5 | 7.1 | 1.2 | 0.6 | 0.9 | 1.1 | 1 | 1 | 1 | 3.1 |
| Rb | 1.7 | 1.6 | 1.4 | 1.7 | 3.3 | 2.6 | 1 | 7.2 | 4.4 | 8.3 | 3.7 | 2.8 | 2.9 | 1 | 2.5 | 2.7 | 0.4 | 0.4 | 2 | 0.7 |

## 3. Results and Discussion

### *3.1. Assessment of sediment contamination*

In the interpretation of geochemical data, it is important to compare concentrations between contaminated stream sediment and uncontaminated rock. Because stream sediments can contaminate both mineralization and weathering of rocks, principal component analysis orfactoring (according to correlation matrix) techniques can be used to identify the source of metals in stream sediments. Stream sediments were determined using multivariate statistical techniques and pollution indicators and presented a wide range of metal contaminants. The data obtained from the study area were evaluated by the contamination assessment methods below. These values have been estimated using uncontaminated background values and the average content of ultramafic and mafic rocks due to outcropping ophiolites and volcano-sedimentary rocks in the study area. Background values were taken from Başpınar (2006), and the average values were calculated from the content of trace elements in harzburgite, dunite, pyroxenite, gabbros, diabase, and basalts.

### *3.1. Contaminant factor (CF)*

The CF is the ratio obtained by dividing the concentration of each metal in the sediment by the background value .

$$\mathrm{CF} = \mathrm{C\ heavy\ metal}\ /\mathrm{C\ backgraund}$$

CF values were interpreted as sug gested by Hakanson (1980), where: CF<1 indicates low contamination; 1<CF<3 is moderate contamination; 3<CF<6 is considerable contamination; and CF>6 is very high contamination (Hakanson 1980).

### *3.2. Pollution load index (PLI)*

PLI has been determined as the nth root of the product of the n CF:

$$\mathrm{PLI} = \sqrt{}(\mathrm{CF1} \times \mathrm{CF2} \times \mathrm{CF3} \ldots\ldots \times \mathrm{CFn})$$

When PLI> 1, it means that pollution exists; otherwise, if PLI< 1, there is no metal pollution (Tomlinson et al. 1980).

### *3.3. Geoaccumulation index (Igeo)*

The geoaccumulation index (Igeo) is defined by the following equation:

$$\mathrm{Igeo} = \mathrm{Log2}(\mathrm{Cn})/1.5(\mathrm{Nn})$$

Cn, Bn and 1.5 value, respectively, is the concentration of metals examined in sediment samples, the metal's geochemical background concentration, and the background matrix correction factor due to lithospheric effects. According to Muller (1981), the geoaccumulation index consists of seven classes. These were Igeo≤ 0 indicates practically unpolluted; 0< Igeo< 1 is unpolluted to moderately polluted; 1< Igeo< 2 is moderately polluted; 2< Igeo< 3 is moderate to heavy polluted; 3< Igeo< 4 is heavily polluted; 4< Igeo< 5 is heavy to extremely polluted; 5>Igeo is extremely polluted (Buhiyan 2010, Varol 2011, Kalender and Çiçek Uçar 2013).

### *3.4. Enrichment factor (EF)*

The enrichment factor (EF) is essential for determining the extent of heavy metal contamination deposition in river sediments (Sakan et al. 2009).

The relationship shown below is used to calculate the EF:

$$EF = \left(\frac{Cx}{Cref}\right) sediment / \left(\frac{Cx}{Cref}\right) backgraund$$

Where Cx is the concentration of element x, and Cref and background values (uncontaminated regional host rock) are the concentrations of the reference element in sediment (s) and mafic and ultramafic rocks on the Earth's crust, respectively. The reference elements are those whose concentration in the sample medium is only affected by crustal sources, meaning they are unaffected by anthropogenic activity and have little occurrence variability. Ti, Ce, Sc, Mn, Zr, and Hf have all been utilized for this project (Romero 2013). Al and Fe are the most often utilized reference elements (Sterckeman et al. 2006, Sutherland 2000).

EF values were calculated using Al as a reference element and normalising the local background proposed by Sağıroğlu et al. (2009).

Iron (Fe) was used in this work as a reference for conservative element's geochemical normalization because of its relationship with fine solid surfaces, similar geochemistry to that of numerous trace elements, and tendency for uniform natural concentration (Buhiyan et al. 2010). Sakan et al. (2009) stated that the following was the interpretation of the EF values: EF 1 stands for minimal enrichment, 3, moderate enrichment, 5, moderately severe enrichment, 10, severe enrichment, 25, and > 50, extremely severe enrichment.

### *3.5. Sediment quality guidelines*

The significance of screening for sediment contamination by comparing sediment concentration with the relevant quality standard is emphasized by sediment quality assessment guidelines (SQGs) (Swartz 1999, Mac Donald et al. 2000).

Persuad et al. (2000) and Mac Donald et al. (2000) discuss the reliability of the threshold effect level (TEL), probable effect level (PEL), lowest effect level (LEL), minimal effect threshold (MET), threshold effect concentration (TEC), and probable effect concentration (PEC) for assessing sediment quality conditions (1993).

The result of the chemical analysis of the Inci stream sediment samples is shown in Table 2. Table 3 shows the correlation matrix for each element. The elements' correlation coefficient results show a positive relation between Mo and Zn, Th, and Rb (r> 0.74). The highest negative relation is shown between Cu and Ni (r= -0. 83) but the positive correlation coefficients between Cu and Sr (r= 0.75), Cr (r= 0.84), Ti (r= -0.86), Ga (r=0.88) are shown in the studied sediments. There are positive correlation relation between Ni and Mn (r=0.57), Fe (r= 0.62); between Cr and Ti (r= 0.68), Ga (r=0.69); between Mn and Fe (r=0.93); between Th and Ba (r=0.82), Rb (r=0.99); between Sr and Ti (r=0.85), Ga (r=0.95); between Ba and Ga (r=0.73), Rb (r=0.79), As (r=0.75), Zn (r= 0.77); between Ti and Ga (r=0.93). Th and Rb results indicate the effect on metal enrichments of crustal contamination. Between Cu and Ni negative relation shows that these two metals behave differently in an aqueous environment due to their ionic potential values ($Cu^{1+}$=1.041; $Ni^{2+}$=2.89). Therefore, Cu and Ni can't precipitate together in the stream sediments. Between Cu and Sr, Ti and Ga relationship indicates the source rock is in mafic composition. Ni and Mn ionic radii are very close to each other (Ni $^{2+}$; r= 0.69 Å; Ni $^{3+}$; r= 0.62Å-Mn $^{2+}$ r= 0.80 Å; Mn $^{4+}$ r= 0.60 Å) that is considered the metals may be concentrated in the same minerals from volcano-sedimentary units just like Fe and Mn; Th, As, Ba, Ga, Rb, Zn; Sr, Ti, and Ga. High Ga indicates these elements are associated with clay minerals in the studied stream sediments. According to Clay minerals and Fe-oxy-hydroxide coated films function as element adsorbers, according to Alexakis (2011). Iron gave both anthropogenic and natural sources of resources some thought. Fe-oxides and hydroxides can form thin coating films on clays and other minerals, acting as carriers of elemental pollutants (Lazzari et al. 2004, Galan et al. 2003).

Cr mineralizations are dominant in the area, but Ni and Ti enrichment may be considered to originate from the Maden Group's basaltic and andesitic source rocks in the study area. The average Cr value is nine times higher than the Earth's crustal average; the average Ni value is eight times higher than the Earth's crustal average. However, the average Cr value is lower than the background values, and the average Ni value is 1.78 times higher than the background values. This case explains the importance of regional lithological features when determining metal contaminations. For this reason, three different rock averages (background values, ultramafic and mafic rocks) and the median values of the studied sediment samples were used while calculating the pollution indices. The results of contamination factors (CFs, Igeo, and EF) values are present in Table 4. Table 4 summarises the calculated values of EF, Igeo, and EF for elements in the studied stream sediments according to the three different rock compositions. Among the studied metals, Mn>Ba>Th>Pb>Rb reported the highest ecological risk based on the calculations according to the ultramafic rock averages. The CF values (1<CF<3) for Cu, Zn, Ni, Cr, and Mn when based on background values, Cu, Zn, and Cr based on ultramafic rock average, and Ba based on mafic rock average, which denotes "moderate contamination"; the CF values >3 for As and Ga based on both background and the average of ultramafic rock compositions, and As base on the average.

**Table 3.** Correlation matrix of elements in the Inci stream sediment.

| Element | Mo | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 0.14 | Cu | | | | | | | | | | | | | |
| Pb | 0.49 | -0.24 | Pb | | | | | | | | | | | | |
| Zn | **0.64** | 0.17 | **0.77** | Zn | | | | | | | | | | | |
| Ni | 0.15 | -0.83 | 0.46 | 0.23 | Ni | | | | | | | | | | |
| Mn | 0.58 | -0.17 | **0.74** | **0.89** | **0.57** | Mn | | | | | | | | | |
| Fe | 0.48 | -0.17 | **0.65** | **0.81** | **0.62** | **0.93** | Fe | | | | | | | | |
| As | 0.42 | 0.48 | 0.44 | **0.67** | -0.3 | 0.4 | 0.25 | As | | | | | | | |
| Th | **0.8** | 0.17 | **0.69** | **0.87** | 0.09 | 0.77 | 0.62 | 0.67 | Th | | | | | | |
| Sr | 0.06 | **0.75** | -0.19 | 0.1 | -0.84 | -0.22 | -0.41 | 0.51 | 0.22 | Sr | | | | | |
| Cr | 0.17 | **0.84** | -0.52 | -0.17 | **-0.82** | -0.44 | -0.41 | 0.21 | -0.02 | 0.61 | Cr | | | | |
| Ba | 0.63 | 0.54 | 0.45 | **0.77** | -0.31 | 0.51 | 0.35 | **0.75** | **0.82** | 0.63 | 0.29 | Ba | | | |
| Ti | 0.08 | **0.86** | -0.16 | 0.22 | -0.82 | -0.15 | -0.23 | 0.58 | 0.26 | **0.85** | **0.68** | 0.58 | Ti | | |
| Ga | 0.18 | **0.88** | -0.12 | 0.27 | **-0.84** | -0.07 | -0.21 | **0.61** | 0.36 | **0.95** | **0.69** | **0.73** | **0.93** | Ga | |
| Rb | **0.82** | 0.11 | **0.69** | **0.86** | 0.15 | **0.78** | 0.64 | **0.63** | **0.99** | 0.16 | -0.05 | **0.79** | 0.18 | 0.29 | Rb |

Note: ($p < 0.01$)

**Table 4.** Statistical, CF, Igeo and EF values and some sediment quality standards for analysing Guleman Inci stream sediment samples. Background values (natural rocks/ Guleman Ophiolites and Maden Group); ** Clark values of the ultramafic rocks and mafic rock values were taken from Başpınar 2006,$^+$ Ertürk et al. 2018, Mason 1966, Turekian and Wedepohl 1961, respectively.

| | Mo | Cu | Pb | Zn | **Ni** | Cr | Mn | Fe (%) | As | Th | Sr | Ba | Ti (%) | Rb | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Arithmetic Mean | 0.134 | 19.34 | 4.64 | 32.95 | **1656.49** | 68.07 | 883.8 | 5.65 | 1.78 | 0.57 | 12.56 | 16.185 | 0.014 | 2.62 | 2.27 |
| Minimum | 0.01 | 6.2 | 0.73 | 10.3 | **318.5** | 37.9 | 373 | 2.55 | 0.7 | 0.1 | 2 | 3.9 | <0.1 | 0.4 | 0.6 |
| Maximum | 0.36 | 50.95 | 11.65 | 61.4 | **2393.3** | 165 | 1464 | 8.5 | 3 | 1.6 | 44.1 | 41.6 | 0.06 | 8.3 | 7.5 |
| Standard dev. | 0.08 | 14.27 | 3.29 | 12.35 | 716.38 | 35.56 | 275.46 | 1.54 | 0.74 | 0.42 | 11.98 | 10.46 | 0.02 | 2.07 | 2.12 |
| Threshold val. | 0.29 | **47.88** | 11.21 | **57.64** | **3089.26** | **143.87** | **1434.72** | 8.74 | **3.26** | 1.4 | 36.53 | 37.1 | 0.05 | 6.76 | 6.5 |
| **Median** | 0.185 | 28.58 | 6.19 | 35.85 | 1355.9 | 101.45 | 918.5 | 5.525 | 1.85 | 0.85 | 23.05 | 22.75 | 0.03 | 4.35 | 4.05 |
| **Background v. Ultramafic rock av.** | ***1.4<br>0.2*** | ***14.5<br>10*** | ***0.6<br>0.1*** | ***33*** | ***926;76,41$^+$*** | ***100;190$^+$*** | ***900; 1158$^+$*** | ***0.16*** | ***0.6*** | ***<0,1;<br>1.27$^+$*** | ***3;283$^+$*** | ***1.7;115.38$^+$*** | ***0.073;0.43$^+$*** | ***0.6;15.54$^+$<br>0.2*** | ***16.2;17,9$^+$<br>1.5*** |
| **Mafic rock av.** | ***1.5*** | ***90*** | ***7*** | ***30<br>115*** | ***75<br>130*** | ***100<br>23.5*** | ***0.5<br>0.15*** | ***9.85<br>8.63*** | ***0.5<br>2*** | ***0.004<br>1.18*** | ***10<br>342*** | ***0.05<br>0.15*** | ***0.03<br>8.63*** | ***32.72*** | ***342.4*** |
| **Assessment indices were calculated based on background values** | | | | | | | | | | | | | | | |
| CF | 0.13 | **1.97** | **10.32** | **1.09** | **2.26** | 1.01 | 1.2 | **34.53** | **3.08** | _ | **7.68** | **13.38** | 0.19 | **7.25** | **4.05** |
| Igeo | -1.16 | 0.23 | ***2.93*** | 0.02 | 0.01 | 0.045 | 0.003 | ***11.27*** | 0.98 | _ | 1.09 | 1.88 | -0.85 | 2.36 | 1.34 |
| EF | 0.14 | 1.97 | **10.31** | 1.11 | 2.26 | 0.93 | 0.026 | Reference | 3.08 | _ | **7.68** | **14.3** | 0.005 | **7.26** | **4.05** |
| **Assessment indices were calculated based on average ultramafic rock values** | | | | | | | | | | | | | | | |
| CF | 0.925 | **2.86** | **61.9** | 1.195 | **18.07** | 1.02 | **6123.3** | 0.56 | **3.7** | **212,5** | **7.68** | **1082** | **11.1** | **21.75** | 7.56 |
| Igeo | -8.11 | 0.32 | ***17.53*** | 0.11 | 0.09 | 0.04 | ***43.75*** | 0.17 | 1.18 | -39,08 | 1.09 | ***14.6*** | -35.25 | ***7.07*** | 1.56 |
| EF | 1.65 | **5.09** | **110.36** | 2.13 | 2.26 | 1.01 | **10916.71** | Reference | 3.08 | **378.85** | 4.11 | **1079.46** | **11.07** | **38.78** | 7.54 |
| **Assessment indices were calculated based on average mafic rock values** | | | | | | | | | | | | | | | |
| CF | 0.12 | 0.32 | 0.88 | 0.31 | **10.43** | 0.6 | **6123.33** | 0.64 | 0.93 | 0.72 | 0.07 | 2.28 | 0.24 | 0.13 | 0.65 |
| Igeo | -1.08 | 0.04 | 0.25 | 0.03 | 0.05 | 0.03 | ***43.75*** | 0.19 | 0.3 | -0.13 | 0.01 | 0.03 | -0.77 | 0.04 | 0.13 |
| EF | 0.19 | 0.5 | 1.38 | 0.49 | **16.29** | 0.52 | **9564.59** | Reference | 1.44 | 1.13 | 0.11 | 1.99 | 0.21 | 0.21 | 0.57 |
| PEL | | 108* | 91 | 315 | 42.80* | 160.4* | - | - | 17 | - | - | - | - | - | - |
| TEL | - | 18.7* | 35 | 123 | 15.9* | 52.3* | - | - | 5.9 | - | - | - | - | - | - |
| PEC | - | 32 | 36 | 120 | 23 | - | - | - | 33 | - | - | - | - | - | - |
| TEC | - | 150 | 130 | 460 | 49 | - | - | - | 9.8 | - | - | - | - | - | - |

PEL= Probable effect level (Smith et al. 1996). TEL= Threshould effect level (Smith et al. 1996). PEC= Probable effect concentrations (from Mac Donald et al. 2000). TEC=Threshold effect concentrations (from Mac Donald et al. 2000). PEL*= Probable effect level (Essien et al. 2009). TEL*= Threshould effect level (Essien et al. 2009).

of mafic rock composition, which denotes "considerable contamination"; the CF values>6 for Pb, Fe, Sr, Ba, and Rb based on background values, Pb, Ni, Mn, Th, Sr, Ba, Ti, Rb, Ga base on the average of ultramafic rock composition, and Ni and Mn base on the average of mafic rock composition which indicates a considerable risk. The Igeo values show that Ba, Sr, and Ga were "moderately to heavy polluted"; Rb and Pb were "heavily polluted"; Fe was "extremely polluted" for sediment according to base on background values. Mn, Pb, Ba, and Rb were the highest ecological risk according to base on the average of the ultramafic rock composition, and also Mn was a considerable risk due to the average of the mafic rock composition. EF values indicate that Ga was moderate enrichment, Rb and Sr were moderate-severe enrichment, and Pb and Ba were severe enrichment based on the background. Cu was moderate enrichment; Ti and Ga were severe enrichment; Rb was severe enrichment; Ba, Mn, Pb and Th were extremely enriched based on the ultramafic rock composition. Ni and Mn were extremely enrichment based on the mafic rock composition. Ni and Mn are important metals in the studied stream sediments. Many sample sites in the Middle Eocene Maden Group consist of basaltic and andesitic volcano-sedimentary rock. Calculated EF values show that Ni and Mn may be indicator metals in the studied stream sediments as Pb. Calculated threshold values according to Ni and Cr values are indicated that the calculated threshold values of Ni and Cr are higher than 72, 0.89 times PEL values, and 194; 2.57 times TEL values, respectively. The threshold value of Cu is 2.26 times higher than TEL and 1.49 times PEC as Pb and Zn threshold values are below PEL, TEL, PEC, and TEC values. The threshold values indicate that Ni, Cr, and Cu may be both ecotoxicological risks to the studied sediments and indicators for a new exploration mineral source. Giesy and Hoke (1990) determined that As > 8 and Cu > 50 "heavily polluted", and Cr; 25-75 "moderately polluted". In addition to As, Cu, and Cr median values (1.85, 28, and 240.5, respectively) in the Inci stream, sediment was heavily polluted only in terms of Cr. Sediment quality assessment guidelines (SQGs) are an important and useful parameter for sediment pollution for determination and interpretation (Swartz 1999, Mac Donald et al. 2000). Extensive anthropogenic activities characterise chromite mining in the Guleman region since 1936. This is shown that the stream sediment has the highest metal concentrations, both natural and anthropogenic. Primary mineralization is chromites. There are many secondary minerals, pentlandite, magnetite, hematite, and ilmenite, around the Guleman chromite mining area (Başpınar 2006, Özek et al. 2017). At this moment, Cr and Ni enrichments were determined in the Inci stream area due to weathering of the chromites and pentlandite, millerite (nickel sulfide minerals), and the other Cr and Ni minerals. The higher Ti and Fe values are by weathering of the ilmenites. The high Cr, Mn, Ni, and Zn contents have been stated by the presence of montmorillonite in stream sediments by Alexakis (2011). This study is shown that lithological features and mineralization are effective on stream sediment metal concentrations. It is well-known that low mobility elements in flow direction and mechanically enrichment next to the source can be used as path-finder elements. In contrast, in locations away from the source, more mobile elements have low ionic potential values (<3) and are enriched in fine-grained sediments. They consider average ophiolite concentration a lithogenic source, especially observed Cr and Ni concentrations. " High Cr and Ni concentrations in the stream sediments of East Attica represent a case of pollution that occurs naturally", and As content is both natural and anthropogenic (Förstner and Müller 1981, Alexakis 2011). It was determined that the enrichment factor value was not expected when compared to the background (basic value) values. It has been determined that this situation is due to the high Cr concentration in the basement rocks in the region.

## 4. Conclusion

The study summarizes the discussion of the normalization values in the equations of the assessment pollution index. Hereby, the background values were selected from the average of regional ophiolitic and basaltic rocks and used the average of the Earth's crust ultramafic and mafic rocks. The assessment of contamination values was calculated in three stages. Due to many sample sites in mafic lithology, the highest contamination values in the Inci stream sediments were obtained from calculations by the average ultramafic rock compositions. Also, Guleman ophiolites are an important factor in the source of metals. Different ionic properties of metals and possible mineralizations have been the cause of contamination or high concentration in the Inci Stream sediments. Between Ni and Mn, Fe; Cu and Cr; Pb and Zn, Mn, Fe, Th, and Rb, positive correlation relationships suggest that they were transported from the same source. EF, CF, and Igeo values indicate that Pb represents primary ore metals; Cu, Mn, Ni, and Cr accompany the accessory elements such as Rb, Sr, Ba, Ga, Ti, and Th. All these elements have a high concentration to create an atoxic effect on the Inci stream sediments' ecosystem. The calculated Cu, Ni, and Cr threshold values are higher than PEL and TEL. These data suggest that Cu, Ni, and Cr are characteristic elements in terms of the background influences and ecotoxicological risks. There is a lot of factor on metal concentrations through drainage systems. Both lithologically anthropogenically and mineralizingly produced hazardous heavy metals in stream sediment are transported and accumulated under the control of the stream sediments. Of course, contamination is not an obstacle to mineral exploration. A possible Cu, Pb-Zn, Mn, Ni, and Cr mineralization may be explored. More multidisciplinary studies involving biologists, biochemists, and geologists are required in light of the growing understanding of the connections between human health and geochemistry in order to comprehend the biogeochemical cycle of specific metals and evaluate the effects of urbanization on the sediments of these streams.

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