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Evaluation of Potential Ecological Risk Index of Toxic Metals Contamination in the Soils †

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Abstract: Toxic metal pollution in the soil and associated health risk is a global problem, with the majority of cases occurring in developing nations. The current work focuses on a contaminated site in Mexico which is used for recreational purposes. The contaminated site in Cerrito Blanco in San Luis Potosi, Mexico is close to an abandoned mining area surrounded by non-cultivated farmland. Analyses of topsoil samples indicated the presence of arsenic (As), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn). This work has estimated the potential harmful impacts of toxic metals by using the Contamination factor (C_f), Ecological risk factor (E_r), and Potential ecological risk index (*RI*) by Hakanson's method. The results indicate that the soil contamination factors (C_f) of toxic metals were: As >Zn >Cu >Pb >Ni. It is concluded that Cu, Pb, and Zn have been found in the soil samples because of past mining activities. The highest contamination factor (C_f) of As (11.94 mg/kg) in the soil was in the extremely high contamination category. It is also believed that the As concentration in the soil is high because arsenic-contaminated water was regularly used for irrigating the land. The Ecological risk factors (E_r) for toxic metals were: As >Cu >Pb >Zn >Ni. In the surface soils of this region, As posed a considerable ecological concern and contributed the most to potential ecological risk indices (*RI*). It is also acknowledged that various anthropogenic factors contributed significantly to the potential ecological risk index (*RI*). The spatial distribution of toxic metal contamination in the soil was also mapped using a Geographic Information System (GIS). This study concludes that a regular assessment is needed to estimate the risk level of toxic metal contamination in the soil.

Keywords: Toxic metals; Soil contamination; Potential Ecological Risk Index (*RI*); GIS; San Luis Potosi

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1. Introduction

One of the most serious environmental issues facing the world today is soil contamination. The toxic contaminants in the soil spread to other parts of the ecosystem and pose a direct or indirect threat to human health [1,2]. Industrial emissions, illegal dumping, municipal disposal of wastes, and the improper use of agrochemicals collectively contribute to the concentration and absorption of heavy toxic metals in the environment [3,4,5]. Severe heavy metal accumulation in the soil surface will degrade the soil ecosystems and raise the possible exposure and significant risk of heavy metals to humans [6]. Toxic metal contamination has been linked to serious health consequences in humans, including cardiac diseases, skeletal illnesses, infertility as well as neurological disorders [2,7]. Some elements like Cd, Hg, Cu, and As, etc., are poisonous and harmful to people, even at low concentrations [8,9]. These metals concentrate in adipose tissues, bones, muscles, and joints after entering the body, causing a variety of disorders [10,11].

The technique for estimating the injury or damage from a possible health threat is referred to as risk assessment. In general, risk assessment is a scientific framework for environmental policy [2]. The overall purpose of risk evaluation is to assess the environmental impact of contamination in water, air, soil, or sediment [12]. Several studies have been conducted across the world to examine the potential ecological risk of heavy metals. Rostami et al. [2] studied the concentrations of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn, and As) in agricultural soils in the Kamfiruz district of Fras in Iran and assessed their ecological risk. The findings revealed that Cd was the main contaminant, which might be attributable to human activities such as the use of chemical fertilisers and pesticides in the sampling area. Qi et al. [9] investigated the levels of heavy metal contaminations (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) and ecological risks in agricultural soil in Shanxi Province, China. A total of 33 surface soil samples were collected from 11 cities in Shanxi. The soil-heavy metals pollution levels were evaluated using a geo-accumulation index and their ecological risks were assessed using respective risk indices. This study found that the metals Cd and Hg were present in higher concentrations and posed higher ecological concerns in agricultural soil in Shanxi. The conclusions of this study will give fundamental information on agricultural soil pollution management and control. Tisha et al. [13] performed a study in Savar tannery industrial estate, Bangladesh to assess the concentrations of heavy metals, such as Cd, Cr, Pb, Cu, and Ni in the surface soils and to evaluate the level of contamination and ecological risks. This study concluded that continuous heavy metal contamination monitoring should be conducted to estimate the risk of heavy metal contamination in the soil.

The multivariate statistical technique, along with a variety of indices, provides a modern framework for assessing toxic metal contamination in the field soils that may also be used in similar soil pollution systems. In the present study, toxic metals in the soil were chosen as they cause public health concerns and influence the ecological balance. This study aims to: (i) determine the concentrations of toxic metals, including arsenic (As), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) in the surface soil, (ii) evaluate the status of contamination by using the contamination factor (C_f), (iii) assess the ecological risk factor (E_r), and (iv) evaluate the potential ecological risks and spatial distributions of target toxic metals in the soil of the study area.

2. Study Area

Soil samples were collected from the fields close to an abandoned mining area surrounded by non-cultivated farmland in Cerrito Blanco, Matehuala municipality, San Luis Potosi, Mexico. It has a total geographical area of around 4.84 hectares and is positioned within 23°40'30" N latitude and 100°35'27" W longitude (Figure 1). The study area is Joya Verde soccer sports club, which comprises irrigated lands, including three half-hectare soccer grounds, and vegetative areas, known as non-irrigated lands, surrounding the soccer pitches [14]. Massive amounts of recent as well as historical tailings are reported to have been deposited on the surrounding terrains as a result of mining activities on an unmanaged privately owned land with no restrictions on public access [15,16,17]. Slags, wastes, construction debris from a dormant metal ore smelter that operated within Matehuala City until the 1960s have accumulated on the site and further contaminated the environment [17,18]. The area has a semi-arid climate, and the predominant vegetation is michrophyllus scrub that is mixed with agricultural lands and susceptible to mild cattle grazing [19]. The types of soil in this area include Calcisol and Gypsisol, and the area receives limited precipitation, ranging from 300 to 500 mm per year [20,21].

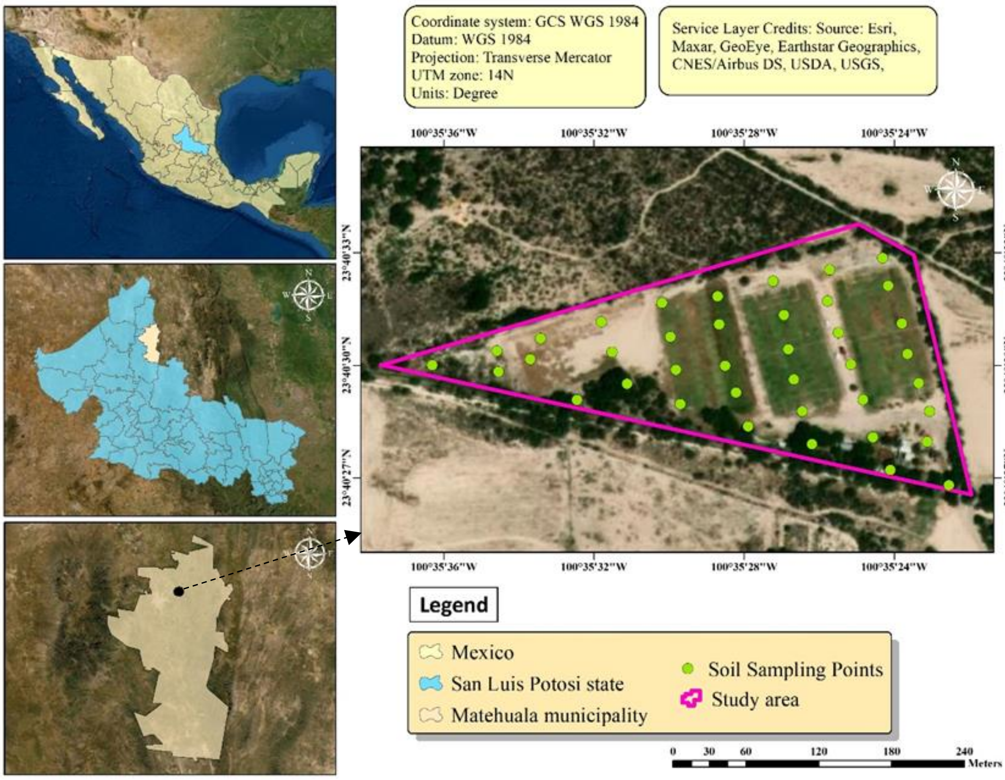

Figure 1. Locations of soil samples are shown on a map of the study area.

3. Materials and Methods

3.1. Soil Sampling and Chemical Analyses

A total of 39 surface soil samples were collected with an auger at a depth of 0–5 cm from the study area including soccer fields. A Garmin Etrex Personal navigator global positioning system receiver was used to geo-locate all of the soil sampling locations. For data quality concerns, duplicate samples were taken from every fifth sampling point to make a total of 77 soil surface samples [14]. As a typical sample, a 1 kg specimen of fresh topsoil was taken from each location and packaged in a sealed plastic bag to preserve it clean before being transferred to the testing laboratory. All soil samples were dried at room temperature and sieved for fractions less than 2 mm. In a beaker, 1.0 gm of soil was poured, followed by 10 mL of aqua regia (HNO_3:HCl) with a ratio of 3:1. For assessing total accessible toxic metals in soils, this digestion process is acceptable [14,22]. The different concentrations of digested samples were evaluated for As, Cu, Ni, Pb, and Zn after dilution with deionised water using inductively coupled plasma optical emission spectroscopy (ICP-EOS) [14,23].

3.2. Assessment of Soil Contamination Risk

3.2.1. Contamination factor (C_f)

Contamination factor (C_f) is described as a basic and useful tool for detecting toxic metal contamination. C_f is used to evaluate the individual toxic metal contamination in soils. Several previous papers have done extensive use of the C_f [5,13,24]. The following equation 1 is used to compute it:

$$C_f = \frac{C_{metal}}{C_{background}} \tag{1}$$

Where, C_{metal} denotes the measured metal concentration of the soil sample, $C_{background}$ is the background reference concentration values of the individual metals. The study of Hakanson [25] demonstrated the C_f values. Table 1 shows the seven different classifications into which the contamination factor (C_f) is categorised.

Table 1. Contamination indices classification for the soil.

Index	Category	Description	References
Contamination factor (C_f)	$C_f < 1$	Low contamination	[25,26]
	$1 \leq C_f < 2$	Low to moderate contamination	
	$2 \leq C_f < 3$	Moderate contamination	
	$3 \leq C_f < 4$	Moderate to high contamination	
	$4 \leq C_f < 5$	High contamination	
	$5 \leq C_f < 6$	High to very high contamination	
	$C_f \geq 6$	Extreme contamination	
Ecological risk factor (E_r)	$E_r < 40$	Low risk	[2,27]
	$40 \leq E_r < 80$	Moderate risk	
	$80 \leq E_r < 160$	Considerable risk	
	$160 \leq E_r < 320$	High risk	
	$E_r \geq 320$	Very high risk	
Potential Ecological Risk Index (RI)	$RI < 150$	Low risk	[28,29]
	$150 \leq RI < 300$	Moderate risk	
	$300 \leq RI < 600$	Considerable risk	
	$RI \geq 600$	High risk	

3.2.2. Ecological risk factor (E_r)

The ecological risk factor (E_r) is a technique for assessing the ecological risk in soil based on metal toxicity and environmental response factors. According to the study of Hakanson [25], the E_r was calculated using the following equation 2:

$$E_r = T_r \times C_f \quad (2)$$

Where, T_r is the toxic response factor values for each different metal, which are described in Table 2, and C_f is the contamination factor, which has been discussed in the previous section. The classification of the soil contamination based on E_r is specified in Table 1.

Table 2. Toxic-response factor values of toxic metals by Hakanson [25].

Metals	As	Cu	Ni	Pb	Zn
Toxic-response factor	10	5	5	5	1

3.2.3. Potential Ecological Risk Index (RI)

The potential ecological risk index (RI) is a method for assessing risks to the environment from soil. It is a comprehensive assessment of a contaminated site to assess the possible ecological risk [13]. According to the study of Hakanson [25], the RI was calculated using the following equation 3:

$$RI = \sum E_r \quad (3)$$

Where E_r is the ecological risk factor of a toxic metal element in each soil sampling point. Table 1 shows the classification levels of toxic metals for possible ecological impact.

4. Results

4.1. Descriptive Analysis of Toxic Metal Concentrations

The concentrations of toxic metals in the soils are indicated in Table 3. The mean concentrations of As, Cu, Ni, Pb, and Zn were 119.54, 20.65, 3.20, 36.95, and 58.93 mg/kg, respectively. The concentrations of As and Zn were higher than the permissible limit for this study area, while the concentrations of Cu, Ni, and Pb were lower than the permissible limit. The permissible limits of As, Cu, Ni, Pb, and Zn were 10, 36, 35, 85, and 50 mg/kg [30]. The mean concentrations of As were found to be 12 times greater, which showed a serious contamination level in the study area. The coefficient of variation (CV) was the most important factor in influencing the variance of toxic metal properties. According to descriptive statistics of toxic metals (Table 3), all metals of this study area showed a considerably high variation. The box and whisker plots in Figure 2 describe the primary information for the toxic metals assessments in this analysis. The high concentration of As was probably due to effluents of nonferrous metal smelting, past mining activities as well as the use of As-contaminated irrigation water [14].

Table 3. Descriptive statistics for selected toxic metals of soil samples.

	Arsenic (As)	**Copper (Cu)**	**Nickel (Ni)**	**Lead (Pb)**	**Zinc (Zn)**
Mean (Measured)	119.44	20.65	3.20	36.95	58.93
Standard Error	17.54	1.56	0.30	3.97	5.56
Median	90.51	18.10	3.07	30.86	54.57
Standard Deviation	109.54	9.75	1.87	24.79	34.71
Kurtosis	8.37	3.63	0.93	5.73	15.38
Skewness	2.43	1.68	0.93	2.12	3.27
Range	578.17	47.85	8.13	126.30	209.81
Minimum	13.14	7.88	0.24	8.99	20.53
Maximum	591.31	55.73	8.37	135.29	230.34
Sum	4658.01	805.17	124.90	1440.99	2298.24
Coefficient of variation (CV) (%)	91.71	47.22	58.32	67.10	58.90
Samples	39	39	39	39	39
Confidence Level (95.0%)	35.51	3.16	0.61	8.04	11.25
Permissible Limits (mg/kg)	10	36	35	85	50

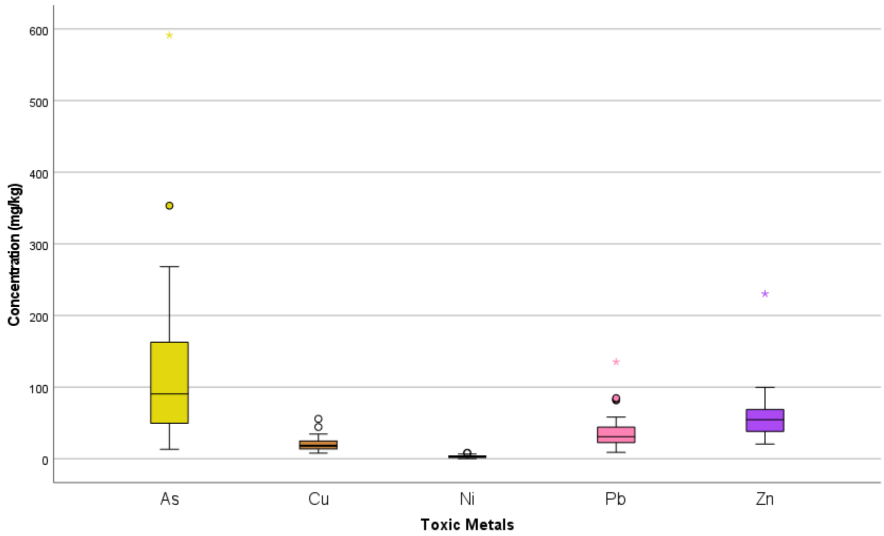

Figure 2. Box and whisker plots showing toxic metal concentrations, with the median at the middle of the box and the lower and upper quartiles at the bottom and top of the box.

The principal component analysis (PCA) revealed the potential relationships between the various environmental conditions and the identified toxic metals. PCA with VARIMAX normalized rotation was used to determine the source of toxic metals in this study soils since it is an efficient technique for evaluating toxic metals source identification. The results of the PCA for the toxic metal concentrations are shown in Table 4. The first principal component (PC1), which contained Cu, Pb, and Zn, represented the most significant variation (50.43%) while Ni and Pb made up the second principal component (PC2), which accounted for 30.35 per cent of the overall variance. The first principal component (PC1) might be interpreted as a combination of anthropogenic and lithogenic sources, with the former originating from non-ferrous mining tailings. In addition, a lithogenic and environmental constituent was also seen in As contamination. The major source of As was As-contaminated irrigation water and past mining activities. This result demonstrates that As and Pb come from both geological and industrial sources.

Table 4. Principal component analysis of toxic metals *(Components with a value larger than 0.32 are bolded)*.

Elements	Principal components		Communalities
	PC1	PC2	
As	0.119	-0.838	0.717
Cu	**0.981**	0.067	0.966
Ni	0.235	**0.816**	0.722
Pb	**0.819**	**0.342**	0.788
Zn	**0.905**	-0.164	0.846
Eigen value	2.522	1.517	
% of variance	50.431	30.347	
Cumulative %	50.431	80.778	

To determine the linear correlation between two metal elements, Pearson's correlation coefficient was performed. The results of Pearson's correlation matrix for the toxic metal concentrations are shown in Table 5. The Pearson coefficient ranges from -1 to 1, with -1 indicating a perfect negative correlation and 1 indicating a perfect positive correlation, while 0 indicating no link [13]. On the basis of correlation matrix, Cu-Pb (r = 0.795), Cu-Zn (r = 0.878), Ni-Pb (r = 0.410), and Pb-Zn (r = 0.537) are significantly correlated and suggests that the contaminants may have the same or comparable sources of contamination.

Table 5. Pearson's correlation matrix of selected toxic metals in the surface soil.

Metals	As	Cu	Ni	Pb	Zn
As	1				
Cu	0.029	1			
Ni	-0.408**	0.264	1		
Pb	-0.137	0.795**	0.410**	1	
Zn	0.130	0.878**	0.054	0.537**	1

**$p<0.01$

4.2. Assessment of Contamination and Environmental Risk

The classifications of contamination factor (C_f) for toxic metal contaminations in the surface soil were shown in Figure 3. Based on the measured data, the C_f varied for the corresponding toxic metals as follows: As, 1.31 - 59.13; Cu, 0.22 - 1.55; Ni, 0.01 - 0.24; Pb, 0.11 - 1.59; and Zn, 0.41 - 4.61. The order of mean C_f was As (11.94) > Zn (1.18) > Cu (0.57) > Pb (0.43) > Ni (0.09). The assessment of C_f values represented that As was the major contaminant in the study soil because the mean concentration level of As represents extreme contamination level (C_f >6). The mean concentration level of Zn was low to moderate ($1 \leq C_f < 2$) while Cu, Ni, and Pb had low contamination levels ($C_f < 1$). For the As, the C_f result showed that 26 sampled locations were in extreme contamination level (C_f >6), two in high to very high contamination, three in high contamination, two in moderate to high contamination, two in moderate contamination, and four in low to moderate contamination, which is shown in Figure 3.

Figure 3. Classifications of contamination factor (C_f) for soil sampling locations.

The toxic metal contamination and potential ecological risk of the surface soils were assessed using C_f, E_r, and *RI*, as shown in Table 6. These three metal evaluation indices based on the soil toxic metal background reference value for the study soil can demonstrate the level of external contamination. The order of mean E_r was As (119.44) > Cu (2.87) > Pb (2.17) > Zn (1.18) > Ni (0.46). The assessment of E_r values also represented that As was the main contaminant in the study soil because the mean concentration level of As was at a considerable risk level ($80 \leq E_r < 160$). Except for As, the mean E_r values of the remaining four metals were all less than 40, indicating that these metals presented a relatively low-risk level in the soil.

Table 6. Contamination factor (C_f), Ecological risk factor (E_r), and Potential Ecological Risk Index (*RI*) assessment of the toxic metals in the study soils.

Heavy metals	**As**		**Cu**		**Ni**		**Pb**		**Zn**		
Contamination indices	C_f	E_r	C_f	E_r	C_f	E_r	C_f	E_r	C_f	E_r	***RI***
Mean ($\bar{x}$)	11.94	119.44	0.57	2.87	0.09	0.46	0.43	2.17	1.18	1.18	126.11
Median (med)	9.05	90.51	0.50	2.51	0.09	0.44	0.36	1.82	1.09	1.09	100.34
Minimum (min)	1.31	13.14	0.22	1.09	0.01	0.03	0.11	0.53	0.41	0.41	17.32
Maximum (max)	59.13	591.31	1.55	7.74	0.24	1.20	1.59	7.96	4.61	4.61	601.34

Standard deviation (SD)	10.95	109.54	0.27	1.35	0.05	0.27	0.29	1.46	0.69	0.69	109.41

The potential ecological risk index (*RI*) indicates the susceptibility of distinct biological ecosystems to toxic contaminants and depicts the possible ecological risk posed by toxic metals in the environment and living organisms [2,5,31]. This index was used to describe the contamination risk level in the soil as classified by Hakanson [25]. The whole study area including the three soccer grounds can be categorized as having a moderate ecological risk level. Most of the locations of this study area can be classified as low ecological risk level ($RI < 150$).

4.3. Spatial Distribution of Potential Ecological Risk Level

The spatial distribution pattern of the potential ecological risk level (*RI*) for five different toxic metals contamination (i.e., As, Cu, Ni, Pb, and Zn) in the soil is shown in Figure 4. For the spatial distribution, the inverse distance weighting (IDW) interpolation technique was applied to evaluate the distribution of potential ecological risk levels for toxic metals in the surface soil, because it is a suitable approach for interpolating regularly spaced specific sampling point data [14]. GIS software was used to map the potential ecological risk level areas and classify them into four categories. According to the results of the potential ecological risk level distribution pattern, 73.52 per cent of the soils were having low ecological risk level, 24.80 per cent was in the moderate ecological risk level, 1.50 per cent of soils had considerable ecological risk level, while 0.19 per cent of soils was in the high ecological risk level. Furthermore, most areas are in the low ecological risk level zone, but specific areas of soccer grounds have moderate ecological risk levels because of the persistent use of As-contaminated irrigated water.

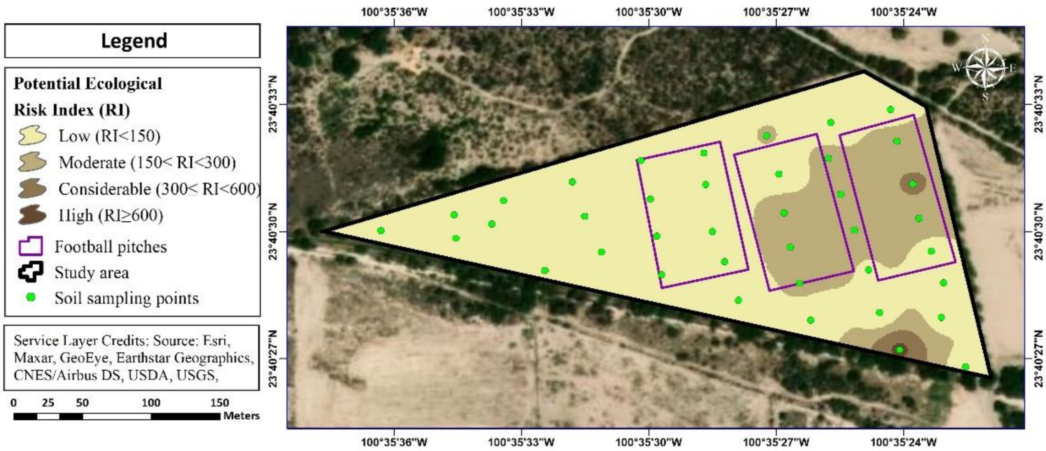

Figure 4. Spatial distribution of potential ecological risk index (*RI*).

5. Conclusions

The toxic metal contamination and accumulation in soils can result in a variety of issues for the environment, plants, and humans. In this study, the sources, as well as the status of contamination, was identified by C_f and E_r of five different toxic metals in the Joya Verde soccer sports club's surface soils. The primary metal contaminants were arsenic (As) and zinc (Zn), with amounts in most of the soil samples above the toxic metal background reference value. The C_f values revealed that the soil had a low range of contamination with Cu, Ni, Pb, a low to moderate range of contamination with Zn, and an extreme level of contamination with As. Additionally, E_r demonstrated that the soil had a low risk of contamination with Cu, Ni, Pb, and Zn, but a very high risk of contamination with As. Based on PCA, the factors influencing the toxic metal accumulation varied across the sampling locations. According to the level of potential ecological risk index (*RI*), arsenic poses the highest risk of toxic metals, while the other metals have a low-risk level. In comparison to the study location, the surrounding areas with intensive industrial operations, past mining activities, and the growth of urban populations were often characterised by a moderate and considerable potential ecological risk. The outcomes of this work provide a better knowledge of toxic metal enrichment and the risk of soil used for sports purposes, which is a significant issue for human health.

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Data Availability Statement: The data and information cited in the paper can be found in the reported literature as references.

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Conflicts of Interest: The authors declare no conflict of interest.

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