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# The importance of using soil series-based geochemical background values when calculating the enrichment factor in agricultural areas

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Abstract The enrichment factor (EF) is one of the most commonly used indices for determining the source of air, water and soil pollution. However, concerns have been raised about the accuracy of the EF results because the formula leaves the choice of background value to the researcher's discretion. The EF was used in this study to assess the validity of such concerns and to determine heavy metal enrichment in five soil profiles with different parent materials (alluvial, colluvial, and quartzite). Moreover, the upper continental crust (UCC) and specific local background values (sub-horizons) were used as the geochemical backgrounds. When UCC values were applied, the soils were moderately enriched in Cr (2.59), Zn (3.54), Pb (4.50) and Ni (4.69), and significantly enriched in Cu (5.09), Cd (6.54) and As (6.64). Using the sub-horizons of the soil profiles as a background value, it was found that the soils had "moderate enrichment" by As (2.59) and "minimally enrichment" by Cu (0.86), Ni (1.01), Cd (1.11), Zn

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(1.23), Cr (1.30), and Pb (1.50). As a result, the UCC reported an inaccurate conclusion indicating that soils were 3.84 times more heavily polluted than they were. In addition, the statistical analyses performed in this study (Pearson correlation analysis and principal component analysis) revealed that the percentage of clay in the soil horizons and the cation exchange capacity had strong positive relationships ( $r \ge 0.670$ , p < 0.05) with certain heavy metals (Al, Zn, Cr, Ni, Pb and Cd). These findings indicated that sampling from the "lowest horizons" or "parent materials" of the soil series would yield the most accurate results in determining the geochemical background values in agricultural areas.

**Keywords** Heavy metals · Pollution indices · Soil contamination · Soil map

# Introduction

Humanity has always exerted pressure on the natural environment (Gałuszka, 2007). Especially over the last century, activities resulting from increased industrialization have intensified this pressure (Jalali & Khanlari, 2008; Kim et al., 2020; Loska et al., 2004). Soil is one of the components of the environment essential to the clean water and food that all living things rely upon and it bears its share of the burden caused by pollution (Aytop, 2022; Soil Survey Staff, 2014). Besides industrialization, fertilization, pesticide, and irrigation activities are among the causes of agricultural soil pollution (Akbay et al., 2022; Ateş et al., 2022; Aytop et al., 2023; Kim et al., 2020). When these activities are carried out intensively and carelessly, they leave high levels of heavy metals in the soil (Varol et al., 2020). Heavy Metals are the leading soil pollutants, and even low concentrations have toxic effects on humans, animals, and plants (Elizabeth Rani et al., 2021; Rajendran et al., 2022). For instance, individuals exposed to high arsenic, chrome, and lead may develop hypertension disorders, internal organ failures, and cancers (Adimalla & Wang, 2018; Huang et al., 2018; Rezapour et al., 2022a; World Health Organization, 2019).

Reclamation of metal-contaminated soils is difficult, time-consuming, and costly (Akbay et al., 2022; Grandclément et al., 2017). Therefore, it is necessary to monitor the pollution levels of agricultural areas at regular intervals and to identify possible pollutant sources (Chen et al., 2015; Varol et al., 2020; Ye et al., 2019). Indices such as enrichment factor (EF), geoaccumulation index (Igeo), and contamination factor (CF) are frequently used by researchers in evaluating the pollution status of agricultural areas. This monitoring also significantly contributes to developing pollution prevention strategies (Kumar et al., 2019).

One of the indices most frequently used by researchers to determine whether pollution is human-made is EF, and its first use dates back to the 1980s (Hakanson, 1980). A simple Google Scholar search for the term "enrichment factor" yields around 3,110,000 results (January 9, 2023). This simple search gives a sense of how often researchers use EF. However, some researchers have concerns about the accuracy of EF results (Blaser et al., 2000; Githaiga et al., 2021; Reimann & Caritat, 2005). One such concern is that there is no standard for selecting reference material and this method leaves the choice of reference material to the researcher. For instance, Reimann and Caritat (2005) reported that EF results indicate different pollution levels depending on the reference material selected. In addition, they argued that EFs have as much to do with the distribution patterns of the reference element(s) as with anthropogenic contamination or pollution. While this idea may seem justified, it should be noted that not using the correct background values in the EF formula may also give spurious results.

The background value is of great importance for accurately estimating metal pollution in soil. Only appropriately selected background values will provide consistency of results. While some researchers consider local background values (Cao et al., 2022; Kowalska et al., 2022; Mavakala et al., 2022; Rezapour et al., 2022b) for their calculations, others use different sources, such as the upper continental crust (UCC) as the basis for their background values (Taşpınar et al., ; Islam et al., 2022; Kafle et al., 2022; Aytop, 2022; Yılmaz, 2022). Regional-that is, those taken from a wider area than local-background values are also used in many studies (Dytłow & Górka-Kostrubiec, 2021; Hu et al., 2019). However, soil can be found to have different physical and chemical properties from one part to another of even a small area. Even soils classified in the same series may differ in topsoil texture (Aytop & Şenol, 2022a). In addition, soils have many features that change daily and seasonally (Soil Survey Staff, 2014). Given such complexity, it would not be the right approach to select the background values needed to determine the pollution level of agricultural areas from different regions and countries.

The general opinion accepted by researchers is that heavy-metal concentrations are higher in the topsoil than in the subsoil. One of the reasons for this thought is the ability of organic matter to retain heavy metals in high concentrations (Kavamura & Esposito, 2010; Kwiatkowska-Malina, 2018). Because, in general, the amount of organic matter is higher in the top horizon of the soil. Although this holds true for areas with anthropogenic pollution, concentrations may yet vary depending on the content of the parent material forming the soil and other factors that are instrumental in soil formation. For example, clay percentage and cation exchange capacity (CEC) can also significantly affect heavy-metal distribution in the profile of a given soil horizon. Let us say that the soil's clay content and CEC increase from the A horizon to the C horizon. This increase causes some cations, including metals, to be present in higher concentrations in the sub-horizons. This being the case, it must be realized that using the UCC and regional background values instead of specific local background values can significantly alter EF results. The word "specific" here denotes the lowest horizon of each sampling point.

The main aims of our study were: (a) to use both background values obtained from the sub-horizon of each soil profile and UCC background values and to show how different background values affect degrees of contamination, and (b) to discuss vertical heavy-metal distribution in soil profiles and the relationship between clay percentages and that distribution.

# Materials and methods

## Study area

The study was carried out in the Mikail Stream Basin located in the Mediterranean region of Türkiye. The Mikail Stream Micro Basin is found between  $37^{\circ}$  27' and  $37^{\circ}$  27' E and  $36^{\circ}$  48' and  $36^{\circ}$  51' N (Fig. 1). The basin is 462 to 886 m above sea level and covers



**Fig. 1** Location of the study area and soil profile sampling points (P1-P5)

an area of 11.80 km<sup>2</sup>. The Mediterranean climate is dominant in the study area. The climate is characterised by humid, cool winters and hot, dry summers. The annual average precipitation and temperature in the study area are 719 mm and 16.7 °C, respectively (Aytop & Şenol, 2022a). The soil temperature regime is thermic, and the soil moisture regime is xeric of study (Soil Survey Staff, 2014). Three different parent materials have been identified in the basin: alluvial, colluvial and quartzite (Fig. 2). While the soils formed on the alluvial parent material are located in the flat and nearly flat areas in the north-eastern part of the basin, the soils formed on the quartzite and colluvial parent material are mainly in the upper parts of the basin.

The study area has been classified into six slope classes based on the slope percentage, which varies from 0 to 73.4%. Most of the study area (78.21%) has a slope of 12%. The basin's flat and nearly flat areas are 10.88% of the total area. Five land-use types were identified in the study area: forest (69.20%), annual plants (10.48%), orchards (9.53%), pasture (9.13%) and settlement (1.04%). Dominant crops in the basin include wheat, barley, maize, vegetables, grapes and olives. The irrigation source of the basin is a stream passing through the middle of the study area. The dominant irrigation system in the study area is flood irrigation. Irrigation is possible in the lower parts of the basin, where the slope is flat, and wheat, corn and

vegetables are grown predominantly in these regions. Türkiye's fertility and its irrigation of olive and grape fields are more limited than in European countries (İrget et al., 2007). There is a similar situation in the study area. There is no irrigation in the higher parts, and mainly olive, barley and grape cultivation is done. There is a more intensive use of fertilizers and pesticides in annual plants in the basin. The basin soils are nonsaline, noncalcareous and have good drainage. There are no mining or industrial activities in the basin.

Soil series were determined according to the traditional soil survey method. First, the slope map, elevation map, geological map and satellite images of the study area were examined. After these examinations, the regions where profile pits would be opened were determined in the field. Later, profile pits were opened in the field and soils with different parent materials and morphological characteristics were defined. Finally, the soil profiles were classified according to the Soil Taxonomy (Soil Survey Staff, 2014). The subgroup of the soil series is presented in Table 1.

## Soil sampling and analyses

This study excavated and sampled five soil profiles. According to the soil taxonomy (Soil Survey Staff, 2014), the soils were classified as entisols





Soil Profiles	Hor	Depth (cm)	Parent Materials	Subgroup of soil series	Soil color (moist)	Texture	CaCO <sub>3</sub> (%)	EC (dS/m)	pH (	(%) WC	Clay (%)	CEC (me/100 g)
P1	A	0-12	Quartzite	Typic Xerorthents	2.5 YR4/6	CL	0.40	0.160	6.55	1.35	27.30	8.70
	C	12-80			2.5 YR4/6	C	0.40	0.099	6.11 (	0.34	50.00	13.16
P2	A	0-12	Quartzite	İnceptic Haploxeralfs	7.5 YR4/4	SL	0.56	0.075	6.11	1.08	19.50	5.08
	$\mathbf{BA}$	12-32			2.5 YR4/6	SCL	0.48	0.077	5.73 (	0.40	26.90	7.76
	Bt	32-60			2.5 YR3/6	C	0.56	0.083	5.68 (	0.56	52.10	19.81
P3	A	6-0	Quartzite	Typic Xerorthents	5 YR4/6	SCL	0.64	0.247	6.91	1.97	28.90	11.28
	U	9–28			2.5 YR4/8	C	0.64	0.244	6.88 (	0.50	54.30	15.17
P4	A	0-15	Colluvial	Ultic Haploxeralfs	10 YR3/4	SL	0.56	0.115	5.67	1.69	17.40	5.75
	Щ	15-42			10 YR5/6	SL	0.56	0.117	5.53 (	).44	16.40	4.24
	Bt1	42–79			2.5 YR4/8	CL	0.48	0.091	5.50 (	0.43	37.40	12.87
	Bt2	79-110			2.5 YR5/8	C	0.48	0.078	4.92 (	0.54	45.80	12.83
P5	Ap	0-20	Alluvial	Typic Xerofluvents	10 YR4/3	L	0.56	0.249	6.73	1.04	22.70	11.76
	A2	20-33			10 YR4/4	SCL	0.64	0.208	6.62	1.41	22.70	9.26
	CI	33-72			10 YR5/6	SCL	0.72	0.170	6.87 (	0.73	20.60	9.24
	C	72-100			10 YR5/6	L	0.48	0.161	6.89 (	0.31	16.40	6.56

Table 1 Basic morphological, physical and chemical properties of soil profiles (Aytop & Senol, 2022b)

(P1, P3 and P5) and alfisols (P2 and P4). Soil horizons and their thicknesses were determined in the study area—see Table 1. From the horizons of each soil profile, 15 degraded soil samples were taken on a horizon basis. Combining three random subsamples created a composite soil sample at each horizon. The collected samples were put in polythene bags and taken to the laboratory for some physical and chemical analysis. The soils were dried (in the air and in the oven) to remove moisture and crushed with a wood mallet. The dried soil samples were sieved through sieves (2 mm and 0.5 mm). The sieved soils were used to determine the organic matter (OM) percentage with the Walkley-Black method, texture (percent clay, percent sand and percent silt) with the hydrometer method (Gee & Bauder, 1979), and pH with a glass electrode (in saturated soil). The sodium acetate method (Rhoades, 1982) determined the cation exchange capacity, and the lime analysis was determined using the Scheibler calcimeter (Soil Survey Lab. Staff, 1992). EC (in saturated soil) measurement was determined using an EC meter (Soil Survey Lab. Staff, 1992). The moist Munsell colour was described in the study area (Soil Survey Staff, 2014).

In addition, in this study, eight heavy metals, including Pb, As, Cr, Ni, Al, Cu and Zn, were analyzed in the soil samples. These metals were chosen due to their substantial role in soil pollution (Aytop, 2022; Rinklebe et al., 2019). The samples were digested in teflon vessels, including a mixture of concentrated 10 ml HCI and HNO<sub>3</sub> (3:1) (USEPA, 1998) the Cem Mars 6 microwave device. After the digested solutions were passed through Whatman filter paper (Grade 42, 2.5  $\mu$ m), their final volume was made up to 50 ml with ultrapure water. Concentrations of elements were measured by an ICP-OES (Agilent 5100, USA).

Quality control was accomplished using certified reference material (LGC6187, river sediment). Certified Reference Material (CRM) was digested and analyzed with every 15 samples in this study. The data were analyzed using mean values. The recovery of elements in the CRM varied from 88.8 to 101.4%. Standard solutions were provided by ICP multi-element standard solution IV (Merck, Germany). Enrichment factor (EF)

The Enrichment Factor is a frequently used tool to determine whether metals sources in soil, sediment and water are of lithogenic or anthropogenic origin. EF is calculated using the formula below.

$$\text{EF} = \text{sample}\left(\frac{C_i}{C_{ref}}\right) \setminus \text{background}\left(\frac{C_i}{C_{ref}}\right)$$
(1)

Here, Ci denotes metal concentration in the soil sample, and Cref denotes the geological background concentration. Since it is more stable, Al was chosen as the reference element (Varol et al., 2020) for this study. The geochemical background is generally referred to as the elemental content of the environment not affected by human activities (Gałuszka, 2007; Gough, 1993). Therefore, in this study, together with The Upper Continental Crust (UCC) values (Rudnick & Gao, 2004), the background values of the sub-horizons dominated by lithogenic effects rather than human activities were used. The background values of the upper continental crust (UCC) were taken as  $81,500 \text{ mg kg}^{-1}$ ,  $92 \text{ mg kg}^{-1}$ ,  $67 \text{ mg kg}^{-1}$ ,  $47 \text{ mg kg}^{-1}$ ,  $28 \text{ mg kg}^{-1}$ ,  $17 \text{ mg kg}^{-1}$ , 4.8 mg kg<sup>-1</sup> and 0.09 mg kg<sup>-1</sup> for Al, Cr, Zn, Ni, Cu, Pb, As and Cd, respectively. EF values can be classified under five groups: (I) EF < 2, minimal enrichment; (II)  $2 \le EF < 5$ , moderate enrichment; (III)  $5 \le EF < 20$ , significant enrichment; (IV)  $20 \le EF < 40$ , very high enrichment; (V)  $40 \le EF$ , extremely high enrichment (Aytop, 2022; Sutherland, 2000).

#### Statistical analysis

This study used Principal Component Analysis (PCA) and Pearson correlation analysis to reveal the relationships between heavy metals and some soil properties. The data set was suitable for PCA based on the KMO score (0.64) and Bartlett's sphericity test value (p < 0.001). Varimax rotation and Kaiser normalization were used to perform PCA. Varimax rotation reduces the amount of variables that place heavy stress on each component, making it easier to interpret PCA results. Two components with eigenvalues > 1 were found by PCA in the current investigation and accounted for 78.13% of the

total variance. All examined data were standardised using z-scale transformation before PCA.

# Results

Basic chemical and physical properties of soil profiles

For this study, five different soil profiles (SPs) were



Fig. 3 Photographs of analysed five soil profiles

examined (Fig. 3). The studied SPs were classified (Soil Survey Staff, 2014) into the following ordos: entisols and alfisols (Table 1). Soils formed on P1, P2 and P3 quartzite parent material, P4 coluvial parent material and P5 alluvial parent material. Since P1, P3 and P5 are very young soils, they do not have a defining horizon other than the ochric epipedon. P2 and P4 have an argillic horizon representing clay deposition. Also, among the defining horizons of P4 is the eluvial horizon albic. The pH of the soil profiles varies between 4.51 and 6.91. The organic matter (OM) content of the soils is very low. Soils are non-saline  $(EC < 1 \text{ dS m}^{-1})$  and non-calcareous  $(CaCO_3 < 1\%)$ throughout the profile (Table 1). Clay percentages and cation exchange capacities (CEC) increase from the top-horizons to the subhorizons in soils except for P5. P5 represents alluvial soils with flat and nearly flat slopes where intensive agricultural practices are performed. These soils consist of materials brought by rivers at different times. Some of the physical and chemical analysis results of the SPs are presented in Table 1 (Aytop & Şenol, 2022b).

# Total metal content of soils

The total metal content of the soils and basic statistical data are shown in Table 2. The mean concentrations of the metals in the SPs in the study area are listed as Al (21,982)>Ni (57)>Zn (52)>Cr (51) > Cu (41) > Pb (16) > As (5.98) > Cd (0.26)from the most abundant to the least abundant (Table 2). The concentration of Al in the soil was higher compared to Ni, Zn, Cr, Cu, Pb, As and Cd; it possibly originates explicitly from natural sources. The metal content of the soils increases gradually towards the sub-horizons, except for P5. In P5, the metal concentrations in the horizons were irregular. In soil P5, the A2 horizon revealed enrichment with As, while in the C2 horizon, a significant decrease in As was observed. There was an albic horizon in P4. This horizon is a mineral layer where clay and some metals suffer eluvial loss (Soil Survey Staff, 2014; WRB, 2015). Therefore, it is expected that some metal contents are less in other horizons than in the E horizon.

Soil Profiles	Hor	Al	Zn	Cr mg/kg	Ni	Cu	Pb	As	Cd
P1	A	19,203	56.35	61.36	77.36	18.06	17.51	3.17	0.003
	С	33,423	88.73	86.82	136.65	32.68	21.84	3.37	0.173
P2	А	14,270	30.24	46.00	35.26	8.76	10.24	2.19	0.043
	BA	21,732	39.75	57.12	57.49	14.70	14.04	2.83	0.087
	Bt	44,289	85.33	91.20	109.60	89.51	15.57	5.78	0.938
P3	А	25,973	57.10	50.32	51.43	76.18	20.79	17.63	0.433
	С	48,036	84.92	73.58	85.62	86.42	26.61	18.43	1.088
P4	А	8553	27.67	32.13	19.82	5.65	10.88	1.88	0.027
	Е	6758	28.37	24.80	25.12	7.94	10.33	0.44	0.065
	$Bt_1$	25,936	45.51	49.96	58.10	18.23	16.20	0.75	0.278
	$Bt_2$	15,191	41.32	41.89	54.61	19.60	17.93	10.16	0.141
P5	Ap	14,226	57.97	35.55	38.63	51.23	14.15	10.49	0.187
	A2	18,652	43.84	39.39	37.54	62.45	15.03	1.51	0.094
	C1	18,579	50.81	45.54	42.36	69.32	14.52	9.65	0.317
	C2	14,913	39.67	34.62	31.24	61.67	9.76	1.36	0.046
Mean		21,982	52	51	57	41	16	5.98	0.261
Maximum		48,036	89	91	137	90	27	18.43	1.088
Minimum		6758	28	25	20	6	10	0.44	0.003
SD		11,944	20.31	19.60	32.56	30.58	4.75	5.96	0.33
CV		54.33	39.18	38.16	56.74	73.69	30.24	99.72	125.86

Table 2Heavy metalconcentrations andintroductory statistics in thehorizons of soil profiles

#### Analysis of enrichment factor

When calculating EF, each profile's top horizon was considered. These horizons were the A horizon for P1, P2, P3, and P4 and the Ap horizon for P5. In this study, two different background values were used. The upper continental crust (UCC) values described by Rudnick and Gao (2004) and metal concentrations of the sub-horizons of each profile were used as the geochemical background value. EF values calculated according to different background values and their basic statistical data are given in Table 3. When UCC was used as the background value, the mean EF values of the metals ranged from 2.59 to 6.64. The maximum EF values were recorded for As, Cd and Cu. According to these results, the soils were moderately enriched in Zn, Cr, Ni and Pb, and significantly enriched in Cu, As and Cd (Table 3). When sub-horizontal soils were used as background values, minimal EF values (<1) were found for metals except for Arsenic (Table 3). The mean EF values of the metals are listed as As (2.59) > Pb (1.50) > Cr(1.30) > Zn (1.23) > Cd (1.11) > Ni (1.01) > Cu (0.86). It was determined that the soils were "moderately enrichment" by As and "minimal enrichment" by Pb, Cr, Zn, Cd, Ni and Cu. In this study, when UCC was used as the background value instead of the sub-horizon, It was observed that metals enriched on average 3.84 times in soils. This ratio was highest in Cd (5.89 times) and Cu (5.92 times). These results showed how different background values could change the EF results.

### Statistical analysis

This study used Pearson correlation analysis and principal component analysis to determine the relationships between metal contents in soil profiles and some physical and chemical soil properties. The results showed that strong positive correlations existed among Clay, CEC, Al, Zn, Cr, Ni, Pb and Cd (r > 0.7; p < 0.01), indicating that these soil properties in the soil profiles were derived from similar sources (Table 4).

The first component (C1) had strong positive loadings (>0.7) on Clay, Al, Cr, Ni, Zn, CEC,

oil Profiles	EF values calculated using UCC*										
	Zn	Cr	Ni	Cu	Pb	As	Cd				
P1	3.57	2.83	6.99	2.74	4.37	2.80	0.14				
P2	2.58	2.86	4.29	1.79	3.44	2.60	2.73				
P3	2.67	1.72	3.43	8.54	3.84	11.52	15.10				
P4	3.94	3.33	4.02	1.92	6.10	3.72	2.86				
Р5	4.96	2.21	4.71	10.48	4.77	12.52	11.88				
Mean	3.54	2.59	4.69	5.09	4.50	6.64	6.54				
Min	2.58	1.72	3.43	1.79	3.44	2.60	0.14				
Max	4.96	3.33	6.99	10.48	6.10	12.52	15.10				
SD	0.98	0.63	1.37	4.11	1.03	4.95	6.53				
CV	27.70	24.26	29.18	80.59	22.77	74.63	99.89				
	EF value	es calculated	l using sub-	norizons							
P1	1.11	1.23	0.99	0.96	1.40	1.64	0.03				
P2	1.10	1.57	1.00	0.30	2.04	1.18	0.14				
P3	1.24	1.26	1.11	1.63	1.44	1.77	0.74				
P4	1.19	1.36	0.64	0.51	1.08	0.33	0.34				
Р5	1.53	1.08	1.30	0.87	1.52	8.06	4.29				
Mean	1.23	1.30	1.01	0.86	1.50	2.59	1.11				
Min	1.10	1.08	0.64	0.30	1.08	0.33	0.03				
Max	1.53	1.57	1.30	1.63	2.04	8.06	4.29				
SD	0.18	0.18	0.24	0.51	0.35	3.11	1.80				
CV	14.21	13.94	23.87	59.68	23.20	119.65	162.39				

 Table 3
 The enrichment

 factor values of soil profile
 according to different

 background values
 background values

\**UCC* Upper continental crust

	pН	OM	Clay	CEC	Al	Zn	Cr	Ni	Cu	Pb	As	Cd
pН	1	_	_	_	_	_	_	_	_	_	_	_
ОМ	0.314	1	_	_	_	_	-	-	_	_	_	_
Clay	- 0.227	-0.376	1	_	_	_	-	_	_	_	_	_
CEC	-0.043	-0.223	0.877**	1	-	-	-	_	-	_	_	_
Al	0.170	-0.264	0.849**	0.837**	1	-	-	-	-	_	-	_
Zn	0.283	-0.215	0.803**	0.835**	0.885**	1	-	-	_	-	-	-
Cr	0.022	-0.266	0.817**	0.748**	0.886**	0.874**	1	-	-	_	-	_
Ni	-0.041	-0.343	0.842**	0.733**	0.801**	0.887**	0.952**	1	-	_	-	-
Cu	0.618*	0.026	0.351	0.610*	0.639*	0.636*	0.389	0.291	1	_	-	-
Pb	0.219	-0.025	0.788**	0.670**	0.760**	0.772**	0.645**	0.683**	0.442	1	-	-
As	0.407	0.209	0.413	0.481	0.466	0.479	0.226	0.176	0.617*	0.695**	1	-
Cd	0.178	-0.175	0.707**	0.783**	0.877**	0.729**	0.631*	0.502	0.742**	0.624*	0.640*	1

Table 4 Pearson's correlation coefficients (r) between heavy metal concentrations with soil properties of different soil profiles

\*\*P<0.01, \*P<0.05

Cd, and Pb, and C1 accounted for 60.1% of the total variance (Table 5). These eight soil properties exhibited strong positive correlations with each other. Thus, they were mainly controlled by natural sources.

The second component (C2) had strong positive loading (> 0.734) on pH, Cu and As, and C1 accounted for 17.9% of the total variance (Table 5). As a result of these data, it was concluded that the

 Table 5
 Principal component analysis of pH, OM, Clay, CEC

 and heavy metals in soil profiles

	C1	C2
pН	-0.052	0.834
OM	-0.400	0.539
Clay	0.957	-0.090
CEC	0.897	0.147
Al	0.936	0.226
Zn	0.912	0.265
Cr	0.917	-0.037
Ni	0.914	-0.141
Cu	0.485	0.734
Pb	0.769	0.351
As	0.398	0.734
Cd	0.773	0.408
Eigenvalues	7.216	2.159
% of Variance	60.137	17.995
Cumulative %	60.137	78.132
As Cd Eigenvalues % of Variance Cumulative %	0.398 <b>0.773</b> 7.216 60.137 60.137	<b>0.734</b> 0.408 2.159 17.995 78.132

Using Kaiser normalization varimax

source of Cu and As, which is dominant in the second component, is anthropogenic and lithogenic.

## Discussion

The present study sought to reveal the inconsistencies that may arise when using different background values to calculate EFs. For this purpose, a number of soil properties and the heavy metal contents of five soil profiles formed from different parent materials were investigated. The geochemical background values of the heavy metals used in this study were obtained from the upper continental crust (UCC) and heavy metal concentrations of the lowest horizons of the soil profiles. In addition, both a Pearson correlation analysis and a principal component analysis were performed to determine the relationships between the heavy metals and certain other soil properties.

The strong correlation between the examined heavy metals indicated that they originated from similar sources or were interdependent (Baltas et al., 2020; Tholkappian et al., 2018; Wang et al., 2020). The Pearson correlation analysis showed that the presence of Al, Zn, Cr, Ni, Pb, and Cd in the soil profiles was significantly correlated with the lithogenic properties (clay content and CEC) of the soils (Table 4). Similarly, Rajmohan et al. (2014) reported that clay exhibits a strong positive correlation with certain heavy metals ( $p \le 0.01$ ) and that a high clay content increases heavy metal concentrations in soils. As a result of this relationship, as the clay percentage increases, the heavy metal concentrations in the soils also increase. This increase is also related to the cation exchange capacity, as soils with high cation exchange capacities can contain high metal concentrations.

The PCA analysis performed using varimax rotation enabled the identification of two main components with eigenvalues > 1 (Table 5). The first was loaded by Al, Zn, Cr, Ni, Pb, Cd, clay content, and CEC. The aforementioned heavy metals were positively correlated with clay content and CEC  $(r \ge 0.670, p < 0.05)$ . PC1 can be better explained by the natural accumulation of heavy metals in soils due to the chemical process occurring in the bedrock. The second component was loaded by As, Cu, and pH. PC2 can be explained by anthropogenic effects (Baltas et al., 2020; Chandrasekaran et al., 2015; Taşpınar et al., 2022). As the pH decreased, the solubility of heavy metals in the soil solution increases (Kiekens, 1983). Many other researchers have found a strong relationship between Cu and pH in soil (Bayraklı et al., 2023; Sungur et al., 2015; Wei et al., 2020). Heavy metals can be released into the environment by anthropogenic processes, such as industrialization, urbanization, and agriculture (Aytop, 2022; Rezapour et al., 2022b), as well as by many natural processes and sources, such as rock weathering and parent material (Wuana & Okieimen, 2011; Durand, 2012; Otunola & Ololade, 2020). No industrial operations occur in the study area, where agriculture is the primary activity. It is also located far from the city center (Aytop & Şenol, 2022a). Therefore, the anthropogenic sources of As and Cu in the soil are thought to be agricultural activities. Some researchers have reported that agricultural soils often have high As and Cu concentrations due to using fertilizers, animal manures and pesticides (Chen et al., 1997; Kabata-Pendias, 2011; Varol et al., 2020; Ateş et al., 2022; Aytop, 2022).

The texture analysis results revealed that the amount of clay increased towards the sub-horizons in all of the profiles except P5, which indicated that the clays in the soil profiles were leaching towards the sub-horizons. The movement of the clay particles to the lower layers is a complex process and is more common in climates with abundant rainfall (Ciolkosz et al., 1996; Elliott & Drohan, 2009). As further evidence of this, an argillic horizon was observed in both

P2 and P4 which is an indicator of clay illuviation (Soil Survey Staff, 2014). The parent material is very effective on clay minerals variety and amounts of the soils (Kome et al., 2019). For instance, soils with the parent material of limestone can be richer by the percentage of clay than soil with serpentine parent material (Soil Survey Staff, 2014).

Similar to our results, those of numerous other researchers indicated that the heavy metal concentration in soil increases in direct proportion to the percentage of clay (Bayraklı et al., 2023; Li et al., 2019; Rajmohan et al., 2014; Tian et al., 2023; Wang et al., 2022). Because there are cations in heavy metals, they can be retained in substantial amounts in clay soils. Clays are often used for water filtration given their heavy metal binding properties (Foorginezhad et al., 2022; Ghasemi et al., 2023; Kinoti et al., 2022; Senanu et al., 2023). They also appear to be one of the most important indicators of soil quality (Blanco-Canqui & Lal, 2008) and heavy metal availability in soil (Kim et al., 2015; Kome et al., 2019). Given that clays are mineral soil colloids with negative electrical charges (Kerr, 1952; Kumari & Mohan, 2021), they retain the nutrients (positively charged cations) necessary for the survival of plants on their surfaces. Hence, soils rich in clay have a high cation exchange capacity (Drake & Motto, 1982). In this study, the accumulation of heavy metals in the subsoil rather than the topsoil pointed to the leaching of mobilized metals into the soil profiles together with the clays (Table 2). Li et al. (2017) reported that certain heavy metals accumulate in the sub-horizons by means of leaching.

In addition, heavy metal concentration and CEC increased in direct proportion to the percentage of clay toward the lower layers of the first four profiles. The amount of clay in P5 did not increase toward the lower horizons and was instead irregularly distributed. These findings are consistent with those of Sağlam and Dengiz (2015), who discovered that the percentages of clay in the horizons of soils with alluvial parent materials are more unevenly distributed than in soils composed of different parent materials. Characteristic differences between profiles indicate the diversity of natural processes involved in forming and developing soils (Hazelton & Murphy, 2016; Rezapour et al., 2022b). Here, P5 comprised soil with alluvial parent materials, which are distinguished by the complexity of their development on the basis of geological and climatic factors (Kumar et al., 2007; Loaiza-Usuga et al., 2022; Villar, 1996). Soils consisting of alluvial parent materials are young soils whose horizons generally reflect the properties of the materials deposited by rivers or streams at different times (Soil Survey Staff, 2014; WRB, 2015). Moreover, considering that P5 is located in the basin area with the most intensive agricultural production, it should not be forgotten that human activities (Aytop, 2022; Rezapour et al., 2022b) can effectively cause differences between profiles. Consequently, the textures of soils with alluvial parent materials may be non-uniform throughout a profile, which can cause irregularities in clay percentage and heavy metal concentration in horizons.

The sources of heavy metal concentrations in soils can be determined using the EF (Rezapour et al., 2022b; Varol et al., 2020), but the selection of background values in EF calculations is left to the discretion of researchers (Anderson & Kravitz, 2010; Githaiga et al., 2021). This approach raises concerns about the accuracy of results (Githaiga et al., 2021). Although no significant heavy metal contamination was found in the soils in this study, the EF values calculated using the UCC revealed that the soils were significantly contaminated (Table 3). Indeed, the concentrations derived using the UCC gave the highest enrichment values for all of the heavy metals, while the sub-horizon background values gave the lowest EFs. Use of the UCC suggested that the soils were 3.84 times more contaminated with heavy metals on average. This result justified our concerns that the use of background values that do not reflect the properties of the parent material will give rise to inaccurate EF results.

Some researchers stated that the use of average concentrations obtained using the UCC overlooks the natural geochemical variation and may yield unrealistic results (Anderson & Kravitz, 2010; Dytłow & Górka-Kostrubiec, 2021; Githaiga et al., 2021). However, to address this problem, they suggested the use of the mean local background values. While this suggestion may appear valid, the use of a single background value for an entire agricultural area is not appropriate because the relief, time, vegetation, climate (precipitation, temperature) and parent material all come to the fore during soil formation processes (Aytop & Şenol, 2022a; Wilson, 2019). These processes also determine the chemical content of soils.

Therefore, choosing the background values from the parent materials of the soil series would be a more appropriate approach. Furthermore, if there is heavy metal contamination in the soils caused by the parent material, it would indicate that the contamination is of lithogenic rather than anthropogenic origin.

## Conclusion

The present study's results revealed that using different background values in agricultural soils changes the EF results. Heavy metal concentrations in the sub horizons of the soil profiles provided the lowest contamination values, whereas the UCC values resulted in the highest EF values. More specifically, using UCC as a background value generated false results, showing that the soils were, on average, 3.84 times more severely contaminated with heavy metals. The statistical methods used in this study revealed that the clay content and cation exchange capacity was strongly related to  $(r \ge 0.670, p < 0.05)$  the heavy metal concentrations in the soils. It was also determined that the vertical distributions of heavy metals in the horizons of soils with different parent materials differed according to their clay percentages and cation exchange capacities.

Based on the results of this study, we offer researchers two suggestions for selecting the background values required when making EF calculations in agricultural areas. First, on the basis of the region's soil series map, a separate background value should be determined for each series. If the region in question does not have a soil series map, samples should be taken from the lowest horizon of each sampling point with the help of a soil auger and then pointwise background values should be calculated. These recommendations are expected to minimise concerns regarding the consequences of using the EFs in agricultural areas. For young soils that do not have a defining horizon other than the A horizon, the background values of similar parent materials could be used.

This study is one of the first attempts to put forward the argument that the background values used for EF calculations in agricultural areas should be determined according to soil series. This study also explained the relationships between heavy metal concentration, clay percentage, and cation exchange capacity. Nevertheless, because clay types are also effective indicators of the chemical properties of soils, similar studies should perform clay-type analyses in soils to more comprehensively shed light on the association between heavy metals and other soil properties.

Author contributions HA put forward the original idea and wrote the manuscript. HA, SŞ and YKK collected the soil samples. YKK and SŞ supervised the work and revised the manuscript. All the authors contributed to the manuscript writing.

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**Availability of data and material** The datasets used during the current study are available from the frst author on reasonable request.

### Declarations

**Conflict of interest** The authors declare that there are no known competing interests.

**Ethical statement** We have conducted ourselves with integrity, idelity and honesty. The submitted work is original and has not been published elsewhere in any form or language.

Consent to participate Not applicable.

Consent for publication Not applicable.

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