# ENVIRONMENTAL CONTAMINATION OF HEAVY METALS AND CHRYSOTILE ASBESTOS IN THE MUNZUR AND PÜLÜMÜR STREAMS (TUNCELI, TURKEY)

**Okay Çimen**[*,**,✉], **Fatma Toksoy Köksal**[*], **Ayten Öztüfekçi Önal**[***] and **Yüksel Örgün Tutay**[°]

[*] *Department of Geological Engineering, Middle East Technical University, Ankara, Turkey.*
[**] *Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Indiana, United States.*
[***] *Department of Metallurgical and Materials Engineering, Tunceli University, Turkey.*
[°] *Department of Geological Engineering, Istanbul Technical University, Turkey.*
[✉] *Corresponding author, email: cokay@metu.edu.tr, ocimen@nd.edu*

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## ABSTRACT

The Munzur and Pülümür streams are essential water supplies of the Tunceli Province (Turkey). Chromite bearing ultramafic rocks and Zn-Cu mineralization products are possible causes of the toxic elements enrichment in the streams. Sediment and soil samples were collected along these streams to determine the level of toxic element enrichment. Multi-element normalized patterns of the samples with respect to the upper crust display enrichments in Cr, Ni, Co, Cs, W, Pb, As, Sb, Au, Hg and Cr, Ni, Co, W, for the Munzur and Pülümür streams, respectively. Also, the calculated Igeo index values show the presence of contaminations of Cr, Ni, As, Hg, Cd and Cr, Ni, As in the Munzur and Pülümür streams, respectively. Elemental grouping in the samples indicates two different effects related to the ultramafic host rocks and mineralization products in the study area. Additionally, mineralogical XRD analyses exhibit the presence of chrysotile, plagioclase, quartz and calcite. The fibrous chrysotile and heavy metal contaminations must be considered as a threat for public health.

## INTRODUCTION

The Munzur and Pülümür streams are located in the Tunceli province (Eastern Turkey). There are around 100 villages and approximately 8000 people that dwell in the Pülümür drainage area. Kırmızıköprü, Büyükyurt, Kocakoç, Sütlüce, close to the Pülümür stream, are significant residential areas for local people. On the other hand, Munzur and its drainage area provide fertile lands for the local people and include 60 villages where about 6000 people live. The construction of several dams is being planned in these two drainage areas. For instance, the Uzunçayır dam was constructed downstream from the junction of two streams utilized by local people for tourism, fishing and partially for agricultural purposes. In this regard, both streams are very crucial for the local community. Except for the chromite mines, the effects of industrial pollutants are negligible for the overall pollution of the streams due to the underdeveloped industry. However, the remarkable contamination detected may stem from the natural compounds associated with the lithology of host rocks in the drainage areas.

Although there is a high possibility of pollution from geological units which are rich in chromite and Zn-Cu mineralization products, no studies related to the geochemical effects on the sediment and soil of these streams have been carried out until now. Therefore, in this study we examined the geochemistry and mineralogy of the sediments and soils to determine their heavy metal and trace element characteristics, and the source of possible pollution in the Munzur and Pülümür streams. The results of this pioneering work will be beneficial for future studies on environmental geochemistry and contamination.

## GEOLOGICAL FRAMEWORK

The geology of the area was extensively examined by Mineral Research and Exploration General Directorate (MTA) in 2008. According to this study, Paleozoic metamorphic rocks (schists, marbles, meta-clastics, meta-basics), serpentinized Late Cretaceous ultramafics together with other ophiolitic rocks (peridotite and dunite) and limestones, Oligo-Miocene flysch sediments, Late Miocene volcanics with interlayered pyroclastic and lacustrine sediments are present in the area. The streams run through these units. The chromite-rich ultramafic units are exposed in both drainage areas (Fig. 1). Additionally, volcanic units and Zn-Cu-Pb mineralizations crop out in the drainage area of the Munzur stream.

In recent years, some studies addressed the petrological characteristics of the Ovacık and Pülümür ophiolitic mélanges (Çimen et al., 2014; Öztüfekçi-Önal et al., 2014). These ophiolitic mélanges are the less-known parts of the Izmir-Ankara-Erzincan-Sevan-Akera Suture Belt which represents the northern branch of the Neo-Tethyan ocean. They contain harzburgites, Cr-bearing dunites, serpentinized peridotites, magmatic rocks (basalt, gabbro, and diabase), limestone blocks and pelagic sediments. These oceanic assemblages were formed in an intra-oceanic subduction zone during the closure of Northern Neo-Tethys (Çimen et al., 2014).

## MATERIALS AND METHODS

All the geological units, including the mineralization products examined by MTA (2008), were considered for sample selection. Samples were collected from various locations throughout the streams from the upstream parts to

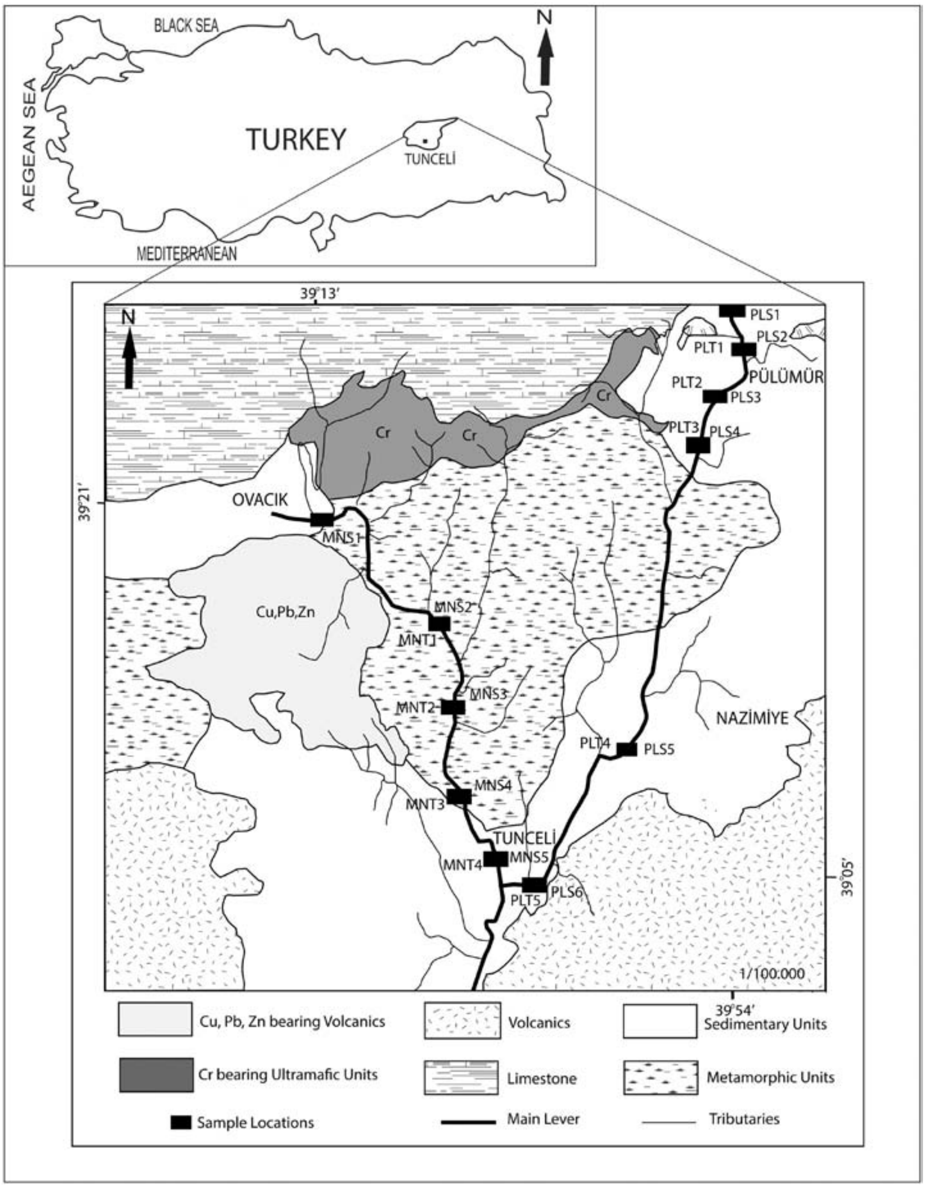



Fig. 1 - Geological map and sampling locations of the Munzur and Pülümür streams (modified from MTA, 2008).

the downstream junction. 5 locations along the Munzur stream, 6 locations along the Pülümür stream were selected for sampling (Fig. 1). 11 sediment and 9 soil samples were taken from these locations. About 1 kg of sediment sample from each location was taken using a hand bucket from a depth of approximately 50 cm under the water surface. Furthermore, about 1 kg of soil sample was taken by excavating down to approximately 50 cm depth from the same locations (Fig. 1).

The collected soil and sediment samples were dried at 100 °C during 24 hours. The dried samples were sieved in sand size with a 10 mesh sieve and grinded under 100 mesh using an agate mortar for chemical and mineralogical analyses. Major and trace elements were analyzed by using an ICP-OES (ICP optical emission spectrometry) and an ICP-MS (ICP mass spectrometry), respectively, at the Acme Analytical Laboratories (Canada). Total abundances of the major oxides and several minor elements were analysed by ICP-emission spectrometry following a Lithium metaborate/tetraborate fusion and dilute nitric digestion. Loss on ignition (LOI) is by weight difference after ignition at 1000°C. The highly precise labware was used to ensure greater precision and accuracy in the analyses. Also, some duplicated samples were analyzed in order to confirm the accuracy of the analyses.

Moreover, the mineralogical contents of the sediments were determined for 8 samples (4 samples for each stream) by performing X-Ray Diffractometer (XRD) analyses at the Central Laboratory in Middle East Technical University (Turkey).

## RESULTS

### Mineralogy

The XRD patterns display the presence of similar mineralogical contents for all the samples (Fig. 2). The identified minerals are fibrous chrysotile, plagioclase, quartz and calcite. It is remarkable that chrysotile is determined from all four samples from the Pülümür stream, while only three of the four samples from the Munzur stream contain chrysotile.

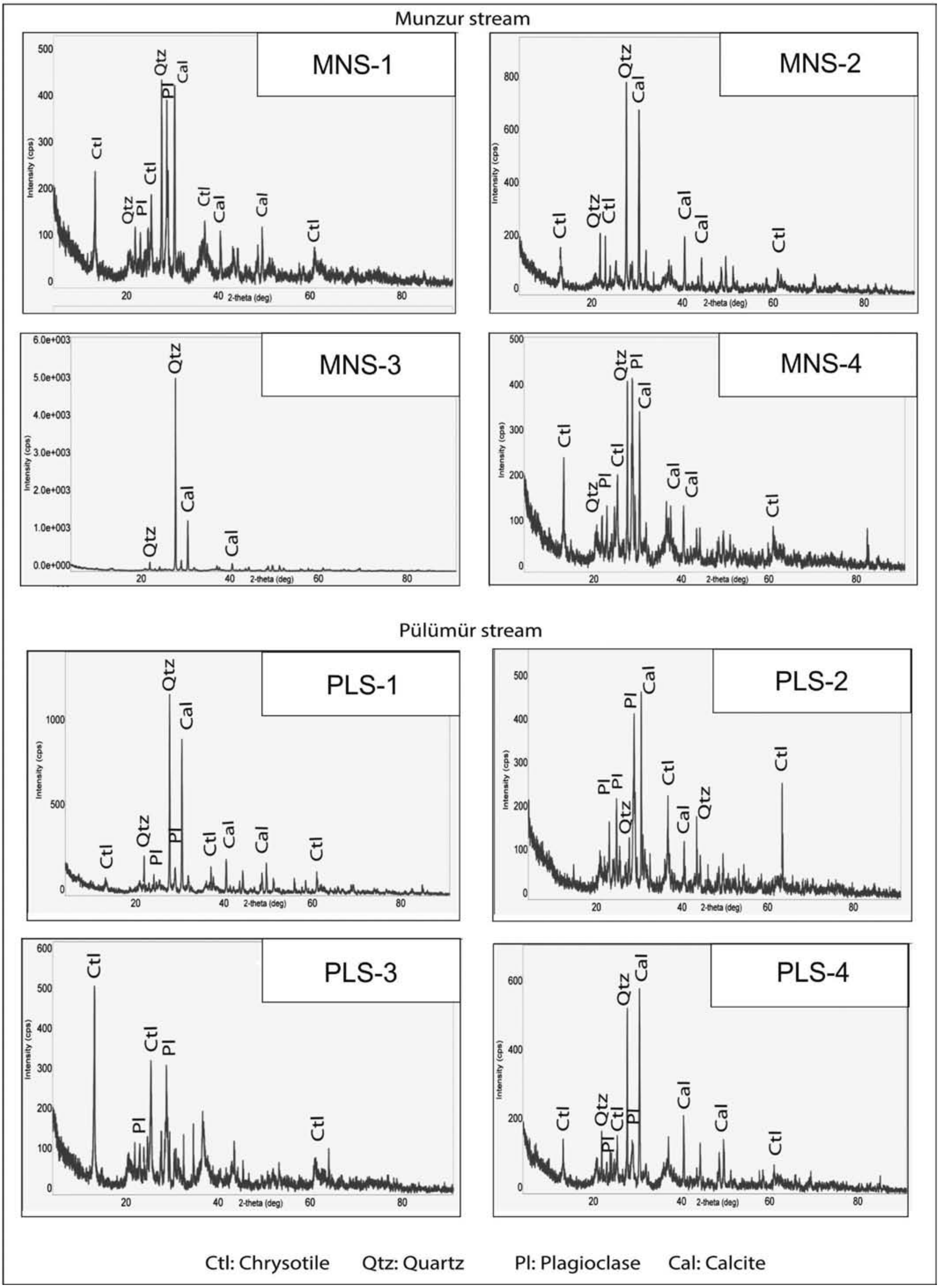



Fig. 2 - XRD analyses of the Munzur and Pülümür sediments.

## Chemical Index of Alteration (CIA)

In the drainage area of the Munzur and Pülümür streams, intense weathering is expected on the chromite bearing ultramafic rocks and on the products of Zn-Cu mineralization. The degree of chemical weathering in a regional source can be expressed by the chemical index of alteration (CIA: Fedo et al., 1995). In the formula of CIA = $[(Al_2O_3) / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$, used in several studies (Nesbitt and Young, 1982; Young and Nesbitt, 1999), $CaO^*$ represents the silicate fraction of the CaO content (Fig. 3). The calculated CIA values of the samples in this study are in the range of 80.3-82.3 and 77.2-78.7 for the Munzur and Pülümür streams, respectively.

## Sediment and soil geochemistry

The geochemical data of the Munzur and Pülümür sediments (Table 1) are used to explain the effective factors controlling the chemical composition of the sediments in the study area. In fact, in drainage areas, the compositional effect of host rocks, natural processes and human activities can be interpreted by evaluating the geochemical properties of the basin sediments (Zhang and Wang, 2001). Enrichment factors for the studied samples were calculated (Fig. 4) by using $(El/Al)_{sample}$ / $(El/Al)_{crust}$ formulae (Turekian and Wedepohl, 1961) and crustal values of Rudnick and Gao (2003).

Rare earth element (REE) data of the sediment samples (Table 2) were also examined in this study. REEs are used as geochemical tracers due to their immobile character during weathering and transportation processes (Taylor and McLennan, 1985; Schatzel and Steward, 2003; Rantitsch et al., 2003; Wang et al., 2008; Kasper-Zubillaga et al., 2008; Zanin et al., 2010; Fu et al., 2010). Enrichment factors for REEs of the studied samples were calculated (Fig. 5) using upper crust (UC) values (Turekian and Wedepohl, 1961) and Post-Archean Australian Shale (PAAS) values (Taylor and McLennan, 1985).

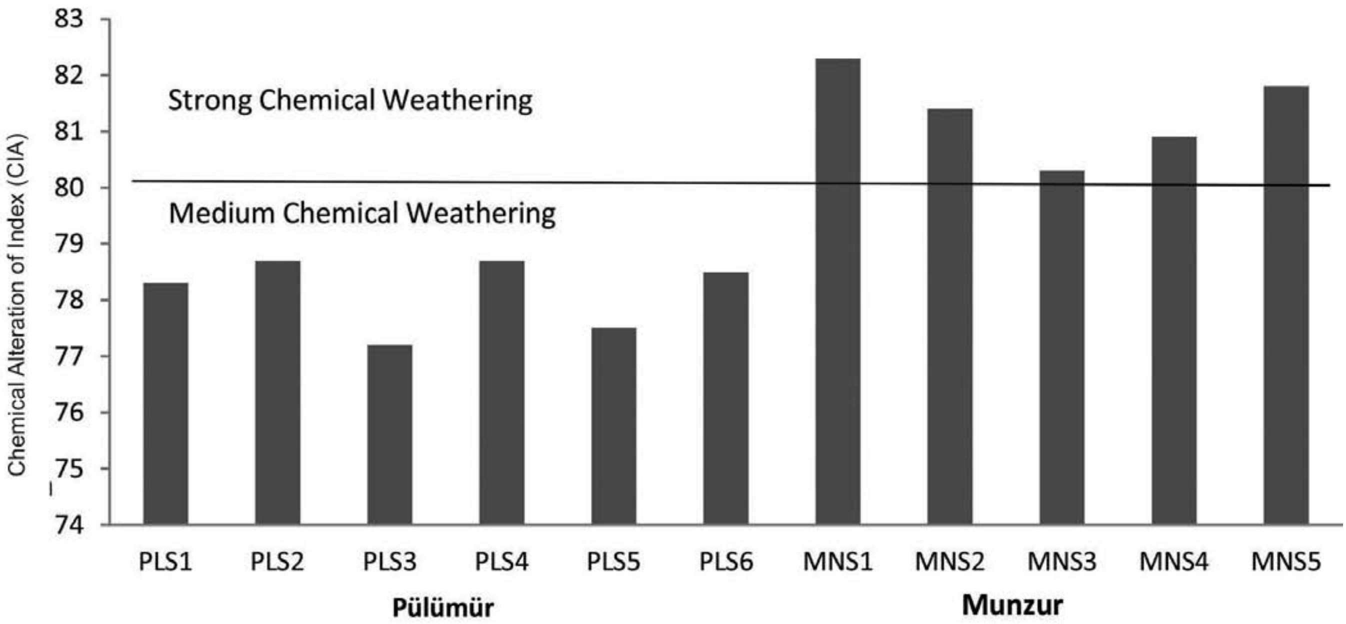
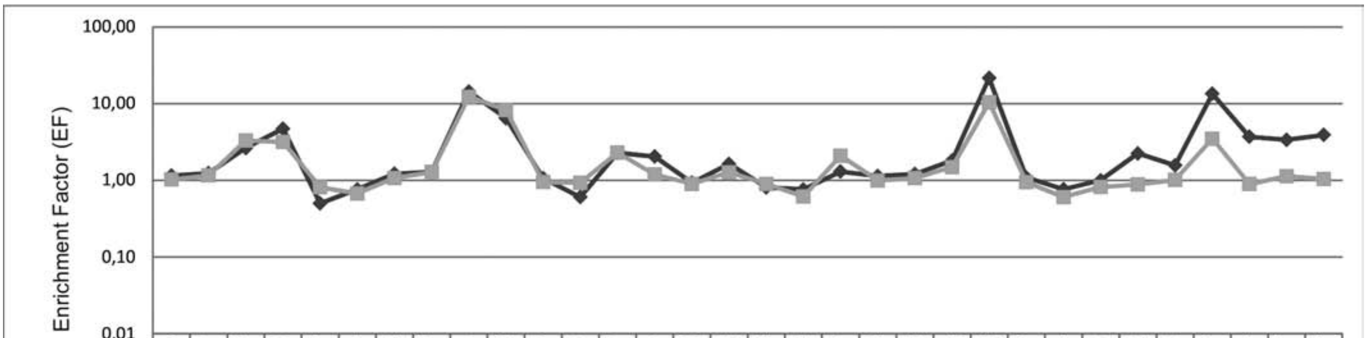



Fig. 3 - Chemical index of alteration (CIA) of the Pülümür and Munzur drainage areas.




| | Si | Fe | Mg | Ca | Na | K | Ti | Mn | Cr | Ni | Sc | Ba | Co | Cs | Ga | Hf | Nb | Rb | Sr | Th | U | V | W | Zr | Y | Cu | Pb | Zn | As | Sb | Au | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Munzur | 1,1 | 1,2 | 2,6 | 4,7 | 0,5 | 0,7 | 1,2 | 1,2 | 14, | 6,4 | 1,0 | 0,6 | 2,2 | 2,0 | 0,9 | 1,6 | 0,8 | 0,7 | 1,3 | 1,1 | 1,2 | 1,8 | 21, | 1,0 | 0,7 | 1,0 | 2,2 | 1,5 | 13, | 3,6 | 3,3 | 3,9 |
| Pülümür | 1,0 | 1,1 | 3,3 | 3,1 | 0,8 | 0,6 | 1,0 | 1,2 | 12, | 8,2 | 0,9 | 0,9 | 2,2 | 1,1 | 0,8 | 1,2 | 0,9 | 0,6 | 2,0 | 0,9 | 1,0 | 1,4 | 10, | 0,9 | 0,6 | 0,8 | 0,8 | 1,0 | 3,4 | 0,8 | 1,1 | 1,0 |

Fig. 4 - Enrichment factors of the elements in the Munzur and Pülümür sediments.

Table 1 - Major and trace element concentrations of the Pülümür (PL) and Munzur (MN) sediments.

| | Sample No. | PLS1 | PLS2 | PLS3 | PLS4 | PLS5 | PLS6 | Average | S.d. | MNS1 | MNS2 | MNS3 | MNS4 | MNS5 | Average | S.d. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | (%) | 45.44 | 45.30 | 42.10 | 39.12 | 39.23 | 42.49 | 42.26 | 2.80 | 39.66 | 40.59 | 42.27 | 39.52 | 37.34 | 39.88 | 1.79 |
| $Al_2O_3$ | | 15.10 | 10.31 | 9.98 | 9.28 | 7.86 | 7.91 | 10.07 | 2.67 | 10.51 | 8.37 | 8.52 | 8.56 | 8.03 | 8.80 | 0.98 |
| $Fe_2O_3$ | | 6.64 | 7.84 | 5.82 | 5.64 | 4.55 | 5.37 | 5.98 | 1.14 | 4.84 | 6.59 | 5.84 | 5.08 | 5.78 | 5.63 | 0.69 |
| MgO | | 2.84 | 16.31 | 10.38 | 8.40 | 4.71 | 9.42 | 8.68 | 4.72 | 2.19 | 9.54 | 5.13 | 6.14 | 10.63 | 6.73 | 3.41 |
| CaO | | 11.41 | 5.96 | 10.15 | 14.32 | 19.62 | 15.41 | 12.81 | 4.72 | 14.26 | 14.21 | 17.47 | 16.66 | 14.09 | 15.34 | 1.60 |
| $Na_2O$ | | 2.76 | 1.87 | 1.78 | 1.32 | 1.19 | 1.30 | 1.70 | 0.59 | 0.98 | 0.87 | 0.97 | 0.95 | 0.86 | 0.93 | 0.06 |
| $K_2O$ | | 1.41 | 0.92 | 1.16 | 1.18 | 1.09 | 0.86 | 1.10 | 0.20 | 1.27 | 1.03 | 1.11 | 1.06 | 0.92 | 1.08 | 0.13 |
| $TiO_2$ | | 0.96 | 0.61 | 0.51 | 0.53 | 0.45 | 0.48 | 0.59 | 0.19 | 0.60 | 0.61 | 0.62 | 0.52 | 0.48 | 0.57 | 0.06 |
| $P_2O_5$ | | 0.33 | 0.19 | 0.15 | 0.18 | 0.11 | 0.06 | 0.17 | 0.09 | 0.22 | 0.12 | 0.11 | 0.10 | 0.11 | 0.13 | 0.05 |
| MnO | | 0.11 | 0.12 | 0.10 | 0.09 | 0.10 | 0.09 | 0.10 | 0.01 | 0.11 | 0.10 | 0.07 | 0.08 | 0.10 | 0.09 | 0.02 |
| $Cr_2O_3$ | | 0.03 | 0.33 | 0.10 | 0.09 | 0.07 | 0.09 | 0.12 | 0.11 | 0.04 | 0.17 | 0.18 | 0.13 | 0.11 | 0.13 | 0.06 |
| LOI | | 12.70 | 9.70 | 17.40 | 19.50 | 20.80 | 10.10 | 15.03 | 4.76 | 25.20 | 17.50 | 17.50 | 20.70 | 19.40 | 20.06 | 2.94 |
| Sc | (ppm) | 14.00 | 14.00 | 13.00 | 13.00 | 10.00 | 12.00 | 12.67 | 1.51 | 12.00 | 13.00 | 12.00 | 12.00 | 12.00 | 12.20 | 0.45 |
| Ba | | 453 | 313 | 294 | 239 | 260 | 153 | 285 | 99 | 221 | 148 | 166 | 162 | 141 | 168 | 32 |
| Be | | 2.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.17 | 0.41 | 2.00 | 1.00 | 1.00 | 1.00 | 5.00 | 2.00 | 1.73 |
| Co | | 25.00 | 52.90 | 37.20 | 32.00 | 22.40 | 28.10 | 32.93 | 11.09 | 17.80 | 46.00 | 25.90 | 25.90 | 41.90 | 31.50 | 11.92 |
| Cs | | 2.30 | 1.30 | 2.30 | 3.10 | 3.00 | 1.30 | 2.22 | 0.79 | 3.40 | 2.40 | 4.20 | 4.10 | 4.10 | 3.64 | 0.76 |
| Ga | | 15.90 | 10.40 | 10.00 | 9.40 | 8.50 | 8.30 | 10.42 | 2.81 | 11.00 | 9.80 | 8.90 | 8.80 | 8.80 | 9.46 | 0.96 |
| Hf | | 3.90 | 2.30 | 2.20 | 2.30 | 2.10 | 1.60 | 2.40 | 0.78 | 3.40 | 2.30 | 2.50 | 2.20 | 1.60 | 2.40 | 0.65 |
| Nb | | 19.80 | 10.50 | 11.30 | 10.30 | 8.50 | 9.20 | 11.60 | 4.14 | 10.80 | 9.30 | 8.80 | 8.30 | 9.20 | 9.28 | 0.94 |
| Rb | | 46.00 | 28.00 | 35.00 | 41.00 | 36.00 | 26.00 | 35.33 | 7.58 | 50.00 | 35.00 | 37.70 | 34.70 | 32.00 | 37.88 | 7.07 |
| Sn | | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 0.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 0.00 |
| Sr | | 647 | 383 | 477 | 524 | 603 | 345 | 497 | 119 | 195 | 264 | 318 | 348 | 235 | 272 | 62 |
| Ta | | 1.10 | 0.60 | 0.70 | 0.60 | 0.50 | 0.50 | 0.67 | 0.23 | 0.80 | 0.60 | 0.60 | 0.60 | 0.50 | 0.62 | 0.11 |
| Th | | 8.70 | 4.50 | 5.10 | 5.40 | 4.70 | 3.50 | 5.32 | 1.78 | 7.10 | 4.90 | 6.00 | 4.30 | 4.00 | 5.26 | 1.28 |
| U | | 2.30 | 1.80 | 1.90 | 1.90 | 1.80 | 1.60 | 1.88 | 0.23 | 2.00 | 1.90 | 1.80 | 1.80 | 1.90 | 1.88 | 0.08 |
| V | | 130 | 130 | 101 | 101 | 87 | 104 | 109 | 17 | 102 | 128 | 125 | 102 | 102 | 112 | 13 |
| W | | 5.40 | 6.90 | 0.80 | 1.60 | 27.10 | 0.50 | 7.05 | 10.16 | 28.20 | 5.30 | 14.10 | 12.10 | 1.00 | 12.14 | 10.40 |
| Zr | | 176 | 91 | 92 | 90 | 75 | 70 | 99 | 39 | 129 | 115 | 92 | 75 | 80 | 98 | 23 |
| Y | | 19.60 | 12.50 | 12.60 | 13.60 | 12.80 | 12.40 | 13.92 | 2.82 | 18.80 | 14.50 | 14.40 | 13.70 | 13.70 | 15.02 | 2.15 |
| Mo | | 0.50 | 0.40 | 0.40 | 0.50 | 0.70 | 0.50 | 0.50 | 0.11 | 0.70 | 0.60 | 0.70 | 0.70 | 0.40 | 0.62 | 0.13 |
| Cu | | 28.70 | 29.90 | 26.80 | 27.20 | 24.70 | 22.10 | 26.57 | 2.81 | 33.00 | 31.00 | 24.40 | 26.60 | 30.70 | 29.14 | 3.53 |
| Pb | | 5.80 | 5.10 | 7.10 | 8.80 | 10.40 | 15.30 | 8.75 | 3.75 | 21.50 | 12.80 | 17.60 | 12.50 | 12.00 | 15.28 | 4.14 |
| Zn | | 53.00 | 47.00 | 43.00 | 50.00 | 45.00 | 44.00 | 47.00 | 3.85 | 72.00 | 58.00 | 60.00 | 62.00 | 53.00 | 61.00 | 7.00 |
| Ni | | 71 | 890 | 453 | 371 | 213 | 404 | 400 | 278 | 76 | 472 | 224 | 264 | 546 | 316 | 191 |
| As | | 1.70 | 1.40 | 3.70 | 5.20 | 9.10 | 7.10 | 4.70 | 3.04 | 13.00 | 10.50 | 16.50 | 15.70 | 10.00 | 13.14 | 2.94 |
| Cd | | 0.10 | 0.10 | 0.20 | 0.10 | 0.20 | 0.20 | 0.15 | 0.05 | 0.70 | 0.30 | 0.30 | 0.30 | 0.30 | 0.38 | 0.18 |
| Sb | | 0.10 | 0.10 | 0.10 | 0.10 | 0.20 | 0.10 | 0.12 | 0.04 | 0.60 | 0.40 | 0.40 | 0.30 | 0.10 | 0.36 | 0.18 |
| Bi | | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.30 | 0.13 | 0.08 | 0.20 | 0.20 | 0.10 | 0.10 | 0.10 | 0.14 | 0.05 |
| Ag | | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.00 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.01 |
| Au (ppb) | | 2.80 | 0.50 | 0.50 | 1.60 | 6.10 | 2.80 | 2.38 | 2.09 | 8.20 | 8.00 | 3.10 | 4.00 | 4.10 | 5.48 | 2.42 |
| Hg | | 0.01 | 0.02 | 0.01 | 0.01 | 0.02 | 0.03 | 0.02 | 0.01 | 0.06 | 0.03 | 0.04 | 0.05 | 0.05 | 0.05 | 0.01 |
| Tl | | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.00 | 0.10 | 0.10 | 0.10 | 0.20 | 0.10 | 0.12 | 0.04 |
| Se | | 0.50 | 0.50 | 0.50 | 0.60 | 0.50 | 0.50 | 0.52 | 0.04 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.01 |

Trace element concentrations of soil samples from the Munzur and Pülümür streams (Table 3) were normalized to the soil standard (Kabata-Pendias and Pendias, 1992) to detect the level of possible contamination (Fig. 6).

### Geoaccumulation Index (Igeo)

Toxic and pollutant effects of heavy metals are observed when they exceed certain concentrations. To investigate these effects of the heavy metals in the studied samples, the geoaccumulation index (Igeo) values were calculated (Fig. 7) using Igeo = $\log_2$Cn/1.5Bn formulae (Grzebisz et al., 2002; Apostoae and Iancu, 2009; Fagbote and Olanipekun, 2010). In this formula, Bn represents the crust values (Rudnick and Gao, 2003) and Cn represents the element concentrations in the sample.

Additionally, The Soil Pollution Standards of Turkey (MEUP, 2012) was used in order to compare the results with local background values (Fig. 8).

## DISCUSSION

In drainage areas, where water activity is high, mechanical and chemical weathering are intense. Thus, sediments and soils in stream basins are expected to be affected by mineralogical and geochemical characteristics of the host rocks. Mineralogical characterization of the sediment samples from the Munzur and Pülümür streams shows the presence of chrysotile, plagioclase, quartz and calcite (Fig. 2). It is remarkable that chrysotile was determined in all samples of the Pülümür stream. On the other hand, three samples of the Munzur stream contain fibrous chrysotile mineral. The presence of chrysotile (Fig. 2) in the samples indicates ultramafic rocks as the source, precisely, from the upstream part of the drainage area. The fibrous chrysotile from the asbestos group is well known because of its adverse effects on human beings (Nolan et al., 2001). Considering the projects about construction of numerous dams on the Munzur and Pülümür streams, the presence of fibrous chrysotile has to be taken into consideration, because of its danger on public health.

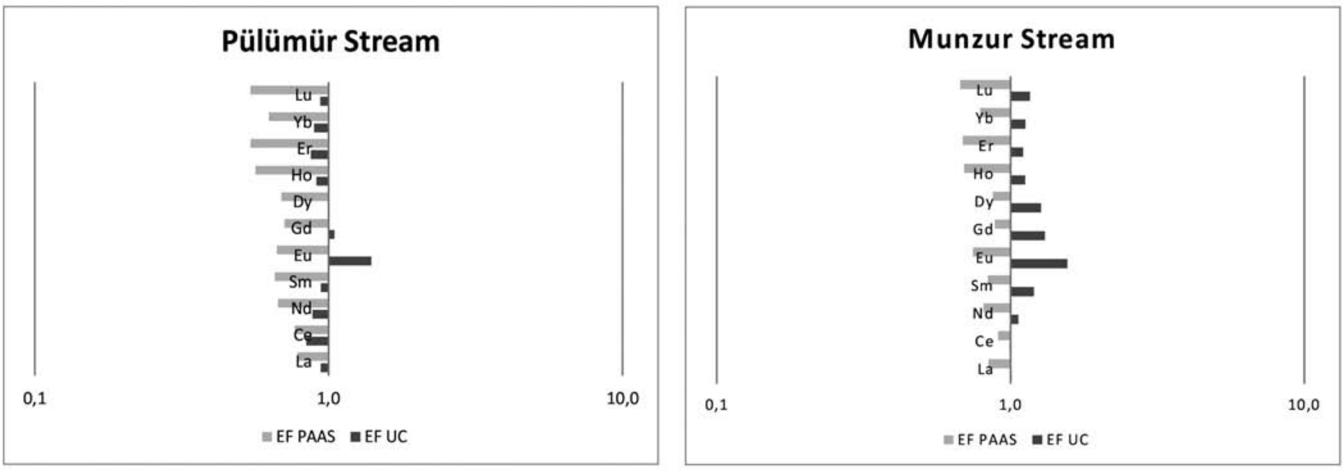
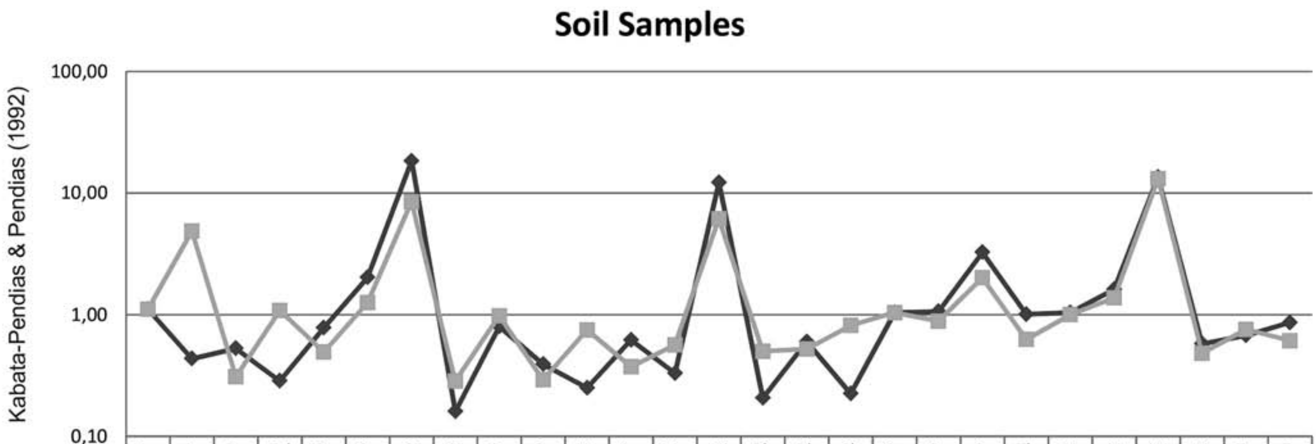



Fig. 5 - Enrichment factors of the REE in the Pülümür and Munzur sediments.




| | Ag | As | Ba | Cd | Ce | Co | Cr | Cs | Cu | Ga | Hg | La | Mo | Ni | Pb | Rb | Sb | Se | Sn | Sr | Th | U | V | W | Y | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pülümür | 1,11 | 0,44 | 0,53 | 0,29 | 0,78 | 2,03 | 18,3 | 0,16 | 0,80 | 0,39 | 0,25 | 0,62 | 0,33 | 12,2 | 0,21 | 0,60 | 0,22 | 1,04 | 1,06 | 3,26 | 1,01 | 1,04 | 1,62 | 13,5 | 0,58 | 0,68 | 0,86 |
| Munzur | 1,11 | 4,88 | 0,31 | 1,08 | 0,49 | 1,26 | 8,46 | 0,28 | 0,98 | 0,29 | 0,75 | 0,37 | 0,57 | 6,15 | 0,50 | 0,52 | 0,82 | 1,04 | 0,88 | 2,01 | 0,63 | 1,00 | 1,38 | 13,1 | 0,48 | 0,76 | 0,61 |

Fig. 6 - Enrichments of the trace elements in the Pülümür and Munzur soils.

Table 2 - REE concentrations of the Pülümür (PL) and Munzur (MN) sediments.

| Sample No. | PLS1 | PLS2 | PLS3 | PLS4 | PLS5 | PLS6 | Average | S.d. | MNS1 | MNS2 | MNS3 | MNS4 | MNS5 | Average | S.d. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (ppm) | | | | | | | | | | | | | | | |
| La | 29.4 | 17.3 | 16.4 | 16.6 | 15.2 | 11.6 | 17.75 | 6.06 | 19.4 | 15.1 | 21.4 | 13.8 | 13.7 | 16.68 | 3.51 |
| Ce | 55.9 | 32.2 | 32.1 | 32 | 28.8 | 23.7 | 34.12 | 11.17 | 41.5 | 30.3 | 46.7 | 28.1 | 29.3 | 35.18 | 8.38 |
| Pr | 6.12 | 3.44 | 3.54 | 3.63 | 3.31 | 2.83 | 3.81 | 1.17 | 4.57 | 3.55 | 5.17 | 3.26 | 3.37 | 3.98 | 0.84 |
| Nd | 23.7 | 13.4 | 13.5 | 13.7 | 12.9 | 9.7 | 14.48 | 4.76 | 17.4 | 13.6 | 19.8 | 12.9 | 12.6 | 15.26 | 3.19 |
| Sm | 4.1 | 2.57 | 2.55 | 2.64 | 2.4 | 2.29 | 2.76 | 0.67 | 3.51 | 2.67 | 3.77 | 2.51 | 2.66 | 3.02 | 0.57 |
| Eu | 1.24 | 0.77 | 0.75 | 0.73 | 0.65 | 0.66 | 0.80 | 0.22 | 0.86 | 0.7 | 0.95 | 0.66 | 0.6 | 0.75 | 0.15 |
| Gd | 3.77 | 2.39 | 2.37 | 2.5 | 2.37 | 1.9 | 2.55 | 0.63 | 3.25 | 2.53 | 3.22 | 2.47 | 2.37 | 2.77 | 0.43 |
| Tb | 0.62 | 0.39 | 0.39 | 0.41 | 0.39 | 0.38 | 0.43 | 0.09 | 0.53 | 0.41 | 0.47 | 0.4 | 0.39 | 0.44 | 0.06 |
| Dy | 3.29 | 2.11 | 2.13 | 2.3 | 2.05 | 1.94 | 2.30 | 0.50 | 3.06 | 2.37 | 2.54 | 2.28 | 2.42 | 2.53 | 0.31 |
| Ho | 0.69 | 0.43 | 0.43 | 0.48 | 0.42 | 0.48 | 0.49 | 0.10 | 0.6 | 0.51 | 0.5 | 0.46 | 0.45 | 0.50 | 0.06 |
| Er | 1.89 | 1.17 | 1.19 | 1.29 | 1.2 | 0.31 | 1.18 | 0.50 | 1.68 | 1.42 | 1.37 | 1.38 | 1.43 | 1.46 | 0.13 |
| Tm | 0.28 | 0.18 | 0.18 | 0.19 | 0.17 | 0.21 | 0.20 | 0.04 | 0.27 | 0.21 | 0.2 | 0.21 | 0.22 | 0.22 | 0.03 |
| Yb | 1.76 | 1.14 | 1.23 | 1.31 | 1.17 | 1.15 | 1.29 | 0.24 | 1.74 | 1.36 | 1.31 | 1.29 | 1.28 | 1.40 | 0.19 |
| Lu | 0.27 | 0.18 | 0.19 | 0.19 | 0.18 | 0.21 | 0.20 | 0.03 | 0.25 | 0.21 | 0.2 | 0.2 | 0.2 | 0.21 | 0.02 |
| ΣLREE | 119.22 | 68.91 | 68.09 | 68.57 | 62.61 | 50.12 | 72.92 | 23.78 | 86.38 | 65.22 | 96.84 | 60.57 | 61.63 | 74.128 | 16.47 |
| ΣHREE | 12.57 | 7.99 | 8.11 | 8.67 | 7.95 | 6.58 | 8.645 | 2.04 | 11.38 | 9.02 | 9.81 | 8.69 | 8.76 | 9.532 | 1.12 |
| ΣREE | 131.79 | 76.9 | 76.2 | 77.24 | 70.56 | 56.7 | 81.565 | 25.81 | 97.76 | 74.24 | 106.65 | 69.26 | 70.39 | 83.66 | 17.32 |
| ΣLREE/ΣHREE | 9.48 | 8.62 | 8.40 | 7.91 | 7.88 | 7.62 | 8.43 | 0.68 | 7.59 | 7.23 | 9.87 | 6.97 | 7.04 | 7.78 | 1.22 |
| PAAS Ce/Ce* | 0.85 | 0.84 | 0.87 | 0.85 | 0.83 | 0.84 | 0.85 | 0.01 | 0.92 | 0.86 | 0.93 | 0.87 | 0.91 | 0.90 | 0.03 |
| PAAS Eu/Eu* | 1.49 | 1.46 | 1.44 | 1.34 | 1.28 | 1.32 | 1.39 | 0.09 | 1.2 | 1.27 | 1.28 | 1.25 | 1.23 | 1.25 | 0.03 |
| UC Ce/Ce* | 0.91 | 0.9 | 0.93 | 0.92 | 0.89 | 0.91 | 0.91 | 0.01 | 0.99 | 0.93 | 1 | 0.93 | 0.95 | 0.96 | 0.03 |
| UC Eu/Eu* | 1.48 | 1.46 | 1.43 | 1.34 | 1.28 | 1.31 | 1.38 | 0.08 | 1.2 | 1.27 | 1.28 | 1.25 | 1.27 | 1.25 | 0.03 |

*Eu/Eu*= EuCN/(SmCN*GdCN)$^{0.5}$*
*Ce/Ce*= 3CeCN/(2LaCN + NdCN)*

Regarding geochemical composition of sediments, it is known that trace element concentrations are controlled by chemical weathering of the source rocks and basin (Yang and Rose, 2005). The heavy metal enrichments in the stream sediments suggest an efficient chemical alteration in the drainage area. The CIA values of the samples for the Munzur (80.3-82.3) and Pülümür streams (77.2-78.7) indicate a strong and medium chemical alteration in the drainage area (Fig. 3). The higher degree of alteration in the Munzur drainage area, where flow rate is more intense, strongly suggests a higher mobility of elements from the host rocks.

Normalized patterns of the enrichment factors display similar trends for both basin sediments of the Munzur and Pülümür streams (Fig. 4). All the sediments are enriched in Mg, Ca, Cr, Ni, Co, W and As. Additionally, the sediments from the Munzur stream are also enriched in Pb, Zn, Sb, Au and Hg. These similarities in enrichment factors indicate a lithological control for the Cr, Ni, Co, W and As enrichments (Fig. 4). The control of the host rock is well demonstrated by the presence of similar geological units in both drainage areas. Limited and insignificant industrial and agricultural activities support the role of the host rocks as major contamination factor. Among these geological units, the chromite bearing ultramafic rocks, located north of the drainage areas, are the main source of the Cr, Ni and Co enrichments. On the other hand the Pb, Zn, As, Sb, Au and Hg enrichments in the sediments of the Munzur drainage area can be explained by the presence of Cu-Pb-Zn mineralization. Lastly, significant W enrichments are observed in both streams, possibly because of unknown W-bearing deposits present in the drainage areas (Fig. 1). For instance, W-bearing deposits mostly occur in contact metamorphic zones

Table 3 - Trace element concentrations of the Pülümür (PL) and Munzur (MN) soils, comparison with the Kabata-Pendias values.

| Element (ppm) | Pülümür | Munzur | Kabata-Pendias& Pendias (1992) |
|---|---|---|---|
| Ag | 0.1 | 0.1 | 0.09 |
| As | 4.96 | 55.65 | 11.4 |
| Ba | 328.2 | 192.25 | 622 |
| Cd | 0.14 | 0.53 | 0.49 |
| Ce | 39.1 | 24.73 | 50.2 |
| Co | 25.54 | 15.85 | 12.6 |
| Cr | 1300 | 600 | 70.9 |
| Cs | 2.08 | 3.7 | 13 |
| Cu | 22.56 | 27.6 | 28.2 |
| Ga | 10.96 | 8.18 | 28 |
| Hg | 0.03 | 0.09 | 0.12 |
| La | 20.68 | 12.48 | 33.4 |
| Mo | 0.66 | 1.13 | 2 |
| Ni | 217.14 | 109.55 | 17.8 |
| Pb | 5.86 | 14.23 | 28.4 |
| Rb | 37.46 | 32.6 | 62.5 |
| Sb | 0.22 | 0.8 | 0.98 |
| Se | 0.5 | 0.5 | 0.48 |
| Sn | 1.2 | 1 | 1.13 |
| Sr | 560.64 | 346.18 | 172.1 |
| Th | 6.4 | 3.98 | 6.35 |
| U | 2.06 | 1.98 | 1.98 |
| V | 110.2 | 94 | 68.2 |
| W | 20.28 | 19.73 | 1.5 |
| Y | 15.16 | 12.68 | 26.3 |
| Zn | 45.8 | 51.25 | 67.8 |
| Zr | 120.44 | 85.65 | 140 |

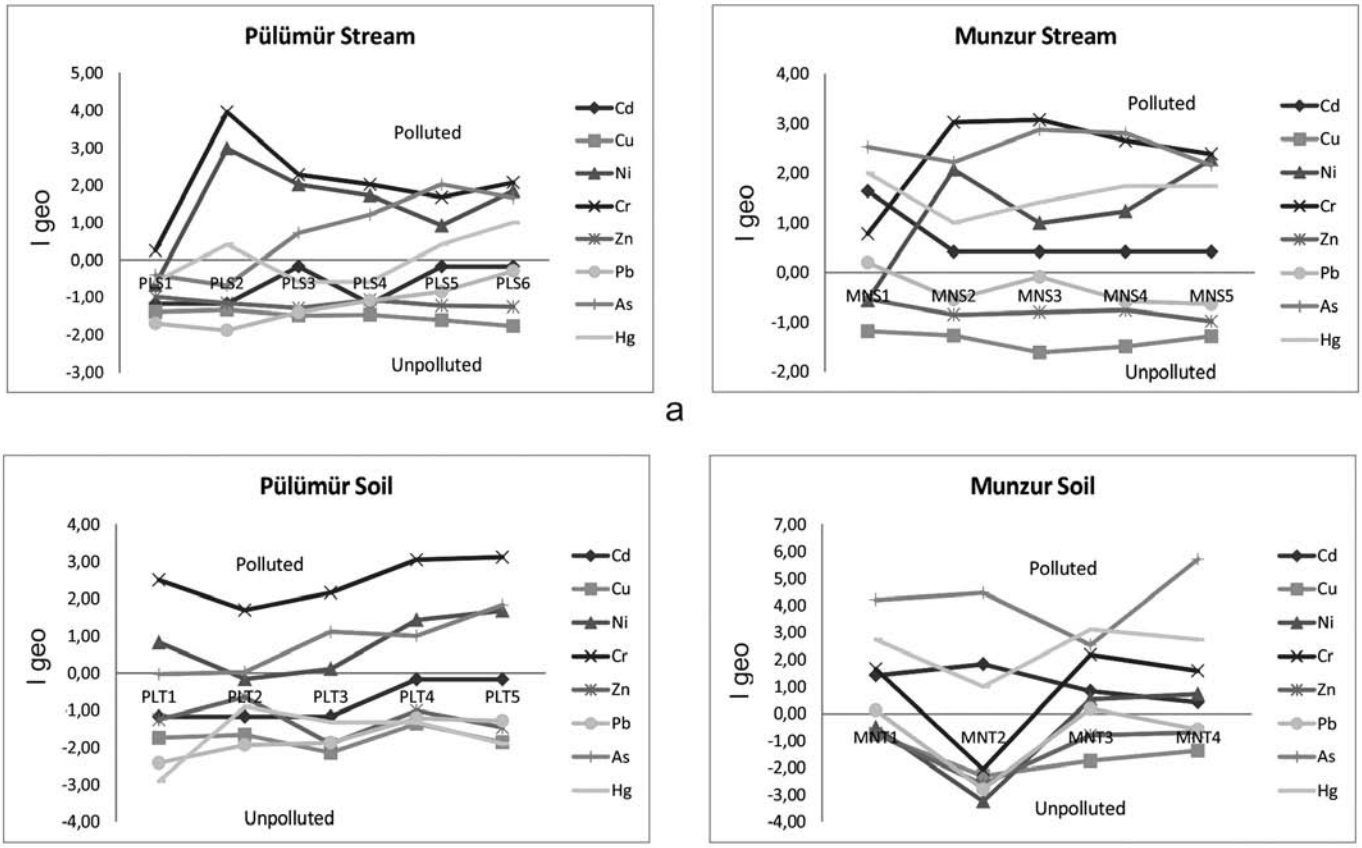



Fig. 7 - Geoaccumulation index (Igeo) values for the sediments (a) and soils (b).

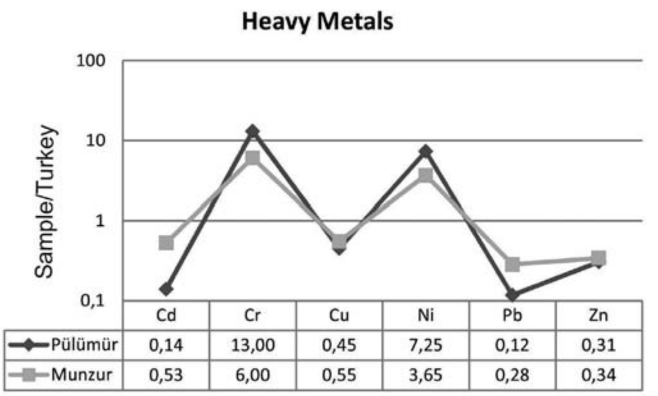



Fig. 8 - Comparison of the heavy metal concentrations in the Pülümür and Munzur soils with “The Soil Pollution Standards of Turkey” (MEUP, 2012).

(Kwak, 1987), and the drainage areas contain many limestone units and marbles which can be host rock of this kind of mineralization.

The enrichment factors of REEs indicate that the sediments of both streams were depleted compared to PAAS. However, the enrichment factors compared to UC show enrichment in Eu for the Pülümür sediments, enrichment in middle (Sm, Eu, Gd, Dy) and heavy (Ho, Er, Yb, Lu) rare earths for the Munzur sediments (Fig. 5). The most important factor for concentration of REE is transportation by clay minerals to the depositional environment (Gromet et. al., 1984; Condie, 1991; Ketris and Yudovich, 2009). The patterns indicate that volcanic rocks, cropping out on the drainage area of the Munzur stream (Fig. 1), control the REE concentrations in the sediments. The ultramafic rocks in the drainage area cannot account for the REE enrichments because of their primary chemical compositions highly depleted in REE. The slightly negative Ce anomalies (Ce/Ce*) (Table 2) of the sediment samples from both streams is likley related to Ce leaching from sediment after oxidation of $Ce^{+3}$ to $Ce^{+4}$ (Thomas et al., 2003). The positive Eu anomalies (Table 2) suggest the presence of Ca-rich plagioclase in the sediments as inferred by the XRD mineralogical characterization.

The normalized patterns of the soil samples show enrichments in Co, Cr, Ni, Sr, V and W for both streams. However, Arsenic appears enriched only in the soils of the Munzur stream. Cd, Hg and Sb display depletion in the soils of both streams, nevertheless the samples of the Munzur stream have relatively higher concentrations. The soils of the drainage areas are also enriched in Cr, Ni and Co, which reflects the ultramafic units as natural contaminants (Fig. 6). The source of As enrichment, detected only in the soil samples of the Munzur stream, could be conceivably attributed to the Cu-Pb-Zn mineralization.

Evaluation of the geochemical data reveals the heavy metal enrichments in sediment and soil samples of the Munzur and Pülümür streams. Environmental pollution by heavy metals is a worldwide problem due to their toxic effects on human health (Schuurmann and Market, 1998; MacFarlane and Burchett, 2000). The calculated Igeo values for the sediments of the Pülümür stream indicate that Cr and Ni concentrations are at pollution level except for one sample (PLS1). Non-pollution levels of Cr and Ni contents in sample PLS1 can be due to the absence of ultramafic units in this sampling location. Igeo values clearly indicate that As, Hg, Cd, Cu, Zn and Pb are below the pollution level in the Pülümür drainage area (Fig. 7a). The Igeo values, for the sediments of the Munzur stream except for sample MNS1, show pollutant levels of Cr and Ni contents similar to the sediments of the Pülümür stream. All samples of the Munzur sediments also have pollutant levels of As, Hg and Cd heavy metals. The concentrations of Cu, Zn and Pb in the Munzur sediments are below the pollutant levels. The pollutant heavy metals are significantly controlled by host rocks in the drainage areas of the streams. The anthropogenic pollution is not considered in the study area because of the limited and insignificant industrial and agricultural activities.

Cr and Ni are defined as pollutant in the soil samples of the Pülümür stream, similar to the sediments (Fig. 7b). In contrast, Igeo values of the other heavy metals (i.e. Cd, Hg, Cu, Zn and Pb) indicate non-pollutant levels. Igeo index values for the soils of the Munzur stream are not consistent among the samples. In detail; the concentrations of As, Hg, Cr, Ni and Cd for the MNT1; As, Cd and Hg for the MNT2; As, Hg, Cr, Ni and Cd for the MNT3 and MNT4 exhibit pollutant levels (Fig. 7b). The common heavy metals (Cr, Ni, As, Hg, Cd) can be shown as pollutants in the sediments and soils of both Munzur and Pülümür streams. Moreover, the heavy metal concentrations of the soil samples were compared with the values of "The Soil Pollution Standards of Turkey". This comparison confirms the presence of Cr and Ni enrichments for soil samples of the both streams (Fig. 8). These elements are removed from the source rock as a consequence of alteration process and accumulate in the streams. Both mechanical and chemical weathering processes cause the element enrichments. The natural lithological distribution is the main reason for the pollutants in the study area. Additionally, the geochemical behaviour of As may indicate a partially anthropogenic source for the Pülümür drainage area, because the concentration of As slightly increases not only in soils but also in the sediments along the stream flow (Fig. 1 and Fig. 7) where small-scale residential areas and agricultural activities exist.

## CONCLUDING REMARKS

To sum up, the subject of this study is to determine the geochemical and mineralogical characteristics of the sediments and soils of the Munzur and Pülümür streams which are essential water supplies of Tunceli Province (Turkey). The identified heavy metal contaminations (Cr, Ni, As, Hg, Cd) and the presence of fibrous chrysotile are caused by the natural lithology due to the absence of significant industrial and agricultural activities. Elemental grouping in the samples point out two different sources related to the Cr-bearing ultramafic host rocks and Zn-Cu mineralization in the study area. The fibrous chrysotile and heavy metal contaminations must be considered as a threat for the public health.

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