ISSN: 2634 - 8845

Journal of Earth and Environmental Science Research

SCIENTIFIC Research and Community

Research Article

Open Access

Assessment of Heavy Metal Contamination in the Soils of an Agricultural Field Near the Bargny Cement Plant (Senegal)

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ABSTRACT

In this study, the concentrations of heavy metals Fe, As, Mn, Cr, Ni, Zn, Ti, and Cu were measured in soil samples from an agricultural site located near a cement plant that has been operating in the area for several decades. The results of the analyses showed the following decreasing ranking of average concentrations: Fe > Ti > Cr > Ni > As > Mn > Zn > Cu. The maximum concentrations of As (54.79 mg/kg) and Cr (148.86 mg/kg) exceeded the limits set by the World Health Organization and the Food and Agriculture Organization of the United Nations (FAO). The analysis of correlations between the concentrations of the different heavy metals studied indicated anthropogenic origins for the metallic elements As, Zn, and Cr. The agricultural field showed moderate enrichment by Ni, significant enrichment by Cr, and very high enrichment by As, with enrichment factors of 4.725, 8.315, and 20.599, respectively. Approximately 33.33% of the study area had an as concentration exceeding the permitted limit. The individual pollution index (PI) indicated moderate as pollution of the agricultural field. The overall Neme row pollution index (PN) placed the study site within the precautionary range for the trace metal Cr. Regarding As, the site was in the area of severe pollution, with a PN of 3.097. However, the potential ecological risks were low.

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Received: April 14, 2026; **Accepted:** April 20, 2026; **Published:** April 28, 2026

Keywords: Heavy Metals, Risk Assessment, Soils, Agricultural Field, Cement Industry

Introduction

Soil is an essential part of the Earth's environment, crucial for agricultural practices and the development of terrestrial wildlife. Soil quality has a direct impact on crop yields and food security. However, soil degradation is a significant issue in some agricultural areas. Most agricultural sites are exposed to pollution, particularly from heavy metals, which contribute significantly to the destruction of environmental and human health. Heavy metals are produced naturally through rock weathering, but also through human activity [1]. The cement industry is one such human-caused source, due to its dust emissions containing high levels of heavy metals and its chimney emissions [2-4]. A typical raw cement contains 25 mg/kg of chromium (Cr), 21 mg/kg of copper (Cu), and 53 mg/kg of zinc (Zn) [5]. Other anthropogenic sources exist: vehicle emissions, fertilizers, pesticides, etc. High levels of heavy metals in an environment can lead to ecosystem alteration. Indeed, soil contamination by heavy metals can cause long-term problems in the biogeochemical cycle, thus affecting ecosystem functioning and leading to changes in soil fauna [6]. Heavy metal pollution is also characterized by its persistence, its insidious nature, its resistance to decomposition, and its high toxicity [7]. Exposure to toxic metals poses risks to human health through the food chain [8,9]. According to Jomova et al., long-term accumulation of heavy metals in the body can cause various diseases such as neurological, cardiovascular, hepatic, and renal disorders [10]. For example, chromium (Cr) is carcinogenic even at low concentrations with prolonged exposure; nickel (Ni) can cause skin diseases; and arsenic (As) can cause lung and bladder cancer [11-13]. Heavy metals are easily absorbed by plants through their roots and eventually accumulate in leaves and fruits [14]. With industrial development, urbanization, and the overexploitation of agricultural land, heavy metals concentrations are constantly increasing in agricultural areas. The accumulation of heavy metals in the soil is due to their non-biodegradable nature [15]. Heavy metal pollution results in decreased productivity and soil quality in agricultural fields, disruption of the ecological balance, and poses a significant threat to animal, plant, and human health [16].

The level of soil pollution by heavy metals is estimated using soil condition assessment indices. Soil quality depends on the calculated index value. Therefore, pollution indices can be considered tools that convey raw environmental information to managers, decision-makers, technicians, and the public [17]. The indices used in this paper are: the geoaccumulation index (Igéo), the enrichment factor (EF), the Nemerow individual (PI) and global pollution indices (PN), the potential ecological risk index (E), and the global potential ecological risk index (RI).

In this study, the objectives are to: 1) determine the concentrations of the heavy metals Mn, Cu, Zn, Cr, As, Ni, Ti, and Fe; 2) map their spatial distribution using Surfer software; and 3) assess the soil contamination levels in the agricultural field.

Method and Materials

Study Site

The study site is an agricultural field where market garden crops are grown. It is located in the Niayes region of Senegal. The Niayes region is one of Senegal's main vegetable-producing areas. The site is heavily used for agriculture, hence the frequent use of fertilizers, pesticides, and compost.

The study site is located in an urbanized and industrialized area. A cement factory is located near the agricultural field, which could be a potential source of environmental contamination. The site's GPS coordinates are 14°42'52.66"N and 17°14'46.71"W. The region's topography consists of a series of hills and plateaus with elevations below 50 m [18].

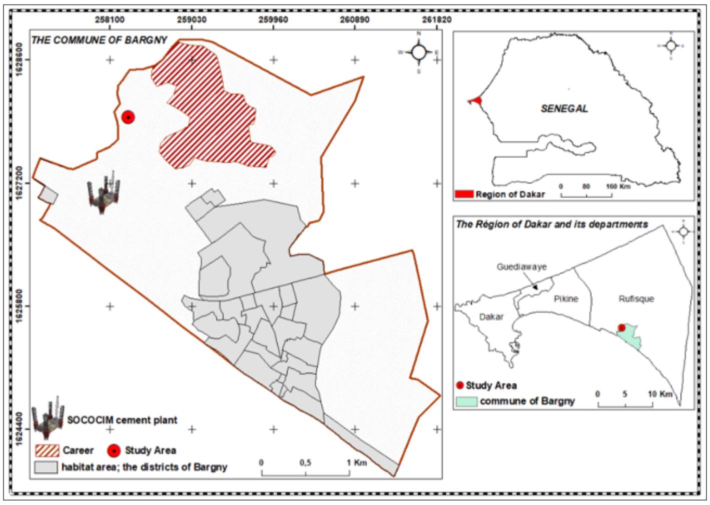


Figure 1: Location Map of the Study Site [19].

Sample Collection and Analysis

Samples were collected at the study site to ensure near-perfect coverage of the entire surface. The distance between sampling points was 10 m. Sampling was carried out using a core drill. Very wet samples were dried in an oven at approximately 80°C, ground, and homogenized. A representative portion of each sample was analyzed using X-ray fluorescence spectroscopy. A set of 30 samples was collected from a depth of 20 cm.

A Niton XLT900s portable XRF spectrometer (P-XRF) was used to perform elemental measurements on all soil samples. The spectrometer provides accurate analysis and displays results instantly on the screen. The measurement time for each sample was 300 seconds. The portable spectrometer has a low detection limit and can analyze a wide range of chemical elements. The X-ray fluorescence instrument has been fully standardized with comprehensive techniques for quantifying fundamental parameters. See Table 1 for specifications and operating conditions of the portable unit.

Table 1: Spectrometer Specification and Operating Conditions

Resolution	178eV at Mn Kα
Window Thickness	12.7µm Be
Rating	50kV, 40µA maximum power of the tube 2W
Beam diameter	7mm
Filter	Element analysis
Ag excitation source	Sb, Sn, Cd, Pd, Ag, Mo, Nb, Zr, Sr, Rh, Bi, As, Se, Au, Pb, W, Zn, Cu, Re, Ta, Hf, Ni, Co, Fe, Mn, Cr, V, Ti, Th, and U
Sandwich of Al, Ti and Mo	Ba, Sb, Sn, Cd, Pd, Ag
Cu Filter	Cr, V, Ti, Ca, K
No Filter	Al, P, Si, Cl, S, Mg

Calculation of Pollution Indices

The geo-accumulation index, the enrichment factor, the individual pollution index, the Nemerow global pollution index, the individual potential ecological risk index and the potential ecological risk index for a set of heavy metals are used to assess the state of pollution or contamination of the soils of the agricultural field of Bargny which is located near anthropogenic sources of heavy metals.

Geo-Accumulation Index Igeo

Using the equation of Muller, the values of the geo-accumulation index of the metals studied were calculated [20]:

$$I_{géo} = log_2(\frac{C_n}{1{,}5B_n}) \qquad (1)$$

Where Cn is the measured concentration of a heavy metal n in the soil sample, Bn is the geochemical background concentration of the heavy metal n in the soil and 1.5 is a correction factor for possible variations due to lithogenic effects. Muller provided the following classification based on the Igeo value [21,22].

Class	Igeo	Soil Quality
0	$I_{géo} \leq 0$	Unpolluted
1	$0 < I_{géo} < 1$	Unpolluted to moderately polluted
2	$1 < I_{géo} < 2$	Moderately polluted
3	$2 < I_{géo} < 3$	Moderately to heavily polluted
4	$3 < I_{géo} < 4$	Heavily polluted
5	$4 < I_{géo} < 5$	Heavily to extremely polluted
6	$5 > I_{géo}$	Extremely polluted

Enrichment Factor EF

The formula established by Simex and Helz for calculating the enrichment factor is [23].

$$EF = \frac{(\frac{C_x}{C_{ref}})sample}{(\frac{B_x}{B_{ref}})Background} \qquad (2)$$

Where Cx is the concentration of heavy metal x in the soil sample from the study site, Cref is the concentration of the reference metal, Bx is the concentration of heavy metal x in the background and Bref is the concentration of the reference metal in the background. In this study, iron was used as the reference metal. Iron is distributed independently of other metals and is abundant in the soil.

Five categories of contamination are recognized based on the enrichment factor [24].

EF<2	Minimal to deficient enrichment
2<EF<5	Moderate enrichment
5<EF<20	Significant enrichment
20<EF<40	Very high enrichment
EF>40	Extremely high enrichment

Pollution Index PI

The pollution index was used to assess the level of soil pollution by a heavy metal. This index is calculated using the formula [25].

$$PI_i = \frac{C_i}{B_i} \qquad (3)$$

Where PI_i is the pollution index of heavy metal i, Ci is the measured concentration of heavy metal i in the sample in $mg.kg^{-1}$, and Bi is the concentration of heavy metal i in the reference (the terrestrial background) in $mg.kg^{-1}$.

The pollution index is divided into four levels:

$PI_i \leq 1$	means no contamination,
$1 < PI_i \leq 2$	means slight contamination
$2 < PI_i \leq 5$	means moderate contamination
$PI_i > 5$	means severe contamination.

Since the soil contains several heavy metals, its pollution can therefore be caused by these different heavy metals. The overall pollution caused by several heavy metals is calculated using Nemerow's formula [26].

$$P_N = \sqrt{\frac{(PI_{i\,max}^2 + \overline{PI_i}^2)}{2}} \qquad (4)$$

Where $PIi\ max$ is the maximum PI and $\overline{PIi}$ is the average PI value of the different heavy metals calculated.

Degree of pollution according to P_N values.

Pollution grade	Pollution index	Pollution level
1	$P_N \leq 0{,}7$	Safety domain
2	$0{,}7 < P_N \leq 1{,}0$	Precautionary domain
3	$1{,}0 < P_N \leq 2{,}0$	Slightly Polluted domain
4	$2{,}0 < P_N \leq 3{,}0$	Moderately Polluted domain
5	$P_N > 3{,}0$	Seriously Polluted domain

Potential Ecological Risk Index

The potential ecological risk index (RI) is a widely used method for assessing soil pollution by heavy metals. This method was proposed by Hakanson in 1980 [27]. This index provides information on the toxicology of heavy metals as well as their ecological and environmental effects [28].

$$E_i = T_i * PI_i \qquad (5)$$

$$RI = \sum_{i=1}^{m} E_i = \sum_{i=1}^{m} T_i * PI_i \qquad (6)$$

Where Ei is the potential environmental risk index for a heavy metal i; Ti is the toxicity coefficient of heavy metal i; and RI is the potential environmental risk index for all m heavy metals analyzed.

The potential environmental risk index Ei is classified into five levels:

$E_i < 40$	Low
$40 \leq E_i < 80$	Moderate
$80 \leq E_i < 160$	High
$160 \leq E_i < 320$	Very high
$320 \leq E_i$	Extremely high

Regarding RI values, there are four grades [29]:

$RI < 150$	Low
$150 \leq RI < 300$	Moderate
$300 \leq RI < 600$	High
$RI \geq 600$	Very high

Results and Discussion

Descriptive Statistical Analysis

The results of the descriptive statistics from the study of agricultural soil samples are presented in Table 2. The coefficients of variation (CV) indicate the degree of variability in heavy metal concentrations. A $CV \leq 20\%$ indicates low variability; $21\% < CV \leq 50\%$ reflects moderate variability; $50\% < CV \leq 100\%$ shows high variability; and $CV > 100\%$ represents exceptionally high variability [30]. According to this classification, Fe has low variability in its concentration; Ni, Mn, and Ti have moderate variability; Cr and Zn have high variability in their concentrations; and as has exceptionally high variability. These results show that the anthropogenic input of as at the study site is greater than that of the other chemical elements. The high variability of Zn and Cr can be explained by agricultural practices: the use of herbicides, pesticides and fertilizers or by discharges from the cement plant.

Based on Table 2, a descending ranking of the average concentrations of heavy metals in agricultural soil samples was established: Fe > Ti > Cr > Ni > As > Mn > Zn > Cu. Fe had the highest average concentration at 2739,305 mg/kg. As concentrations ranged from 5,058 mg/kg to 54,797 mg/kg. The highest concentrations of Ni, Cr, and Zn were 23,508 mg/kg, 145,860 mg/kg, and 7,501 mg/kg, respectively. The lowest concentrations were 6,781 mg/kg for Ni, 15,568 mg/kg for Cr, and 1,790 mg/kg for Zn. The average concentrations of Ni and Cr were lower than the world average [31]. The maximum concentrations of Cu, Zn, Mn, Ni, and Fe were below the maximum limits established by the World Health Organization (WHO) and the Food and Agriculture Organization of the United Nations (FAO). In contrast, the maximum concentrations of As and Cr exceeded the limits established by regulatory organizations [32].

This enrichment of heavy metals such as Cr and as could result from agricultural practices, urbanization, or industrial activities. The Ti at the study site is not of anthropogenic origin.

Table 2: Statistical Description of Heavy Metal Concentrations in Agricultural Soil

Heavy metal	Concentration (mg.kg^{-1})								mg.kg^{-1}	
	Mean	Median	Max	Min	Range	SD	CV (%)	Kurtosis	Référencea	WHO/ FAOb
As	15.51	8.01	54.79	5.06	49.74	16.69	107.61	1.76	6.83	20
Ni	18.65	20.12	23.51	6.78	16.73	5.10	27.35	5.47	29	50
Zn	2.93	2.22	7.50	1.79	5.71	1.59	54.54	4.54	70	300
Cr	43.43	23.67	148.86	15.57	133.29	42.88	98.72	1.67	59.5	100
Mn	11.24	10.03	21.78	7.32	14.46	3.80	33.83	3.72	488	2000
Cu	1.03	1.03	1.03	1.03	0	-	-	-	38.9	100
Ti	165.16	172.82	303.81	70.84	232.97	75.94	45.98	- 0.91	7038	-
Fe	2739.30	2900.60	3438.61	1538.25	1900.36	548.01	20.00	- 0.11	-	50.000

[a] [31].

[b] [32].

The observed variability in the concentrations of the different heavy metals, with the exception of Ti, is visible in the boxplots (see figure 2). This confirms the variety of sources for these chemical elements. The heavy metals Zn, Ni, and Cr originate from industrial emissions as well as road traffic. As, Cr, Mn, Cu, Ni, and Zn can come from fertilizers, pesticides, and quarrying operations [31].

A one-way analysis of variance (ANOVA) also showed a significant difference between the mean concentrations of the heavy metals studied ($p<0.01$).

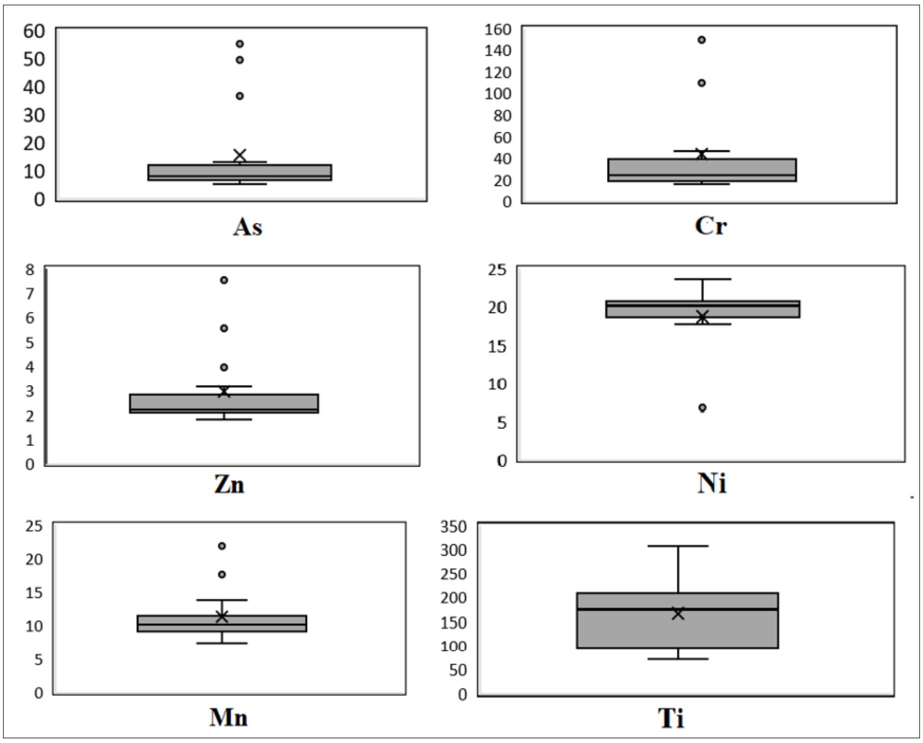


Figure 2: Boxplots of As, Cr, Mn, Zn, Ni and Ti Concentrations in Agricultural Soil

Spatial Distribution of Elements

The high variability of Cr and Zn concentrations is reflected in Figure 3 by their non-uniform spatial distribution across the agricultural field. This is certainly due to human activities. In their study on heavy metals in topsoil surrounding a cement plant, Ogunkunle and Fatoba attribute the presence of heavy metals, including Zn and Cr, to dust emitted by the cement plant [33]. Cr was found at high concentrations in the eastern and southwestern parts of the study site. Cr concentrations were higher than the global Earth background concentration in these areas. The spatial distribution of as was almost identical to that of Cr. Areas whereas concentrations exceeded the Earth background concentration represented 33.33% of the studied area. The maximum concentrations of As (54.80 mg/kg) and Cr (148.86 mg/kg) exceeded the maximum limits established by regulatory organizations, including the World Health Organization (WHO) and the Food and Agriculture Organization of the United Nations (FAO) (see Table 2). Zn and Mn were more concentrated in the southeastern area of the study site. Their average concentrations were lower than at the Earth's surface, and the maximum concentration values were below the maximum limit. The heavy metals Zn, Cr, Mn, and As, whose production originated from human activities, were carried by runoff to the lowest surface of the study site, which was not the case for Ti, which appears to have originated solely from natural sources. Heavy metals can be easily transported by soil erosion [19,34,35].

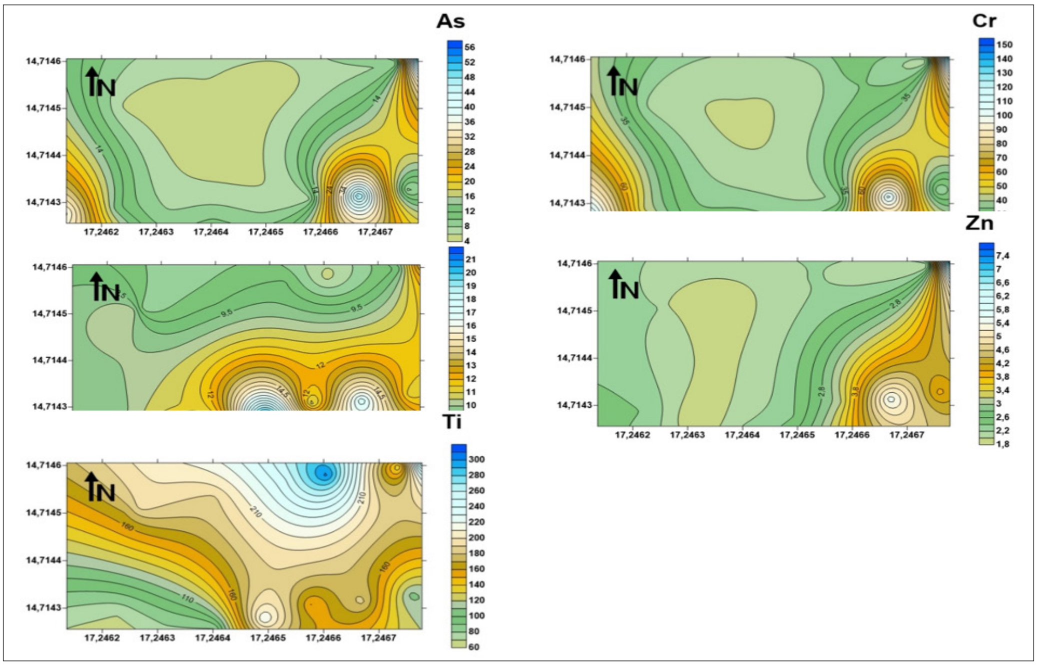
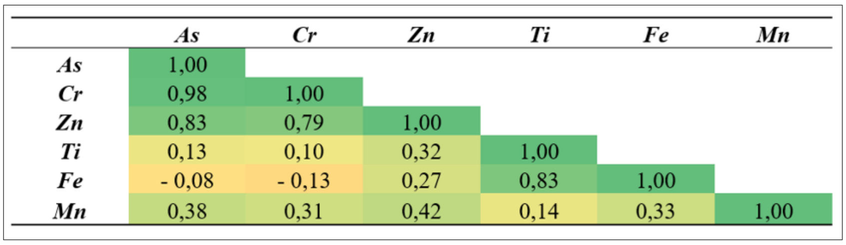


Figure 3: Spatial Distribution of As, Cr, Mn, Zn and Ti Concentrations in Agricultural Soil

In Table 3, the very strong positive correlation of As with Cr and Zn indicates their common origin. Ti and Fe also have a very strong positive correlation. Ti has a positive but very weak correlation with As and Cr. The source of Ti is different from that of As and Cr. Observation of Table 3 shows that As and Cr are negatively and very weakly correlated with Fe. In this case, when the concentration of As or Cr increases the concentration of Fe decreases. Mn has a weak positive correlation with the heavy metals As, Cr, and Fe, and a moderately positive correlation with Zn. The significant positive correlations observed in this study suggest that some of these heavy metals come from the same source. This source could be vehicle emissions, agricultural practices or cement production.

Table 3: Pearson Correlation Coefficient between the different Heavy Metals



	As	*Cr*	*Zn*	*Ti*	*Fe*	*Mn*
As	1,00					
Cr	0,98	1,00				
Zn	0,83	0,79	1,00			
Ti	0,13	0,10	0,32	1,00		
Fe	- 0,08	- 0,13	0,27	0,83	1,00	
Mn	0,38	0,31	0,42	0,14	0,33	1,00

The amount of organic matter at the study site averaged 76% and the average pH was 6.9. The soil texture was predominantly sand at 63%, silt represented 17% while clay was 19%.

Assessment of Contamination and Ecological Risks

An assessment of soil contamination by bioavailable heavy metals is essential for formulating measures to prevent and control soil pollution and protect soil ecosystems [36].

In Table 4, the geoaccumulation indices (Igeo) showed values below 0 ($Igeo<0$) for all metallic elements. The soil samples from the study site were not contaminated by any of the heavy metals in this study. However, the agricultural site showed moderate enrichment in Ni ($2 < EF = 4.725 < 5$), significant enrichment in Cr ($5 < EF = 8.315 < 20$), and very high enrichment in As ($20 < EF = 20.599 < 0.40$). Rashed indicates that an enrichment factor greater than 1.5 in soil samples suggests a strong human influence [37]. Regarding the pollution index (PI), with the exception of arsenic (As) which showed moderate contamination of the studied area, no contamination was observed for the other heavy metals. A pollution index value of 1.193 indicates slight arsenic contamination of the studied agricultural site. According to Jin et al. and Tian et al. chromium (Cr), zinc (Zn), nickel (Ni), copper (Cu), manganese (Mn), and titanium (Ti) originated from natural sources; anthropogenic input was negligible, as their PI was less than 1[38,39]. The Nemerow PN global pollution indices for the different heavy metals studied were ranked in the following descending order: As < Cr < Ni < Zn < Ti < Cu < Mn. For the heavy metals Ni, Zn, Ti, Cu, and Mn, the study site was within the safe range, while Cr placed the site within the precautionary range. As for the as which has a PN = 3.097 the site was in the area of serious pollution.

The potential ecological risk index is used to assess the sensitivity of biological communities to metal toxicity [40]. Table 4 shows the ecological risk index values of 0.965, 1.645, 0.031, 0.114, 11.932, 0.013, and 0.035 for the chemical elements Cr, Ni, Zn, Cu, As, Mn, and Ti, respectively. The potential ecological risk was low ($E < 40$) for all heavy metals in this study. The potential ecological risk index ($RI = 14.74$) for all heavy metals was also low.

Table 4: Assessment of Agricultural Soil Contamination by Heavy Metals

Heavy metal	Igéo	EF	PI	PN	E
Cr	-1.636	8.315	0.483	1.218	0.965
Ni	-2.451	4.725	0.274	0.312	1.645
Zn	-5.605	0.531	0.031	0.059	0.031
Cu	-6.035	0.394	0.0228	0.023	0.114
As	-0.330	20.559	1.193	3.097	11.932
Mn	-6.795	0.232	0.013	0.020	0.013
Ti	-5.384	0.618	0.035	0.053	0.035

Conclusion

The average concentrations of the different metals studied in this work are lower than the global average concentrations. However, some heavy metals, such as chromium (Cr) and arsenic (As), had peak concentrations higher than the limit established by the World Health Organization (WHO). The degree of variability in concentrations was exceptional for As, high for Cr and zinc (Zn), and moderate for nickel (Ni), manganese (Mn), and titanium (Ti). The spatial distribution of As, Cr, and Zn concentrations was heterogeneous. Approximately 33.33% of the study site area had as concentrations exceeding the global limit. Regarding the pollution assessment, the geo-accumulation index (Igeo) indicated an unpolluted site. Different enrichments were observed on the site: moderate enrichment for Ni, significant enrichment for Cr, and very high enrichment for As. The individual pollution index (PI) reflected moderate contamination for As. Regarding the overall pollution index of Nemerow National Park, the study site was classified as having severe pollution for arsenic (As), within the precautionary range for chromium (Cr), and within the safe range for the remaining heavy metals. Based on the results of this study, it is crucial to establish control strategies aimed at limiting soil pollution by heavy metals in the Niayes region.

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