RESEARCH ARTICLE

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# Heavy metals in tailings and soils in the Pb-Zn mining areas of North-west Türkiye and health risk evaluations

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**Abstract**

Improper mining waste and tailing management in Pb-Zn mining areas (Balya and Koru) in the north-west Türkiye have not been researched sufficiently. Accordingly, concentrations of heavy metal were determined in mine tailing and soils taken from Balya and Koru, and a health risk evaluation caused by heavy metals was performed. Average Cd, Cr, Cu, Mn, Ni, Pb, and Zn concentrations in mine tailings in Balya are 35.2, 17.8, 354.7, 1735, 10, 10089, 3730 mg kg$^{-1}$ and these values were determined as 9.9, 8.9, 101.5, 1308, 4.5, 1871, 1375 mg kg$^{-1}$ in the tailings in Koru, respectively. The concentrations of heavy metals in the soil samples taken from both Balya and Koru were determined to be lower. The evaluation of heavy metals' health risks was performed according to both non-carcinogenic and carcinogenic effects. The primary route of heavy metals in adults and children has been determined by oral intake. For both children and adults, the order of the carcinogenic effects of heavy metals in mine tailings and soils in Balya and Koru was Cd > Pb > Ni > Cr. As the carcinogenic risk values of Cd and Pb for adults and children in mine tailing and soils in Balya were above the limit value, the children's Cd carcinogenic risk values were found above the limit value in mine tailing and soils in Koru. The mining area in both Balya and Koru poses a risk to human health since it is close to settlements.

**Keywords:** Heavy metals, Lead–zinc mine, Soil pollution, Health risk assessment, Türkiye

## INTRODUCTION

Human activities including agricultural activities, vehicular emissions, inappropriate waste removal and disposal, fossil fuels and mining facilities generate serious damage on environmental matrices (soil, plant, water and sediment). Mining activities constitute the most striking and the primary source of heavy metals in receiving bodies (Azhari et al. 2017; Nassiri et al. 2021). Mine wastes such as tailing, soil and dust result in water, air and soil pollution, loss of biodiversity and various health problems for people living around mining facilities (Du et al., 2019; Tran et al., 2022).

Exposure of human body to excessive concentrations of heavy metals can damage nervous system, cause kidney dysfunction, hypertension, cancer and increase the risk of fetal death (Kapwata et al., 2020; Zhao et al., 2019). Heavy metals are taken into human body through ingestion, inhalation or dermally (Botsou et al., 2020; Kan et al., 2021; Parlak et al., 2022, 2023). Qi et al. (2016) conducted a health risk assessment study for children exposed to soil heavy metals in a Pb-Zn mine district of Yunnan Province of south-west China. It was found that long-term Pb/Zn mining activities caused serious soil pollution. It was also determined that children were exposed to greater health risks than adults and the highest hazard index was encountered in Pb (57-74%). Jahromi et al. (2020) calculated health index values for heavy metals (Cd, Pb, and Zn) of the soil samples taken from the nearest mining area of Isfahan (Iran) and determined that all health index values were higher than 1, indicating negative impacts on human health.

In recent years, number of studies on Pb-Zn mining areas of different countries such as Nigeria (Adewumi et al., 2021), Algeria (Arab et al., 2021), China (Cao et al., 2022), Spain (Garcia-Lorenzo et al., 2019) and Iran (Tehrani et al., 2023) has increased. There are also previous studies on heavy metals in Pb-Zn mining regions of Türkiye (Hanilçi and Öztürk, 2011; Koz, 2014; Çelebi and Öncel, 2016; Çiçek and Oyman, 2016; Hanilçi et al., 2019), but none of them focused on potential health risks of heavy metals. Therefore, this study will be the first comprehensive study in Pb-Zn mining areas of north-west Türkiye. Objectives of the present study was set as to assess spatial distribution and concentrations of heavy metals in tailings and soils of lead-zinc mining area in Balya (Balıkesir) and Koru (Çanakkale) districts; to evaluate possible sources of contamination in tailings and soils in Pb-Zn mining areas using principal component analysis and to evaluate the possible impacts of heavy metals in tailing and soils of the research areas on human health (adults and children).

## MATERIALS AND METHODS

### Study Area

Balya-Balıkesir Pb-Zn Mine: Balya is located in the Southern Marmara part of the Marmara Region, within the borders of Balıkesir province. It is surrounded by Manyas and Gönen in the north, Central district of Balıkesir in the east, İvrindi in the south, Yenice and Havran districts in the west. Balya is located between 27°20ˈ - 27°50ˈ east longitudes and 39°35ˈ - 39°55ˈ north latitudes (Figure 1). More or less 70% of Balya consists of mountainous areas, the rest consists of rough terrains. At 225 meters above sea level, Balya has hot, dry summers and cool, rainy winters. According to the long-term average (1938-2020), the average temperature of Balya is 14.7 ºC and the monthly total precipitation is 524 mm (GDM, 2022). There are Paleozoic, Mesozoic and Tertiary formations in the study area. There are mainly Permian-aged (Balya Formation) allochthonous limestones. A series of Triassic-aged (Karakaya Formation) claystone, sandstone, limestone and pebble stones unconformably are located on the parent rock (Budakoğlu and Pratt, 2005). The distance of mining site to Balya district is 1.6 km. Balya mining site lies between the villages of Patlak and Çakallar (Figure 1). Oak (Quercus) is the primary tree species in Balya. Red pine (*Pinus nigra*) species are encountered in the south and southwest of the mountains and there are also black pine (*Pinus nigra*) trees at higher altitudes. Hungarian oaks (*Quercus frainetto*) and Turkish oaks (*Quercus cerris*) are observed at relatively high altitudes and in the plateaus extending up to 600 m. These species have the appearance of clustered shrubs in areas with high level of destruction. Maquis lands have expanded their borders as a result of the destructions in the area where the primary vegetation is dry forest due to climate conditions. Maquis species include mock privet (*Phillyrea latifolia*), Greek strawberry tree (*Arbutus andrachne* L.), strawberry tree (*Arbutus unedo* L.), juniper (*Juniperus oxycedrus*) and Spanish broom (*Spartium junceum*) (Öncel, 2016). Balya mining site is an uncontrolled dumping site that has been in direct interaction with the receiving environment for many years (Figure 2A). The tailings interact with surface waters (rain water, Sarısu/Maden Stream, Kocaçay, Madra, Manyas Dam Reservoirs), groundwater, soil through dusting and therefore with humans and living things. Amount of tailing at Balya mining site is estimated to be between 1.000 - 2.355 million tons (Aka, 2020). Balya tailings contain pyrite ($FeS_2$), sphalerite (ZnS), galena (PbS), and chalcopyrite ($CuFeS_2$) minerals (Budakoğlu and Pratt, 2005).

Balya Pb-Zn mine is a mine known to exist since ancient times and operated by primitive ways. In the modern sense, it was first started to be operated by a French company in the 1880s. It was operated by the French company at intervals until 1939. The mine was closed in 1940 because the production revenues did not cover the operating costs (Arslan, 2010). The Pb-Zn mine was reactivated in 2005 and two private companies obtained the license to operate it. It is still the largest and oldest Pb-Zn deposit discovered in Türkiye (Çelik Balcı et al., 2014).

Koru (Lapseki-Çanakkale) Pb-Zn Mine: It is located in the north-west of Türkiye, on the Biga Peninsula, within the borders of Çanakkale province and in Korukoy area of Lapseki district (Figure 1). The geology of Biga Peninsula generally consists of metamorphic assemblages, ophiolitic rocks, overlying Neogene basin sediments and the products of magmatic activity that started from the Eocene and continued until the Pliocene (Bozkaya et al., 2020). Lapseki district has a typical Mediterranean climate with a high precipitation density in autumn and spring, cold in winters, hot in summers and air movements throughout the year (Türkeş, 1996). According to long-term average (1938-2020), the average temperature of Koru is 15.6 ºC and the monthly total precipitation is 620 mm (GDM, 2022). The distance of Koru mining site to the nearest settlement, Asmalı village, is 2.9 km. Koru mining site is located between the villages of Asmalı, Eskikışla and Karaömerler (Figure 1). The distance between Koru mining site and the village of Eskikışla and Karaömerler is 3.3 km and 4.3 km, respectively. In Lapseki, natural vegetation consists of a few maquis species of christ's thorn (*Paliurus spina-christi*), Greek strawberry tree (*Arbutus andrachne* L.), kermes oak (*Quercus coccifera*), erica (*Erica* L.), mock privet (*Phillyrea latifolia*), rockrose (*Cistus* spp.), strawberry tree (*Arbutus unedo* L.), Spanish broom (*Spartium junceum*), cotoneaster (*Cotoneaster*), rhododendron (*Rhododendron*), wild blackthorn (*Prunus spinosa*), blackberry (*Rubus fruticosus*), wild olive (*Olea aleaster*), sumac (*Rhus coriaria* L.), styrax tree (*Styrax officinalis* L.) and red pine (*Pinus brutia*) (Koca, 2003). The tailings are discharged into receiving environments and there is no data on the amount of tailing for Koru mining site (Figure 2B). Koru tailings contain galena, sphalerite (ZnS), chalcopyrite, bornite ($Cu_5FeS_4$), and tennantite ($Cu_{12}As_4S_{13}$) minerals (Çiçek and Oyman, 2016).

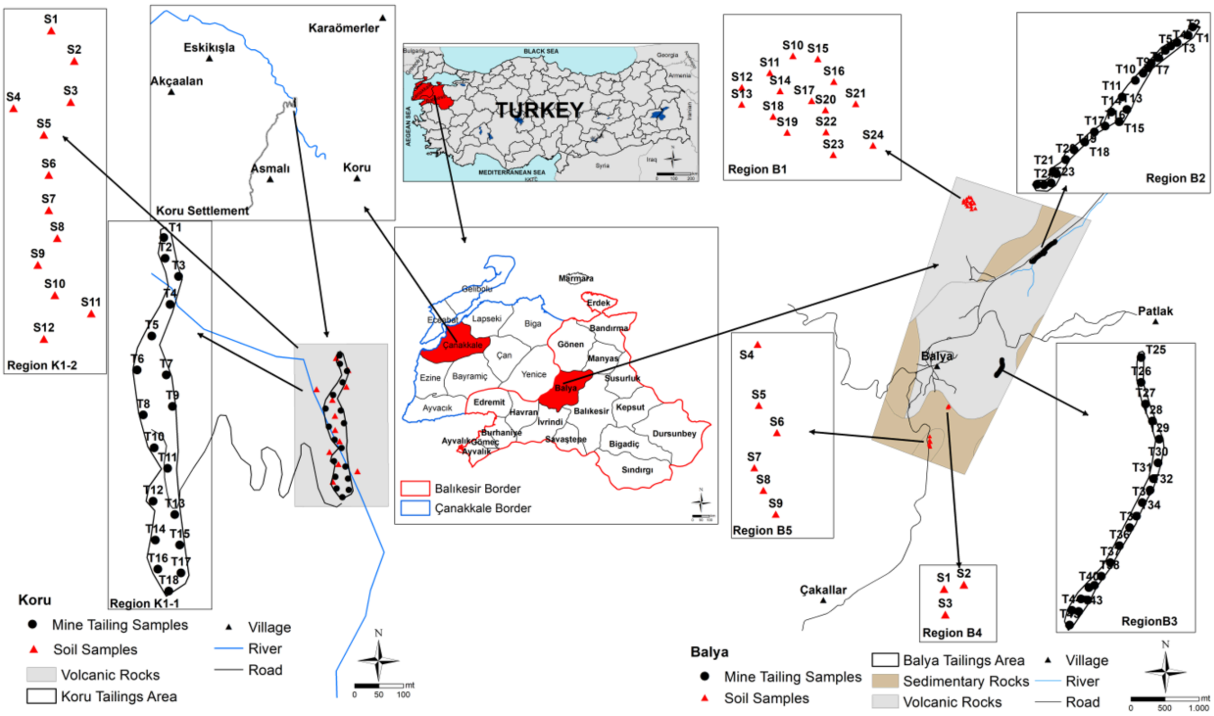


**Figure 1.** The location of the case areas and the places where mine waste and soil samples were taken


**Figure 2.** A. Tailings in the Balya mining area, B. Tailings in the Koru mining area

### Sampling, Soil and Tailing Analysis

Soil and tailing samples were taken from the Pb-Zn mining regions Balya and Koru between April 2018 and May 2019 with the use of random sampling method. Totally, 45 tailing and 24 soil samples were taken from 5 different regions of Balya and 18 tailing and 12 soil samples were taken from 1 region of Koru mining site. About 1 kg sample was taken from 0-20 cm depth. Each sample was divided into 3 sub-samples. Soil samples were taken from close vicinity of mining areas. Especially for Koru mining area, soil and tailing sampling points were quite close to each other. Coordinates of all sampling points were determined with a Global Positioning System (GPS).

Tailing and soil samples were then to laboratory, air dried, large particles were broken into small pieces with a wooden hammer and passed through 2 mm sieve. Some physicochemical analyses were performed on these samples. For soil texture (fine sand, coarse sand, silt and clay; %), Bouyoucos Hydrometer method was used (Gee and Or, 2002). Soil EC (dS $m^{-1}$) and pH values were measured from saturation paste extract and lime content (%) was determined in accordance with the procedures outlined in Burt (2004). Organic matter (OM) was determined in accordance with Nelson and Sommers (1996).

For heavy metal analyses (Cd, Cr, Cu, Mn, Ni, Pb, and Zn), samples were passed through 100 µm sieve and subjected to acid-digestion in aqua regia ($HNO_3$:HCl mixture, 1:3 ratio) (USEPA, 1996). Heavy metal concentrations of tailing and soil samples were measured in an ICP-OES device (Varian 710-ES model). Method validity was tested with the use of a verified reference material (NIM-GBW07425, soil). Percent recoveries are provided in Table 1. Recoveries varied between 88 - 104% and the findings were acceptable.

**Table 1.** Certified and measured values ( in mg $kg^{-1}$) and recovery rate (%) of heavy metals of various standard reference materials (NIM-GBW07425, soil)

| Metals | Certified values | Measured values | Recovery(%) |
|---|---|---|---|
| Cd | 0.13±0.01 | 0.14±0.01 | 95.2±4.1 |
| Cr | 59±3 | 62.6±2.5 | 94.3±3.8 |
| Cu | 21.4±1.2 | 24.3±1.5 | 88.2±5.4 |
| Mn | 572±14 | 553.3±22.5 | 103.8±4.2 |
| Ni | 25.4±1.3 | 27.3±0.6 | 92.9±2.1 |
| Pb | 24.7±1.4 | 24.2±0.9 | 102.3±3.6 |
| Zn | 65±5 | 67.6±4.5 | 96.3±6.5 |

### Health Risk Evaluation

Adults and children are walking around mining sites, children are also playing and livestocks are grazing on mining sites. In addition, people collect fruit from the shrubs and trees around the mining site and also collect edible wild plants. Therefore, health risk assessment of heavy metals was also performed in this study. Non-carcinogenic and carcinogenic health risks have been estimated for adults and children exposed to tailing and soil heavy metals (USEPA 1997, 2011). Several researchers stated the most important potential exposure pathways as ingestion and dermal pathway (Li et al. 2014; Jahromi et al. 2020). Therefore, ingestion and dermal pathways were used in present study to determine adverse health effects. The average daily dose ($ADD_{ingestion}$ and $ADD_{dermal}$) was calculated with the use of the following equation (USEPA, 1989, 1997, 2011, 2019).

$$ADD_{ingestion} (mg\ kg^{-1} d^{-1}) = Cx\ (IngRxEFx\ ED)/BWxAT\ xCF \quad (1)$$

$$ADD_{dermal} (mg\ kg^{-1} d^{-1}) = Cx\ SAxAFxABSxEFxED/BWxAT\ xCF \quad (2)$$

The parameters used to calculate the average daily dose ($ADD_{ingestion}$ and $ADD_{dermal}$) are shown in Table 2.

**Table 2.** Exposure factors of heavy metals (in mg $kg^{-1}$ $d^{-1}$) used in this study

| Parameters | Symbols | Units | Values | References |
|---|---|---|---|---|
| Heavy metal concentration | C | $mg^{-1}$ $kg^{-1}$ | Present value | - |
| Ingestion rate-adult | $IngR_a$ | $mg^{-1}$ $day^{-1}$ | 20 | USEPA, 1997 |
| Ingestion rate-child | $IngR_c$ | $mg^{-1}$ $day^{-1}$ | 200 | USEPA, 1997 |
| Skin surface available for exposure-adult | $SA_a$ | $cm^2$ | 6032 | USEPA, 2004 |
| Skin surface available for exposure-child | $SA_c$ | $cm^2$ | 2800 | USEPA, 2004 |
| Skin adherence factor-adult | $AF_a$ | mg $cm^{-2}$ | 0.07 | USEPA, 2004 |
| Skin adherence factor-child | $AF_c$ | mg $cm^{-2}$ | 0.2 | USEPA, 2004 |
| Dermal absorbsion factor | ABS | unitless | 0.001 | De Miguel et al., 2007; Botsou et al.,2020 |

| | | | | |
|---|---|---|---|---|
| Exposure frequency-adult | $EF_a$ | days year$^{-1}$ | 350 | USEPA, 2011 |
| Exposure frequency-child | $EF_c$ | days year$^{-1}$ | 104 | USEPA, 2011 |
| Exposure duration-adult | $ED_a$ | year | 20 | De Miguel et al., 2007; Botsou et al.,2020 |
| Exposure duration-child | $ED_c$ | year | 6 | De Miguel et al., 2007; Botsou et al.,2020 |
| Conservation factor | CF | kg mg$^{-1}$ | $10^{-6}$ | USEPA, 2011 |
| Body weight-adult | $BW_a$ | kg | 70 | USEPA, 2011 |
| Body weight-child | $BW_c$ | kg | 15 | USEPA, 2011 |
| Average time for non-carcinogenic effects-adult | $AT_a$ | day | 7300 | USEPA, 1989 |
| Average time for non-carcinogenic effects-child | $AT_c$ | day | 2190 | USEPA, 1989 |

Potential health risks for both adults and children who were exposed to heavy metal- contaminated soils were assessed through hazard quotient, calculated with the use of Eq. 3:

Hazard Quotient (HQ)=ADD/RfDs (3)

In equation, $RfD_s$ is reference dose for heavy metals, which is provided in Table 3.

**Table 3.** Values of $RfD_s$ (mg kg$^{-1}$ d$^{-1}$) and SF (mg kg$^{-1}$ d$^{-1}$) for seven heavy metals (De Miguel et al, 2007; Ferreira-Baptista and De Miguel, 2005; Cheng et al., 2018; Cao et al., 2015; Jiang et al., 2017).

| | Cd | Cr | Cu | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|
| $RfD_s$ for ingestion | 1.00E-03 | 3.00E-03 | 4.00E-02 | 4.60E-02 | 2.00E-02 | 3.50E-03 | 3.00E-01 |
| $RfD_s$ for dermal absorption | 1.00E-05 | 6.00E-05 | 1.20E-02 | 1.84E-03 | 5.40E-03 | 5.25E-04 | 6.00E-02 |
| SF for ingestion | 6.10E+00 | 5.00E-01 | - | - | 1.70E+00 | 8.50E-03 | - |
| SF for dermal absorption | 6.10E+00 | 2.00E+01 | - | - | 4.25E+01 | - | - |

The hazard index was then determined by adding the HQs for each variable within study. HI values of below 1.0 indicate that significant additive or harmful interactions were exceedingly improbable and HI values of > 1.0 imply that undesirable, non-carcinogenic health effects were probable (USEPA, 2007; USEPA, 2011).

The carcinogenic risk (CR) was calculated (Eq. 4) by combining the average daily doses (ADD) with the slope factor.

Carcinogenic risk (CR) = Average Daily Dose (ADD) x Slope Factor (SF) (4)

Computed carcinogenic risk values of between $1x10^{-6}$ and $1x10^{-4}$ are considered to be within the acceptable and tolerable risk range for human health (USEPA, 2011).

## Statistical Analysis and Spatial Distribution

Descriptive statistics (average, minimum, maximum, standard deviation) were used to determine the distribution of parameters. Data normality was checked and a transformation was performed for some parameters. Then a factor analysis was performed. Principal component analysis (PCA) was performed to identify possible sources of heavy metals. In factor analysis, Barlett and Kaiser–Meyer–Olkin (KMO) tests were used to determine the suitability of the data set, the principal component analysis method was used to determine the factors, and the Varimax technique was used for the rotation process. As a result of factor analysis, groups with eigen values equal to or greater than 1 were accepted as factors. Pearson correlation analysis was performed to determine the relationships between parameters. Statistical analyses were performed with the use of IBM SPSS 17.0 software (SPSS Inc., 2007). Spatial distribution of heavy metal concentrations in mine tailings and soils was performed with the use of ArcGIS 10.1 software (ESRI, 2009).

## RESULTS AND DISCUSSION

Some physical and chemical properties of tailing and soil samples taken from Balya and Koru mining areas are provided in Table 4. Balya tailings were 33% loamy-sand, 60% sandy-loam and 7% sandy in texture. Average pH, lime (%), EC (dS m$^{-1}$) and OM (%) content of mine tailings were found to be 6.1, 2.1, 0.7 and 1, respectively. Average Cd, Cr, Cu, Mn, Ni, Pb and Zn content of tailings were determined to be 35.2, 17.8, 354.7,1734.9, 10, 10089 and 3730 mg kg$^{-1}$, respectively. Balya soils were all sandy-loam in texture. Soil pH values varied between 6 - 7.3 and EC values varied between 0.3 - 0.9 dS m$^{-1}$. Average lime (%) and OM (%) content of the soils were determined to be 7.7 and 2.2. Soil heavy metal concentrations were ordered as Pb > Zn > Mn > Cu > Cd > Cr > Ni.

Koru tailings were 33% sandy-clay-loam and 67% sandy-loam in texture. Tailing pH values varied between 4.2 - 6.6, EC values varied between 0.1 - 0.8 dS $m^{-1}$, lime contents between 0.1 - 1.4% and organic matter contents between 0.4 - 4.7%(Table 1). Average Cd, Cr, Cu, Mn, Ni, Pb, and Zn concentration of tailings were determined to be 9, 8.9, 101.5, 1308, 4.5,1871 and 1375 mg $kg^{-1}$, respectively. Koru soils were 50% sandy-loam, 25% sand and 25% loamy-sand in texture. Soil average pH, EC (dS $m^{-1}$), lime (%) and OM (%) contents were determined as 5.7, 0.6, 0.5 and 0.9, respectively. Soil average Cd, Cr, Cu, Mn, Ni, Pb of Zn concentrations were determined to be 4.6, 3.4, 57.5, 1190, 1.6, 431.4 and 909 mg $kg^{-1}$, respectively.

**Table 4.** Some physicochemical properties of tailings and soils in Balıkesir-Balya and Çanakkale-Koru Pb-Zn mining areas

| | Balya | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Tailing | | | | | Soil | | | | |
| Parameters | Mean | Std.Deviation | Min. | Max. | Median | Mean | Std.Deviation | Min. | Max. | Median |
| Clay(%) | 9.7 | 3 | 4.1 | 16.7 | 10.2 | 14 | 3 | 6.3 | 18.7 | 14.3 |
| Silt(%) | 14.2 | 6 | 4.2 | 27.1 | 12.8 | 18.7 | 4.1 | 12.3 | 30.6 | 18.4 |
| F.S(%) | 71.2 | 8.7 | 56.2 | 86.2 | 70.3 | 61 | 5.7 | 53.3 | 76.3 | 60.4 |
| C.S(%) | 4.9 | 2.4 | 1.5 | 11.2 | 4.3 | 6.3 | 3 | 1.1 | 15.5 | 6.3 |
| pH | 6.1 | 0.8 | 3.4 | 7 | 6.4 | 6.9 | 0.3 | 6 | 7.3 | 7 |
| EC(dS $m^{-1}$) | 0.7 | 0.3 | 0.2 | 1.9 | 0.7 | 0.6 | 0.2 | 0.3 | 0.9 | 0.5 |
| Lime(%) | 2.1 | 2.8 | 0.1 | 15 | 1.3 | 7.7 | 5.4 | 1.1 | 21.1 | 7 |
| O.M(%) | 1.0 | 0.8 | 0.03 | 4.3 | 0.9 | 2.2 | 1.2 | 0.6 | 5.1 | 2 |
| Cd | 35.2 | 29.2 | 0.2 | 98.9 | 30.9 | 20.4 | 33.2 | 5.1 | 172.7 | 13 |
| Cr | 17.8 | 23.2 | 0.2 | 112.7 | 8.3 | 14.4 | 6.7 | 2.8 | 27.1 | 13.5 |
| Cu | 354.7 | 252.7 | 18 | 1207.5 | 348.4 | 168.5 | 259 | 39.7 | 1349.5 | 127.8 |
| Mn | 1734.9 | 640.2 | 171.8 | 3182 | 1878 | 1271 | 635 | 321 | 2558 | 1120 |
| Ni | 10 | 10.9 | 0.1 | 39.2 | 7.8 | 5.6 | 5.2 | 0.1 | 24.3 | 4.1 |
| Pb | 10089 | 6299 | 612 | 27845 | 9045 | 6824 | 4495 | 1890 | 26850 | 6242 |
| Zn | 3730 | 1946 | 134 | 6531 | 4397 | 2204 | 1246 | 1002 | 6338 | 1920 |
| | Koru | | | | | | | | | |
| | Tailing | | | | | Soil | | | | |
| Parameters | Mean | Std.Deviation | Min. | Max. | Median | Mean | Std.Deviation | Min. | Max. | Median |
| Clay(%) | 15.3 | 6.3 | 10.2 | 26.1 | 12.3 | 7.6 | 3.6 | 4.1 | 16.3 | 6.2 |
| Silt(%) | 17.6 | 2.1 | 12.3 | 20.8 | 18.4 | 11.7 | 5.8 | 4.1 | 20.2 | 11.1 |
| F.S(%) | 57.4 | 5.7 | 43.2 | 66.5 | 58.8 | 75.8 | 9.1 | 59.1 | 90.2 | 77 |
| C.S(%) | 9.7 | 4.1 | 1.9 | 15.2 | 10.6 | 4.9 | 2.8 | 1 | 10.5 | 5.2 |
| pH | 5.1 | 0.7 | 4.2 | 6.6 | 5 | 5.7 | 0.6 | 4.5 | 6.3 | 6 |
| EC(dS $m^{-1}$) | 0.2 | 0.1 | 0.1 | 0.8 | 0.2 | 0.6 | 0.4 | 0.1 | 1.4 | 0.3 |
| Lime(%) | 0.3 | 0.2 | 0.1 | 1.4 | 0.2 | 0.5 | 0.3 | 0.1 | 0.9 | 0.5 |
| O.M(%) | 2.1 | 1.2 | 0.4 | 4.7 | 1.9 | 0.9 | 0.7 | 0.2 | 1.9 | 0.6 |
| Cd | 9.9 | 11 | 1 | 46.4 | 5 | 4.6 | 2.5 | 1.2 | 9.8 | 4.4 |
| Cr | 8.9 | 6.3 | 4.5 | 28.3 | 6.7 | 3.4 | 1.9 | 1.5 | 8.5 | 2.8 |
| Cu | 101.5 | 46.5 | 28.6 | 176.6 | 88 | 57.5 | 36 | 12.9 | 114.3 | 49.9 |
| Mn | 1308 | 519 | 448 | 2254 | 1261 | 1190 | 685 | 185 | 2024 | 1331 |
| Ni | 4.5 | 1.8 | 2.8 | 8.9 | 3.8 | 1.6 | 0.6 | 0.6 | 2.7 | 1.4 |
| Pb | 1871 | 1425 | 397 | 4964 | 1526 | 431.4 | 256.8 | 17.9 | 773.9 | 528.9 |
| Zn | 1375 | 824 | 706 | 3598 | 1054 | 909 | 589 | 30 | 1548 | 1194 |

F.S: Fine sand, C.S: Coarse sand, EC: electrical conductivity, O.M: Organic matter

Forghani et al. (2015) took soil samples from agricultural fields and Pb-Zn mining sites of Iran and reported that mining site soils had greater heavy metals levels than the agricultural soils. Sebei et al. (2020) performed heavy metal analyses in soil samples taken from an abandoned mine of Fedj Lahdoum, northern Tunisia and reported heavy metal contamination order as Zn > Pb > Cd. Nassiri et al. (2021) performed heavy metal analyses in soil samples taken from High Moulouya, Zeida abandoned mining area in northeastern Morocco. The hazards index for both adults and children was determined in the order of Mn > Co > Pb > Ni > other heavy metals. The hazards of dermal and inhalation cancer were designated to be negligible.

Comparisons of present heavy metal concentrations with the findings of previous studies conducted on the other Pb-Zn mining regions throughout the world are presented in Table 5. For Balya tailings, Cd concentrations were lower than Slovenia and higher than China, Slovakia, Spain and India; Cr concentrations were higher than China and lower than Slovakia, Spain and India; Cu concentrations were higher than China, Slovakia, Spain and India; Mn contents were higher than Spain and lower than India; Ni contents were higher than China and lower than Spain and India; Pb contents were lower than Slovenia and higher than China, Slovakia, Spain and India; Zn contents were lower than Slovenia and higher than China, Slovakia, Spain and India. For Balya soils, Cd concentrations were higher than the other countries (China, Morocco, Iran, Türkiye and worldwide); Cr concentrations were lower than the others (China, Türkiye and worldwide); Cu contents were higher than the others (China, Morocco, Iran, Türkiye and worldwide); Mn concentrations were higher than Iran and worldwide; Ni contents were lower than the others (China, Türkiye and worldwide); Pb and Zn contents were found to be higher than the other countries (China, Morocco, Iran, Türkiye and worldwide).

**Table 5.** Average heavy metal concentrations of tailings and soils in Pb-Zn mining areas in the world (in mgkg$^{-1}$)

| Material | Location | Cd | Cr | Cu | Mn | Ni | Pb | Zn | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Tailing | Meza,Slovenia | 176.3 | - | - | - | - | 12192 | 26166 | Miler and Gosar, 2012 |
| | Liaoning, China | 11 | 0.7 | 15.9 | - | 1.7 | 649.5 | 2285 | Zhang et al., 2016 |
| | Zlataldka, Slovakia | 2.8 | 69.4 | 156.6 | - | - | 1283.1 | 66.8 | Rapant et al., 2006 |
| | Linares, Spain | 0.8 | 50 | 145 | 1211 | 20.6 | 4077 | 124 | Martinez et al., 2007 |
| | Zawar, India | 8.9 | 41.7 | 29.5 | 1798 | 41 | 1435 | 1442 | Anju and Banerjee, 2012 |
| | Balya, Türkiye | 35.2 | 17.8 | 354.7 | 1342.4 | 6 | 10089 | 3730 | This research |
| | Koru, Türkiye | 9.9 | 3.9 | 78.2 | 1308 | 2.6 | 1871 | 1375 | This research |
| Soil | Huan, China | 0.2 | 59.8 | 30 | - | 28.4 | 39.2 | 112.3 | Lu et al., 2015 |
| | Moulouya, Morocco | 0.4 | - | 26.2 | - | - | 1935.7 | 47 | Azhari et al., 2017 |
| | Irankouh, Iran | 2.5 | - | 38.4 | 1212.1 | - | 281.7 | 1035.2 | Jahromi et al., 2020 |
| | Türkiye | 3 | 100 | 140 | - | 75 | 300 | 300 | SPCR, 2005 |
| | Worldwide | 0.5 | 54 | 19.8 | 437 | 22 | 28.6 | 64 | Kabata-Pendias and Pentias, 2011 |
| | Balya, Türkiye | 20.4 | 14.4 | 168.5 | 1864 | 14.4 | 6824 | 2204 | This research |
| | Koru, Türkiye | 4.6 | 10.8 | 92.5 | 1190 | 4.5 | 431 | 909 | This researh |

For Koru tailings, Cd concentrations were found to be lower than Slovenia and China and higher than Slovakia, Spain and India; Cr and Cu contents were higher than China and lower than Slovakia, Spain and India; Mn concentrations were higher than Spain and lower than India; Ni contents were higher than China and lower than Spain and India; Pb concentrations were lower than Slovenia and Spain, but higher than China and India; Zn contents were lower than the other countries (Slovenia, China, Spain, and India. For Koru soils, Cd concentrations were higher than the other countries (China, Morocco, Iran, Türkiye and worldwide); Cr contents were lower than the others (China, Türkiye, worldwide); Cu contents were lower than the other countries (China, Morocco, Iran, Türkiye and worldwide); Mn contents were lower than Iran and higher than the other countries; Ni concentrations were lower than the others (China, Türkiye, worldwide); Pb contents were higher than the others (China, Morocco, Türkiye and worldwide); Zn contents were higher than the others, except for Iran (Table 5).

Correlations between physicochemical properties and heavy metals of mine tailings and soils Balya mining site are demonstrated in Table 6. For Balya tailings, a negative correlation was determined between clay and fine sand (r=0.79), clay and pH (r=0.40), clay and Cd (r=0.32), clay and Cu (r=0.49), clay and Pb (r= 0.50) and clay and Zn (r=0.47); a negative correlation was determined between fine sand and silt (r=0.91), pH and silt (r=0.49), Cd and silt (r=0.43), Cu and silt (r=0.32), Pb and silt (r=0.40), Pb and Zn (r=0.46); a positive correlation was found between silt and EC (r=0.31); a negative correlation was determined between fine sand and coarse sand (r=0.39), fine sand and EC (r=0.32), fine sand and Cd (r=0.43), fine sand and Cu (r=0.41), fine sand and Cr (r=0.42); a positive correlation was determined between fine sand and pH (r=0.44), fine sand and Pb (r=0.46), fine sand and Zn (r=0.50); a positive correlation was determined between coarse sand and Cr (r=0.54); a negative correlation was determined between pH and EC (r=0.49), pH and Ni (r=0.35); a positive correlation was determined between pH and lime (r=0.39), pH and Cd (r=0.61), pH and Cu (r=0.37), pH and Zn (r=0.69); EC and SOM (r=0.37), EC and Cd (r=0.40), EC and Cu (r=0.48), EC and Ni (r=0.29), EC and Pb (r=0.47); a negative significant correlation was determined between EC and Zn (r=0.53); a positive significant correlation was determined between lime and Ni (r=0.61); a significant positive correlation was determined between Cd and Cu (r=0.66), Cd and Pb (r=0.68), Cd and Zn (r=0.89); a positive significant correlation was determined between Cu and Pb (r=0.86), Cu and Zn (r=0.76); a negative significant correlation was determined between Mn and Zn (r=0.24); a positive significant correlation was determined between Pb and Zn (r=0.77). For Balya soils, a positive correlation was determined between clay and silt (r=0.41), a negative significant correlation was determined between clay and fine sand (r=-0.72), clay and Cu (r=0.51), clay and Pb (r=0.40); a negative significant correlation was determined between silt and fine sand (r=0.74), silt and EC (r=0.25); a negative significant correlation was determined between fine sand and Cd (r=0.52), fine sand and Cu (r=0.56); a negative significant correlation was determined between coarse sand and OM (r=0.41), coarse sand and Cu (r=0.19), pH and Cu (r=0.11); a positive significant correlation was determined between pH and lime (r=0.56), pH and Cr (r=0.67), pH and Zn (r=0.45); a positive significant correlation was determined between pH and Cr (r=0.67); a positive significant correlation was determined between lime and Cr (r=0.75), lime and Ni (r=0.45); a negative significant correlation was determined between lime and Zn (r=0.46); a significant positive correlation was determined between Cd and Cu (r=0.99), Cd and Pb (r=0.93), Cd and Zn (r=0.83); a positive significant correlation was determined between Cr and Ni (r=0.41); a positive significant correlation was determined between Pb and Zn (r=0.64).

**Table 6.** Pearson correlation coefficient between physicochemical properties of tailings/soils and heavy metals contents for Balya tailings and soils*

| Type | Parameters | Clay | Silt | F.S | C.S | pH | EC | $CaCO_3$ | OM | Cd | Cu | Cr | Mn | Ni | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tailing | Silt | 0.60 | | | | | | | | | | | | | |
| | F.S | -0.79* | -0.91* | | | | | | | | | | | | |
| | C.S | 0.15 | 0.09 | -0.39* | | | | | | | | | | | |
| | pH | -0.40* | -0.49* | 0.44* | 0.12 | | | | | | | | | | |
| | EC | 0.25 | 0.31* | -0.32* | 0.08 | -0.49* | | | | | | | | | |
| | $CaCO_3$ | -0.01 | -0.12 | 0.02 | 0.23 | 0.39* | -0.12 | | | | | | | | |
| | OM | 0.29 | 0.17 | -0.16 | -0.20 | -0.05 | -0.37* | -0.26 | | | | | | | |
| | Cd | -0.32* | -0.43* | -0.43* | -0.07 | 0.61* | -0.40* | -0.04 | 0.03 | | | | | | |
| | Cu | -0.49* | -0.32* | -0.41* | -0.08 | 0.37* | -0.48* | -0.16 | -0.01 | 0.66* | | | | | |
| | Cr | 0.28 | 0.25 | -0.42* | 0.54* | 0.12 | 0.14 | 0.21 | -0.22 | 0.04 | 0.12 | | | | |
| | Mn | 0.23 | 0.20 | -0.24 | 0.06 | -0.25 | 0.01 | 0.13 | 0.20 | -0.20 | -0.02 | 0.05 | | | |
| | Ni | -0.16 | -0.15 | 0.12 | 0.17 | -0.35* | -0.29* | 0.61* | -0.09 | 0.14 | 0.12 | 0.05 | 0.12 | | |
| | Pb | -0.50* | -0.40* | 0.46* | -0.05 | 0.45 | -0.47* | 0.02 | -0.11 | 0.68* | 0.86* | 0.07 | -0.03 | 0.23 | |
| | Zn | -0.47* | -0.46* | 0.50* | -0.07 | 0.69* | -0.53* | -0.09 | -0.01 | 0.89* | 0.76* | 0.05 | -0.24* | 0.16 | 0.77* |
| Soil | Silt | 0.41* | | | | | | | | | | | | | |
| | F.S | -0.72* | -0.74* | | | | | | | | | | | | |
| | C.S | -0.18 | -0.36 | -0.19 | | | | | | | | | | | |
| | pH | 0.19 | -0.21 | -0.03 | 0.15 | | | | | | | | | | |
| | EC | -0.37 | -0.25* | 0.24 | 0.24 | -0.14 | | | | | | | | | |
| | $CaCO_3$ | -0.11 | -0.24 | 0.08 | 0.28 | 0.56* | 0.23 | | | | | | | | |
| | OM | 0.35 | 0.33 | -0.19 | -0.41* | 0.11 | -0.29 | -0.21 | | | | | | | |
| | Cd | -0.51- | -0.23 | -0.52* | -0.16 | -0.13 | 0.19 | -0.14 | -0.03 | | | | | | |
| | Cu | -0.51* | -0.27 | 0.56* | -0.19* | -0.11* | 0.19 | -0.15 | 0.03 | 0.99* | | | | | |
| | Cr | -0.28 | -0.28 | 0.21 | 0.26 | 0.67* | 0.21 | 0.75* | -0.21 | 0.03 | 0.01 | | | | |
| | Mn | -0.11 | -0.22 | 0.04 | 0.33 | -0.21 | -0.06 | -0.39 | -0.18 | 0.02 | 0.01 | -0.16 | | | |
| | Ni | -0.33 | -0.42 | 0.35 | 0.23 | 0.09 | 0.31 | 0.45* | -0.36 | 0.20 | 0.18 | 0.41* | 0.13 | | |
| | Pb | -0.40* | -0.19 | 0.40* | -0.11 | 0.16 | 0.11 | 0.12 | 0.09 | 0.93* | 0.93* | 0.24 | -0.09 | 0.21 | |
| | Zn | -0.37 | -0.13 | 0.37 | -0.15 | -0.45* | 0.35 | -0.46* | -0.02 | 0.83* | 0.83* | -0.38 | 0.07 | 0.06 | 0.64* |

F.S: fine sand, C.S: coarse sand, EC: electrical conductivity, OM: organic matter, *$p < 0.05$

Correlations between physicochemical properties and heavy metals of tailings and soils of Koru mining site are demonstrated in Table 7. For Koru tailings, a negative correlation was determined between clay and fine sand (r=0.71), clay and coarse sand (r=0.53); a positive significant correlation was determined between clay and pH (r=0.55), clay and EC (r=0.59), clay and lime (r=0.51); a negative significant correlation was determined between fine sand and coarse sand (r=0.13); a significant negative correlation was determined between coarse sand and pH (r=0.66), coarse sand and EC (r=0.63), coarse sand and lime (r=0.73), coarse sand and Zn (r=0.60); a positive significant correlation was determined between coarse sand and OM (r=0.60); a positive significant correlation was determined between pH and lime (r=0.72), pH and Cr (r=0.54), pH and Zn (r=0.66); a positive significant correlation was determined between EC and lime (r=0.52); a negative significant correlation was determined between EC and OM (r=0.57); a negative significant correlation was determined between lime and OM (r=0.49); a positive significant correlation was determined between Cd and Pb (r=0.65); a positive significant correlation was determined between Cu and Zn (r=0.49); a positive significant correlation was determined between Mn and Zn (r=0.54). For Koru soils, a negative correlation was determined between clay and fine sand (r=0.84), clay and pH (r=0.77), clay and lime (r=0.60); a positive correlation was determined between clay and OM (r=0.87), clay and Cd (r=0.73); a negative correlation was determined between silt and fine sand (r=0.82); a positive correlation was determined between silt and OM (r=0.58); a negative correlation was determined between fine sand and OM (r=0.87); a negative correlation was determined between fine sand and Cd (r=0.60); a positive correlation was determined between fine sand and pH (r=0.79); a positive correlation was determined between pH and lime (r=0.87); a negative correlation was determined between pH and OM (r=0.83), pH and Cd (r=0.76); a positive correlation was determined between EC and lime (r=0.19); a negative correlation was determined between EC and Cu (r=0.72), EC and Zn (r=0.64); a negative correlation was determined between lime and OM (r=0.70), lime and Cd (r=0.69); a positive correlation was determined between OM and Cd (r=0.78); a positive correlation was determined between Cu and Ni (r=0.71); a positive correlation was determined between Cr and Mn (r=0.64), Cr and Pb (r=0.74), Cr and Zn (r=0.76); a positive correlation was determined between Mn and Zn (r=0.89); a positive correlation was determined between Pb and Zn (r=0.92).

**Table 7.** Pearson correlation coefficient between physicochemical properties of tailings/soils and heavy metals contents for Koru tailings and soils*

| Type | Parameters | Clay | Silt | F.S | C.S | pH | EC | Lime | OM | Cd | Cu | Cr | Mn | Ni | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tailing | Silt | -0.03 | | | | | | | | | | | | | |
| | F.S | -0.71* | -0.32 | | | | | | | | | | | | |
| | C.S | -0.53* | -0.02 | -0.13* | | | | | | | | | | | |
| | pH | 0.55* | 0.02 | -0.14 | -0.66* | | | | | | | | | | |
| | EC | 0.59* | 0.33 | -0.31 | -0.63* | 0.34 | | | | | | | | | |
| | Lime | 0.51* | 0.02 | -0.04 | -0.73* | 0.72* | 0.52* | | | | | | | | |
| | OM | -0.44 | 0.15 | -0.01 | 0.60* | -0.32 | -0.57* | -0.49* | | | | | | | |
| | Cd | 0.02 | -0.08 | 0.05 | -0.04 | -0.08 | 0.14 | 0.12 | -0.40 | | | | | | |
| | Cu | 0.06 | 0.25 | -0.16 | 0.01 | 0.01 | 0.02 | 0.26 | 0.28 | 0.10 | | | | | |
| | Cr | 0.11 | -0.14 | 0.05 | -0.16 | 0.54* | -0.09 | 0.65* | -0.14 | 0.04 | 0.03 | | | | |
| | Mn | 0.36 | 0.39 | -0.37 | -0.24 | 0.42 | 0.22 | 0.32 | -0.27 | 0.02 | 0.30 | 0.12 | | | |
| | Ni | -0.05 | 0.09 | -0.36 | 0.53* | -0.15 | -0.28 | -0.21 | 0.42 | -0.12 | 0.35 | -0.15 | 0.01 | | |
| | Pb | -0.16 | -0.33 | 0.34 | -0.06 | 0.06 | -0.15 | 0.38 | -0.19 | 0.65* | 0.44 | 0.17 | -0.11 | -0.06 | |
| | Zn | 0.16 | 0.06 | 0.24 | -0.60* | 0.66* | 0.18 | 0.61* | -0.52* | 0.40 | 0.49* | -0.08 | 0.54* | -0.34 | 0.38 |
| Soil | Silt | 0.48 | | | | | | | | | | | | | |
| | F.S | -0.84* | -0.82* | | | | | | | | | | | | |
| | C.S | 0.42 | -0.02 | -0.46 | | | | | | | | | | | |
| | pH | -0.77* | *0.66* | 0.79* | -0.21 | | | | | | | | | | |
| | EC | -0.23 | -0.25 | 0.34 | -0.28 | 0.15 | | | | | | | | | |
| | Lime | -0.60* | -0.43 | 0.53 | -0.04 | 0.87* | 0.19* | | | | | | | | |
| | OM | 0.87* | 0.58* | -0.87* | 0.48 | -0.83* | -0.34 | -0.70* | | | | | | | |
| | Cd | 0.73* | 0.28 | -0.60* | 0.44 | -0.76* | -0.52 | -0.69* | 0.78* | | | | | | |
| | Cu | -0.08 | 0.06 | -0.09 | 0.27 | -0.11 | -0.72* | -0.22 | 0.25 | 0.35 | | | | | |
| | Cr | 0.15 | 0.57 | -0.38 | -0.14 | 0.04 | -0.21 | 0.12 | 0.10 | -0.33 | -0.07 | | | | |
| | Mn | 0.12 | 0.05 | -0.07 | -0.05 | -0.18 | -0.77 | -0.30 | 0.26 | 0.56 | -0.12 | 0.64* | | | |
| | Ni | 0.42 | 0.35 | -0.42 | 0.10 | -0.19 | 0.06 | -0.11 | 0.20 | -0.13 | 0.71* | -0.30 | -0.24 | | |
| | Pb | 0.21 | 0.23 | -0.28 | 0.16 | -0.44 | -0.73 | -0.55 | 0.48 | 0.71 | -0.22 | 0.74* | 0.88* | -0.29 | |
| | Zn | -0.08 | 0.13 | -0.01 | -0.01 | -0.18 | -0.64* | -0.36 | 0.24 | 0.42 | -0.15 | 0.76* | 0.89* | -0.38 | 0.92* |

F.S: fine sand, C.S: coarse sand, EC: electrical conductivity, OM: organic matter, *$p < 0.05$

For Balya mining site, three factors explained 78.61% of total variation in tailings and 74.79% of the total variance in soils (Table 8). It is known that Cd mainly occurs in association with sphalerite (ZnS) (Tran et al., 2022). Pb and Cu originate from galena (PbS) and chalcopyrite ($CuFeS_2$) minerals. These elements are also known to be often originated from Pb–Zn mining activities (Cao et al., 2022; Jahromi et al., 2020; Nassiri et al., 2021). For Balya tailings, the first factor included Cd, Pb and Cu (41.85% of total variance), the second factor included Mn (20.70% of total variance) and the third factor included Zn (16.04% of total variance). For Balya soils, Factor 1 (32.51% of total variance) included Cr; Factor 2 (24.70% of total variance) included Ni; Factor 3 (17.58% of total variance) included Mn.

**Table 8.** Principal components of mine tailings and soil samples in Balya

| | Mine tailing | | | Soil | | |
|---|---|---|---|---|---|---|
| | **Factor 1** | **Factor 2** | **Factor 3** | **Factor 1** | **Factor 2** | **Factor 3** |
| Mn | -0.303 | **0.738** | 0.290 | -0.038 | -0.088 | **0.925** |
| Cr | 0.235 | 0.694 | -0.460 | **0.795** | 0.353 | -0.056 |
| Cd | **0.895** | -0.154 | 0.109 | 0.178 | -0.806 | 0.308 |
| Pb | **0.909** | 0.225 | -0.080 | 0.493 | -0.453 | -0.577 |
| Zn | 0.032 | 0.017 | **0.935** | -0.764 | 0.003 | 0.032 |
| Ni | 0.403 | 0.657 | -0.056 | 0.264 | **0.807** | 0.325 |
| Cu | **0.892** | 0.177 | -0.116 | -0.775 | 0.195 | 0.063 |
| Eigenvalues | 2.930 | 1.450 | 1.123 | 2.275 | 1.729 | 1.231 |
| % of variance | 41.858 | 20.708 | 16.039 | 32.506 | 24.701 | 17.580 |
| % cumulative variance | 41.858 | 62.566 | 78.606 | 32.506 | 57.208 | 74.788 |
| Kaiser- Meyer- Olkin measure of sampling adequacy | | | 0.638 | | 0.488 | |
| Bartlett's test of sphericity | | | 0.000 | | 0.003 | |

*Bold values are factor loadings of the principal components

For Koru mining site, three factors explained 71.78% of total variance in tailings and two factors explained 64.85% of total variance in soils (Table 9). For Koru tailings, Factor 1 (33.33% of total variance) included Mn and Cr; Factor 2 (20.17 % of total variance) included Cd, Pb, and Zn; Factor 3 (18.28% of total variance) included Ni. For Koru soils, Factor 1 (42.22% of total variance) included Mn and Cu; Factor 2 (22.63% of total variance) included Cr and Ni (Table 4). Tran et al. (2022) reported that heavy metals originate from combination of anthropogenic and geogenic sources in soils near Pb-Zn mining areas.

**Table 9.** Principal components of mine tailings and soil samples in Koru

| | Mine tailing | | | Soil | |
|---|---|---|---|---|---|
| | **Factor 1** | **Factor 2** | **Factor 3** | **Factor 1** | **Factor 2** |
| Mn | **0.872** | 0.006 | 0.080 | **0.921** | 0.034 |
| Cr | -0.777 | -0.022 | 0.202 | -0.085 | **0.872** |
| Cd | 0.210 | **0.809** | -0.197 | 0.634 | -0.182 |
| Pb | -0.272 | **0.769** | 0.045 | 0.122 | -0.769 |
| Zn | 0.602 | **0.704** | 0.023 | -0.548 | 0.264 |
| Ni | -0.057 | -0.221 | **0.809** | -0.224 | **0.886** |
| Cu | 0.030 | -0.091 | -0.794 | **0.814** | -0.111 |
| Eigenvalues | 2.333 | 1.412 | 1.280 | 2.956 | 1.584 |
| % of variance | 33.325 | 20.171 | 18.281 | 42.223 | 22.626 |
| % cumulative variance | 33.325 | 53.497 | 71.778 | 42.223 | 64.849 |
| Kaiser- Meyer- Olkin measure of sampling adequacy | | | 0.407 | | 0.473 |
| Bartlett's test of sphericity | | | 0.094 | | 0.078 |

*Bold values are factor loadings of the principal components

Local distribution maps of heavy metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) of Balya mining site are presented in Figure 3. For Balya tailings, the lowest Cd, Cr, Cu, Pb and Zn values were found in Region 2 and the lowest Mn and Ni levels were seen in Region 3. The highest Cd and Cu values were seen in Region 5 (S8- Region 5 with 172.70 mg $kg^{-1}$ Cd and 1349.5 mg $kg^{-1}$ Cu). The highest Pb, Zn and Mn concentrations were seen in Region 3 (27845 mg $kg^{-1}$ Pb, 6530.5 mg $kg^{-1}$ Zn and 3182 mg $kg^{-1}$ Mn). In general, average of heavy metal concentrations of tailings were higher than the soils. Although heavy metal concentrations were low in Region 1, it is noteworthy that the heavy metal concentrations in Region 3 were high.

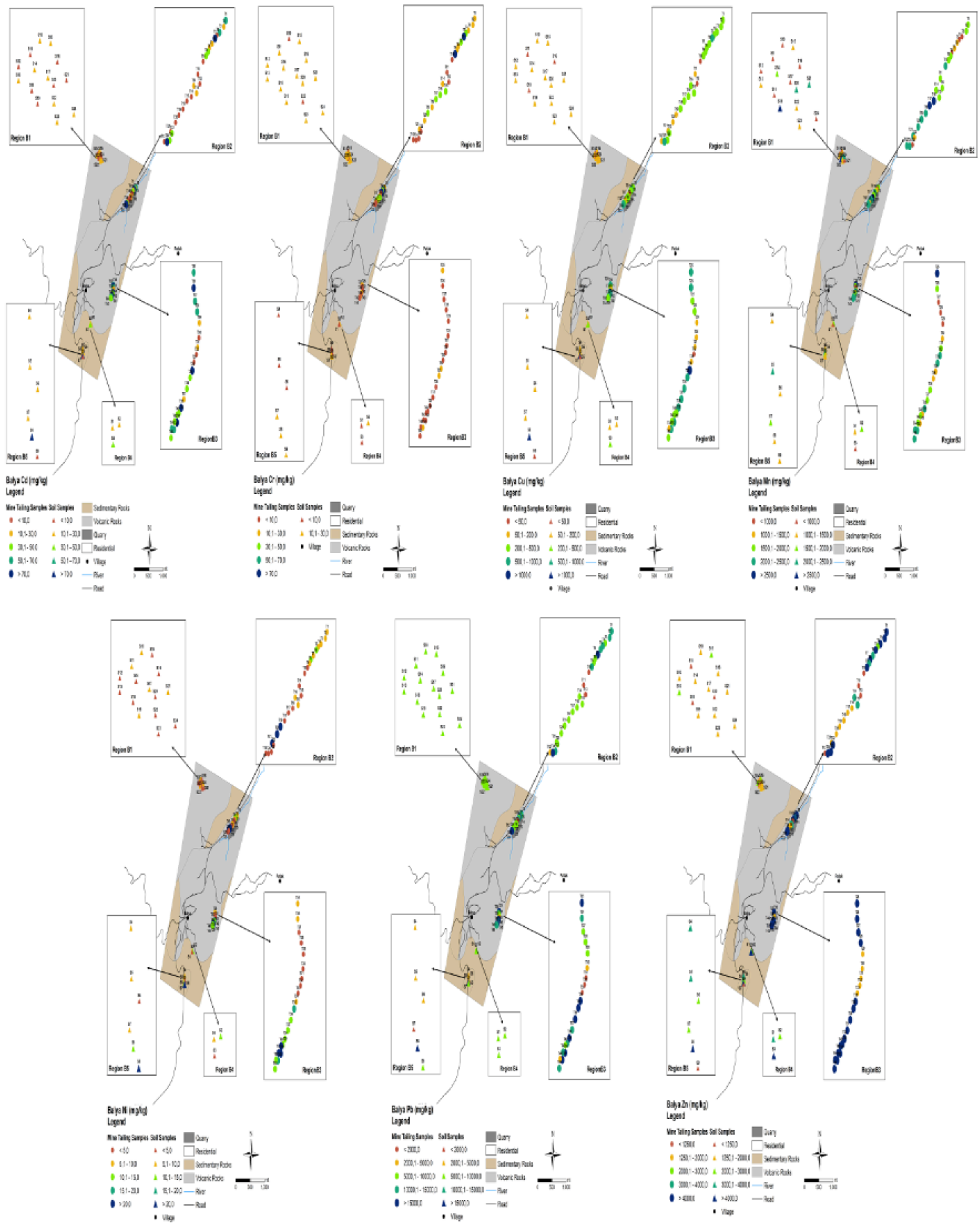

**Figure 3.** Spatial distribution of heavy metals in tailings and soils in the Balya mining area

Local distribution maps of heavy metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) of Koru mining site are presented in Figure 4. The lowest Cr and Ni concentrations were found in soil samples (S4) and the highest concentrations were found in tailing samples T2 and T7. The lowest Mn and Zn concentrations were found in soil sample S8 (185.28 mg $kg^{-1}$ and 30.09 mg $kg^{-1}$) and the highest Mn and Zn concentrations were found in T2 tailing sample (2254 mg $kg^{-1}$ and 3598 mg $kg^{-1}$). The lowest Cu and Pb concentrations were found in soil sample S7 (12.89 mg $kg^{-1}$ and 17.88 mg $kg^{-1}$) and the highest Cu and Pb concentrations were found in T18 and T2 tailing samples (176.62 mg $kg^{-1}$ and 4963.5 mg $kg^{-1}$). In general, average Cd, Cr, Cu, Mn, Ni, Pb and Zn concentrations of tailing samples were greater than the soil samples.

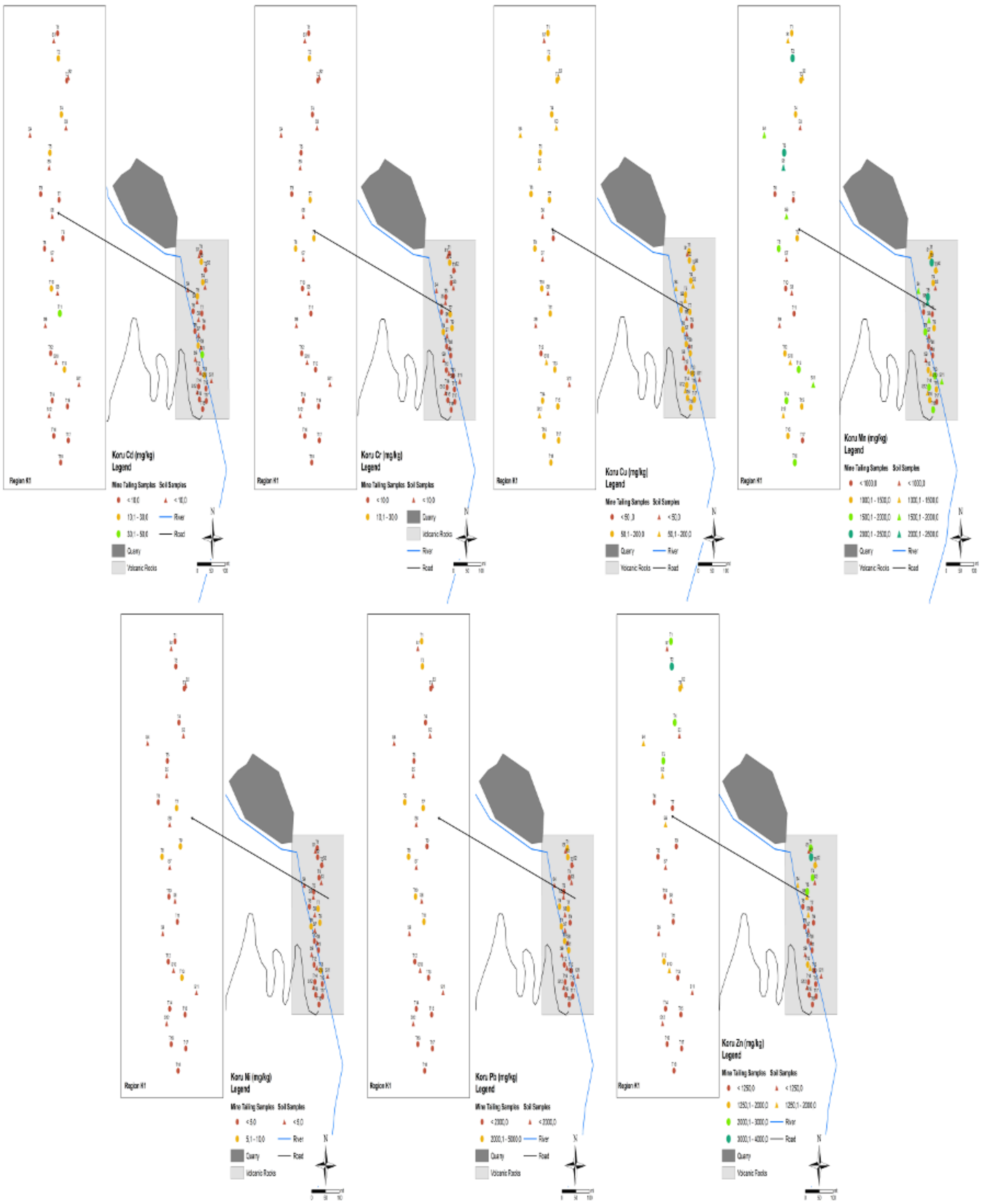

**Figure 4.** Spatial distribution of heavy metals in tailings and soils in the Koru mining area

The ADD values for adults are presented in Table 10. For Balya mining site, ADD values varied between 1.02E-03 and 1.65E-10 in tailing samples and between 9.32E-01 and 2.39E-10 in soil samples. For Koru mining site, ADD values for adults varied between 3.58E-04 and 7.46E-11 in tailing samples and between 1.18E-04 and 2.65E-11 in soil samples.

**Table 10.** ADD values for adults in mine tailing and soils in Balya and Koru mining areas

| Sample Type | Heavy metals | Balya | | Koru | |
|---|---|---|---|---|---|
| | | $ADD_{ing}$ | $ADD_{derm}$ | $ADD_{ing}$ | $ADD_{derm}$ |
| Mine tailing | Cd | 9.64E-06 | 5.82E-10 | 2.73E-06 | 1.64E-10 |
| | Cr | 4.88E-06 | 2.94E-10 | 2.45E-06 | 1.48E-10 |
| | Cu | 9.72E-05 | 5.86E-09 | 2.78E-05 | 1.67E-09 |
| | Mn | 4.75E-04 | 2.86E-08 | 3.58E-04 | 2.16E-08 |
| | Ni | 2.74E-06 | 1.65E-10 | 1.24E-06 | 7.46E-11 |
| | Pb | 2.76E-03 | 1.67E-07 | 5.13E-04 | 3.09E-08 |
| | Zn | 1.02E-03 | 6.16E-08 | 3.77E-04 | 2.27E-08 |
| Soil | Cd | 5.60E-06 | 3.38E-10 | 1.27E-06 | 7.69E-11 |
| | Cr | 3.96E-06 | 2.39E-10 | 9.20E-07 | 5.55E-11 |
| | Cu | 4.62E-05 | 2.78E-09 | 1.58E-05 | 9.50E-10 |
| | Mn | 3.48E-04 | 2.10E-08 | 3.26E-04 | 1.96E-08 |
| | Ni | 1.54E-06 | 9.32E-01 | 4.39E-07 | 2.65E-11 |
| | Pb | 1.87E-03 | 1.13E-07 | 1.18E-04 | 7.13E-09 |
| | Zn | 6.04E-04 | 3.64E-08 | 2.49E-04 | 1.50E-08 |

The ADD values for children are presented in Table 11. For Balya mining site, ADD values for children varied between 3.83E-02 and 9.15E-10 in tailing samples and between 2.59E-02 and 5.77E-10 in soil samples. For Koru mining site, ADD values for children varied between 7.11E-03 and 9.15E-10 in tailing samples and between 4.52E-03 and 1.64E-10 in soil samples.

**Table 11.** ADD values for children in mine tailing and soils in Balya and Koru mining areas

| Sample Type | Heavy metals | Balya | | Koru | |
|---|---|---|---|---|---|
| | | $ADD_{ing}$ | $ADD_{derm}$ | $ADD_{ing}$ | $ADD_{derm}$ |
| Mine tailing | Cd | 1.34E-04 | 3.60E-09 | 3.78E-05 | 1.02E-09 |
| | Cr | 6.77E-05 | 1.82E-09 | 3.40E-05 | 9.15E-10 |
| | Cu | 1.35E-03 | 3.62E-08 | 3.86E-04 | 1.03E-08 |
| | Mn | 6.59E-03 | 1.77E-07 | 4.97E-03 | 1.33E-07 |
| | Ni | 3.80E-05 | 1.02E-09 | 1.71E-05 | 4.61E-10 |
| | Pb | 3.83E-02 | 1.03E-06 | 7.11E-03 | 1.91E-07 |
| | Zn | 1.42E-02 | 3.82E-07 | 5.22E-03 | 1.41E-07 |
| Soil | Cd | 7.76E-05 | 2.09E-09 | 1.77E-05 | 4.76E-10 |
| | Cr | 5.49E-05 | 1.48E-09 | 1.28E-05 | 3.44E-10 |
| | Cu | 6.40E-04 | 1.72E-08 | 2.19E-04 | 5.88E-09 |
| | Mn | 4.83E-03 | 1.29E-07 | 4.52E-03 | 1.21E-07 |
| | Ni | 2.14E-05 | 5.77E-10 | 6.08E-06 | 1.64E-10 |
| | Pb | 2.59E-02 | 6.98E-07 | 1.64E-03 | 4.41E-08 |
| | Zn | 8.37E-03 | 2.25E-07 | 3.46E-03 | 9.30E-08 |

Health risk assessments for carcinogenic and non-carcinogenic elements of Balya mining site are presented in Table 12. For non-carcinogenic effects on adults, heavy metals were ordered as Pb > Ni > Mn > Cd > Zn > Cu > Cr in tailing samples and Pb > Cd > Mn > Zn > Cr > Cu > Ni in soil samples. For children, heavy metals were ordered as Cd > Pb > Mn > Zn > Cu > Cr > Ni in tailing samples and Cd > Pb > Mn > Zn > Cr > Cu > Ni in soil samples. For children and adults, carcinogenic effects of heavy metals were ordered as Cd > Pb > Ni > Cr. The values of the cancer threat of Cd and Pb were found to be above $1\times10^{-4}$.

**Table 12.** Health risk assessment of heavy metal based on total heavy metals in mine tailing and soil for adults and children in Balya

| Sample type | Heavy metals | Adults | | | | Children | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $HQ_{ingest}$ | $HQ_{dermal}$ | HI | Risk | $HQ_{ingest}$ | $HQ_{dermal}$ | HI | Risk |
| Mine tailing | Cd-non cancer | 9.64E-03 | 5.82E-05 | 9.70E-03 | | 1.34E-01 | 1.34E+04 | 1.34E+04 | |
| | Cd-cancer | 5.88E-05 | 3.54E-09 | | 5.88E-05 | 8.16E-04 | 2.19E-08 | | 8.16E-04 |
| | Cr-non cancer | 1.63E-03 | 4.91E-07 | 1.63E-03 | | 2.26E-02 | 3.04E-06 | 2.26E-02 | |
| | Cr- cancer | 2.44E-06 | 5.88E-09 | | 2.44E-06 | 3.38E-05 | 3.64E-08 | | 3.38E-05 |
| | Cu | 2.43E-03 | 4.88E-06 | 2.43E-03 | | 3.37E-02 | 3.02E-05 | 3.37E-02 | |
| | Mn | 1.03E-02 | 1.56E-05 | 1.03E-02 | | 1.43E-01 | 9.64E-05 | 1.43E-01 | |
| | Ni-non cancer | 1.37E-03 | 3.06E-08 | 1.37E-03 | | 1.90E-02 | 1.90E-07 | 1.90E-02 | |
| | Ni- cancer | 4.66E-06 | 7.03E-09 | | 4.66E-06 | 6.46E-05 | 4.35E-08 | | 6.46E-05 |
| | Pb-non cancer | 7.90E-01 | 3.18E-04 | 7.90E-01 | | 1.10E+01 | 1.97E-03 | 1.10E+01 | |
| | Pb- cancer | 2.35E-05 | | | 2.35E-05 | 3.26E-04 | | | 3.26E-04 |
| | Zn | 3.41E-03 | 1.03E-06 | 3.41E-03 | | 4.72E-02 | 6.36E-06 | 4.72E-02 | |
| Soil | Cd-non cancer | 5.60E-03 | 3.38E-05 | 5.63E-02 | | 7.76E-02 | 7.76E+03 | 7.76E+03 | |
| | Cd-cancer | 3.41E-05 | 2.06E-09 | | 3.41E-05 | 4.73E-04 | 1.27E-08 | | 4.73 E-04 |
| | Cr-non cancer | 1.32E-03 | 3.98E-07 | 1.32E-03 | | 1.83E-02 | 2.46E-06 | 1.83E-02 | |
| | Cr- cancer | 1.97E-06 | 4.78E-09 | | 1.98E-06 | 2.31E-04 | 6.20E-09 | | 2.74E-05 |
| | Cu | 1.15E-03 | 2.31E-06 | 1.16E-03 | | 1.60E-02 | 1.43E-05 | 1.60E-02 | |
| | Mn | 7.57E-03 | 1.14E-05 | 7.58E-03 | | 1.05E-01 | 7.06E-05 | 1.05E-01 | |
| | Ni-non cancer | 7.72E-04 | 1.73E-08 | 7.73E-04 | | 1.07E-02 | 1.07E-07 | 1.07E-02 | |
| | Ni- cancer | 2.63E-06 | 3.96E-09 | | 2.63E-06 | 3.64E-05 | 2.45E-08 | | 3.64E-05 |
| | Pb-non cancer | 5.34E-01 | 2.15E-04 | 5.34E-01 | | 7.41E+00 | 1.33E-03 | 7.41E+00 | |
| | Pb-cancer | 1.59E-05 | | | 1.59E-05 | 2.20E-04 | | | 2.20E-04 |
| | Zn | 2.01E-03 | 6.07E-07 | 2.01E-03 | | 2.79E-02 | 3.76E-06 | 2.79E-02 | |

Health risk assessments for carcinogenic and non-carcinogenic elements of Koru mining site are presented in Table 13. For non-carcinogenic effects on adults, heavy metals were ordered as Pb > Mn > Cd > Zn > Cr > Cu > Ni in tailing samples and Pb > Mn > Cd > Zn > Cu > Cr > Ni in soil samples. For children, heavy metals were ordered as Cd > Pb > Mn > Zn > Cr > Cu > Ni in tailing samples and Cd > Pb > Mn > Zn > Cu > Cr > Ni in soil samples. For children and adults, carcinogenic effects of heavy metals were ordered as Cd > Pb > Ni > Cr. . Cd has a carcinogenic effect for children in both tailings and soils in Koru. Wang et al. (2017) conducted a study in Huedehong lead-zinc mining area (Yunnan-Southwest China) and reported heavy metal contents in the order of Zn > Pb > Cr > Cu > Cd. Cd had the highest non-carcinogenic effect in the study area and Cr had the least cancer risk. Baghaie and Aghili (2019) determined that Cd and Pb concentrations of soil samples taken from Shahin (Iran) mine were higher than the background. Non-cancerogenic hazard quotient values of Pb and Cd were less than 1 for the soils examined. Kan et al. (2021) conducted health risk assessment of heavy metals in Pb-Zn mining areas located in the southern and eastern regions of China and indicated that heavy metals in mine tailings were mostly taken by oral ingestion and children were more sensitive to adverse effects. Nassiri et al. (2021) performed heavy metal analyses in the soil samples taken from the Zeida abandoned mining area in northeastern Morocco, High Moulouya. The hazard index for children and adults was determined in the order of Mn > Co > Pb > 1 > other heavy metals. Inhalation and dermal carcinogenic risks were found to be negligible. Nikolaidis et al. (2013) conducted heavy metal analyses in the samples taken from a lead-zinc mining area in Kirki region (NE Greece) and indicated that arsenic caused health risks.

**Table 13.** Health risk assessment of heavy metal based on total heavy metals in mine tailing and soil for adults and children in Koru

| Sample type | Heavy metals | Adults | | | | Children | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $HQ_{ingest}$ | $HQ_{dermal}$ | HI | Risk | $HQ_{ingest}$ | $HQ_{dermal}$ | HI | Risk |
| Mine tailing | Cd-non cancer | 2.73E-03 | 1.64E-05 | 2.74E-03 | | 3.78E-02 | 3.78E+03 | 3.78E+03 | |
| | Cd-cancer | 1.66E-05 | 1.001E-09 | | 1.66E-05 | 2.31E-04 | 6.20E-09 | | 2.31E-04 |
| | Cr-non cancer | 8.17E-04 | 2.46E-07 | 8.17E-04 | | 1.13E-02 | 1.52E-06 | 1.13E-02 | |
| | Cr- cancer | 1.22E-06 | 2.95E-09 | | 1.22E-06 | 1.70E-05 | 1.82E-08 | | 1.70E-05 |
| | Cu | 6.95E-04 | 1.39E-06 | 6.97E-04 | | 9.64E-03 | 8.65E-06 | 9.65E-03 | |
| | Mn | 7.79E-03 | 1.17E-05 | 7.80E-03 | | 1.08E-01 | 7.27E-05 | 1.08E-01 | |
| | Ni-non cancer | 6.18E-04 | 1.38E-08 | 6.18E-04 | | 8.57E-03 | 8.55E-08 | 8.57E-03 | |
| | Ni- cancer | 2.10E-06 | 3.16E-09 | | 2.10E-06 | 2.91E-05 | 1.96E-08 | | 2.91E-05 |
| | Pb-non cancer | 1.46E-01 | 5.89E-05 | 1.47E-01 | | 2.03E+00 | 3.65E-04 | 2.03E+00 | |
| | Pb- cancer | 4.36E-06 | | | 4.36E-06 | 6.04E-05 | | | 6.04E-05 |
| | Zn | 1.26E-03 | 3.79E-07 | 1.26E-03 | | 1.74E-02 | 2.34E-06 | 1.74E-02 | |
| Soil | Cd-non cancer | 1.27E-03 | 7.69E-06 | 1.28E-03 | | 1.77E-02 | 1.77E+03 | 1.77E+03 | |
| | Cd-cancer | 7.78E-06 | 4.69E-10 | | 7.78E-06 | 1.08E-04 | 2.90E-09 | | 1.08E-04 |
| | Cr-non cancer | 3.07E-04 | 9.25E-08 | 3.07E-04 | | 4.25E-03 | 5.73E-07 | 4.25E-03 | |
| | Cr- cancer | 4.60E-07 | 1.11E-09 | | 4.60E-07 | 6.38E-06 | 6.87E-09 | | 6.38E-06 |
| | Cu | 3.94E-04 | 7.92E-07 | 3.95E-04 | | 5.46E-03 | 4.90E-06 | 5.47E-03 | |
| | Mn | 7.09E-03 | 1.07E-05 | 7.10E-03 | | 9.83E-02 | 6.62E-05 | 9.84E-02 | |
| | Ni-non cancer | 2.19E-04 | 4.90E-09 | 2.19E-04 | | 3.04E-03 | 3.03E-08 | 3.04E-03 | |
| | Ni- cancer | 7.45 E-07 | 1.12E-09 | | 7.45 E-07 | 1.03E-05 | 6.95E-09 | | 1.03E-05 |
| | Pb-non cancer | 3.38E-02 | 1.36E-05 | 3.38E-02 | | 4.68E-01 | 8.41E-05 | 4.68E-01 | |
| | Pb-cancer | 1.00E-06 | | | 1.00E-06 | 1.39E-05 | | | 1.39E-05 |
| | Zn | 8.31E-04 | 2.51E-07 | 8.31E-04 | | 1.15E-02 | 1.55E-06 | 1.15E-02 | |

## CONCLUSION

In this study, heavy metal concentrations of tailing and soil samples taken from Balya and Koru mining sites were determined and effects of heavy metals on human health were assessed. In both mining sites, heavy metal concentrations were generally higher in tailing samples than in soil samples. The shortcoming of this research is that no sampling was done from the water and sediment in the study area and heavy metal contents were not determined. Mine tailings and soils in the study areas were heavily polluted by Pb and Zn. The non-carcinogenic risk was determined to be at the highest level for Pb and the carcinogenic risk was determined to be at the highest level for Cd and Pb. An environmental management plan should be applied and a soil remediation strategy should be developed to reduce the effects of mining activities on human health.

## COMPLIANCE WITH ETHICAL STANDARDS

### Peer-review

Externally peer-reviewed.

### Declaration of interests

The authors declare that they have no competing, actual, potential or perceived conflict of interest.

### Author contribution

The contribution of the authors to the present study is equal. All the authors read and approved the final manuscript. All the authors verify that the Text, Figures, and Tables are original and that they have not been published before.

### Ethics Committee Approval

Ethics committee approval is not required.

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