How to cite: Sadig, M., 2024. Heavy metal content of mountainous agricultural soils and ecological risk assessment in Gadabay district, Azerbaijan. Ege Univ. Ziraat Fak. Derg., 61 (1): 73-86, https://doi.org/10.20289/zfdergi.1386603

Research Article
(Araştırma Makalesi)

Ege Üniv. Ziraat Fak. Derg., 2024, 61 (1): 73-86
https://doi.org/10.20289/zfdergi.1386603

Heavy metal content of mountainous agricultural soils and ecological risk assessment in Gadabay district, Azerbaijan

Azerbaycan'ın Gedebay ilçesinde dağlık tarım topraklarının ağır metal içeriği ve ekolojik risk değerlendirmesi

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Received (Alınış): **28.11.2023** **Accepted** (Kabul Tarihi): **28.03.2024**

ABSTRACT

Objective: The objective of this study was to i) investigate the distribution characteristics of heavy metals, ii) examine their relationships with basic soil properties, and iii) characterize their potential sources and ecological risks.

Material and Methods: A total of 85 samples were collected from the surface horizon (0-15 cm) of Chernozem soil in a representative agricultural area located in the Lesser Caucasus Mountains (Gadabay district), and heavy metal contents and basic soil properties were determined.

Results: The mean of the heavy metals followed a decreasing order: Mn>Zn>Cu>Cr>Ni>Co>Pb>As>Se>Cd and some heavy metals (As, Cd, Se) exhibited a fragmented distribution. Co, Cr, Mn, Se and Zn contents were higher than the background concentration, while others (As, Cd, Co, Cu, Pb and Zn) exceeded the maximum permissible concentration.

Conclusion: The spatial distribution of heavy metals was characterized by their typical and element-specific distribution. The noted variability was likely related to geologic features (soil mineralogy), mining history and agricultural practices. Notably, the presence of limestone and clay minerals contributed to the association of Cd, Cu and Se and Mn and Pb, respectively. Sand content influenced the mobility of Cr and Cu. The relations between pH and Cr, Ni and Se was the indication of the influence of the parent material on the distribution of these metals.

Keywords: Caucasus Mountains, environmental indices, heavy metals, soil properties

ÖZ

Amaç: Amaç: Çalışmanın amacı, i) ağır metallerin dağılım özelliklerini araştırmak, ii) temel toprak özellikleri ile ilişkilerini incelemek ve iii) potansiyel kaynaklarını ve ekolojik risklerini karakterize etmektir.

Materyal ve Yöntem: Kafkas Dağları'nda (Gadabay bölgesi) yer alan temsili bir tarım alanında Çernozem toprağının yüzey katmanından (0-15 cm) toplam 85 örnek toplanmış, ağır metal içerikleri ve temel toprak özellikleri belirlenmiştir.

Araştırma Bulguları: Ağır metallerin ortalamaları azalan bir sıra izlemiştir: Mn>Zn>Cu>Cr>Ni>Co>Pb>As>Se>Cd ve bazı ağır metaller (As, Cd, Se) parçalı bir dağılım sergilemiştir. Co, Cr, Mn, Se ve Zn içerikleri arka plan konsantrasyonundan daha yüksek iken diğerleri (As, Cd, Co, Cu, Pb ve Zn) izin verilen maksimum konsantrasyonu aştı.

Sonuç: Ağır metallerin uzaysal dağılımı, tipik ve elemente özgü dağılımlarıyla karakterize edilmiştir.. Belirtilen değişkenlik muhtemelen jeolojik özellikler (toprak mineralojisi), madencilik geçmişi ve tarımsal uygulamalarla ilgilidir. Kireçtaşı ve kil minerallerinin varlığı sırasıyla Cd, Cu ve Se ile Mn ve Pb'nin birlikteliğine katkıda bulunmuştur. Kum içeriği Cr ve Cu'nun hareketliliğini etkiledi. pH ile Cr, Ni ve Se arasındaki ilişkiler, ana materyalin bu metallerin dağılımı üzerindeki etkisinin göstergesiydi.

Anahtar sözcükler: Kafkas Dağları, çevresel indeksler, ağır metaller, toprak özellikleri

INTRODUCTION

Heavy metal contamination and accumulation is a serious problem around the world due to the potential threat to food safety and its detrimental effects on human and animal health (Hu et al., 2017). The natural concentrations of metals in soils tend to remain low depending on the geological parent material composition (Shan et al., 2013). However, as reported by Borůvka et al. (2005) and Kabata-Pendias (2011), the main sources of heavy metals in the soil beside geogenic also includes various anthropogenic factors. As known, heavy metal content and distribution in soils are influenced by several factors including organic matter content, types of land management, particle-size distribution, parent material, drainage, soil age, vegetation and aerosol input (Esser et al., 1991; Lee et al., 1997; Sun et al., 2019). Understanding the presence and origin of specific heavy metals in soils is a priority for the European Union, as it aligns with its goals of promoting sustainable agriculture and restoring landscapes. Thus, monitoring land quality in mountain areas affected by agricultural practices and mining require a systematic investigation of heavy metal concentrations in the soils, since (i) mountainous ecosystems provide the vital functions and services, such as water supply and biodiversity conservation, and (ii) contribute to local food security, and directly impact downstream and lowland areas through ecosystem services.

Although most of agricultural lands are related to livestock production (e.g., pastures and hays), in the mountainous areas of the Caucasus region, yet the dry farming agriculture is the main type of practice in these areas. However, long-term intensified and blind use of mineral fertilizer and manure, driven by variable soil fertility level, runoff and erosion damage (i.e., onsite and offsite impact), has raised concerns about increased heavy metal pollution. Excessive use of agrochemicals and manure, as documented by Nicholson et al. (2003) and Hani & Pazira (2010), can lead to elevated levels of toxic heavy metals like Pb, Ni, Cr and Zn in agricultural soils. Such practices further complicate the assessment of soil health or quality in mountainous regions due to a critical lack of data on spatial and temporal variation of heavy metal content (Zinn et al., 2020; Mammadov et al., 2022).

Soil quality is related to the physical, chemical and biological soil properties, and hence to soil fertility, which is traditionally managed by applying organic amendments and mineral fertilizers. Healthy soil with high organic matter can enhance biological (microbial activity and community) and physical (bulk density, water holding capacity, infiltration and drainage capacity) and chemical properties (Celik et al., 2004; Herencia et al., 2011; Li et al., 2018). However, not only soil organic matter content and fertility elements (e.g., N, P, Ca, K), but also concentration of heavy metals should be considered, since the elevated concentration of the heavy metal and its availability (i) can be associated with certain soil chemical properties, land use and environmental processes, (ii) can negatively affect plant development, soil biota and biological processes and quality, and (iii) create various environmental and ecological risk (Sungur et al., 2014; Kars & Dengiz, 2020; Kandziora-Ciupa et al., 2021).

In this study, it was studied to evaluate heavy metal content of agricultural soils in the Gadabay district, Azerbaijan. It is a typical mountainous agricultural land, a representative of those situated in the Lesser Caucasus Mountains. The study area, has been long cultivated with predominantly potato, cereals, and to some extend cabbage, beet and carrot, yet the majority of lands are used under pasture and hay depending on slope conditions. The cultivated lands are distributed on mountain plateau where typical soil groups are Chernozems (with high soil organic matter) according to the International Soil Classification System (IUSS, 2015). This region is well-known with its mineral deposits (Ismayil et al., 2018; Veliyev et al., 2018) and historical mining activity (started as long as 2000 years ago). More recent activity was during 1849-1917 when the Mekhor Brothers, followed by the German Siemens Bros Company developed and operated a copper mine in Gadabay. The area includes the first operating gold mine as well as a number of exploration targets in Azerbaijan. An open pit mine and a conventional heap leach activity commenced once more in 2008 and it is presently operational.

As obvious, the studied region is rather complex in terms of the combined effect of these factors. A long-term mining activity, traditional agricultural practices, blind use of mineral and organic fertilizers, land use variety in association with erosion processes and parent material diversity make this region more impedimental area in view of soil health and regular soil monitoring. Given that the region was not studied in view of the impact of the long-term mining as well the agricultural practices on soil properties, it can be stated that the present pioneering study may play an important role in future environmental studies. Thus, the determination of background levels of heavy metals is an important approach to prevent environmental pollution and physiological disorders in plant and grazing animals, and to establish an initial or modified threshold levels for studying heavy metal concentrations (Kabata-Pendias, 2011; Bayraklı & Dengiz, 2019). Furthermore, the basic soil properties, such as texture (clay), pH, organic matter, carbonates and salinity significantly affect the concentrations and availability of heavy metals in the soil (Omran, 2016; Kars & Dengiz, 2020; Lasota et al.. 2020; Mammadov et al., 2022). Therefore, the basic soil properties were also studied. The objectives of this study were to (i) asses the concentrations of heavy metals in the study area, (ii) evaluate relationships between heavy metal concentration and basic soil properties, and (iii) estimate the level of environmental and ecological risk posed by heavy metals and sources of heavy metals in agricultural lands.

MATERIALS and METHODS

Study area

The study site is situated within the administrative area of Gadabay district (Figure 1), known for its abundant mineral deposits in the Caucasus region. Geographically located in the western part of Azerbaijan, within the Lesser Caucasus Mountains, the site spans elevations ranging from 1060 to 3271 m above sea level. In general, the study area is complicated due to the tectonic structure of anticlinal pattern and magmatic occurrences in three different periods as Bajocian, Batonian (Middle Jurassic) and Upper Jurassic-Early Cretaceous (Karimov, 1976).

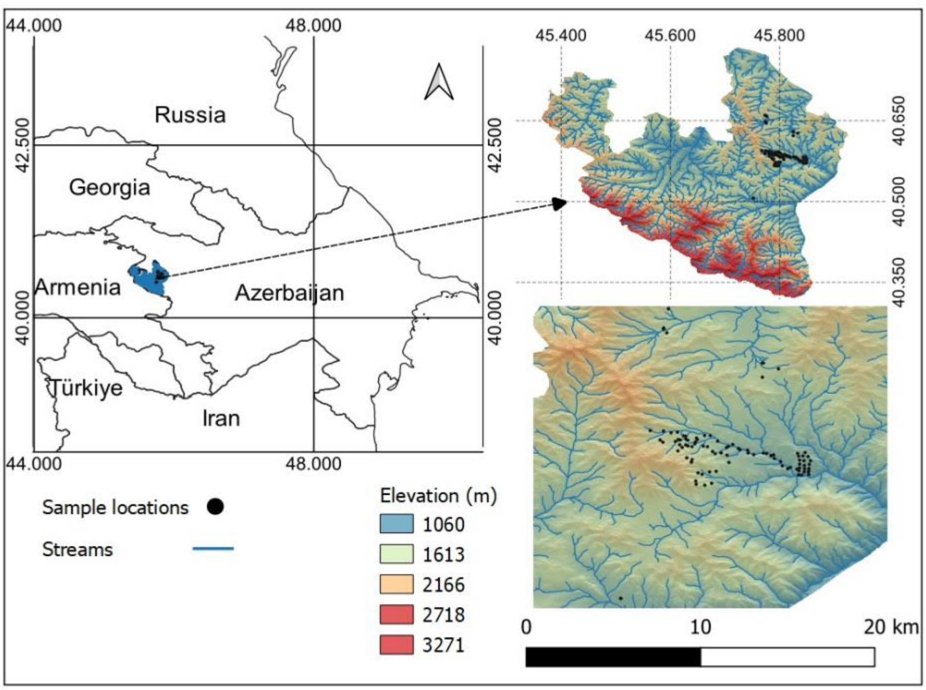

Figure 1. Geographical location of the study area and sampling points.

Şekil 1. *Çalışma alanının coğrafi konumu ve örnekleme yerleri.*

Therefore, in the geological setting of the area alluvium of Quaternary, quartz porphyry and granodiorite-diorite of Upper Jurassic and Lower Cretaceous, andesitic tuff-conglomerate, andesite, rhyolite and rhyodacite of Middle Jurassic/Bathonian stages played an important role. The study area is characterized by predominantly grasslands, mountainous forests, cultivated lands and locally occurring shrubbery areas. Given the region's extensive involvement in agriculture, soil erosion is typical, and all rates of soil erosion occurred in the region. The climate in the region is moderate, featuring dry winters. The annual precipitation is 650 mm, and average air temperature is 7.8°C.

Soil sampling and chemical analyses

As the lack of previous information on heavy metal content of soils in this study area, a simple sampling procedure was applied to avoid deliberate bias and partially fill the data gaps in this region. The elevation of sampling site varied between 1450-1800 m. The samples (85) were randomly collected from the soil surface horizon (0-15 cm) of the representative land uses (pastures, hays, cultivated-potato, wheat, cabbage, carrot and beet) within Gadabay district, including neighboring agricultural lands of the copper-gold mine (Figure 1). The cultivated lands primarily were small patches associated with traditional land tenure. Soil samples were subjected to microwave acid digestion with HNO_3 (Moral et al., 1996), and the concentration of heavy metals (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, and Zn) was measured through ICP-OES analysis. In addition to heavy metals content, basic soil properties were analyzed to characterize relationships between heavy metals and basic properties. The soil organic carbon (SOC) was determined by Walkley-Black method (Nelson & Sommers, 1996), soil reaction (pH) by using a pH-meter, $CaCO_3$ content by a pressure-calcimeter method (Sherrod et al., 2002), and texture (sand, silt and clay contents) by the hydrometer method (Gee & Bauder, 1986).

Statistical analysis and environmental risk assessment

Descriptive statistics of environmental variables, especially the concentration of heavy metals in soil is important in view of the nature and spatial distribution. Therefore, the results of chemical tests were analyzed in terms of minimum (Min), maximum (Max), mean, median, standard deviation (SD) and coefficient of variation (CV). The CV values were classified as low (<15%), medium (15-35%) and moderate (>35%) according to Mallants et al. (1996). To elucidate the relations between basic soil properties and heavy metals the Spearman Rho correlation coefficients were calculated. Furthermore, different environmental indexes were calculated to characterize the nature, sources and environmental risk of heavy metal content of the soils in the area.

A single pollution index was calculated to characterize the present status of each heavy metal concentrations. The pollution index (P_i) was computed as the ratio between the metal concentration and its reference value (national criteria of the metal).

$$P_i = C_i/S_i$$

where, P_i is the pollution index, C_i is the metal concentration in a given sample, and S_i is the maximum permissible concentrations (MPC) of pollutants established by Azerbaijan legislation (GN 2.1.7.2041-06, 2000).

An enrichment factor (E_f) was used to assess the contribution of anthropogenic sources to natural levels of heavy metals in the soil:

$$E_f = \frac{C_i/C_r}{B_i/B_r}$$

where, C_i and C_r are the concentrations of the target metal and the reference metal in the sample, while B_i and B_r are the background concentrations (BC) of the target metal and the reference metal for the natural soils of the study area. In this study, the BC values for target heavy metals were adopted from the Azerbaijan legislation (GN 2.1.7.2041-06, 2000) which referred to the existing studies. Commonly, the concentrations of immobile elements such as, Al, Ti, Fe and Mn are used to compute enrichment factor (Hu et al., 2013). Thus, in this study, the concentration of Mn was used as the reference.

The geoaccumulation (I_{geo}) and potential ecological risk indexes were calculated to evaluate the environmental and ecological risk for the soils of the study area. The geoaccumulation index was introduced by Müller, (1979) and is widely used to assess the contamination level of heavy metals in soils:

$$I_{geo}=\log 2\left(\frac{C_n}{1.5B_n}\right)$$

where C_n is the measured concentration of the given heavy metal, B_n is the local geochemical background concentration. It is commonly accepted that the constant of 1.5 can minimize the possible variations in the background concentration derived from lithological effect.

Ecological risk index (R_i) was also computed to assess the potential risk of the given heavy metal according to Hakanson (1980):

$$R_i=\sum E_i\ ,\ E_i=T_i f_i=T_i\frac{C_i}{B_i}$$

where, E_i is the risk factor of the given element i, T_i is the toxic effect factor of the given metal i, f_i is the measured concentration of the given metal (C_i), B_i is the background concentration.

The maximum permissible and background concentrations (BC) of heavy metals in the soils of Azerbaijan as well the values of T_i for the given heavy metals were adopted from the national standard ((GN 2.1.7.2041-06, 2000)) and presented in Table 1. The values of the pollution and geoaccumulation indexes (I_{geo}), enrichment (E_f) and potential ecological risk (R_i) factors (Table 2) were classified according to Hakanson (1980) and Brady et al. (2015).

Table 1. Background concentration and maximum permissible concentration of heavy metals in Azerbaijani soils

Çizelge 1. *Azerbaycan topraklarındaki ağır metallerin arka plan konsantrasyonu ve izin verilen maksimum konsantrasyonu*

Element	BC	MPC considering BC	MPC (without BC)	T_i
As	15	2	2.0	10
Cd	3	2*	2.0	30
Co	8	5*	5	5
Cr	40	6	6	2
Cu	100	3	3	5
Hg	0.4	2.1	2.1	40
Mn	250	1500	1500	1
Ni	45	4	4	5
Pb	20	32	32	5
Se	0.1	3		
Zn	70	23*	23	1

* MPCs according to other standards

Table 2. The classification of pollution (P_i), enrichment (E_f) and geoaccumulation ($İ_{geo}$) indexes and potential ecological risk (R_i)

Çizelge 2. *Kirlilik (P_i), zenginleşme (E_f) ve jeoakümülasyon ($İ_{geo}$) endekslerinin sınıflandırılması ve potansiyel ekolojik risk (R_i)*

P_i		E_f		I_{geo}		R_i	
<1	Unpolluted/weakly polluted	<2	Depletion to mineral enrichment	<0	Unpolluted/slightly polluted	<40	Low potential ecological risk
1-3	Moderate-strong	2-5	Moderate enrichment	0-1	Moderately polluted	40-80	Moderate potential ecological risk
3-6	Strong	5-20	Significant enrichment	1-3	From moderately to strongly polluted	80-160	Considerable potential ecological risk
>6	Very strong	20-40	Very high enrichment	3-5	Strongly polluted	160-320	High potential ecological risk
		>40	Extremely high enrichment	>5	Extremely polluted	>320	Very high potential ecological risk

RESULTS and DISCUSSION

Descriptive statistics of the reference data

The descriptive statistics of basic soil properties and heavy metals are tabulated in Table 3, and the heavy metals in Chernozem soil samples with the clay-loam and loam-clay texture showed their both typical and element-specific distribution. Except soil pH, the spatial distribution of basic soil properties and heavy metal concentration was characterized with medium and moderate variation. Among others, only the pH (mean value of 6.4) showed a low variability (10%), i.e., smooth spatial continuity. The soil reaction were charasterized as slightly acidic, however 6% of the samples were slightly alkaline, showing the importance of land use and soil processes, and local environmental condition (Mammadov et al., 2022). Soil clay, $CaCO_3$ and SOC content were moderately, while sand and silt content were medium variable. As the main driver for many processes in soil medium, the large variation in SOC (1.3−9.1%) was related to elevation, vegetation cover, land use and slope (Mammadov et al., 2021).

The $CaCO_3$ content varied in between 1% to 15% in surface soils owing to parent material, erosion and slope condition (Table 3). Recent studies in the adjacent district revealed that $CaCO_3$ content was typically associated with parent material, elevation, slope and land use (Mammadov et al., 2021; Mammadov et al., 2022,). The mean value of $CaCO_3$ content (8.6%) was an affirmative indication of carbonate-rich parent material and its dominance in the study area (Ismayil et al., 2018). However, silt content (20−45%), which has $CaCO_3$ size, showed medium variation (16.5%), while sand (16−65%) and clay (9−47%) content displayed medium and moderate variation, respectively. The mean value (21%) of clay content was lower than those of silt (33 %) and sand (45%) content. This can be attributed to erosion and selective transport of eroded particles in the surface soils, typical of the study area (Mammadov et al., 2021).

Based on the mean values, the heavy metals followed the sequence of Mn > Zn > Cu > Cr > Ni > Co > Pb > As > Se > Cd. The Hg was not detected in the samples (Table 3). The content of As (detected in 31 samples) varied in a narrow range (7.10-19.70 mg/kg) and its overlapping mean and median values as well skewness value confirmed unimodal distribution (Table 3, Figure 2). Among the tested soil samples, the concentration of As in one sample slightly exceeded the MPC that might be related to mining activity. Occurrence of elevated As level is typical to soils around gold and copper mines, and As occurs as arsenopyrite (FeSAs), realgar (As_2S_2) and orpiment [As_2S_3] in gold bearing rock (Fashola et al., 2016).

The Cd was detected in 24 out of 85 samples which confirms its fragmented distribution, whereas its histogram showed unimodal distribution (Figure 2). One of the tested samples (very close to mining area) exceeded the MPC. Cd is reported as one of the most toxic heavy metals to most organisms and occurs in gold bearing orebodies as an isometric trace element in sphalerite and its concentration depends on the concentration of the sphalerite in the ore body (Fashola et al., 2016). The specific distribution of Cd is presumably associated with the local geology, topography and soil moisture regime. As reported by Han et al. (2007) soil moisture could greatly affect the solubility, toxicity, bioavailability, and mobility of Cd and cause it redistribution in soils.

The typically distributed in the study area, Co content (not detected only in one sample and symmetric unimodal pattern, Figure 2) varied between 6.48 and 34.30 mg/kg with a mean value of 18.91 mg/kg (Table 3). Given that the BC, Co content was double higher than the MPC in 36 samples. It was assumed that the noted higher Co concentration is typical to the study because the BC for Co according to Azerbaijani legislation is 8 mg/kg and additionally MPC for Co is not indicated from unknown reasons. Therefore, other standards from other regions were used (Table 1). As well, mean concentration of Co in Europe is reported to vary between 1 and 20 mg/kg and this range can be higher in geologically Co-rich areas (Angelone & Bini, 2009). The concentration of Co in soil is dependent on several factors, such as local geological features, precipitation and Co-rich dust, soil moisture regime, soil age and texture, land-use and application of chemicals. Bradley, (1980) reported that Co concentration exceeds the value of 2500 mg/kg in Northern Wales and the ecosystem of those areas have been adapted to such high concentration and healthy. Thus, geological setting of the region and the existence of gold-copper mine in Gadabay district presumably causes high Co concentration in the study area.

Table 3. Descriptive statistics of basic soil properties and heavy metals

Çizelge 3. *Temel toprak özellikleri ve ağır metallerin tanımlayıcı istatistikleri*

Element	Min	Max	Mean	Median	SD	CV
Basic soil properties						
$CaCO_3$ (%)	1.06	15.00	8.61	9.00	3.98	46.25
Sand (%)	16.00	65.00	44.85	46.00	12.18	27.15
Silt (%)	20.00	45.00	33.69	33.00	5.56	16.51
Clay (%)	9.00	47.00	21.46	21.00	8.81	41.05
pH	5.31	8.30	6.36	6.30	0.67	10.50
SOC (%)	1.32	9.10	4.34	3.94	2.02	46.61
Heavy metals						
As (mg/kg)	7.10	19.70	10.81	10.68	2.63	24.33
Cd (mg/kg)	0.58	6.60	1.08	0.76	1.17	108.56
Co (mg/kg)	6.48	34.30	18.91	17.40	5.52	29.19
Cr (mg/kg)	5.30	110.00	44.28	42.26	18.09	40.85
Cu (mg/kg)	34.59	180.20	68.73	67.00	25.40	36.95
Mn (mg/kg)	326.08	1214.27	690.26	653.40	204.51	29.63
Ni (mg/kg)	11.49	67.00	37.74	38.20	10.82	28.68
Pb (mg/kg)	3.60	77.90	12.26	10.89	9.01	73.53
Se (mg/kg)	0.63	3.02	1.48	1.33	0.58	39.52
Zn (mg/kg)	4.90	2655.09	107.15	71.51	282.23	263.39

In the study area, Cr was detected in all tested samples, ranging from 5.30 to 110 mg/kg and the content exceeded the BC in 50% of the samples (Table 3). The unimodal and symmetric distribution (Figure 2) showed its typical distribution that was attributed to the geological features of the study area (Karimov, 1976).

The Cu was the third abundant heavy metal in terms of mean value (67.32 mg/kg, Table 3). Its moderate variability and bimodal distribution (peaks centered around 40 and 75 mg/kg, Figure 2) evidently reflected local geological features of the study area (Figure 2). The Cu concentration exceeded the MPC in 9 samples that can be attributed to the lithological features of the parent material or mining as Cu is widely distributed in sulphides, arsenites, chlorides and carbonates (Fashola et al., 2016). On other hand, gold mining leads greatly increased Cu concentration in the environment which upon release binds to particles of organic matter, clay minerals and sesquioxides leading to great accumulation in the soil (Fashola et al., 2016).

The most abundant heavy metal, Mn ranged from 326 to 1214 mg/kg with a mean value of 690 mg/kg (Table 3). Overall, Mn content in the study area was averagely higher than the BC, however the tested samples showed no values exceeding the MPC. The medium variability and unimodal, yet large spread pattern (Figure 2) showed its typical distribution. A similar distribution pattern was also found for Ni, the fifth abundant heavy metal with a mean value of 37.74 mg/kg. However, Ni content slightly exceeded the MPC in some samples. The noted high concentration for heavy metals such as Ni, Co and Cr was in line with previous studies (Bayraklı & Dengiz, 2019; Kars & Dengiz, 2020). Such characteristics of the heavy metals are associated with the nature of parent material as reported by Chen et al. (2005), the Ni concentration in volcanic rocks is 20-40 times greater as compared to other ones.

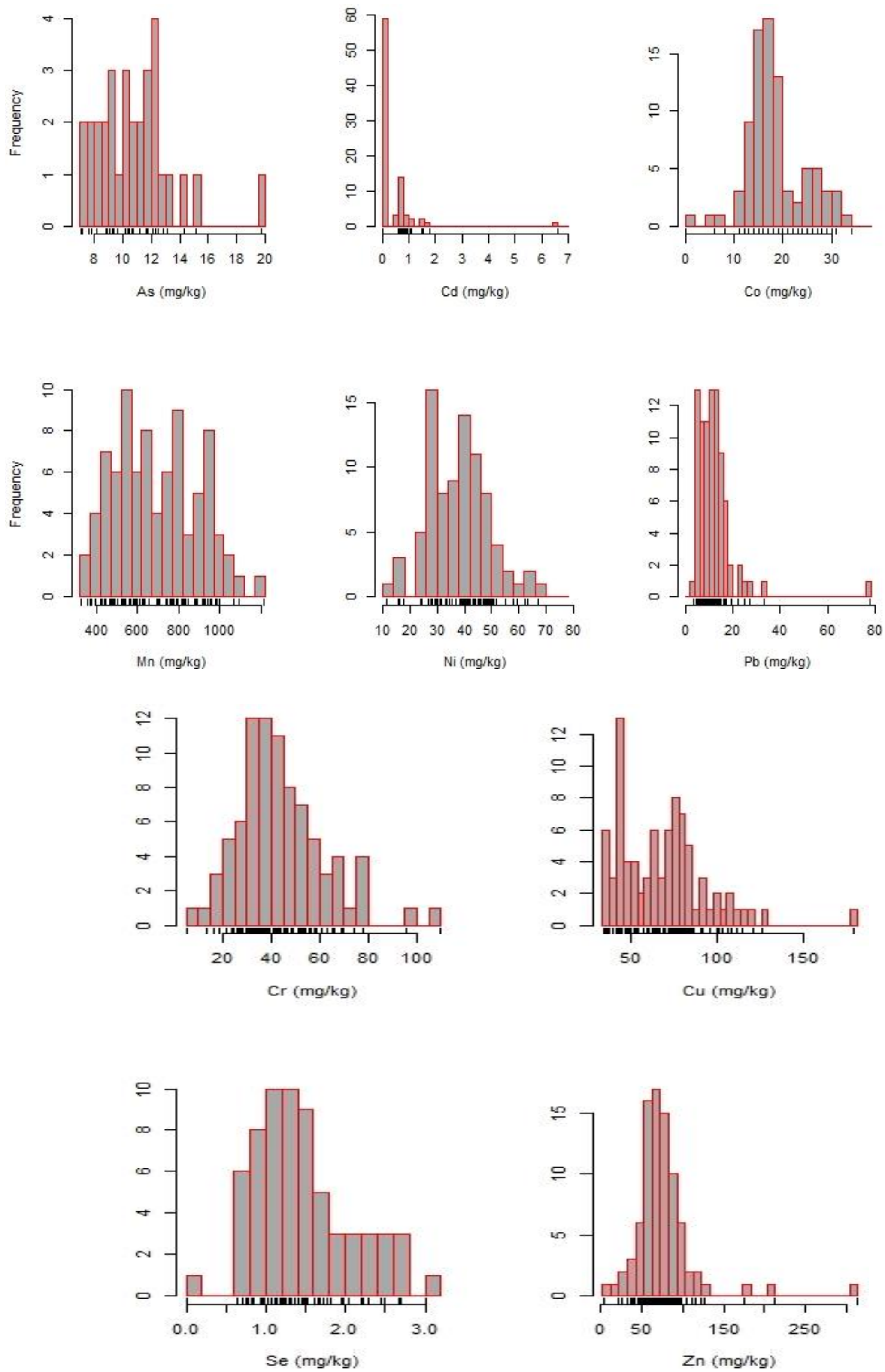

Figure 2. Histogram of the tested heavy metals.

Şekil 2. *Test edilen ağır metallerin histogramı.*

The soils in the study area can be considered abundant with Pb content, e.g., the range (3.60-77.90 mg/kg, Table 3) was concordant with a range of 10-67 mg/kg in surface soils worldwide (Fashola et al., 2016). The Pb content showed moderate variability and associated with Mn and Zn. In addition, the elevated concentration was found for one sample and exceeded the MPC that maybe related to the parent material in severely eroded pastureland.

Unlike other heavy metals, Se content showed specific distribution, and it was not detected in 3 samples. Its content varied from 0.63 to a maximum of 3.02 mg/kg and the mean value (1.48 mg/kg) was ten times higher than the BC according to the native regulation (Table 1 and Table 3). Besides that the MPC is missing in the native regulation. A unimodal symmetric pattern and spatial continuity may confirm its naturally higher concentration in the study area. On the other hand, we assume that significant gaps exist in compiling native regulation of BC and MPC as noted in Vodyanitskii (2016).

As there exists data scarcity on Se content of soils in Azerbaijan, it is important to provide a brief overview from different study examples. According to the studies from different regions of the world, Se content ranges between 0.1-0.6 mg/kg and the background value of 0.4 mg/kg (Fordyce, 2013). It was reported that Se content in Canada varies from 0.02 to 3.70 mg/kg with a mean value of 0.30 mg/kg (Haluschak et al., 1998). Tan (1989) and Dinh et al. (2018) reported that Se content is in toxic level in the Hubay region of Chine, mean concentration is about 2.3 mg/kg. Another characteristic making Se specific is the narrow range between Se toxicity and deficiency. According to Fleming (1980), a high Se concentration and its main origin in soil is associated with limestones, shales and other volcanic rocks of the Jurassic and Cretaceous stages. Summarizing above-mentioned studies and considering predominating rocks in the study region, the noted Se content maybe related to the nature of the study area.

The soils in the Gadabay district are characterized by a remarkable high Zn content, the second abundant element following Mn. A large range (4.90-2655 mg/kg) and high CV value made its distribution different from others (Table 3). The mean content (107.15 mg/kg) was higher than the BC (70 mg/kg). According to the national standards (GN 2.1.7.2041-06, Table 1), the present status of Zn content in the study area is indicative of massive pollution. Because the MPC is accepted 23 mg/kg considering BC, in this case the Zn concentration of majority of the samples is higher than the MPC. Therefore, it would be reasonable to pay attention to the MPC of other standards. For example, MPC for Zn in Soil Code DEFRA standard is 200 mg/kg. This level is also accepted in other standards. Bos et al. (2005) found that the toxic effect of heavy metals on soil ecosystem is dependent on soil type and considering the changes in BC of Zn depending on soil types, the authors prepared special methodology for determining MPC for Zn content. The presented approach showed that the difference between BC of Zn for different soil types reaches to 7.5 times thereby MPC ranges from 44 mg/kg to 208 mg/kg depending on soil type.

Summarily, the distribution of heavy metals in the study area was basically attributed to the geologic settings and heavy metal levels were to some extent higher compared to the BC both in nationally and internationally. The presented study found that the content of some heavy metals such as Co, Se and Zn is considerably higher, however the comparisons made between the studies from different regions of the world showed that there is great need to study those elements in the country and the native standards need to be improved.

Relations between the soil properties and heavy metals

The significant correlations were found not only between basic soil properties themselves, but also between basic soil properties and heavy metals (Table 4). As expected, very close relations were found between the particle sizes, sand content was inversely correlated with silt (r = -0.76) and clay (r = -0.91) while the silt and clay (r = 0.45) occur associated in soil medium. This is in line other studies and typical case for the region where calcareous parent material occurs (Mammadov et al., 2022).

The relations between $CaCO_3$ and sand content (*r* = 0.45), $CaCO_3$ and SOC (*r* = -0.56), SOC and clay content (r = 0.72) apparently represent characteristic features of soil-forming processes in the mountainous temperate climate where a favorable ratio of precipitation to temperature in the background of topography and parent material formalize Chernozems. Meanwhile, the significant relationships between clay and pH (*r* = -0.34), sand and pH (*r* = 0.29), SOC and pH (*r* = -0.39) well characterize soil-forming environment and weathering process. These relations also ascertained the relations between basic soil properties and heavy metals.

The positive correlation coefficients between clay and Mn, clay and Pb confirmed the importance of clay mineralogy. The study conducted in the adjacent district found out the similar relations between clay content and plant available forms of Mn and Pb (Mammadov et al., 2022). However, Cu, Cr and Co showed inverse relations, e.g., decrease with increasing the clay content. Among the studied heavy metals, solely Cr and Cu was found associated with sand content, their concentration increases with sand content. The impact of calcareous parent material on heavy metal content was evident through the correlation coefficients found between $CaCO_3$ and solely three elements (Cd, Cu and Se). The elements As, Zn and Ni showed no significant relationships with basic soil properties. As regards the relationships between pH and heavy metals, the significant correlations were solely found for Cr, Ni and Se. Although the total content of most heavy metals showed no relations to pH in our study area, the availability of Cd, Pb and Mn content was significantly affected by pH in this region (Mammadov et al., 2022).

The correlation coefficients indicated that most heavy metals occur associated in soil medium, e.g., As content increases with increasing the content of all heavy metals (Table 4). The tested heavy metals presented evident grouping e.g., Pb and Mn, Pb and Zn, Cr and Ni, Cd and Zn couples showed significant relations that was presumably attributed to the geogenic factor leading to their similarly bonding in parent material and soil (e.g., Karimov 1977). The close relations found between those couples were in line with other studies (Hadzi et al., 2019, Mammadov et al., 2022). Hadzi et al., (2019) reported associated distribution of Cd and Zn in surface soil of mining areas. As well, Mammadov et al. (2022) found significant relations between Zn and Pb, Pb and Cd in the surface soils of the Caucasus Mountains. In addition, the relations found between other heavy metals (for example Co, Cu, Mn and Ni; Cd, Se and Zn; Cr, Ni and Cu) were in line with previous studies. The associated distribution of Cd, Cr, Cu and Zn was reported regardless of land use types (farmland, grassland and woodland) in Southwest Chine (Sun et al., 2019).

Environmental risk assessment

According to the mean value of pollution index, the studied samples were related to the unpolluted and weakly polluted class (P_i<1.0) except Co, which was characterized with moderate-strong (P_i = 1.44) pollution (Table 5). As noted before, the MPC for Co is missing in the national standard, and the MPC value was taken from another country's standard. The interpretation of P_i values of individual samples also showed a moderate-strong point-source pollution: the pollution was noted in one location for As and Cd, and in four locations for Zn. The three Zn-polluted samples were in mine-adjacent areas that may be linked to mining activity (Omwene et al., 2018). The contamination levels of heavy metals and other major elements (Pb, As, B, Cd, Zn, Cr, Mo, Co, Ni, Cu, and Ag) in surface sediments and their possible pollution sources was studied in Mustafakemalpaşa catchment in Türkiye. The highest I_{geo} values were recorded for Cr, B, Ni, As and Zn, and occurred near urban settlements and mining sites. The sources of Pb, Zn and Cu in the sediments were attributed to weathering of sulfide ore minerals (Omwene et sl., 2018). Thus, the gaps in the national standards for MPCs of heavy metals and absence of earlier soil data (one or several decades ago) appeared as a limiting factor in calculating and evaluating other environmental indices (Han et al., 2021). Han et al. (2021) encountered the similar issue to study spatial distribution of soil salinity and heavy metals in the lowland region of Azerbaijan. The study found that among the studied 20elements Ca, Cl, and S and the heavy metals Cr, Ni, and Pb were classified as problematic on the basis of I_{geo} index, and As was also identified as posing a possible risk on the basis of the potential ecological risk index. Soil guideline values were proposed to monitor soil pollution in lowland areas of Azerbaijan (Han et al., 2021), however to fill the gaps concerning the monitoring of mountainous regions an extensive study is required.

Table 4. The Spearman Rho correlation coefficients between soil properties and heavy metals

Çizelge 4. *Toprak özellikleri ile ağır metaller arasındaki Spearman Rho korelasyon katsayıları*

	$CaCO_3$	Sand	Silt	Clay	pH	SOC	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Se
$CaCO_3$	1														
Sand	0.45^{**}	1													
Silt	-0.27^{*}	-0.76^{**}	1												
Clay	-0.43^{**}	-0.91^{**}	0.45^{**}	1											
pH	0.12	0.29^{**}	-0.08	-0.34^{**}	1										
SOC	-0.56^{**}	-0.65^{**}	0.31	0.72^{**}	-0.38^{**}	1									
As	-0.04	0.18	-0.13	-0.16	0.22	-0.11	1								
Cd	0.51^{**}	-0.13	0.07	0.19	-0.11	-0.01	-	1							
Co	-0.25^{*}	0.12	0.10	-0.27^{*}	0.04	-0.37^{**}	0.54^{**}	-0.27^{*}	1						
Cr	0.24	0.31^{**}	-0.09	-0.36^{**}	0.25^{*}	-0.22^{*}	0.30	-0.02	0.24	1					
Cu	0.44^{**}	0.40^{**}	-0.22^{*}	-0.41^{**}	0.05	-0.38^{**}	0.42^{*}	0.16	0.35^{**}	0.24^{*}	1				
Mn	-0.46^{**}	-0.44^{**}	0.35^{**}	0.35^{**}	-0.14	0.24^{*}	0.48^{**}	-0.23^{*}	0.35^{**}	-0.28^{**}	-0.24^{*}	1			
Ni	-0.03	0.06	0.12	-0.16	0.37^{**}	-0.11	0.44^{*}	-0.13	0.32^{**}	0.75^{**}	-0.05	0.16	1		
Pb	-0.35^{**}	-0.62^{**}	0.42^{**}	0.60^{**}	-0.15	0.40^{**}	0.38^{*}	0.17	-0.12	-0.20	-0.37^{**}	0.45^{**}	0.10	1	
Se	0.33^{**}	0.11	0.02	-0.17	-0.29^{*}	0.04	0.30	0.42^{**}	0.10	0.01	0.31^{*}	-0.04	-0.05	-0.05	1
Zn	0.18	-0.13	0.15	0.13	-0.01	0.04	0.48^{**}	0.46^{**}	-0.10	-0.19	0.16	0.08	-0.05	0.44^{**}	0.41^{**}

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

The geoaccumulation index for Se (3.19) showed strong pollution ($3.0<I_{geo}<5$) while I_{geo} values for As, Cd, Cr, Cu, Ni, Pb and Zn presented unpolluted or slightly polluted class ($I_{geo}<0$). Based on I_{geo}, the soils were moderately polluted with Co and Mn. According to E_f values, Co and Cr were in the moderately enrichment class ($2.0 < E_f < 5$) while other heavy metals showed a depletion to mineral enrichment ($E_f<2.0$). The potential ecological risk for all the studied heavy metals was low while moderate for only Se (Table 5). The result was in line with other studies showing the impotance of land use (Sun at el., 2019) and mining history on onsite and offsite pollution potential (Omwene et al., 2018), as well water erosion and aeolian processes.

Table 5. Environmental indices calculated for the heavy metals

Çizelge 5. *Ağır metaller için hesaplanan çevresel endeksler*

Element	BC	P_i	E_f	$İ_{geo}$	R_i
As	15	0.63	1.24	-1.09	7.21
Cd	3	0.35	0.99	-2.35	10.75
Co	8	1.44	3.34	0.57	11.72
Cr	40	0.96	2.35	-0.56	2.21
Cu	100	0.67	1.63	-1.22	3.44
Mn	250	0.46	1.00	0.81	2.76
Ni	45	0.77	1.80	-0.90	4.19
Pb	20	0.24	0.53	-1.50	3.06
Se	0.1	0.48	1.14	3.19	72.70
Zn	70	0.53	1.41	-0.53	1.53

BC-background concentration, P_i-pollution index, E_f-enrichment factor, I_{geo}-geoaccumulation index, R_i-ecological risk factor

CONCLUSIONS

The spatial distribution of heavy metals in the study area was characterized by their typical and element-specific distribution. The order of means, and medium to moderate variation of heavy metal concentrations in this mountainous area were intricated and related to land use and past mining history, and erosion and aeolian processes, along with environmental condition and geologic features. The concentration of heavy metals were (i) fragmentary (As, Cd and Se), (ii) higher than the BC (Co, Cr, Mn, Se and Zn), and (iii) higher than MPC (Co: 36, Cu: 9, and Zn: 47 samples). The correlation between basic soil properties and heavy metals concentration revealed their association with $CaCO_3$ (Cd, Cu and Se), clay (Mn and Pb), sand (Cr and Cu), SOC (Co, Mn, Pb) and pH (Cr, Ni and Se). The significant correlations with pH were attributed to the bedrocks and parent material. The soils were non- and slightly-polluted (excluding three metals). Except two, the metals displayed as depletion to mineral enrichment. In general, the potential ecological risk for the studied heavy metals was low. Moreover, the sole weathering effect of parent material and anthropogenic activity in the regions leaded to high spatial heterogeneity of heavy metals in the soil, thus increasing the difficulty of extrapolation uncertainty by descriptive statistical method.

The evaluation of pollution and ecological risks was impeded by the gaps in the national standards. Further studies are needed to thoroughly investigate the impact of agricultural practices and mining by means of extensive, purposive sampling and cluster analysis.

Data Availability

Data will be made available upon reasonable request.

Author Contributions

Conception and design of the study: MS; sample collection: MS; analysis and interpretation of data: MS; statistical analysis: MS; visualization: MS; writing manuscript: MS.

Ethical Statement

I declare that there is no need for an ethics committee for this research.

Financial Support

The author thanks the Institute of Soil Science and Agrochemistry, Ministry of Science and Education of Azerbaijan Republic for the laboratory support.

Article Description

This article was edited by Section Editor Assoc. Prof. Dr. Ali Rıza ONGUN.

REFERENCES

Angelone, M. & C. Bini, 2009. “Trace Elements Concentrations in Soils and Plants of Western Europe, 19-44”. In: Biogeochemistry of Trace Metals. (Eds. D.C. Adriano), London, Tokyo, Boca Raton, Ann Arbor, Lewis Publishers, 59 pp.

Bayraklı, B. & D. Dengiz, 2019. Determination of heavy metal risk and their enrichment factor in intensive cultivated soils of Tokat Province. Eurasian Journal of Soil Science, 8 (3): 249-256.

Borůvka, L., O. Vacek & J. Jehlička, 2005. Principal component analysis as a tool to indicate the origin of potentially toxic elements in soils. Geoderma, 128 (3-4): 289-300.

Bos, R., M. Huijbregts & W. Peijnenburg, 2005. Soil type-specific environmental quality standards for zinc in Dutch soil. Integrated Environmental Assessment and Management, 1 (3): 252-258.

Bradley, R. I., 1980. Trace elements in soils around, Llechryd, Dyfed, Wales. Geoderma, 24: 17-23.

Brady, J.P., G.A. Ayoko, W.N. Martens & A. Goonetilleke, 2015. Development of a hybrid pollution index for heavy metals in marine and estuarine sediments. Environmental Monitoring and Assessment, 187 (5): 306.

Celik, I., I. Ortas & S. Kilic, 2004. Effects of compost, mycorrhiza, manure and fertilizer on some physical properties of a Chromoxerert soil. Soil and Tillage Research, 78: 59-67.

Chen, T.B., Y.M. Zheng, M.Lei, Z.C. Huang, H.T. Wu, H. Chen, K.K. Fan, K. Yu, X. Wu & Q.Z. Tian, 2005. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. Chemosphere, 60 (4): 542-551.

Dinh, Q.T., Z. Cui, J. Huang, T. Tran, D. Wang, W. Yang, F. Zhou, M. Wang, D. Yu & D. Liang. 2018. Selenium distribution in the Chinese environment and its relationship with human health: A review. Environment International, 112: 294-309.

Esser, K.B., J.G. Bockheim & P.A. Helme, 1991. Trace element distribution in soils formed in the Indiana dunes. United States of America Soil Science, 152: 340-350. http://dx.doi.org/10.1097/00010694-199111000-00005.

Fashola, M.O., V.M. Ngole-Jeme & O.O. Babalola, 2016. Heavy metal pollution from gold mines: environmental effects and bacterial strategies for resistance. International Journal of Environmental Research and Public Health, 13 (11): 1047. https://doi:10.3390/ijerph13111047.

Fleming, G.A., 1980. “Essential Micronutrients, 199-234”. In: Applied Soil Trace Elements (Eds: B.E. Davis), Vol 2, New York, John Wiley&Sons, 482 pp.

Fordyce, F.M., 2013. “Selenium Deficiency and Toxicity in the Environment, 375-416”. In: Essentials of Medical Geology (Eds. O. Selinus), Dordrech, Springer, 805 pp.

Gee, G.W., & J.W. Bauder, 1986. “Particle Size Analysis, 383-409”. In: Methods of Soil Analysis: Part 1 Physical and Mineralogical Methods (Eds. A. Klute), Madison, WI, ASA and SSSA, 1188 pp.

GN 2.1.7.2041-06. Native Standard on Maximum Permissible Concentrations of Toxic Substances in Atmosphere Air, Soils and Surface Water Resources Annexes to the Resolution of Cabinet of Ministers of the Republic of Azerbaijan about Confirmation of Legislative Regulatory Documents on the Maximum Permissible Concentrations of Toxic Substances in Atmosphere Air, Soils and Surface Water Resources. Baku, 2000, 58 pp.

Hadzi G.Y., G.A. Ayoko, D.K., Essumang & S.K.D. Osae, 2019. Contamination impact and human health risk assessment of heavy metals in surface soils from selected major mining areas in Ghana. Environmental Geochemistry and Health, 41: 2821-2843. https://doi:10.1007/s10653-019-00332-4.

Hakanson, L., 1980. An ecological risk index for aquatic pollution control: A sedimentological approach. Water Research, 14 (8): 975-1001.

Haluschak, P., R.G. Eilers, G.F. Mills & S. Grift, 1998. Status of Selected Trace Elements in Agricultural Soils of Southern Manitoba. Technical Report 1998-6E, Land Resource Unit. Brandon Research Centre, Research Branch. Agriculture and Agri-Food Canada, 70 pp.

Han, F.X., W.L. Kingery, J.E. Hargreaves & T.W. Walker, 2007. Effects of land uses on solid-phase distribution of micronutrients in selected vertisols of the Mississippi River Delta. Geoderma, 142: 96-103. https://doi:10.1016/j.geoderma.2007.08.006.

Han, J., Z. Mammadov, M. Kim, E. Mammadov, S. Lee, J. Park, G. Mammadov, A. Guliyev & H.M. Ro, 2021. Spatial distribution of salinity and heavy metals in surface soils on the Mugan Plain, the Republic of Azerbaijan. Environmental Monitoring and Assessment, 193 (95): 1-20. https://doi.org/10.1007/s10661-021-08877-7.

Hani, A. & E. Pazira, 2010. Heavy metals assessment and identification of their sources in agricultural soils of Southern Tehran, Iran. Environmental Monitoring and Assessment, 176: 677-691.

Herencia, J.F., P.A. García-Galavís & C. Maqueda, 2011. Long-term effect of organic and mineral fertilization on soil physical properties under greenhouse and outdoor management practices. Pedosphere, 21: 443-453.

Hu, B., X. Jia, J. Hu, D. Xu, F. Xia & Y. Li, 2017. Assessment of heavy metal pollution and health risks in the soil-plant-human system in the Yangtze River Delta, China. International Journal of Environmental Research and Public Health, 14 (9): 1042.

Hu, Y., X. Liu, J. Bai, K. Shih, E. Zeng & H. Cheng, 2013. Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization. Environmental Science Pollution Research, 20: 6150.

Ismayil, J., F. Arik & J. Özen, 2018. Preliminary geological and mineralogical features of Gedabek (western Azerbaijan) Au-Cu deposit. Omer Halisdemir University Journal of Engineering Sciences, 7 (1): 475-482.

IUSS Working Group WRB, World Reference Base for Soil Resources 2014, Update 2015, International Soil Classification System for Naming Soils and Creating Legends for Soil Maps; World Soil Resources Reports No. 106, FAO, Rome, Italy, 192 pp.

Kabata-Pendias, A., 2011. Trace Elements in Soils and Plants IV. Boca Raton, FL, USA, CRC Press, Taylor and Francis Group, 548 pp.

Kandziora-Ciupa, M., A. Nadgórska-Socha & G. Barczyk, 2021. The influence of heavy metals on biological soil quality assessments in the *Vaccinium myrtillus* L. Rhizosphere under different field conditions. Ecotoxicology, 30: 292-310. https://doi.org/10.1007/s10646-021-02345-1

Karimov, G.I., 1976. Gədəbəy Filiz Rayonunun Petrologiyası və Minerallaşması [Petrology and mineralization of Gadabay ore district]. Baku, Azerbaijan: Elm, 175 pp.

Kars, N. & O. Dengiz, 2020. Assessment of potential ecological risk index based on heavy metal elements for organic farming in micro catchments under humid ecological conditions. Eurasian Journal of Soil Science, 9 (3): 194-201.

Lasota, J., E. Błońska, S. Łyszczarz & M. Tibett, 2020. Forest humus type governs heavy metal accumulation in specific organic matter fractions. Water, Air, and Soil Pollution, 231 (80): 1-13.

Lee, B.D., B.J. Carter, N.T. Basta & B. Weaver, 1997. Factors influencing heavy metal distribution in six Oklahoma benchmark soils. Soil Science Society of America Journal, 61: 218-223. http://dx.doi.org/10.2136/sssaj1997.03615995006100010030x

Li, Z., R.L. Schneider, S.J. Morreale, Y. Xie, C. Li & J. Li, 2018. Woody organic amendments for retaining soil water, improving soil properties and enhancing plant growth in desertified soils of Ningxia, China. Geoderma, 310: 143-152.

Mallants, D., B.P. Mohanty, D. Jacques & J. Feyen, 1996. Spatial variability of hydraulic properties in a multi-layered soil profile. Soil Science, 161 (3): 167-181.

Mammadov E., J. Nowosad & C. Glaesser, 2021. Estimation and mapping of surface soil properties in the Caucasus Mountains, Azerbaijan using high-resolution remote sensing data. Geoderma Regional, 26: e00411. https://doi.org/10.1016/j.geodrs.2021.e00411.

Mammadov, E., M. Denk, F. Riedel, C. Kažmierowski, K. Lewinska, R. Łukowiak, W. Grzebisz, A.I. Mamedov & C. Glaesser, 2022. Determination of Mehlich 3 extractable elements with visible and near ınfrared spectroscopy in a mountainous agricultural land, the Caucasus Mountains. Land, 11 (363): 1-24. https://doi:10.3390/land11030363

Moral, R., N. Javarro-Pedreño, I. Gómez & J. Mataix, 1996. Quantitative analysis of organic residues: effects of samples preparation in the determination of metal. Communications in Soil Science and Plant Analysis, 27: 753-761.

Müller, G., 1979. Schwermetalle in den Sedimenten des Rheins-Veränderungen seit 1971 [Heavy metals in the sediments of the Rhine-changes since 1971]. Umschau, 24: 778-783.

Nelson, D.W. & L.E. Sommers, 1996. “Total carbon, organic carbon, and organic matter, 961-1010”. Part 3. In: Methods of Soil Analysis. (Eds. D.L. Sparks). Chemical Methods, Madison, WI, USA, SSSA, 1358 pp.

Nicholson, F.A., S.R. Smith, B.J. Alloway, C. Carlton-Smith & B.J. Chambers, 2003. An inventory of heavy metals inputs to agricultural soils in England and Wales. Science Total Environment, 311: 205-219.

Omran, E.E., 2016. Environmental modelling of heavy metals using pollution indices and multivariate techniques in the soils of Bahr El Baqar, Egypt. Modeling Earth Systems and Environment, 2: 119.

Omwene, P.I., M.S. Öncel, M. Çelen, & M. Kobya, 2018. Heavy metal pollution and spatial distribution in surface sediments of Mustafakemalpaşa stream located in the world's largest borate basin (Turkey). Chemosphere, 208: 782-792. https://doi.org/10.1016/j.chemosphere.2018.06.031.

Shan, Y., M. Tysklind, F. Hao, W. Ouyang, S. Chen & C. Lin, 2013. Identification of sources of heavy metals in agricultural soils using multivariate analysis and GIS. Journal of Soil Sediments, 13: 720-729.

Sherrod, L.A., G. Dunn, C.A. Peterson & R.L Kolberg, 2002. Inorganic carbon analysis by modified pressure-calcimeter method. Soil Science Society of America Journal, 66: 299-305.

Sun, C., S, Zhu, B. Zhao, W. Li, X. Gao & X. Wang, 2019. Effect of Land Use Conversion on Surface Soil Heavy Metal Contamination in a Typical Karst Plateau Lakeshore Wetland of Southwest China. International Journal of Environmental Research and Public Health, 17 (1): 84. https://doi:10.3390/ijerph17010084.

Sungur, A., M. Soylak & H. Ozcan, 2014. Investigation of heavy metal mobility and availability by the BCR sequential extraction procedure: relationship between soil properties and heavy metals availability. Chemical Speciation & Bioavailability, 26 (4): 219-230.

Tan, J., 1989. The atlas of Endemic Diseases and their Environments in the People’s Republic of China. Beijing/Chine, Science Press, 216 pp.

Veliyev, A., A. Bayramov, J. Ibrahimov, S. Mammadov & G. Alizadeh, 2018. Geological setting and ore perspective of the new discovered Gadir Low sulfidation epithermal deposit, Gedabek NW Flank, Lesser Caucasus, Azerbaijan. Universal Journal of Geoscience, 6 (3): 78-101.

Vodyanitskii, Y.N., 2016. Standards for the contents of heavy metals in soils of some states. Annals of Agrarian Science, 14: 257e263.

Zinn, Y.L., J.A. Faria, M.A. Araujo & A.L.A. Skorupa, 2020. Soil parent material is the main control on heavy metal concentrations in tropical highlands of Brazil. Catena, 185: 104319.