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Sources Apportionment and Pollution Status of Potentially Toxic Elements in Agricultural Surface Soils

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ABSTRACT

This study assessed potentially toxic elements (PTEs) contamination in Tummina's agricultural area and discussed the sources and spatial distribution of the targeted elements. The study results revealed that the median concentrations of arsenic, cadmium, chromium, lead, cobalt, nickel, copper, and zinc found in the soils align with the local geochemical baseline levels (LGB) of PTEs, indicating the lack of enrichment of these PTEs. Our comprehensive analysis of the soil pollution indices indicated that the study area is moderately enrichment with arsenic, cadmium, and lead. The ecological risk factor (Er) highlighted that Cd in the surficial soils poses a high risk ($80 \leq Er < 160$), whereas the other PTEs had a low Er. The investigation area had a median potential ecological risk index (RI) value of 69.45 in the surface soils, representing a moderate ecological risk. However, the P90 of the RI value was significantly higher, signifying a high ecological risk at 134.31. Cd was the primary contributor to RI, followed by As, Co, Pd, Ni, and Cu. PCA and HCA results demonstrated that Co, Cr, and Ni could originate from lithogenic sources. This study provides a confident understanding of the PTE levels and the need for further investigation in the study area.

التلوث بالعناصر السامة في التربة السطحية الزراعية ومصدرها وتوزيعها المكاني

خليفة الصديف الأطرش

تهدف هذه الدراسة الى تقييم التلوث الناتج عن العناصر السامة (PTE) في التربة السطحية لمنطقة طمينة الزراعية ومناقشت المصادر والتوزيع المكاني للعناصر المستهدفة. كشفت نتائج الدراسة أن قيم الوسيط لتركيزات كل من الزرنيخ والكادميوم والكروم والرصاص والكوبالت والنيكل والنحاس والزنك الموجودة في التربة متقاربة مع مستويات خط الأساس الجيوكيميائية المحلية (LGB)، مما يدل على عدم حدوث اثراء لهذه العناصر في منطفة الدراسة. وأشار التحليل الشامل لمؤشرات تلوث التربة إلى أن منطقة الدراسة تم اثرائها بشكل معتدل بالزرنيخ والكادميوم والرصاص. من ناحية اخرى اشار معامل الخطر البيئي (Er) الى أن الكادميوم في التربة السطحية يشكل خطرا كبيرا ($80 \geq 160 > Er$)، بينما العناصر الأخرى كانت منخفضة من حيث معامل الخطر البيئي. في حين ان قيم الوسيط لمؤشر المخاطر البيئية المحتملة (RI) كان 69.45، مما يشير إلى وجود مخاطر بيئية بدرجة معتدلة, ومع ذلك ، فإن التركيزات المئوية التسعين (P90) لمؤشر المخاطر البيئية المحتملة كانت أعلى بكثير (134.31)، مما يشير إلى وجود مخاطر بيئية عالية. وكان Cd المساهم الرئيسي في قيمة مؤشر المخاطر البيئية المحتملة، يليه As و Co و Pd و Ni و Cu. وأظهرت نتائج تحليل المكون الاساسي (PCA) و الهرمي العنفودي (HCA) أن عناصر Co و Cr و Ni يمكن أن تكون قد نشأة في التربة من مصادر طبيعية.

INTRODUCTION

Human interference with the natural state of soil through chemicals or other alterations poses a grave threat to the ecosystem and the living species that depend on it. Intensive human activity has resulted in global agricultural soil pollution, impeding agriculture's sustainable development (Tilman *et al.,* 2017). Trace metals, a category of PTEs, are one of the crucial causes responsible for soil pollution and environmental degradation. Several factors contribute to PTEs' prominence as the most significant pollutants in agricultural soils, including their widespread distribution, high toxicity, non-biodegradability, and bioavailability (Alengebawy *et al.,* 2021; Alloway, 2012; Srivastava *et al*., 2017). Soil plays a crucial role in the cycle of PTEs as it can function as both a sink and a source of these elements. (González Henao and Ghneim-Herrera, 2021). PTEs can originate from either anthropogenic or lithogenic sources. They can, therefore, be processed on-site and transferred over long distances due to their capability to be restricted by dust (Kumari, and Mishra, 2021). These components are biologically toxic and highly environmentally persistent owing to their non-biodegradable inclination and quickly accumulate to toxic concentrations in the soil (Zhao *et al.,* 2022). Toxic metals can build up in soil due to pesticides, herbicides, excessive fertilization, and improper agricultural waste disposal. This accumulation typically occurs in the upper layers of soil profiles. Toxic metal accumulation on the soil surface can severely influence crop quality and yield and the health of plants, animals, and humans. Toxic metals such as cadmium, lead, copper, and zinc contaminate agricultural soil, posing environmental and human health problems (Alengebawy *et al.,* 2021). Certain trace metals, including Pb, Hg, As, and Cd, can lead to serious health issues such as kidney failure, liver damage, skin cancer, and severe osteoporosis (Bayrakli, 2021; Isley *et al.,* 2022). On the other hand, Cu and Zn are crucial for properly functioning plants and animals, but excessive amounts can harm organisms (Okereafor *et al.,* 2020). As a result, the pollution of farmland soils with PTEs has become a worldwide issue that affects human health and food security (Khan *et al.,* 2021). Given the high time and economic cost of remediation of PTEs polluted soils, it is vital to conduct precautions to avoid further soil PTEs enrichment in farmland soils (Rajendran *et al.,* 2022). Understanding the pollution levels, spatial patterns, and sources could instruct the prevention and reduction of new metal input. Previous studies utilized different indicators to estimate the contamination level caused by PTEs. Depending on the calculation method, these indicators can provide helpful information about the pollution level. The indicators mentioned are the geo-accumulation index (Igeo), contamination factor (CF), pollution load index (PLI, enrichment factor (EF), and potential ecological risk index (PERI) (Cai *et al.,* 2023; Hakanson, 1980; H. Liu *et al.,* 2021; Müller, 1969; Sinex and Helz, 1981; Tholley *et al.,* 2023; Tomlinson *et al.,* 1980; Varol *et al.,* 2021).

The most common method for estimating pollution levels using the indicators above is to contrast the actual pollution concentration with comparable "natural benchmark" values. However, obtaining these "natural background" values is difficult precisely due to regional variation and significant anthropogenic influences (Tian *et al.,* 2017). Another approach to assessing soil quality from pollution indices is utilizing the upper continental crust (UCC) chemical composition data derived from sedimentary, igneous, and metamorphic rocks as a direct benchmark, e.g.; (Kabata-Pendias and Pendias, 2001; Rudnick, 2003; Taylor and McLennan, 1995; Turekian and Hans, 1961). Various regions have conducted soil studies and estimated the Earth's crust geochemical composition to provide the given values. These surveys typically cover minimal areas and consist of small sample size, according to Kabata-Pendias and Pendias in 2001. There is disagreement about whether these values represent actual soils from vast and diverse regions, entire continents, or even all continents, as using UCC can only provide general information about the scale of an anthropogenic impact on the environment (Bern et al., 2019; Reimann and de Caritat, 2017). Currently, there is a growing emphasis on the implementation of local geochemical baseline (LGB) strategies. In such cases, the LGB value may be used as an indicator of ambient background "actual background" for measuring present levels of environmental quality and for quantifying the future changes in soil concentrations of trace metals (Alizadeh-Kouskuie *et al.,* 2020; Karim *et al.,* 2015; Li *et al.,* 2021; Tian *et al.,* 2017; S. Wang *et al.,* 2019; Zhang *et al.,* 2020). Tommina, being a typical agricultural area with intensive farming practices, may have experienced resource depletion and environmental damage. Thus, farmland soils in this area deserve special attention concerning trace elements pollution. Researchers have yet to conduct any corresponding research to identify the pollution status, sources of pollution, and associated risks in the agricultural region of Tommina. Such knowledge is necessary to implement risk management practices for the farmland soils in the Tommina agricultural area. This study aimed to evaluate the extent of PTEs pollution in agricultural soil using collective and individual indicators, such as geo-accumulation index (Igeo), contamination factor (CF), pollution load index (PLI), enrichment factor (EF), potential ecological risk index (RI), and to discuss the sources and spatial distribution of the PTEs targeted. These indicators are normalized based on the average local geochemical baseline (GBL) we characterized in our previous work (Alatresh, 2023).

MATERIALS AND METHODS

Study location soil sampling, and analysis

In May 2022, we collected 52 surface soil samples from the Tummina agricultural area in the northwestern region of the Libyan Sahel, which is situated southeast of Misrata city. The properties of the 52 samples have been evaluated in our previous work in terms of concentration, setting the most proper normalizing element for this area, and establishing the local geochemical baseline (LGB) for Co, Zn, Cr, Pb, Cu, Ni, Cd, and As using four techniques: box-whisker plot, reference metal normalization, iterative removal, and cumulative frequency curve. Alatresh's (2023) publication has comprehensive information regarding the study area, fieldwork, soil sampling, soil analysis, and the methods used to define the local geochemical baseline (LGB).

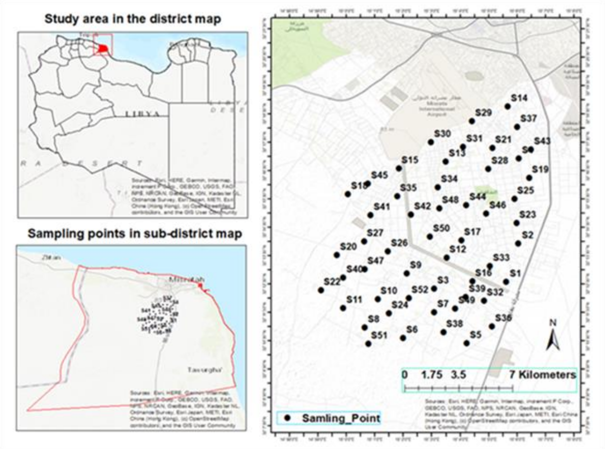


Fig. 1. Location map of the soil sampling points in the Tummina agricultural area

PTEs pollution assessment methods

We applied the following contamination indices with different scopes to assess soil contamination status.

The geo-accumulation index (Igeo) is the ultimate geochemical indicator for a specific metal (n). Müller invented the Igeo test in 1969 to assess the presence of heavy metal and metalloid elements in sediment by comparing current and pre-industrial levels. Since then, researchers worldwide have extensively employed Igeo to evaluate the pollution status of terrestrial, aquatic, and marine ecosystems (Birch, 2013; Gupta *et al.,* 2014). It is a good index for qualifying soil enrichment but is not sensitive to minor contamination (Brady *et al.,* 2015)

$$I_{geo} = log_2 \frac{C_n}{1.5 \times B_n} \qquad (1)$$

Where: Cn and Bn are the investigated concentration of PTE "n" and local geochemical baseline (LGB) value of PTE (n), respectively. The 1.5 factor is the background matrix correlate factor, which considers the natural fluctuation in the content of a chemical element in the environment with minimal human influence (Müller, 1969). Figure 3 displays the various grades or classes for Igeo interpretation. Considering the conservative element concentration, the enrichment factor (EF) compares each concentration value with the background or reference level from the local or regional average composition. The formula for calculating the EF was developed by Chesselet in 1979 as follows:

$$EF = \frac{C_{sample}/C_{C\,(sample)}}{C_{LGB}/C_{C\,(LGB)}} \qquad (2)$$

Where: C_{sample} is the element concentration in the sample, $C_{C\ (sample)}$ is the conservative element concentration in the sample, C_{LGB} is the element concentration in the LGB, and $C_{C\ (LGB)}$ is the conservative element concentration in the LGB. Figure 3 displays the interpretation categories of the EF.

The contamination factor (CF) and pollution load index (PLI) were applied to evaluate the soil's element contamination. The CF is a sample's PTE (n) concentration ratio to the individual LGB value. Figures 3 and 4 demonstrate the various classes of the CF and PLI.

$$CF_n = \frac{C_n}{B_n} \qquad (3)$$

The CF calculates the PLI value to evaluate the total degree of PTEs pollution. The PLI is calculated as the geometric mean of individual CF values and expressed by the following equation (Hakanson, 1980):

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times \ldots \ldots CF_n} \qquad (4)$$

Ecological risk assessment method

The potential ecological risk factor (E_r^i) represents the degree of ecological risk caused by a single metal in the soil using its contamination factor (C_f^i) (Hakanson, 1980):

$$E_r^i = T_r^i \times C_f^i \qquad (5)$$

Where: T_r^i is the toxic-response factor of metal (*i*): Cd = 30, As = 10, Cr = 2, Cu, Ni, Co, Pb = 5, and Zn = 1. We used the potential ecological risk index (RI) to determine the degree of environmental risk caused by multi-metals in the soil (Hakanson, 1980):

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \times C_f^i \qquad (6)$$

Where: *n* is the number of metals (*n = 8*), and E_r^i is the ecological risk factor of metal (*i*). Figures 3 and 4 illustrate the Eri and RI interpretation categories, respectively, based on the works of Hakanson (1980) and (Ramdani *et al.,* (2018).

Statistical analyses

We thoroughly analyzed the data, including the PTE contents, and calculated pollution and ecological risk indices. To ensure accuracy, we employed a range of techniques, including graphical (boxplots) and numerical (mean and median, 50th, 90th, skewness, and kurtosis) tools, as well as the formal Shapiro-Wilk test to test the normality of the distribution of PTE contents and calculated indices. We utilized nonparametric tests because these did not follow a normal distribution.

We utilized the robust SPSS 19.0 software by IBM, Microsoft Excel, and the highly efficient Origin Pro 2021 by OriginLab Company for statistical analyses. Finally, for visualizing the spatial distribution of the targeted PTEs in agriculture soils, we performed spatial interpolations (IDW) using ArcGIS Map 10.4 software.

Table 1. Descriptive statistics of metals concentration (mg/kg) and average local soil geochemical baseline (LGB) (n = 52).

Element	Co	Zn	Cr	Pb	Cu	Ni	Cd	As
Mean	6.8	8.9	5.2	10.3	8.7	6.2	2.8	2.1
Standard Deviation	3.9	3.7	2.9	5.5	4.1	2.7	2.2	2.4
Coefficient of Variation	57%	41%	55%	53%	47%	44%	80%	116%
Minimum	0.9	2.7	1.5	1.8	1.7	2.0	0.1	0.3
Median	6.2	8.8	4.5	9.8	8.7	6.0	2.1	1.2
Maximum	14.5	18.8	13.8	22.5	18.1	13.2	7.7	11.0
P90 (90th percentile)	12.1	13.7	9.3	18.5	14.6	10.2	5.9	6.4
Skewness	0.3	0.4	1.2	0.4	0.5	0.7	0.7	2.5
Kurtosis	-0.9	-0.4	0.9	-0.4	-0.5	0.0	-0.7	5.6
Local geochemical baseline (LGB)	6.61	8.53	4.81	9.50	8.73	5.59	1.98	1.74

RESULTS AND DISCUSSION

PTEs in the study area

Table 1 displays the descriptive statistical results of the total element contents of topsoil samples from the study area. In this study, the most abundant metals were Pb (18.5) > Cu (14.6) > Zn (13.7) > Co (12.1) > Ni (10.2) > Cr (9.3) > Cd (5.9) > As (6.4) in terms of the P90 concentrations (mg/kg). This contribution may vary between the sampling sites since the levels of the eighth metals went between (0.9 to 14.5), (2.7 to 18.8), (1.5 to 13.8), (1.8 to 22.5), (1.7 to 18.1), (2.0 to 13.2), (0.1 to 7.7), (0.3 to 11.0) mg/kg for Co, Zn, Cr, Pb, Cu, Ni, Cd, and As, respectively. It is common practice in several fields to measure distribution variability using the coefficient of variation. Guo et al. (2012) and Niu et al. (2019) have suggested using the classical coefficient of variation (CV) to study the elements' distribution variability. In contrast to the relatively high CV of metals impacted by anthropogenic sources, they evaluate comparatively low CV values for metals dominated by natural sources. These authors divide the degree of variability into four categories: low variability (CV < 20%), moderate variability 20% ≤ CV ≤ 50%, high variability CV > 50%, and very high variability (CV > 100%). In the present study, according to this classification, Zn (41%), Ni (44%), and Cu (47%) show moderate variability, while Pb (53%), Cr (55%), Co (57%) Cd (80%) and As (116%) show very high variability. The results above indicate that the topsoil's distribution of (Pb, Cr, Co, Cd, and As) is uneven and profoundly influenced by human activities. On the contrary, the CV value of (Zn, Ni, and Cu) was smaller, the value of which indicates that they are less affected by human activities. The variability in the PTEs concentration may be due to human activities, growing vegetable crops, and different agricultural practices. The content of some PTEs, such as Cd and As in farmlands, may be attributed to fertilizer and agrochemical applications (Ahmadi et al., 2019; Alengebawy et al., 2021; Weissengruber *et al.*, 2018). Long-term application of fertilizers, fungicides, and metal-containing pesticides can accumulate PTEs in agricultural soils (Alengebawy *et al.*, 2021). The above results show that human activities have significantly impacted the distribution of Pb, Cr, Co, Cd, and Arsenic in the topsoil, which is not uniform. However, the CV value is lower for Zn, Ni, and Cu, indicating that human activities have a less significant effect on these elements. Skewness is a fundamental statistical measure that accurately portrays the symmetry of a distribution. It is worth noting that Co, Zn, Pb, Cu, Ni, and Cd exhibited the right positive skewness values that were less than one. This result implies that most data points for these PTEs clustered towards the lower end of the scale, with a few extreme values towards the higher end. In contrast, Cr and As exhibited skewness values exceeding one, signifying that their data points were significantly dispersed and had a greater incidence of extreme values on the upper end of the spectrum (Table 1 and Fig. 2). The absolute kurtosis values of Cr and As are primarily positive; Cr tends to reach 1 (0.9), whereas arsenic's kurtosis value is higher than 1, specifically 5.6. Cr and arsenic have positive kurtosis values, indicating more extreme values in their distribution. In contrast, other elements Co, Zn, Pb, Cu, and Cd, have negative kurtosis values, indicating fewer extreme values. The platykurtic distribution of nickel kurtosis is evident in its zero value. This distribution signifies a flatter shape, with fewer values in its shorter tails than the normal distribution.

In Figure 2, the boxplots displaying PTEs contents indicate unusually high values (represented by red stars), especially for Cr and As.

Table 2. Igeo, Cf, EF, Er, RI, and PLI values of PTEs in topsoil samples from the study area (n = 52).

		Co	Zn	Cr	Pb	Cu	Ni	Cd	As
Geo-accumulation index (I_{geo})	Mean	-0.8	-0.7	-0.7	-0.7	-0.8	-0.6	-0.7	-0.9
	Minimum	-3.5	-2.2	-2.2	-3.0	-2.9	-2.0	-4.7	-3.0
	Median	-0.7	-0.5	-0.7	-0.5	-0.6	-0.5	-0.5	-1.2
	Maximum	0.6	0.6	0.9	0.7	0.5	0.7	1.4	2.1
	P90	0.3	0.1	0.4	0.4	0.2	0.3	1.0	1.3
Contamination factor (Cf)	Mean	1.0	1.0	1.1	1.1	1.0	1.1	1.4	1.2
	Minimum	0.1	0.3	0.3	0.2	0.2	0.4	0.1	0.2
	Median	0.9	1.0	0.9	1.0	1.0	1.1	1.1	0.7
	Maximum	2.2	2.2	2.9	2.4	2.1	2.4	3.9	6.3
	P90	1.8	1.6	1.9	2.0	1.7	1.8	3.0	3.7
Enrichment factor (EF)	Mean	1.0	1.0	1.1	1.1	1.0	1.1	1.4	1.2
	Minimum	0.1	0.3	0.3	0.2	0.2	0.4	0.1	0.2
	Median	0.9	1.0	0.9	1.0	1.0	1.1	1.1	0.7
	Maximum	2.2	2.2	2.9	2.4	2.1	2.4	3.9	6.3
	P0	1.8	1.6	1.9	2.0	1.7	1.8	3.0	3.7
Ecological risk factors (Er)	Mean	5.2	1.0	2.2	5.4	5.0	5.6	41.8	12.1
	Minimum	0.7	0.3	0.6	0.9	1.0	1.8	1.7	1.9
	Median	4.7	1.0	1.9	5.1	5.0	5.4	32.0	6.8
	Maximum	11.0	2.2	5.8	11.8	10.4	11.8	117.3	63.1
	P90	9.1	1.6	3.9	9.8	8.4	9.2	89.3	36.9

	Mean	Minimum	Median	Maximum	P90
Ecological Risk Index (RI)	78.3	14.9	63.5	212.2	155.5
Pollution load index (PLI)	1.0	0.3	0.9	2.1	1.5

These outliers may result from anthropogenic activities such as farming, leading to anthropogenic contamination due to varying farming practices, including using fertilizers and pesticides. According to research by L. Wang et al. (2022), using manure as fertilizer can significantly increase the soil's PTEs, like Cu, As, Cd, Cr, and Zn levels. Researchers have found that inorganic fertilizers contain higher levels of PTEs like arsenic, cadmium, and lead than other fertilizers (Gimeno-García et al., 1996; Mortvedt, 1995). The study by L. Wang et al. (2022) also found that using inorganic fertilizers led to higher Pb concentrations than using a combination of manure and inorganic fertilizers. However, studies have proven that utilizing organic fertilizers like compost and farmyard manure can effectively decrease the presence of PTEs in the soil. Singh et al. conducted a study in 2010 which highlighted this information.

PTEs pollution status evaluation

Fig. 3, 4, and Table 2 display the various indices and factors utilized to assess the current state of PTEs in the Tommina agricultural area. The EF median values of Co, Zn, Cr, Pb, Cu, Ni, As, and Cd indicated low enrichment (EF < 2).

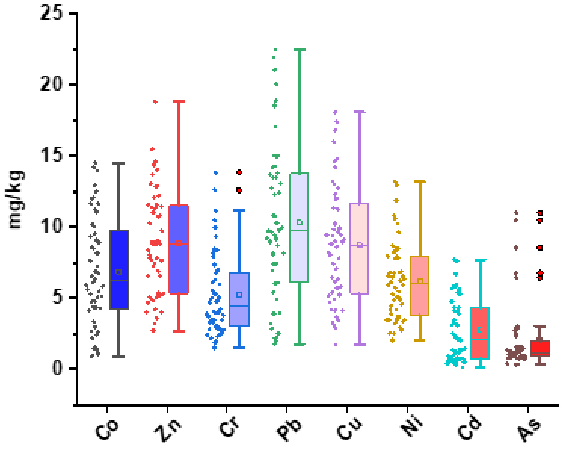


Fig. 2. Boxplots of PTEs concentrations in topsoil within the research area (mg/kg-1) (n = 52).

The EF sequence of the P90 values were As (3.7) > Cd (3.0) > Pb (2.0) > Cr (1.9) > Co (1.8) = Ni (1.8) > Cu (1.7) > Zn (1.6), representing that As, Cd and Pb showed moderate enrichment (2 ≤ EF < 5), whereas Ni, Co, Cu, and Zn had the "P90" value of low enrichment (EF < 2) (Table 2).

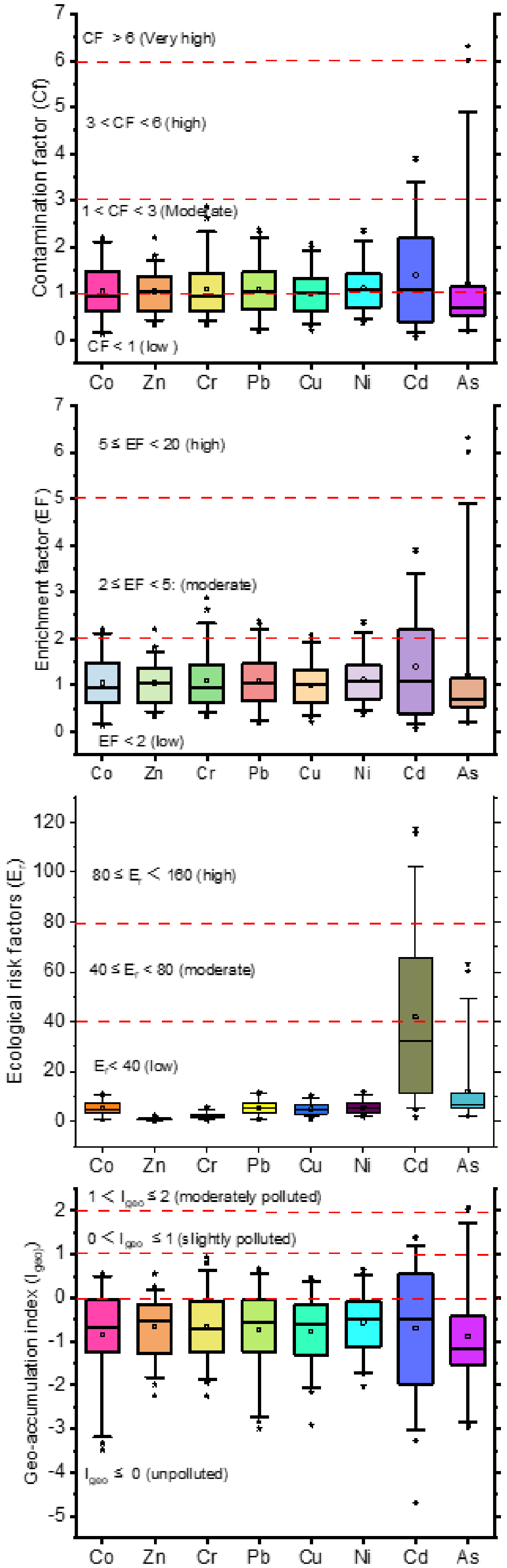


Fig. 3 Boxplots of PTEs contamination factor (Cf), enrichment factor (EF), ecological risk factors (Er), and geo-accumulation index (Igeo) in topsoil samples from the study area (n = 52).

The Igeo median values of Co, Zn, Cr, Pb, Cu, Ni, As, and Cd were negative (Igeo ≤ 0), signifying that the surficial soils of the investigation area were "unpolluted" with all PTEs. The Igeo sequence of the P90 values were As (1.3) > Cd (1.0) > Cr (0.4) = Pb (0.4) > Co = Ni (0.3) > Cu (0.2) > Zn (0.1). These results show that the surface soil samples of the study area are slightly polluted (0 < Igeo ≤ 1) with (Cd, Cr, Pb, Co, Ni, Cu, and Zn) and moderately polluted 1 < Igeo ≤2), with As. The study found that EF and Cf consistently produced similar results. Among the various PTEs studied, As, Co and Cr had median Cf values ranging from 0.7 to 0.9, indicating low contamination (CF < 1). The other PTEs had Cf values higher than one, denoting moderate contamination (1 < CF < 3). The PTEs were ranked based on their P90 values for Cf, with As having the highest value at 3.7, followed by Cd at 3.0, Pb at 2.0, Cr at 1.9, Ni and Co tied at 1.8, Cu at 1.7, and Zn at 1.6. Suggesting that Co, Zn, Cr, Pb, Cu, and Ni had low contamination (CF < 1) in the soil, while As and Cd showed moderate contamination (1 < CF < 3) (Fig. 3 and Table 2). The median and P90 values of the soil pollution load index (PLI) at each sampling point were 0.9 and 1.5, respectively. While the median values suggest no contamination (PLI < 1) in the soils of the research area, the P90 values indicate otherwise, revealing that the soil is polluted (PLI > 1) (Table 3 and Fig. 3). Our thorough analysis of the soil pollution indices shows that contamination in the study area is associated with moderate enrichment of As, Cd, and Pb. We must promptly tackle this problem and guarantee the safety of the environment and the people in the vicinity. Multiple studies have shown that agrochemicals significantly increase certain elements known as PTEs in agricultural soils. These studies include Dayani and Mohammadi (2010), Keshavarzi and Kumar (2018), and Varol et al. (2020). Additionally, using contaminated water for irrigation can also contribute to the presence of these elements in the soil. Studies by Cecchi et al. (2008), Mekki and Sayadi (2017), and Woldetsadik et al. (2017) support this claim. In the study region, soil contamination with arsenic, Cd, and Cr may be due to using fertilizers, pesticides, and contaminated irrigation water.

Ecological risk evaluation

Hakanson's procedure for assessing soil contamination using the potential ecological risk index (RI) considers various metals' contents and potentially hazardous consequences. Table 2, Fig. 3, and Fig. 4 demonstrate the results of the ecological risk factors (Er) and the potential ecological risk index (RI) of eight PTEs in the topsoil of the study area. The Er of (Co, Zn, Cr, Pb, Cu, Ni, and As) were < 40, showing that these metals posed a low Er. In contrast, Cd modelled a moderate ecological threat (40 ≤ Er < 80) (Table 2 and Fig.3).

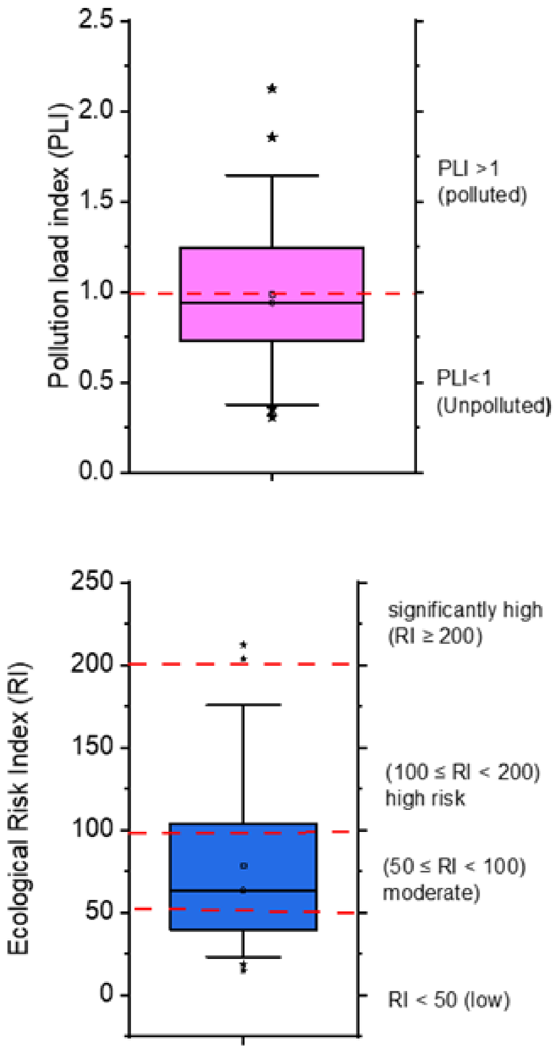


Fig. 4 Boxplots of PTEs ecological risk index (RI) and pollution load index (PLI) in topsoil samples from the study area (n = 52).

The overall labeling of Er levels within the research area's topsoil, however, varied in the following order: Cd > As > Ni > Pb > Co > Cu > Cr > Zn. The order of the P90 Er values were Cd (89.3) > As (36.9) > Pb (9.8) > Ni (9.2) > Co (9.1) > Cu (8.4) > Cr (3.9) > Zn (1.6), indicating that Cd in the surficial soils had a high Er (80 ≤ Er < 160). In contrast, the other metals had low Er (Er<40). In the same vein, studies conducted by Yuanan *et al.* (2020) and Varol *et al.* (2021) found that Cd was the metal with the highest Er level in agricultural soils in Handan (China) and Malatya (Turkey), respectively. Kumar *et al.* (2019) reported the highest Er value for Cd, tailed by Ni and Arsenic, in agricultural soils in India due to chemical fertilizers and pesticides. The median RI value was 69.45, indicating "moderate ecological risk," while the P90 of RI value was 134.31, signifying "high ecological risk" in the surface soils of the investigation area. Contrary to our RI results, very high RI values were reported for agricultural soils in China (Wu *et al.*, 2020) and India (Kumar *et al.*, 2019). The most significant contributor to RI is Cd, followed by As, Co, Pd, Ni, and Cu, as shown in Figure 5. These six elements accounted for 53%, 16%, 7%, 7%, 7%, and 6% of the total ecological risk values. Other elements, such as Cr and Zn, had relatively lower contribution rates to RI, with 3% and 1%, respectively. The contribution rate of PTEs to RI was consistently related to their toxicity response factors, not just their contents. Among the elements, Cd and As posed the most significant ecological risks (Er) and should be closely monitored. Cd had a higher potential ecological risk (41.85) than the other metals. The high toxicity coefficient and low local GBL identify Cd as a critical factor for potential ecological hazards.

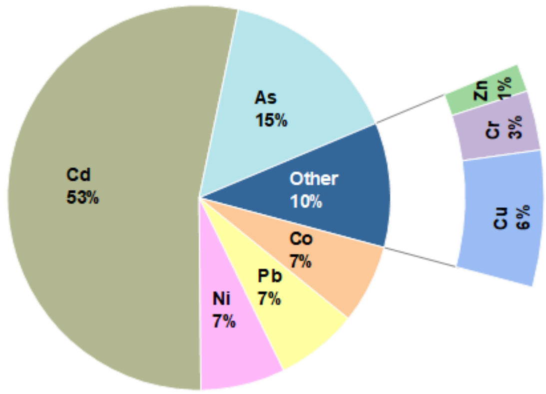


Figure 5. Contribution of PTEs to the Ecological risk index (RI.

Sources and distribution pattern of PTEs

Pearson correlation study

Table 3 displays the outcome of the analysis of relationship coefficients for the PTEs concentrations in the study province at P < 0.05 and P < 0.01. Correlation analysis is an effective tool for identifying commonalities between various pathways or sources of environmental pollutants. Numerous studies, such as Dong *et al.* (2019) and Egbueri *et al.* (2022), have conducted thorough analyses of the relationships between the factors under investigation, utilizing Pearson's correlation matrix to ascertain the degree of similarity. Egbueri *et al.* (2022) divided correlation coefficients into strong (r > 0.7), moderate (0.5 < r < 0.7), and weak (r < 0.5) relations. However, from the correlation analysis results, the following parameter pairs were observed to have a positive significant strong correlation (P < 0.01) between Cd - Zn (0.92), Ni - Cr (0.82), As - Cd (0.79), As - Zn (0.79). Furthermore, Table 3 shows that there is a significant positive correlation (P < 0.01) between Cd - Cu (0.60), Cu - Zn (0.60), Cu - Pb (0.59), Pd - Zn (0.58), Cd - Pb (0.53), Co-Ni (0.33, P 0.05), and Co - Cr (037), As - Pb (0.37), and As - Cu (0.49)7, while As and Pb have a coefficient of 0.37 and As and Cu have a coefficient of 0.49. Additionally, there were adverse relations between Cd / Co, Ni / Pb, Pb / Co, Pb / Cr, / Zn / Co. The negative links imply that these metals' input is not governed by a single factor but rather by combining geochemical support phases and their mixed association (H. Chen *et al.*, 2014; Yang *et al.*, 2018). However, the strong to moderate correlation of Cd, Cu, Zn, Pb, Co, Ni, As, and Cr elemental pairings indicate a probable origin from similar sources, mostly geogenic, and a minor contribution of anthropogenic activities (Huang *et al.*, 2020). Nevertheless, more than a single relationship analysis is required to fully comprehend the source of PTEs.

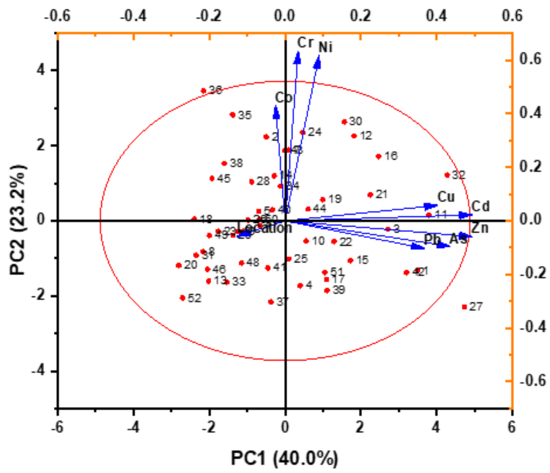
Pierart *et al.* (2015), inappropriate use of pesticides or herbicides may enhance Zn and Cd in topsoil. In this regard, the range of Cd contents in phosphate fertilizers in North America and China is 16-45 and 0.5-3.2 mg/kg, respectively, while the range of Zinc values in fertilizers is 4.87-348.2 mg/kg (Hu *et al.*, 2016; K. Zhao *et al.*, 2010). The remaining PTEs loading is relatively modest, possibly due to an unusual origin from geogenic and anthropogenic origin.

Table 3. Pearson's correlation matrix for PTEs in the surface soils of the Tommina agricultural area. *Indicates significance at 0.05 probability level and **indicates significance at 0.01 probability level (n = 52).

Element	Co	Zn	Cr	Pb	Cu	Ni	Cd
Co							
Zn	-0.12						
Cr	**0.38****	-0.02					
Pb	-0.1	**0.58****	-0.08				
Cu	0.05	**0.60****	0.11	**0.59****			
Ni	**0.33***	0.11	**0.82****	-0.02	0.16		
Cd	-0.02	**0.92****	0.08	**0.53****	**0.60****	0.2	
As	-0.09	**0.79****	-0.06	**0.37****	**0.49****	0	**0.79****

Principal component analysis.

Principal component analysis (PCA) is a widely used tool among researchers for identifying the sources of metals in soils - whether they are natural or anthropogenic, and to determine the unique characteristics of their constituent elements (X. Chen et al., 2012; dos Santos *et al.*, 2017). Moreover, PCA can effectively eliminate the spatial diversity of sample variables and facilitate extracting information among sample variables. The significant PCs were selected based on the Kaiser criterion (eigenvalue > 1). The component loading plot revealed that two groups could categorize the examined metals' composition, representing 63.2% of the total variation (Fig. 6a and Table 4). The first component (PC1) explained 40.0% of the data variance and demonstrated a substantial positive load for Zn (0.94), Cd (0.93), As (0.83), Cu (0.77), and Pb (0.70). PC2 explained 32.20 % of the overall variation and demonstrated a high positive loading of Co (0.62), Cr (0.92), and Ni (0.90). These results strongly endorse the hypothesis that the PTEs in each component have a similar source since it has high positive loadings. In agricultural soils, cobalt, chromium, and nickel sources can be natural and anthropogenic (Aliu *et al.*, 2021). Therefore, PC2 could likely illustrate the lithogenic component of Co, Cr, and Ni. In comparison, the highly favorable loading in PC1 could signify anthropogenic pollution from agricultural activity, atmospheric deposition, fertilizers, and manure application (Adimalla, 2020; H. Chen *et al.*, 2015). Widespread and continual use of agrochemicals containing Cu, As, Zn, and Pb to improve yield and quality may result in As, Cu, and Pb buildup in soils (Acosta *et al.*, 2011). According to Shomar (2006) and



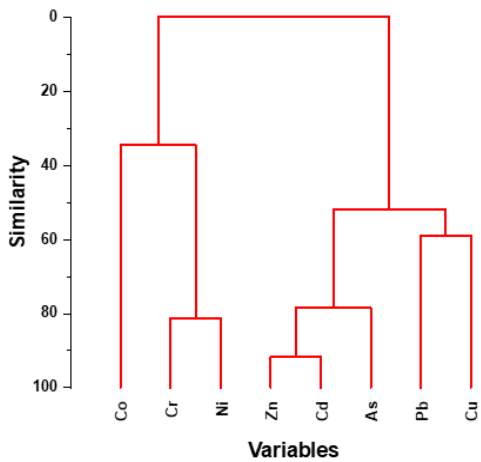


Figure 6 shows the principal component loading plot (a) and Cluster analysis plot (b) of PTEs found in soils in the Tommina agricultural district.

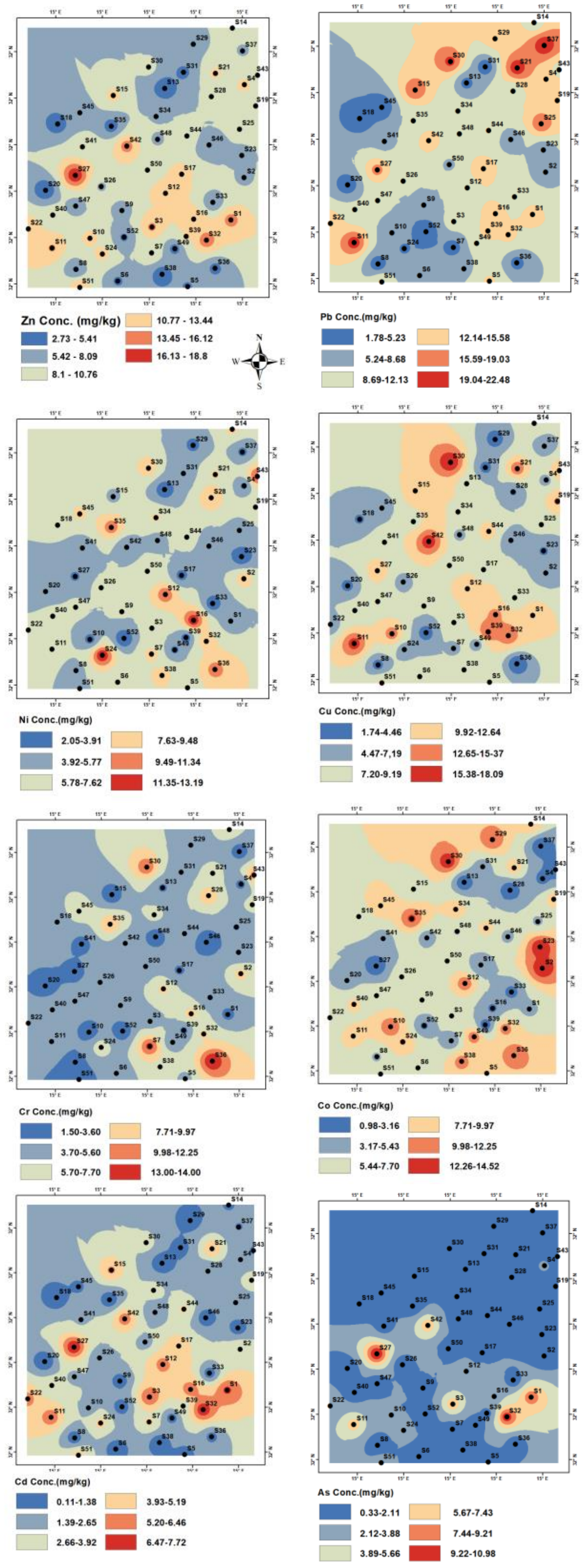


Figure 7 Spatial distributions of PTEs in soils from the Tommina agricultural region.

Hierarchical cluster analysis

The HCA (Fig. 6b) made it possible to identify two separate clusters. Cluster (C1) consists of Zn, Cd, As, Pb, and Cu, while set (C2) contains Cr. Ni, and Co. The conclusions of the PCA and the results of the HCA are consistent.

Spatial distribution

Spatial distribution mapping is crucial in pinpointing safe and unsafe areas and establishing fundamental data for preventing and managing soil contamination. Figure 7 shows the geographic distribution maps of Pb, Co, Cr, Cu, Zn, Ni, As, and Cd in surface agricultural soils in the present research location. The distribution patterns of Co, Zn, Pb, Cu, Ni, and Cd content are generally identical, with the only difference being the concentration and the transit area. The middle of the eastern map has relatively high concentrations, whereas the center of the western map has relatively low concentrations. There are also significant concentrations in the northern half of the region. The distribution pattern of Cr reveals that two locations have a higher concentration than others, after which the spread becomes less widespread. The practice of As's distribution seems to have a higher concentration in the east and west parts of the study area at three distinct places, although this concentration does not appear to be dominant. Those with higher Cd, however, were mainly distributed at the eastern and western corners (Fig. 7). PTE levels in the soils frequently differed significantly from site to site. Co, Cu, Cr, Ni, Pb, As, Zn, and Cd levels in the surficial soil samples had coefficients of variation (CV) of more than 40%, with Zn (41%), Ni (44%), Cu (47%), (53%), Cr (55%), Co (57%) Cd (80%), and As (116%) having the highest. The coefficients of variation (CV) suggest that the anthropogenic activities have significantly influenced the geochemical properties of Tummina's surficial soils (Table 1). The rate of sampling points with the content of PTEs exceeding the LGB was in the decreasing order of Cd (55.8%) > Zn (53.8%) > Cu (51.9%) > Ni (50.0%) > Pb (48.1%) > Co (46.2%) > Cr (42.3%) >As (25.0%).

CONCLUSION

The study reveals that the median concentrations of arsenic, cadmium, chromium, lead, cobalt, nickel, copper, and zinc found in the soils align with the local geochemical baseline levels of PTEs, indicating the lack of enrichment of these PTEs. Furthermore, the median PLI values indicate no contamination in the study region's soils, except those found in soils associated with P90 PLI (1.5). The study also shows that based on the P90 values of PTEs, Cd poses the highest potential ecological risk (Er = 89.3), whereas the other PTEs have a low Er. The RI value was fair at the median and high at the P90, with cadmium contributing the most to the overall ecological risk values. Thus, cadmium and arsenic should be the priority focus for risk management in the study area. PCA and HCA results demonstrate that Co, Cr, and Ni could originate from lithogenic sources.

In contrast, arsenic, cadmium, lead, copper, and zinc could come from both natural origins and anthropogenic sources such as agricultural activity, atmospheric deposition, fertilizers, and manure application. These findings suggest that anthropogenic activities significantly impact the geochemical characteristics of Tummina's surficial soils, resulting in significant variance in PTEs levels throughout sites. In conclusion, the study area requires additional investigations to assess the potential health risks of PTE contamination. The soil has high concentrations of cadmium and arsenic, which is concerning and requires attention to mitigate potential risks. Overall, the study provides a confident understanding of the PTEs levels and the need for further investigation in the study area.

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