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Ecological Risk Assessment of Potentially Toxic Metals in Arable Soils around Adudu Lead–Zinc Mine, North-Central Nigeria

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Abstract: Mining is a major source of toxic heavy metals into the soil when mine wastes are discharged into the nearby farmlands used for the cultivation of food crops. This study investigated the influence of Pb–Zn mining on the quality and ecological risk of arable soils around active mining sites in Adudu, Nasarawa State, Nigeria. Composite soil samples were collected at 0–20 cm depth, pulverized, and analyzed for heavy metal (Al, As, Cr, Cu, Fe, Mn, Pb, and Zn) concentration using X–ray fluorescence technique. Enrichment factor, geo–accumulation index, improved Nemerow index (IIN), contamination factor (CF), degree of contamination (Cd), pollution load index (PLI), and ecological risk assessment (ERA) were used to evaluate the effect of the mining activities on the environment. Results showed elevated levels of Pb, Zn, Cu, Fe, Mn, and Cr in arable soils around the mine and lower levels of these metals in the control soil. IIN, Cd, and PLI showed that the mine and the nearby arable soils were the most deteriorated, and soil quality improved away from the mining vicinity. ERA revealed that the mine and the closest arable soils (sites F1 and F4) have significant to high ecological risk index as a result of the dominant presence of Pb, Zn, and Cu at the sites. Thus, arable soils which are disposal channels for mine wastes are not good for growing food crops. This study clearly shows that Pb–Zn mining activities introduced heavy metals into the arable soils surrounding the mine.

Keywords: Mining; Heavy metal; Ecological risk; Soil contamination; Arable soils.

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1. INTRODUCTION

Globally, harnessing mineral resources (solid, liquid, and gas) significantly contributes to economic growth development and sustainability through income generation from increased business and foreign exchange earnings, provision of industrial raw materials, enhanced employment opportunities, poverty alleviation, etc. (1, 2). Mineral exploitation is of great importance in a developing nation like Nigeria because of its economic potential. This is why it is on the exclusive list of the Federal Government of Nigeria. Nigeria is endowed with about fifty (50) economically potential solid minerals across all states of the country (3). Nigeria's dependence on oil caused the decline of solid mineral exploitation and consequently, the country's economy became a mono-product economy (3). The recent global decline in crude oil prices due to the COVID-19 pandemic has intensified the efforts of the Federal Government of Nigeria to diversify the country's economy from crude oil exploration to solid mineral exploration. Consequently, the Federal Government has introduced various policies such as tax holidays for miners, waivers on imported mining equipment, financial assistance to artisanal miners, etc., to encourage investors in the mining sector. However, the authorities pay little attention to the adverse environmental and health impacts of these mining activities on the host communities.

The impacts of mineral exploration and processing activities on the environment are similar globally depending on the chemical attributes of the ore, method of extraction, and environmental conditions (4, 5). It is a global concern because they cause physical degradation of the ecosystem (6) and more importantly, they produce large amounts of tailings and wastes (7) which are principal anthropogenic sources of heavy metals (such as Pb, Zn, Cd, Mn, Cr, Co, Cu, Ni, Hg, As, Al and Fe) that have adverse effect on the environment (8). Studies have recorded

higher concentrations of heavy metals in soils around the Pb– Zn mine in Enyigba, southeastern Nigeria (9), Ameri, Abakaliki (10), Mkpuma Ekwoku, southeastern Nigeria (11), Abakaliki, Lower Benue Trough, Nigeria (12) and various sites, southeast Missouri, USA (13). Similarly, Oyebamiji et al (5) and Eludoyin et al. (14) reported elevated concentrations of heavy metals in soils around tantalum-niobium and gold mining sites of Iludun-Oro and Itagunmodi communities respectively, in southwestern, Nigeria.

Elevated levels of these heavy metals (pollutants) can have severe negative effects on human and animal health, water quality, aquatic life, land use and agriculture, and other aspects of ecosystem imbalance (15). The elevated levels of these heavy metals increase the risk of soil pollution in and around the mining site, depending on their mobility and bioavailability. Their mobility and bioavailability in the environment are determined by some physicochemical characteristics of the soil such as pH, textural characteristics, organic matter content, speciation or chemical form, and electrical conductivity (16).

Nasarawa State is located in then orth–central region of Nigeria and is known as "The Home of Solid Minerals" because it is blessed with abundant solid minerals that are of high economic significance. The prominent mineral deposits of the State are coal, barytes, salt, limestone, clays, glass, tantalite, columbite, cassiterite, copper, iron ore, lead, and zinc (17). The rocks in Nasarawa State are the host to gold in Wamba; baryte at Azara, Wuse, and Aloshi; coals (of the highest rank in Nigeria) at Obi, Jangerigeri, Jangwa, and Shankodi; Tantalite at Afu, Udege Beki, and Wamba; Gemstone in Keffi; Nasarawa Eggon and Kokona; salt deposits in Ribi, Keana, and Awe; Limestone deposits at Adudu, and Jangwa; at Keffi, Akwanga, Nasarawa Eggon, Tudu Uku, etc. (18). Thus, illegal, indiscriminate and unregulated mining are issues bedeviling several villages/towns in Nasarawa State which are endowed with these solid minerals. It was reported that out of 64 active mining licenses in Nasarawa State, only ten (10) had environmental impact assessments (19). Surface mining such as open-cast mining is predominantly employed in the mining of these solid mineral resources because the solid minerals do not seem to lie deep beneath the earth. Open-cast mining involves the excavation of vegetation (topsoil) with heavy equipment and hard implements to mine a target mineral (20). During this process, pits and dumps are created which causes physical degradation of the land (21). The excavation of soil causes atmospheric depositions of metals and also generates huge quantities of wastes (such as waste rocks, tailings mine wastewater, etc. that contain harmful minerals and chemicals that pollute the environment) which are discharged directly into nearby farmlands, streams, and river channels. Thus, open-cast mining has serious adverse consequences on the environment of the host communities.

Pb–Zn ores are mined using the open cast mining method, in the Adudu community, Awe, North – central Nigeria. This situation has persisted for decades, resulting in the presence of abandoned mines and the generation of significant amounts of mine waste, including waste rocks, tailings, and mine wastewater. These wastes have been haphazardly and indiscriminately disposed of in farmlands (as shown in Figure 1), streams, and river channels.

These increased the possibility of elevated levels of heavy metals in the arable soils around the mine. The community dwellers are ignorant of the adverse consequences of these mining activities on their health and environment. Obasi et al. (22) reported that health challenges such as miscarriages, selenosis in infants, the decline in infertility, and physiological and mental imbalance, were common among inhabitants around Pb–Zn mine in Enyigba community, southeastern Nigeria. Yet until this research, no study has been carried out on the environmental risk of heavy metal-polluted agricultural soils around the Pb–Zn mining site in the Adudu community.

(a) **(b)**

Figure 1: Pb–Zn Mine at Adudu Showing Mine Wastewater Discharged or pumped to Nearby Farmlands (a) and the Pb–Zn ore (b) being mined.

Therefore, this research investigated the influence of opencast mining activities on the heavy metal pollution and environmental risk of arable soils around the Pb–Zn mine site at Adudu, North Central, Nigeria.

2. EXPERIMENTAL SECTION

2.1. Description of Study Area

Adudu is a community in Obi Local Government Area in Nasarawa State. However, geographical coordinates show that the Adudu Pb–Zn mine is located in Awe Local Government Area although it is a boundary between the Obi and Awe Local Government Areas of Nasarawa. The geographical coordinates of the Pb–Zn mine lie within latitude 08°13'83.3''N and longitude 009°01'00.0''E and 169 m above sea level.

Adudu is a low-income community with farming, mining, cattle rearing, and trading as the sources of income. The predominant land uses in the community are agriculture and mining. Mining is the second source of income for the inhabitants of this community. The average temperature of the area is 32 °C. Awe has two distinct seasons which are the dry and the rainy seasons. The soil varies from loam to sandy loam which is good for crop production and crops such as yam, maize, and rice grown in substantially large quantities.

Adudu is located within the middle region of Benue Trough of Nigeria which contains up to 6000 M of Cretaceous-Tertiary Sediment (23). Adudu is within the southern part of Nasarawa State which is part of the low plains of Benue origin and volcanic cones (24) and is also the sedimentary part of the State as the area is covered by sedimentary rocks of Cretaceous-Tertiary ages (2).

2.2. Sample Collection and Preparation

Eleven (11) study sites were investigated in this study. The study sites include the mining site, nine (9) cultivated arable farms around the Pb–Zn active mining site, and one (1) cultivated arable farm located about 3 km away from the active mining site which serves as the control. The cultivated arable farms around the mining site are not less than 150 m apart from each other and 100 m from the mine. Ten (10) composite soil samples were collected from each of the study sites using soil augar. Thus, a total of 110 composite samples were collected and analyzed. At each location in each studied site (active mining site and cultivated arable farms), six (6) quadrats were marked and, in each quadrat, four (4) core soil samples were collected randomly at depth of 0–20 cm and mixed to give a composite sample of that location in the studied site. Foreign materials such as waste polythenes and plastics, plant debris, pebbles, etc were removed from the soil samples. The soil samples were air–dried for 10 days, pulverized, sieved to less than 2 mm, and then, stored in plastic containers for analysis. The coordinates of the sample locations were marked with a handheld global positioning system (GPS) and are shown in Figure 2.

Sampling Site	Latitude (North)	Longitude (East)
Mine	08°13'83.3''	009°01'00.0''
F1	08°13'54.6''	009°01'02.6''
F2	08°13'79.8''	009°01'12.9''
F3	08°13'99.2''	009°01'01.8''
F4	08°14'22.7''	009°01'09.6''
F5	08°14'36.0''	009°01'35.7''
F6	08°14'55.9''	009°01'56.8''
F7	08°14'87.6''	009°01'63.4''
F8	08°15'20.9''	009°01'63.9''
F9	08°15'53.2''	009°01'65.7''
F10 (Control)	08°15'88.3''	009°01'61.5''

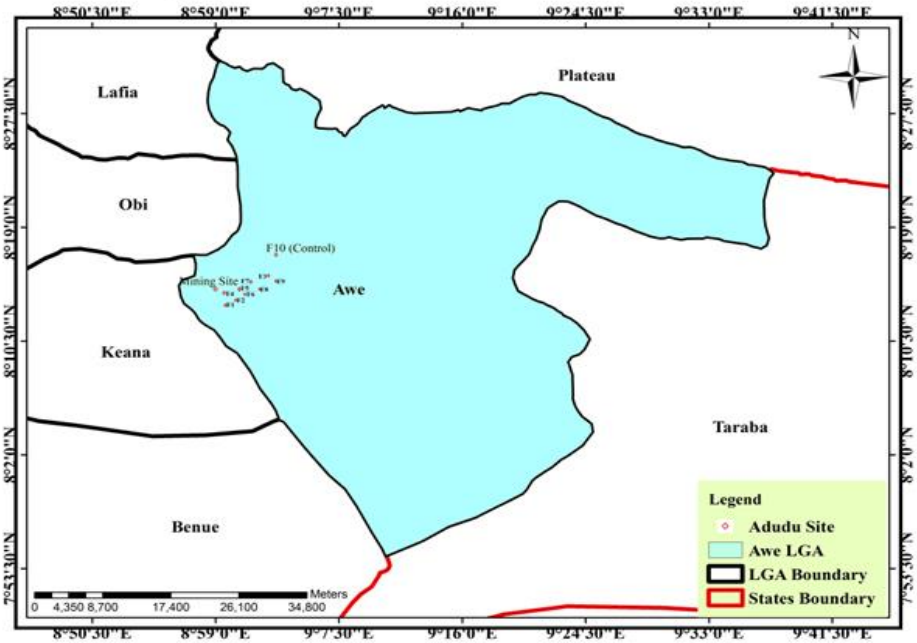

Figure 2: Maps of Nigeria, Nasarawa State and Awe Local Government Area Showing Location of Sampling Sites with Their Coordinates

2.3. Heavy Metal Analysis

About 5 g of the finely ground soil sample was pelletized at a pressure of about 19.4 kg/m^2 using a pelletizing machine. The pelletized sample was placed in a standard sample holder and loaded into the energy dispersive X–ray fluorescence (EDXRF) spectrometer (Minipal 4 model) [Detection limit: 0.0001 % (1 ppm) – 99.9999 %]. The EDXRF spectrometer was switched on and allowed to stabilize for 2 hours. It was set at the default mode to analyze the compositions of the soil samples by irradiating the sample with X-rays generated from the Rh tube (Maximum power: 9 W; window: 75 µm Be; maximum high voltage: 30kV; maximum current: 300 µA; cooling medium: air). A recovery test was carried out on the EDXRF machine as a quality control measure by spiking analyses to ensure the reliability of the result.

2.4. Environmental Risk Assessment

2.4.1. Enrichment factor (EF)

EF is used to differentiate the natural and anthropogenic sources of the heavy metals in the soils by normalizing the heavy metal concentration in the sample concerning a reference heavy metal [6]. The most commonly used reference elements are Sc, Mn, Ti, Al, and Fe (25). The EF of the analyzed heavy metals in the investigated soil samples from the study area was calculated using Eq.1:

$$\mathbf{EF} = \left[\frac{\mathbf{C_{n(sample)}}/\mathbf{C_{ref(sample)}}}{\mathbf{B_{n(Background)}}/\mathbf{B_{ref(Background)}}}\right] \quad (1)$$

Where, $C_{n(sample)}$ is the concentration of the investigated heavy metal "*n*" in the study site, $C_{ref(sample)}$ is the concentration of the reference heavy metal in the study site; $B_{n(background)}$ is the background concentration of the investigated heavy metal (usually the average shale value of the investigated heavy metal) and $B_{ref(background)}$ is the background concentration of the reference heavy metal (usually the average shale value of the reference heavy metal). In this study, Fe is the most naturally abundant element in all the studied soils and thus, was used as the reference heavy metal while the average shale value described by Turekian and Wedepohl, (26) was adopted as the reference value.

2.4.2. Geo–accumulation index (Igeo) and improved Nemerow index (I_{IN})

Igeo is a single-factor contamination index proposed by Muller (27) for qualitative assessment of heavy metal pollution in soils using Eq. 2.

$$\mathbf{I_{geo}} = \mathbf{log_2}\left[\frac{\mathbf{C_n}}{\mathbf{1.5B_n}}\right] \quad (2)$$

Where C_n is the concentration of the heavy metal "*n*" in the sample; B_n is the geochemical background concentration for heavy metal "*n*" which is either directly measured in fossil argillaceous sediments of the area or adopted from literature (world average shale value); 1.5 is a correction factor used to reduce the possible geogenic effect on the variations in background concentration of a given metal. The world average shale values of the analyzed heavy metals as provided by Turekian and Wedepohl (26) were adopted in this study as shown in Table 1.

I_{IN} is a comprehensive index method employed for general assessment of the pollution integrity of the study area (28,29). It was computed using Eq. 3 proposed by Nemerow (30).

$$\mathbf{I_{IN}} = \sqrt{\frac{(\mathbf{I^2_{geomax}} + \mathbf{I^2_{geoave}})}{2}} \quad (3)$$

Where I_{IN} is the comprehensive contamination index of a sample, I_{geomax} is the maximum I_{geo} value of such sample, and I_{geoave} is the arithmetic mean value of I_{geo}.

2.4.3. Contamination factor (CF), degree of contamination (C_d), and pollution load index (PLI)

The extent of soil contamination by each of the analyzed heavy metals was determined using the contamination factor (CF). It was calculated using Eq. 4.

$$\mathbf{CF} = \frac{\mathbf{C_n}}{\mathbf{C_b}} \quad (4)$$

Where C_n is the concentration of the heavy metal "*n*" in the sample, C_b is the background concentration of the heavy metal "*n*". Nigerian Directorate of Petroleum Resources (31) target values for heavy metals in soils (Table 1) were adopted as the background values "C_b".

The sum of all contaminants factors of the various heavy metals is referred to as the degree of contamination (C_d) (32). The generalized form of Hakanson's (33) equation for computing C_d was used in this study. It is given in Eq. 5:

$$\mathbf{C_d} = \sum_{\mathbf{i=1}}^{\mathbf{n=8}}(\mathbf{CF_i}) \quad (5)$$

Where *n* is the number of heavy metals studied and CF_i is the contamination factor for heavy metal "*i*" in the sample.

Pollution Load Index (PLI) was used to estimate the magnitude of contamination by the simultaneous presence of analyzed heavy metals in a sampling site (5). PLI was calculated using Eq. 6 as proposed by Tomlinson *et al*. (34).

$$\mathbf{PLI} = (\mathbf{CF_1} \times \mathbf{CF_2} \times \mathbf{CF_3} \times \mathbf{CF_4} \times \ldots \mathbf{CF_n})^{\mathbf{1/n}} \quad (6)$$

Where *n* is the number of metals and *CF* is the contamination factor of each heavy metal.

2.4.4. Ecological risk assessment

Potential hazard(s) from soil heavy metal contamination were quantified using ecological risk factor (Er) and ecological risk index (RI).

Er is a single index quantitative expression of the potential ecological risk of a given contaminant (heavy metal) (33). It was calculated using Eq. 7

$$\mathbf{Er} = \mathbf{Tr} \times \mathbf{CF} \quad (7)$$

Tr is the toxic response factor suggested by Hakanson (33) and presented in Table 1 while *CF* is the contamination factor of the heavy metal.

The potential ecological risk index (RI) index evaluates the general pollution caused by the simultaneous presence of the eight analyzed heavy metals. It was calculated using the expression in Eq. 8

$$\mathbf{RI} = \sum_{i}^{n} \mathbf{Er} \quad (8)$$

n is the number of the heavy metals considered; *Er* and *RI* are potential ecological risk factors of individual and multiple metals respectively.

3. RESULTS AND DISCUSSION

3.1. Heavy Metal Concentration

Table 1 presents the concentrations of the analyzed heavy metals in the investigated soils. Results showed that concentrations of the analyzed heavy metals in the investigated soils varied significantly away from the mine. The highest concentrations of Mn, Pb, and Zn were obtained in the soil from the mine which also recorded significant levels of Cr, Cu, and Fe. However, the control soil (collected 3 km away from the mining site) showed the least Cr, Cu, Fe, and Mn concentrations and also, lower concentrations of Pb and Zn compared to other investigated soils. This is evidence that the concentrations of analyzed heavy metals in the investigated arable soils around the mine, increased beyond their natural levels due to anthropogenic activities from Pb–Zn mineral exploration and processing. Overall, the studied sites (mining and arable sites) showed high concentrations of Al, Cr, Cu, Fe, Mn, and Zn. This is an indication that mine waste is leached under acidic conditions which are induced by acid mine drainage.

Table 1 showed that Al concentration in the studied soils ranged between 7039.12±157.04 to 31754.81±338.65 mg/kg and thus, are below average shale (26) reference value of 80000 mg/kg for Al. This suggests geogenic or lithogenic origin as the possible major source of Al. The mine and control site contained the lowest and highest Al concentrations respectively. Hence, the Al concentration obtained at the mine is appreciably low compared to those of the studied arable farms (F1–F10) which are away from the mine. This implies that weathering and mineralization of the geochemical composition of the rocks in the study area is a major contributing factor to the presence of Al. Human exposure to Al is inevitable as it naturally occurs in soil, water, air, and food (35). Chronic exposure to free Al cation (Al^{3+}) is a huge concern as it has been reported to be essentially toxic and may aggravate the risk of developing Alzheimer's disease and breast cancer (36). Obiora *et al*. (37) reported a similar range of Al level and decline in Al close to the Pb–Zn mine in Enyigba, southeastern Nigeria. According to Abraham and Susan (38), precipitation of metals in the acidic mined zone could be responsible for Al decline near a Cu mine in western Uganda.

The levels of arsenic (As) in the studied sites are below the instrumentation limit of detection (i.e., 1 mg/kg). Consequently, the level in the study area is below the average shale reference value (26) and its acceptable limit for arable soil (31). This is an indication that As presence in the study area may be associated with natural processes such as weathering of rock, volcanic eruptions, geothermal activities, etc (39). Commonly referred to as king of poison (40), occurs naturally in the earth's crust (41).

Low As level was similarly recorded in most of the arable soils around Pb–Zn mining sites of Abakaliki, Lower Benue Trough, Nigeria (12), and Abuni town, Nasarawa State, Nigeria (42). However, elevated range As (6.9–7.7 mg/kg) was reported in stream sediments around the Pb–Zn mining vicinity of Enyigba, southeastern Nigeria (37). Exposure to AS is a global concern as studies that it is inimical to human health. Human exposure to inorganic As increases the risk of skin cancer and other internal tumors of the bladder, liver, kidney, and lung (43, 44), congenital malformations, low birth weight, spontaneous abortion, genotoxicity, mutagenicity, and teratogenicity (45).

In the present study, soil from the mine showed lower Cr concentration than the investigated arable soils (except control soil) (Table 1). This could be attributed to the leaching of mine wastes to the surrounding arable farms under acidic conditions in addition to the dissolution of Cr through Pb–Zn mineralization of the study area. The concentration of Cr varied between 102.63–649.99 mg/kg. Except for the control soil (F10), soils from the mine and the studied arable farms, showed Cr concentrations above the DPR (31) threshold limit for arable soil (100 mg/kg) and the average shale (26) reference value (90 mg/kg). An indication that Cr concentration is related to the mineralization of the Pb–Zn ores in the study area. Cr usually exists in three main forms; Cr, Cr^{3+}, and Cr^{6+}. Cr^{3+} is less toxic and required in minute quantity for human health. Thus, it has little or no adverse effect on human health (46). However, Cr^{6+} is highly toxic and can cause several human health problems such as anemia, cancer, irritations and ulcers in the small intestine and stomach, damage to sperm and the male reproductive system, and possibly death (47). Cr concentration obtained in this study exceeded values reported by Obiora *et al*. (9) for agricultural soils around Pb–Zn mining localities in Enyigba, southeast Nigeria. However, it is less than the Cr range (1112.60–1127. 57 mg/kg) recorded for agricultural soils in Ameri, Abakaliki Pb–Zn mining area, Ebonyi State, southeast Nigeria (10).

Cu levels in soils from the mine site (3594.91±79.48 mg/kg) and site F4 (6710.50±134.02 mg/kg) are appreciably higher compared to other studied sites (Table 1). Thus, the maximum Cu level obtained in site F4 could be attributed to introductions from chalcopyrite, bornite, and azurite through the disposal of mine wastes (such as waste rocks or gangues, tailings, mine wastewater, etc.) at the site. The Cu level is significantly lower in the control site (F10) than in other studied sites but its level in all

the studied sites greatly exceeded its average shale (26) reference value and DPR (31) acceptable limit for arable soils. This implies that anthropogenic activities from Pb–Zn mining are not the only sources of soil contamination with Cu in the area; the underlying geology and mineralization of Pb–Zn ores in the area are significant contributors. The high level of Cu at the mine suggests that Cu-bearing mineral ores associated with Pb–Zn ores such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), azurite [$Cu_3(CO_3)_2(OH)_2$], etc., are among the principal ores exploited in the study area. The Cu range obtained in this study is higher than those reported for agricultural soils around Pb–Zn mines by other researchers (9–12, 22, 37). Overdose of Cu can have adverse effects on human health such as irritations, dizziness, vomiting, stomach cramps, diarrhea, nausea, liver and kidney damage, and even death (48).

Table 1: Mean concentrations (mg/kg) of the analysed heavy metals in the investigated soils.

Sampling Site	No of Samples Per Site	Data Presentation	Al	As	Cr	Cu	Fe	Mn	Pb	Zn
Mine	10.00	Mean	7039.12	BDL	102.63	3594.91	123167.44	4956.49	24786.02	13979.01
		± SD	±157.04		±10.80	±79.48	±3503.58	±18.26	±368.36	±521.93
F1	10.00	Mean	20243.69	BDL	410.52	958.64	75012.54	2323.35	4455.91	401.70
		± SD	±376.21		±21.04	±65.17	±1758.22	±63.49	±89.22	±16.52
F2	10.00	Mean	18311.93	BDL	444.73	734.96	118446.37	1858.68	BDL	241.02
		± SD	±201.03		±8.63	±36.96	±1948.22	±59.71		±7.91
F3	10.00	Mean	14395.51	BDL	342.10	798.87	112081.67	3020.36	BDL	BDL
		± SD	±286.62		±16.99	±21.04	±2417.74	±65.97		
F4	10.00	Mean	13231.17	BDL	338.68	6710.50	169259.06	2865.47	BDL	457.93
		± SD	±477.12		±20.59	±134.02	±4193.55	±34.82		±24.07
F5	10.00	Mean	14231.23	BDL	280.52	798.87	212867.75	3330.14	BDL	BDL
		± SD	±191.88		±9.44	±18.47	±6218.37	±57.02		
F6	10.00	Mean	16009.71	BDL	478.94	734.96	120264.86	1703.79	BDL	BDL
		± SD	±173.36		±35.82	±33.33	±3618.81	±48.17		
F7	10.00	Mean	29108.57	BDL	342.10	615.13	25144.06	1936.13	BDL	BDL
		± SD	±387.11		±27.33	±16.62	±221.64	±37.11		
F8	10.00	Mean	10611.40	BDL	649.99	878.76	137155.80	1703.79	BDL	241.02
		± SD	±161.29		±25.70	±39.05	±2531.77	±66.28		±13.42
F9	10.00	Mean	26118.33	BDL	441.73	519.26	34201.52	3020.36	BDL	BDL
		± SD	±218.74		±31.08	±23.59	±510.06	±71.24		
F10 **(Control)**	10.00	Mean	31754.81	BDL	BDL	375.47	7204.00	1471.46	BDL	BDL
		± SD	±338.65			±13.32	±95.41	±42.87		
Average Shale Values*			**80000.00**	**13.00**	**90.00**	**45.00**	**47200.00**	**850.00**	**20.00**	**96.00**
DPR Target Values (31)			**NA**	**1.00**	**100.00**	**36.00**	**38000.00**	**850.00**	**85.00**	**140.00**
Tr**			**NA**	**10.00**	**2.00**	**5.00**	**NA**	**1.00**	**5.00**	**1.00**

Keys: SD = Standard Deviation**; NA** = Not Available; **BDL** = Below Detectable Limit; **DPR** = Department of Petroleum Resources (Nigeria); **Tr** = Toxic Response Factor; ***** = (26); ****** = (33)

Iron (Fe) is the most abundant heavy metal found in all the investigated soils (except in soil from the control arable site which has Al as the most abundant). This suggests that Fe-rich mineral ores such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), siderite ($FeCO_3$), pyrite (FeS_2), marcasite (FeS_2), etc., are probably among the principal ores exploited in the area. The studied sites showed varied Fe concentrations ranging from 7,204±95.41 to 212,867.75±6218.37 mg/kg (Table 1). The lowest Fe concentration was obtained in the control soil (F10) while most of the investigated soils (except F7, F9, and F10) showed Fe concentration above the DPR (31) regulatory limit for arable soil and the average shale (26) reference value. These observations, especially the high concentration of Fe in sites located away from the mine (sites F4, F5, and F8), suggest possible introductions from chalcopyrite and bornite, siderite, and pyrite via combined effects of the Pb–Zn mining activities in addition to geologic processes and Pb–Zn mineralization of the area. The Fe range obtained in this study falls within the range reported by Obiora *et al*. (37) for stream sediments around the Pb–Zn mine in Enyigba, southeastern Nigeria.

Table 1 shows that Mn level varied between 1471.46±42.87 – 4956.49±18.26 mg/kg. The maximum and minimum Mn levels were obtained in soils from the mine and control site (F10) respectively. However, Mn levels in all the studied sites are above 850 mg/kg which is the average shale (26) reference value and DPR (31) tolerance level for Mn in arable soils. Thus, Mn sources could be of geogenic and anthropogenic origin. The high Mn concentration obtained could be ascribed to the dissolution of Mn from the sulfide and carbonate ores (such as chalcopyrite, bornite, siderite, etc.) which underlie the study area (49). Also, anthropogenic sources such as used batteries, discarded metal scraps, machinery parts, automobile exhaust fumes, and wastes from welding works and spray paintings of the vehicles (50), could have also contributed to the high level of Mn observed in the control soil due to its proximity to the highway. Mn exists in natural deposits as oxides, sulfides, carbonates, and silicates (51). It is an essential element for humans and

animals and is also a global concern because studies have shown that at an elevated level, it can cause Parkinson's disease-like syndrome of tremour, gait disorder, postural, instability, and cognitive and neurological disorder (52).

Lead (Pb) is a prominent toxic heavy metal and highly persistent in the environment due to its non–biodegradable nature. Hence, on continuous exposure, it accumulates to a toxic level (53). Its toxicity causes negative effects on humans such as high blood pressure, brain and kidney damage, miscarriage, anemia, learning deficit, reduced fertility, and behavioral disorders (53–55). A high concentration of Pb was observed only in soils from the mine (24786.02±368.36 mg/kg) and site F1 (4455.91±89.22 mg/kg) which are above the Pb permissible limit for arable soils (31). The other studied sites (F2–F10) had very low Pb concentrations that were below the instrumentation limit of detection (1 mg/kg). The very high concentration of Pb at the mine is evidence that galena (Pbs) is one of the major mineral components explored at the mine. Also, the continuous disposal/dumping of mine wastes and tailings to the nearby arable farm (F1) explains the appreciable level of Pb in the site. The drastic decrease in Pb concentration in studied sites (F2–F9) that are farther away from the mine, could be attributed to the immobility nature of Pb in soil (56), density settling, and elemental precipitation (37) and poor solubility of Pb in water (57, 58). The low solubility of Pb in water affects its amount in the mine wastewater that is discharged or leached to the surroundings while Pb immobility nature makes it difficult for it to be transported via the soil, to a distance farther from the mine. Similarly, at high pH, Pb precipitates thereby reducing the amount of Pb in the leaching effluents. Ambo *et al*. (42) and Obiora *et al*. (37) reported similar drastic decreases in Pb at locations away from the Pb–Zn mine at Abuni town Nasarawa State and Enyigba, southeastern, Nigeria; respectively.

Similar to Pb, the Zinc (Zn) level at the mine (13979.01±521.93 mg/kg) was found to be significantly high compared to other studied arable soils. Also, soils from arable sites (F1 and F4) which serve as disposal channels for mine wastes showed higher levels of Zn (401.70±16.52 mg/kg and 457.93±24.07 mg/kg respectively) than the other studied arable soils (BDL – 241.02±13.42 mg/kg). Hence, the Zn level in the mining site and a few studied arable sites (F1, F2, F4, and F8) exceed the average shale (26) value and DPR (31) tolerance limit of Zn for arable soils. The elevated Zn level at the mine site is an indication that sphalerite (ZnS) which occurs in close association with galena (PbS), is a principal component of the minerals exploited in the area. Elueze (59) reported that sphalerite and galena are often mined together because of their strong association of occurrence. Unlike Pb, a high amount of Zn was observed at some of the studied sites located farther away from the mine. Thus, in addition to site F1, sites F2, F4, and F8 showed significant levels of Zn which can be attributed to the solubility of Zn in water (57, 58). Aloh *et al*. (10) observed elevated Zn levels in agricultural soils in Ameri, Abakaliki Pb–Zn mining area, Ebonyi State, southeast Nigeria. Zn is an essential element to both humans and animals but is toxic in overdose.

3.2. Environmental Risk Assessment

The quality of the investigated soils and their effect on the environment was evaluated using enrichment factor (EF), geo–accumulation index (I_{geo}), contamination factor (CF), degree of contamination (C_d), pollution load index (PLI), ecological risk (Er) and potential ecological risk index (RI) models.

3.2.1. Enrichment factor (EF)

EF is always used to differentiate between natural and anthropogenic sources of metals (60). The EF values close to unity indicate crusted origin, those less than 1.0 suggest a possible depletion of metals, whereas EF > 1.0 indicates that the element is of anthropogenic origin (61). EF values for the analyzed heavy metals are displayed in Table 3 and enrichment levels proposed by Birth (62) (Table 2) were used to classify the level of enrichment of these heavy metals in the investigated soils.

The result shows that the mine is deficient in Al and Cr. However, it is enriched with Pb and Zn at extremely severe levels, and Cu and Mn at very severe and minimal levels respectively (Table 3). This is supporting evidence that Pb–Zn–Cu bearing ores are major components of the minerals explored at the mine. The highest enrichments of Al, Cu, and Mn are observed at the control site. Consequently, the control site is found to be severely and minimally enriched with Mn and Al respectively, and most enriched with Cu at an extremely severe level. This shows that anthropogenic sources of these metals (Al, Cu, and Mn) in the investigated soils, are a consequence of the geological nature and mineralization of the study area. The EF values signify anthropogenic sources (EF >2) for Pb, Zn, Cu, and Mn as well as lithogenic sources (EF <1) for Al and Cr presence at the mine.

EF value for arsenic (As) was not evaluated because As concentration was not empirically ascertained as it is below the instrumentation limit of detection. Fe was used as a reference element in this study. Except for the control site (F10), the studied sites showed no Al enrichment and deficient to moderate levels of Cr enrichment. Cu is the most enriched element in each of the studied sites (i.e., F2–F10) except the mine and site F1. It is enriched at moderate to extremely severe levels in the studied sites. Some of the studied sites (F2, F4, F5, F6, and F8) showed no Mn enrichment while others showed minimal to severe Mn enrichment. Pb enrichment of the mine and site F1 (close to the mine), is at an extremely severe level while it could be deficient at other studied sites (F2–10). Zn is enriched at an extremely severe level at the mine, minimally enriched at sites (F1 and F4) close to the mine, and deficient at the remaining sites. High EF values (>1) of Pb, Zn, Mn, Cu, and Cr at some of the studied sites are an indication of significant anthropogenic contributions from mining activities. Thus, the result shows that the combined effects of Pb–Zn mining activities with

the underlying geology and Pb–Zn mineralization of the study area are the sources of these analyzed heavy metals in the investigated soils.

Table 2: Classes of EF, I_{geo}, I_{IN}, CF, C_d, Er, and RI concerning enrichment, pollution, contamination level, contamination degree, potential ecological risk, and ecological risk levels, respectively (6, 32).

EF Classes	Enrichment Level	Igeo value Classes	Pollution Level
EF < 1	No enrichment	**0**; Igeo ≤ 0	Practically Unpolluted
EF = 1 – 3	Minor enrichment	**1**; Igeo = 0 – 1	Unpolluted to moderately polluted
EF = 3 – 5	Moderate enrichment	**2**; Igeo = 1 – 2	Moderately polluted
EF = 5 – 10	Moderate severe enrichment	**3**; Igeo = 2 – 3	Moderately to Strongly polluted
EF = 10 – 25	Severe enrichment	**4**; Igeo = 3 – 4	Strongly polluted
EF = 25 – 50	Very severe enrichment	**5**; Igeo = 3 – 5	Strongly to extremely polluted
EF > 50	Extremely severe enrichment	**6;** Igeo > 5	Extremely polluted
IIN Classes	**Contamination Level**		
0; $0 < I_{IN} \leq 0.5$	Uncontaminated		
1; $0.5 < I_{IN} \leq 1$	Uncontaminated to moderately contaminated		
2; $1 < I_{IN} \leq 2$	Moderately contaminated		
3; $2 < I_{IN} \leq 3$	Moderately to heavily contaminated		
4; $3 < I_{IN} \leq 4$	Heavily contaminated		
5; $4 < I_{IN} \leq 5$	Heavily to extremely contaminated		
6; $I_{IN} > 5$	Extremely contaminated		
CF Classes	**Contamination Level**	**Cd Classes**	**Degree**
CF < 1	Low contamination	$C_d < 8$	low degree of contamination
CF = 1 – 3	Moderate contamination	$C_d = 8 – 16$	Moderate degree of contamination
CF = 3 – 6	Considerable contamination	$C_d = 16 – 32$	Considerable degree of contamination
CF > 6	High contamination	$C_d \geq 32$	Very high degree of contamination
Er Classes	**Er Level**	**RI Classes**	**Risk Levels**
Er < 40	Low potential ecological risk	RI < 150	Low ecological risk
Er = 40 – 80	Moderate potential ecological risk	RI = 150 – 300	Moderate ecological risk
Er = 80 – 160	Significant potential ecological risk	RI = 300 – 600	Significant ecological risk
Er = 160 – 320	High potential ecological risk	RI > 600	High ecological risk
Er > 320	Very high potential ecological risk		

Table 3: Enrichment Factor (EF) of the Analysed Heavy Metals in the Investigated Soils.

Sampling Site	Al	As	Cr	Cu	Fe	Mn	Pb	Zn
Mine	0.03	–	0.44	30.61	Used as Reference Element	2.23	474.92	55.80
F1	0.16	–	2.87	13.40		1.72	140.19	2.63
F2	0.09	–	1.97	6.51		0.87	–	1.00
F3	0.08	–	1.60	7.48		1.50	–	–
F4	0.05	–	1.05	41.58		0.94	–	1.33
F5	0.04	–	0.69	3.94		0.87	–	–
F6	0.08	–	2.09	6.41		0.79	–	–
F7	0.68	–	7.14	25.66		4.28	–	–
F8	0.05	–	2.49	6.72		0.69	–	0.86
F9	0.45	–	6.82	15.92		4.90	–	–
F10 **(Control)**	2.60	–	–	54.67		11.34	–	–

Key: **–** = Not Calculated

Table 4: Geo-accumulation index (I_{geo}) of the Analysed Heavy Metals and Improved Nemerow Index (I_{IN}) of the Studied Sites.

									Igeoave	**Igeomax**	**IIN**
Sampling Site	**Al**	**As**	**Cr**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**			
Mine	–4.09	–	–0.40	5.74	0.80	1.96	9.69	6.60	2.54	9.69	7.08
F1	–2.57	–	1.60	3.83	0.08	0.87	7.22	1.48	1.56	7.22	5.22
F2	–2.71	–	1.72	3.45	0.74	0.54	–	0.74	0.56	3.45	2.47
F3	–3.06	–	1.34	3.57	0.66	1.24	–	–	0.47	3.57	2.55
F4	–3.18	–	1.33	6.64	1.26	1.17	–	1.67	1.11	6.64	4.76
F5	–3.18	–	1.06	3.57	1.59	1.39	–	–	0.55	3.57	2.55
F6	–2.91	–	1.83	3.45	0.76	0.42	–	–	0.44	3.45	2.46
F7	–2.04	–	1.34	3.19	–1.49	0.60	–	–	0.20	3.19	2.26
F8	–3.50	–	2.27	3.70	0.95	0.42	–	0.74	0.57	3.70	2.65
F9	–2.20	–	1.72	2.94	–1.05	1.24	–	–	0.33	2.94	2.09
F10 **(Control)**	–1.92	–	–	2.48	–3.30	0.21	–	–	–0.32	2.48	1.77

Key: **–** = Not Calculated

Table 5: Contamination Factor (CF), Degree of Contamination (C_d), and Pollution Load Index (PLI) of the Investigated Soils.

									Cd	**PLI**
Sampling Site	**Al**	**As**	**Cr**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**		
Mine	0.09	–	1.03	99.89	3.24	5.83	291.60	99.85	501.53	6.89
F1	0.25	–	4.11	26.63	1.97	2.73	52.42	2.87	90.98	3.49
F2	0.23	–	4.45	20.42	3.12	2.19	–	1.72	32.13	1.99
F3	0.18	–	3.42	22.19	2.95	3.55	–	–	32.29	1.86
F4	0.17	–	3.39	186.40	4.45	3.37	–	3.27	201.05	2.92
F5	0.17	–	2.81	22.19	5.60	3.92	–	–	34.69	1.98
F6	0.20	–	4.79	20.42	3.16	2.00	–	–	30.57	1.83
F7	0.36	–	3.42	17.09	0.66	2.28	–	–	23.81	1.54
F8	0.13	–	6.49	24.41	3.61	2.00	–	1.72	38.36	2.00
F9	0.33	–	4.45	14.42	0.90	3.55	–	–	23.65	1.69
F10 **(Control)**	0.40	–	–	10.43	0.19	1.73	–	–	12.75	1.04

Key: **–** = Not Calculated

Table 6: Ecological Risk (Er) and Potential Ecological Risk Index (RI) of the Analysed Heavy Metals and Investigated Soils.

	Er								RI
Sampling Site	**Al**	**As**	**Cr**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**	
Mine	–	–	2.06	499.45	–	5.83	1458.00	99.85	2065.19
F1	–	–	8.22	133.15	–	2.73	262.10	2.87	409.07
F2	–	–	8.90	102.10	–	2.19	–	1.72	114.91
F3	–	–	6.84	110.95	–	3.55	–	–	121.34
F4	–	–	6.78	932.00	–	3.37	–	3.27	945.42
F5	–	–	5.62	110.95	–	3.92	–	–	120.49
F6	–	–	9.58	102.10	–	2.00	–	–	113.68
F7	–	–	6.84	85.45	–	2.28	–	–	94.57
F8	–	–	12.98	122.05	–	2.00	–	1.72	138.75
F9	–	–	8.90	72.10	–	3.55	–	–	84.55
F10 **(Control)**	–	–	–	52.15	–	1.73	–	–	53.88

Key: – = Not Calculated

3.2.2. Geo–accumulation index (I_{geo}) and improved Nemerow index (I_{IN})

I_{geo} and I_{IN} values for the analyzed heavy metals studied sites respectively are given in Table 4. I_{geo} evaluation for the analyzed heavy metals is used to determine the level of contamination of the study area by individual heavy metals (28, 63).

Using Muller's (27) classification presented in Table 2, I_{geo} values show that the mine is extremely polluted by Pb, Zn, and Cu (I_{geo} >5) and unpolluted by Al and Cr (I_{geo} < 0). However, the control site is unpolluted by Al and Fe but moderately to strongly polluted by Cu and unpolluted to moderately polluted by Mn. All studied sites are unpolluted by Al but are polluted by Cu at moderate to extreme levels (I_{geo} >2). Most of the investigated arable soils are moderately polluted by Cr (Class 2). The level of Fe and Mn pollution in the studied sites ranges from unpolluted to moderately polluted. Sites close to the mine are extremely and moderately polluted by Pb (F1) and Zn (F1 and F4) respectively. These observations ascertained that of all the analyzed heavy metals, Pb and Zn are the most accumulated heavy metals at the mine while Cu is the most accumulated heavy metal in all the studied sites except at the mine and site F1 where Pb is the most accumulated heavy metal. This suggests that Pb, Zn, and Cu could be absorbed by food crops grown in the mine, sites F1 and F4 where they will be accumulated. The concentrations of Cr, Pb, and Zn at the control site are below I mg/kg suggesting that the site could also be unpolluted by these metals in addition to the unpollution of the site by Al and Fe that was ascertained by the result. These show that human activities from Pb–Zn ore mining and processing increase the geological concentrations of these heavy metals in the arable soils (via diffuse pollution, wet and dry deposition of metals, erosion and leaching of mine wastes, etc.) within the study area which leads to the increase in geo–accumulation of the heavy metals over time (63).

I_{IN} gives a comprehensive description of the pollution status of the study area because it considers input from all other pollution indices (28, 29). According to Fostner *et al*. (64) categorization, the mine and site F1 are extremely contaminated (Class 6) while site F4 is heavy to extremely contaminated. These can be attributed to Pb–Zn mining activities at the mine and releases from mine wastes dumped or disposed of at sites F1 and F4. Other studied sites are moderately to heavily contaminated (Class 3) except the control site which is moderately contaminated. The descending sequence for contamination of the studied sites is as follows: mine >F1 >F4 >F8 >F3 and F5 >F2 >F6 >F7 >F9 >F10. Thus, the mining site is the most contaminated while the control is the least contaminated indicating the influence of mining activities.

3.2.3. Contamination factor (CF), degree of contamination (C_d), and pollution load index (PLI)

CF of the analyzed heavy metals, C_d, and PLI of the investigated soils are summarised in Table 5 and interpreted using levels and classes proposed by Hakanson (33) which is presented in Table 2. The mine site is highly contaminated (CF >6) by Pb, Cu, and Zn, considerably contaminated by Fe and Mn and moderately contaminated by Cr. Thus, contamination of the mine is dominated by Pb, Cu, and Zn. However, the control site showed low contamination by Al and Fe, moderate contamination by Mn, and high contamination by Cu.

All studied sites showed low (CF <1) and high (CF >6) contamination of Al and Cu respectively. Most of the studied sites are considerably contaminated by Cr (CF = 3 – 6). The sites showed low to considerable levels of Fe contamination as well as moderate to considerable levels of Mn contamination. The mine and site F1 are highly contaminated by Pb while other studies sites are assumed to be lowly contaminated by Pb since their Pb content is below 1 mg/kg. Zn contaminates the mine at a very high level but the studied arable sites showed low to moderate Zn contamination. The high CF value (>1) for Pb, Zn, Cu, Mn, Cr, and Fe in different studied sites of the study area, is attributed to anthropogenic activities associated with Pb–Zn ore mining and processing which increase the geologic concentration of the heavy metals in arable soil around the mine.

C_d gives the summation of the contamination factor (CF) for all contaminants in a given sampling site (32). Table 5 shows that the studied sites are contaminated in the following decreasing order; mine >F4 >F1 >F8 >F5 >F3 >F2 >F6 >F7 >F9 >F10. This indicates that the mining and control sites are the most and least contaminated respectively. The contamination degrees of most studied sites (mine, sites F1, F2, F3, F4, F5, and F8) are very high (C_d > 32). Their contamination is dominated by Cu (all sites), Pb (mine and site F1 only), and Zn (mine only). The control site shows a moderate degree of contamination dominated by Cu.

A PLI value under zero indicates unpolluted soils; zero indicates perfection; a value of one or unity indicates the presence of only baseline levels of pollutants and values above one would indicate progressive deterioration of the site soil quality (34, 65). PLI values in this study (Table 5) are high (PLI > 1) except the control site with PLI value of approximately one. This indicates that the control site is considered unpolluted since the result suggests that the pollutants at this site are present at baseline levels. PLI values show that pollution of the studied sites follows a descending order: mine >F1 >F4 >F8 >F2 >F5 >F3 >F6 >F9 >F7 >F10. Thus, the mining site is the most polluted due to the Pb–Zn mineral exploration on this site.

3.2.4. Ecological risk assessment

The persistent nature of heavy metals results in their excessive accumulation in arable soils which affects food quality and safety because plants can absorb and store these heavy metals in their tissues. Consequently, when consumed by humans heavy metals increase the risks of severe diseases, such as cancer, leukemia, and kidney or liver damage (66). Soils contaminated by toxic heavy metals can enter the human body via different exposure routes (such as oral ingestion, inhalation, and dermal contact) and cause serious ecological and human health risks (67). Thus, it is necessary to evaluate the ecological risk factor (Er) of the individual analyzed heavy metals and the ecological risk index (RI) of the studied sites.

Er and RI were calculated to estimate the toxicity of the analyzed heavy metals in investigated soils. Er and RI classifications as specified by Hakanson (33) and reported in Table 2, were applied in the interpretation of Er and RI values of the analyzed heavy metals shown in Table 6. At the mine, Cu and Pb pose a very high ecological risk (Er > 320) while Zn has a significant potential for ecological risk. This implies that food crops, animals, and mine workers are exposed to a high risk of Pb, Zn, and Cu poisoning at the mine site (68). However, a low risk of contamination from Cr, Mn, Pb, and Zn and a moderate contamination risk from Cu was observed at the control site.

The Er of Al, As, and Fe were not evaluated because Al and Fe have no certified toxic response factor (Tr) while the levels of As in the investigated soils were below the instrumentation limit of detection. The result shows that the potential ecological risk factors of Cr and Mn in all the studied sites are low (Er < 40). Thus, Cr and Mn do not pose any ecological risk to the environment. Cu has a very high potential ecological risk factor at mine and site F4 (Er > 320) and ranges between moderate to significant levels at other studied sites with the least Er of Cu observed at the control site. There is a very high and high potential risk of Pb contamination at the mine and site F1 respectively. Contamination risk from Pb at other studied sites could be assumed to be low due to the low level of Pb in these sites (< 1 mg/kg). Zn has a significant level of potential ecological risk at the mine (Er= 80–160) and low potential ecological risk at the studied arable soils.

The RI values of the analyzed metals in the investigated soils showed that the mine and control site had the highest and lowest risks of contamination respectively. This indicates that Pb–Zn mining activities affect the risk of contamination of the study area by these heavy metals. The mine and site F4 showed a high ecological risk index (RI > 600) while site F1 is considered to be at risk of contamination with a significant ecological risk index. This signifies that mine workers and Adudu dwellers close to the mine and arable farms used as disposal channels for mine wastes (i.e., sites F1 and F4) are exposed to toxic levels of Pb, Zn, and Cu through inhalation and dermal contact with the soils from the sites. Also, food crops grown on these sites are at high risk of being contaminated by Pb, Zn, and Cu which will be inimical to human health when consumed (6). A low risk of contamination was observed at the other studied arable sites (F2, F3, F5, F6, F7, F8, F9, and F10) due to their low ecological risk index (RI < 150). The high risk of contamination observed in arable sites F1 and F4 could be attributed to the discharge of mine wastes and tailings to these sites due to their proximity to the mine. The decreasing sequence of potential ecological risk index (RI) of the studied sites from the analyzed heavy metals is as follows: mine >F4 >F1 >F8 >F3 >F5 >F2 >F6 >F7 >F9 >F10. This sequence shows a direct relationship between RI and degree of contamination (C_d) due to their similar trends.

4. CONCLUSION

This study clearly showed that Pb–Zn–Cu bearing ores such as galena, sphalerite, chalcopyrite, bornite, smithsonite, cerussite, and azurite are principal minerals exploited in the mine because of the elevated concentrations of Cu, Fe, Mn, Pb, and Zn at the mining site. Concentrations of the analyzed heavy metals varied greatly away from the mine. Thus, the levels of these heavy metals in the arable soils are related to the Pb–Zn mining activities such as washing and erosion of tailings, discharge, and leaching of mine wastewater, atmospheric deposition (wet and dry) of metals, etc. Weathering or fragmentation of the geochemical composition of the rocks in the study area is a significant contributing factor to the source of these heavy metals. In soil quality assessment, the EF, $I_{geo,}$ and CF showed that the mining site is very severely to extremely severely enriched, extremely polluted, and highly contaminated respectively Pb, Zn, and Cu. I_{IN}, $C_{d,}$

and PLI showed that the mine and the nearby arable farms are the most deteriorated (contaminated and polluted) and the quality of soil improves away from the mining vicinity. Er revealed that the level of Pb, Zn, and Cu at the mine present a significant to very high risk of contamination. Cr and Mn in all the investigated soils pose no ecological risk but Cu poses moderate to very high ecological risk in the studied sites. RI showed that the presence of the analyzed heavy metals at the mine and the close arable farms (sites F1 and F4) can have serious adverse effects on plants, animals, and humans on the sites. However, the control and other studied sites had a low ecological risk index. Therefore, anthropogenic activities from Pb–Zn mining and natural processes (geologic weathering and Pb–Zn mineralization of the area) are the sources of these analyzed heavy metals in the arable soils around the mine site. This study has shown that the arable soils within the vicinity of the Pb–Zn mine, are not good for growing food crops because these heavy metals will enter the food chain via their uptake from soil.

5. CONFLICT OF INTEREST

The authors declare that they have no competing interests. All authors have endorsed the publication of this research.

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