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ORIGINAL ARTICLE

Physico-chemical Properties and Heavy Metal Contamination Levels of Soils from Riruwai Mining Area, North-western Nigeria

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Abstract

This study was aimed to investigate the physico-chemical properties and heavy metals contamination levels of the soils around Riruwai mining area, North-western Nigeria. A total of 60 surface soil samples from four (4) sampling sites which include 18 from active mine sites, 12 from abandoned mine sites, 21 from farmlands and 9 from control site were collected during the dry and rainy seasons. The physico-chemical properties (pH, Electrical conductivity, soil organic matter and cation exchange capacity) were determined using various analytical techniques. The concentrations of heavy metals were analysed using Microwave Plasma Atomic Emission Spectrometer (MP-AES) and the measured concentrations were used to evaluate the pollution load index (*PLI*). The findings of the study indicated that mining activities had a significant impact on the physicochemical properties of the soils. The levels of arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc are in the range of 13.40-35.23, 0.91-13.50, 59.52-116.05, 0.01-1.01,115.19-314.49,11.04-26.04, 43.11-245.00 and 135.09-1653.40, and 7.62-29.12, 0.07-11.61, 38.50-96.24, 0.01- 0.35, 114.5-256.00, 7.34 to 24.43, 39.07-237.00 and 115.30-1394.56 during the dry and rainy seasons respectively. Except for mercury, chromium, manganese and nickel, all the heavy metals were above the recommended maximum limit set by FAO/WHO (2011) in both seasons. The *PLI* values indicated that the soils in active and abandoned mining sites are strongly polluted by heavy metals, while farmland soils are moderately polluted, and control site soils were unpolluted. The soils in the study area are significantly contaminated by heavy metals, particularly in active and abandoned mining sites and the contamination had slightly spread to farmland, suggesting a significant need for proper containment of heavy metals pollution levels in the area especially arsenic, cadmium, lead and zinc.

Keywords: Heavy metals, mining activities, physico-chemical properties, Riruwai mining area, pollution load index

Introduction

Mining, despite its economic benefits, is well documented as one of the most significant sources of heavy metal pollution in the soil (Sun et al., 2018; Sihotang et al., 2021). Heavy metals are released into the environment due mining operations through erosion, weathering and leaching (Rodrı´guez et al., 2009). Once absorbed by the body, heavy metals continue to accumulate in key organs such kidney, liver, brain, liver and bones for many years causing serious health challenges (Kabata-Pendias, 2011). For example, acute exposure to arsenic can cause nausea, abdominal pain, muscle spasms and diarrhoea, whereas chronic exposure can cause diabetes. Lead, on the other hand, causes renal cancers and interferes with the normal functioning of reproductive and nervous systems (Ebrahimi et al., 2020). Mercury can harm the endocrine system and cause kidney damage and cause respiratory failure (Kim et al., 2016). Cadmium has been linked to breast, hepatic, pancreatic, lung and skin cancers (Buha et al., 2017). Asthma and shortness of breath are caused by inhaling high levels of chromium (IV) compounds. Similarly, Nickel is known to cause both oral and intestinal cancer. It is also linked to depression, heart attacks, haemorrhages and kidney problems. Even though zinc is essential for human life, excessive consumption may have non-carcinogenic effects on human health. It has the potential to impair growth and reproduction (Cao et al., 2010). The route of exposure to heavy metals of the people living near the mining area are reported to be direct ingestion, dermal contact, inhalation and consumptions of vegetables, water and animals (Halatek et al., 2014).

Soil, as an essential component of the ecological system, functions as a carrier of heavy metals as well as a medium for heavy metals spread to the atmosphere, organisms and water bodies (Adedeji et al., 2019). Heavy metals in soils are potential environmental threats that can harm human health via a variety of absorption pathways, including direct ingestion, dermal contact and inhalation (Wu et al., 2017). Several studies have underscored the importance of soil physico-chemical properties on soil quality and the behaviour of heavy metals in soils (Keskin and Makineci, 2009; Fashola et al., 2020). The concentrations of heavy metals in the soils depend on the soil's physico-chemical properties like pH, Electrical conductivity, organic matter and cation exchange (Bhatti et al., 2016). High organic matter content, for example, can enhance metal adsorption, reducing mobility in the soil, whereas acidic soil conditions (lower pH) reduce soil cation exchange capacities and increase metal solubility in the soil environment, making metals more mobile and toxic (Ayangbenro and Babalola 2017).

There are numerous studies on the extent of heavy metal contamination in the environment caused by mining activities in various parts of the world. However, to the best of our knowledge, no scientific research has been conducted to assess the physicochemical properties and heavy metal contamination levels in the study area. For this reason, this study was aimed to investigate the physico-chemical properties and heavy metals contamination levels of the soils around Riruwai mining area, North-western Nigeria.

Materials and Methods

Description of the study area

Riruwai, the headquarters of Doguwa Local Government Area, is located in Kano State's extreme south. It covers an area of 129 km^2 and is located between latitude 10°43"97"N - 10°45'01"N and longitude 8°43"3"E - 8°47'39" E (Rilwanu, 2017). Riruwai is one of Nigeria's younger granite complexes. The complex is an example of eroded roots of an alkaline volcano that formed as part of an early Jurassic chain of anorogenic centers (Ogunleye et al., 2006). According to the 2006 census, Riruwai has a population of 150,645 people (NPC, 2006).

Riruwai is principally a mining community. Large scale mining began in 1979 and was expanding rapidly with close to 900 tons of Zn-Sn ore production per day. The mining was closed after five years of continued operation. Artisanal and small mining are still taking place in the area. The research carried out by Nigerian Mining Cooperation revealed that close to five million tons of mineral Ore containing tin and zinc were deposited in Riruwai community. Ore mineralogy study confirmed the presence large deposits of columbite, granite, copper, zinc, lead and uranium (Amosu., 2021). The map of Riruwai is shown in Figure 1.

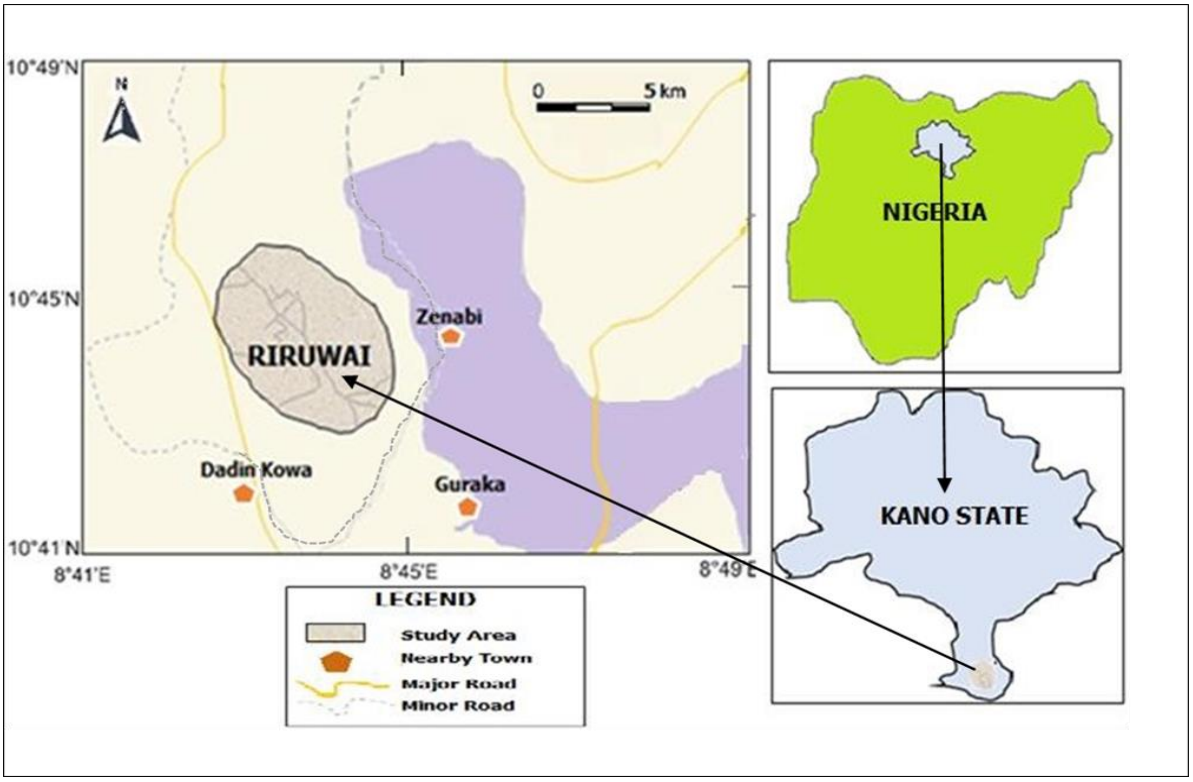

Figure 1. Map of Study Area

Soil Sampling and Collection

A total of 60 surface soil samples from four (4) sampling sites which include 18 from active mine sites, 12 from abandoned mine sites, 21 from farmlands and 9 from control site were collected over a depth of 0-20 cm at the sampling sites using steel soils Auger in two different seasons i.e. rainy season (August, 2020) and dry season (February, 2020). A control samples were collected 6.00 km away from other sampling sites in an area with the same lithology but with no human interference as reported by Ngole-Jeme and Fantke (2017). 1.00 kg of soil were collected from each layer. A grid of equal space lines was constructed and sampling sites were divided into equal sub-areas and an equal distance of 10.00 m was measured at intervals between each sampling site. In order to obtain representative and uniform samples, each soil sample was obtained by mixing 3 sub-samples at each sampling point to form a composite sample. A 1.00 kg from the mixed samples was selected by quartering; stored in a polyethylene bag, labelled and transported to laboratory for analysis. Soil samples were air-dried at room temperature. The large fragments, stones and gravels was removed. The soil was pulverized and sieved through a 2.00 mm polyethylene sieve, homogenized and stored in polyethene bags (Fan and Wang, 2017)

Determination of Physico-chemical Parameters of the Soils

The pH of the soil was measured using pH meter (Hanna HI9921) as described by Beane et al. (2016): a 4.00 g of each sample was agitated in 10.00 cm^3 of deionized water using a 25 cm^3 centrifuge tube and left overnight. The pH of the supernatant was measured and calibrated at pH 4.00 and 7.00. Electrical conductivity was measured based on the procedure outlined by Sani et al. (2012) as follows: 25.00 g of air-dried soils sample was placed into a 250 cm^3 beaker and 50.00 cm^3 of deionized water was added slowly drop by drop evenly over the entire soils surface until the soils appeared wetted. A stainless steel spatula was used to form a homogeneous soils saturated paste. The beaker was then covered with a petri-dish; 50.00 cm^3 deionized water was added and agitated for one hour. The diluted extract (40.00 cm^3) was placed into a 100 cm^3 beaker and the conductivity meter (Hanna HI198331) was inserted and the electrical conductivity of the soils was recorded in µS/cm. For Cation exchange capacity (CEC) determination, a 10.00 g of soil sample was weighed into a 100 cm^3 plastic beaker. A 40.00 cm^3 of 1.00 mol/dm^3 ammonium ethanoate solution pH 7 buffer was added and the suspension was stirred with a glass rod and left overnight. It was suction-filtered with 55 mm Buchner funnel. The residue from filtration was leached with 25.00 cm^3 portions of 1.00 mol/dm^3 NH_4Cl solution. The solution was discarded and the electrolyte washed out of the sample with 150.00 cm^3 concentrated ethanol. The sample was allowed to drain completely and leached gradually with acidified NaCl (acidified with dilute HNO_3) to a 250.00 cm^3. 50.00 cm^3 of 1.00 % boric acid was measured into a 250 cm^3 conical flask and 3 drops of mixed indicator were added. The acidified NaCl leachate was transferred into a 500 cm^3 Kjeldahl flask and 10.00 cm^3 of 1.00 mol/dm^3 NaOH and anti-bumping granules were added. The leachate was distilled over boric acid solution. Ammonium borate distillate (1.50 cm^3) was titrated with standard 0.10 mol/dm^3 HCl and the CEC was determined according to the following equation (Todorovi et al., 2001):

$$\text{CEC}\left(\frac{\text{cmol}}{\text{kg}}\right) = \frac{(\textit{Titre-Blank}) \times M \times 100}{\textit{Weight of the sample}} \quad (1)$$

A loss-on-ignition method adopted by Bakr and El-Ashry (2018) was used to determine the organic matter of the soil. In this method, 3.00 g of the air-dried soils were heated in the oven at 105°C for 24 hours, cooled in a desiccator and weighed to obtain the oven-dried weight. The samples were combusted at 550 ◦C for 2 hours in a muffle furnace. After combustion, the samples were cooled in a desiccator and weighed. The soil organic matter (SOM) was computed based on Schulte and Hopkins (1996) equation:

$$SOM = \frac{SW_{OD}\text{-}SW_{AC}}{SW_{OD}} \times 100\ \% \quad (2)$$

Where: SW_{OD} is the oven-dry weight of the soil sample, SW_{AC} is the weight after combustion at 550 °C

Determination of heavy metals in soil

The sample was air-dried at room temperature and visible materials such as stones, plant root residues and tree leaves were removed. The sample was pulverized, passed through a 0.15 mm nylon screen, sieved and homogenized. The soil sample was digested with a mixture of three concentrated acids (HNO_3, HF and $HClO_4$). Soil sample (0.50 g) was placed in a 200 cm^3 Teflon beaker. 10.00 cm^3 of HNO_3, 10.00 cm^3 of HF and 10.00 cm^3 of $HClO_4$ were added and the mixture was heated on an electric hot plate at 180 °C until the solution was almost dried. The beaker was removed and cooled to room temperature. 5.00 cm^3 of concentrated HNO_3, 5.00 cm^3 of HF and 5.00 cm^3 of $HClO_4$ were added and the mixture was boiled until dense white fumes appeared. The beaker was removed, cooled and 15.00 cm^3 of deionized water was added and boiled for 5

minutes. The digest was filtered using Whatman filter paper no. 42 into a 50 cm^3 volumetric flask. The wall of the beaker was washed three times with 10.00 % dilute HNO_3. The solution was made up to the mark with the HNO_3 for heavy metals analysis. Blank solution was treated and prepared in a similar way. The concentrations of As, Cd, Cr, Hg, Mn, Ni, Pb and Zn were analysed at their respective wavelengths using Microwave Plasma Atomic Emission Spectrometer (MP-AES). The concentrations of heavy metals were reported in mg/kg.

Pollution Load Index

The pollution load index (*PLI*) was used to identify multi-element contamination. It was calculated for every sampling site using the equation adopted by Khalifa and Gad (2018):

$$PLI = \left(C_f^1 \times C_f^1 \times C_f^1 \times \ldots C_f^n\right)\frac{1}{n} \quad (3)$$

where: n = Number of metals investigated and C_f^n = Contamination factor for n^{th} element. The value of contamination factor (C_f) was computed as:

$$C_f = \frac{C_{sample}}{C_{background}} \quad (4)$$

where, C_{sample} = Concentration of heavy metal in sample, $C_{background}$ = Concentration of the heavy metal in the background.

Quality control Statistical analysis

Analytical grade reagents were used throughout the study. All glassware and plastic containers were soaked overnight in 10% (v/v) nitric acid, washed three times with deionized water and oven dried. The containers were further dried in a desiccator for 20 minutes before use for analysis (Ashraf et al., 2011). All samples were analysed in triplicate. The standard solution of each heavy metal was prepared by successive dilution of certified standards (1000 mg/dm^3) procured from Sigma Aldrich and calibration curve of each heavy metal was constructed. The calibration curves with $R^2 > 0.999$ were accepted for concentration calculation. Blank determinations were ran to correct any background contamination from reagents, filter papers or any other systemic source of error. All data were treated as mean ± standard deviation. One-way Analysis of Variance (ANOVA) were carried out using SPSS 23.0 (SPSS Inc., Chicago, USA). One-way Analysis of Variance (ANOVA) and correlation analysis were used to compare heavy metal and physico-chemical parameters contents from the different sampling sites. Statistical significant difference was established using Tukey HSD post-hoc test ($p \leq 0.05$). Microsoft Excel 2013 were used in plotting graphs.

Results and Discussion

Physico-chemical Parameters of Soils

Tables 1 and 2 show the physicochemical properties of the soils at the active mining site, abandoned mining site, farm and control site during the dry and rainy seasons. The pH values of the soil during the dry season ranged from 6.05 (active mining site) to 6.78 (control site) with highest value recorded in the control site while the lowest was found at the active mining sites.

The pH values of 6.26 (abandoned mining site) and 6.48 (farm) fell between the lowest and highest observed values. During the rainy season, the pH values varied from 5.72 (active mining sites) to 6.52 (control sites). The pH values of 5.96 (abandoned mining site) and 6.03 (farms) lied between the highest and lowest experimental values. The pH values observed in this study were closer to the published literature values of 5.91 (mining sites) and 6.85 (control sites) determined in the soils of the Ilesha gold mining site in Osun state, Nigeria (Abiya et al., 2019). The pH values of the soils in all the sampling locations were generally higher during the dry season and decreased in the following order: active mining sites > abandoned mining sites > farms > control sites. The formation of sulfuric acid from the oxidation of pyrite in the ore may be responsible for the low pH values in the active and abandoned mining sites compared to farms and control sites (Boularbah et al., 2006). The acidic nature of mining site soils, particularly during the rainy season, increases the mobility of potentially toxic heavy metals, and hence their potential to harm the environment (Ngole-Jeme and Fantke, 2017).

The electrical conductivity values ranged from 700.68 (control site) to 4400.76 µS/cm (active mining site) with 2300.02 (farm) and 2500.31 µS/cm (abandoned mining site) falling between the lowest and highest values during dry season. During the rainy season, the electrical conductivity values spread from 1000.52 µS/cm (control site) to 4600.11 µS/cm (active mining site). The electrical conductivity values of 2520.02 (farm) and 2607.93 µS/cm (abandoned mining site) fell between the extreme values. The findings of this research revealed that electrical conductivity values decreased during the dry season and increased during the rainy season. This was consistent with the findings of Salem et al. (2020) who reported similar trends when they studied the physiochemical properties and concentration of heavy metals in agricultural soils fertilized with chemical fertilizers.

The organic matter of the soil ranged from 1.11 (active mining site) to 11.13 % (control) with 2.04 (abandoned mining site) and 4.08 (farm) falling between the highest and lowest observed values determined during the dry season. During the rainy season, the organic matter varied from 1.62 (active mining site) to 13.93 % (control site). The percentage organic matter values of 2.27 % (abandoned mining site) and 4.62 % (farm) fell between the maximum and minimum experimental values. The observed values of soil organic matter were slightly lower than reported literature values of 4.7-6.7 % determined in soils of Draa Lasfar Mine in Marrakech, Morocco (Yassir and Alain, 2016). The highest percentage of soil organic matter is generally observed during the rainy season with the maximum value recorded at the control site and the minimum in the active mining sites. Soil organic matter levels less than 3.44 percent are considered very low for tropical soils (Landon, 1991). The soil samples analysed in active and abandoned mining sites were low in organic matter based on this rating. Prematuri et al. (2020) discovered comparable findings when they investigated the impact of nickel mining on soil properties and the growth of two fast-growing tropical tree species.

The cation exchange capacity of the soil varied from 12.59 to 37.45 cmol/kg and 13.87 to 42.35 cmol/kg in dry and rainy season respectively. In the dry season, highest cation exchange capacity value was observed at control site while the lowest was recorded in the active mining site. A similar pattern was also observed during the rainy season. According to the Landon (1991) classification, a soil with a cation exchange capacity value of 5-15 cmol/kg is regarded as low for agricultural soils. Based on this rating, the soils in the active mining sites were low in cation exchange capacity in both seasons. The values decreased in the following order: control site > farm > abandoned mining site > active mining site. Lower cation exchange capacity values in the active and abandoned mining sites might be attributed to the low content of soil organic matter in the sites (Ngole-Jeme and Fantke, 2017). The present findings corroborates the findings of Abah et al. (2014). Cationic exchange capacity represents the soil's ability to absorb or release cations and, as a result, is an important parameter in heavy metal-contaminated sites. It measures the soil's ability to bind or hold exchangeable cations (Salem et al., 2020).

Table 1. Physico-Chemical Parameters of the Soil around Riruwai Mining area during the Dry Season

Sampling Location	pH (H_2O)	EC (µs/cm)	SOM (%)	CEC (cmol/kg)
RSS1	6.05 ± 0.02	4400.76 ± 5.17	1.11 ± 0.02	12.59 ± 0.11
RSS2	6.26 ± 0.03	2500.31 ± 2.83	2.04 ± 0.01	17.61 ± 0.17
RSS3	6.48 ± 0.02	2300.02 ± 2.88	4.08 ± 0.02	22.52 ± 0.12
RSS4	6.78 ± 0.04	700.68 ± 1.281	11.13 ± 0.03	37.45 ± 0.45

Values are mean ± standard deviation (n = 3), **RSS1** = Active mining sites, **RSS2** = Abandoned mining sites, **RSS3** = farm, **RSS4** = Control site. **EC** = Electrical conductivity, **SOM** = Soil organic matter, **CEC** = Cation exchange capacity

Table 2. Physico-Chemical Parameters of the Soil around Riruwai Mining area during the Rainy Season

Sampling Location	pH (H_2O)	EC (µs/cm)	SOM (%)	CEC (cmol/kg)
RSS1	5.72 ± 0.01	4600.11 ± 6.51	1.62 ± 0.02	13.87 ± 0.07
RSS2	5.96 ± 0.04	2607.93 ± 2.65	2.27 ± 0.03	20.01 ± 0.14
RSS3	6.03 ± 0.03	2520.02 ± 4.05	4.62 ± 0.03	24.22 ± 0.11
RSS4	6.52 ± 0.02	1000.52 ± 2.33	13.93 ± 0.06	42.35 ± 0.26

Values are mean ± standard deviation (n = 3), **RSS1** = Active mining sites, **RSS2** = Abandoned mining sites, **RSS3** = farm, **RSS4** = Control site. **EC** = Electrical conductivity, **SOM** = Soil organic matter, **CEC** = Cation exchange capacity

Heavy Metals Concentrations in the Soils

The levels of heavy metals in four sampling locations (active mining site, abandoned mining site, farmland and control site) during dry and rainy seasons are shown in Tables 3 and 4. The concentrations of arsenic during the dry season ranged from 13.40 (control site) to 35.23 mg/kg (active mining site) with 21.54 mg/kg (farm area) and 33.72 mg/kg (abandoned mining site) falling between the lowest and highest experimental values. The highest level of arsenic was found in the active mining area, while the lowest value was observed at the control site. The concentration of arsenic was above the threshold value of 20.00 mg/kg recommended by WHO/FAO (2001) except in the control site, which implied that there was considerable arsenic contamination. During the rainy season, the concentrations of arsenic ranged from 7.62 (control site) to 29.12 mg/kg (active mining site). The levels of 13.09 mg/kg (farm) and 18.50 mg/kg (abandoned) fell between the highest and lowest values of arsenic determined. Except in the active mining site, the level of arsenic in all the sampling locations were below the WHO/FAO (2001) permissible limit. Ameh et al. (2020) observed similar pattern of higher heavy metals concentrations during dry season than the rainy when they studied the seasonal variations of toxic metals in soils of Okaba coal mining area, in Kogi, Nigeria. Eludoyin et al. (2017) also observed similar trends when they studied the effects of artisanal old mining activities on soil properties in Itagunmodi, Southwestern Nigeria.

The levels of cadmium (mg/kg) determined varied from 0.91 (control site) to 13.50 (active mining site). The concentrations (mg/kg) of 1.51 (farm) and 5.01 (abandoned mining site) lied between the lowest and highest cadmium values obtained during the dry season. The concentration of observed cadmium are above the recommended value of 3.00 mg/kg set by WHO/FAO (2001) in agricultural soils for active and abandoned mining sites and below the recommended value for farm and control areas. During the rainy season, the concentrations of cadmium (mg/kg) spread from 0.07 (control site) to 11.61 (active mining site) with 0.09 mg/kg (farm area) and 2.15 mg/kg (abandoned mining site) falling between the extreme experimental values. The concentrations of cadmium in all the sampling sites are below the recommended values except in active mining site where the observed cadmium concentration was more than three times higher than the threshold values. The observed values of cadmium in the present study are slightly lower than reported literature values of 12.62-20.70 mg/kg determined in soils around abandoned Pb-Zn mines in Yelu in Bauchi State, Northern Nigeria (Sanusi et al., 2017).

The concentration of chromium spread from 59.52 to 116.05 mg/kg during the dry season. The highest concentration (59.52 mg/kg) was observed at the active mining site while the lowest concentration (59.52 mg/kg) was found at the control site. The experimental values of 96.44 mg/kg (farm site) and 103.37 mg/kg (abandoned mining site) fell between the highest and lowest obtained concentrations. The observed concentrations of chromium in the active and mining sites were slightly higher than WHO/FAO (2001) threshold concentration of 100.00 mg/kg, whereas the chromium levels in farm and control site were lower than the threshold value. During the rainy season, the levels of chromium ranged from 38.50 to 97.24 mg/kg with 71.36 mg/kg (farm) and 84.73 mg/kg (abandoned mining) values falling between the observed extremes. The levels of chromium in all the sampling were below the threshold value of 100.00 mg/kg established by WHO/FAO (2001). The concentrations of chromium during the rainy season were generally lower than the dry season. The experimental chromium values were relatively close to the literature values of 46.00 to 123.00 mg/kg reported by Fazekaová and Fazekaš (2020) when they studied the soil quality and heavy metal pollution assessment of iron ore mines in Nizna Slana, Slovakia. Olarinoye et al. (2021) also found a chromium content of 151.14 mg/kg in the soils of the Jos mining area, which was relatively similar to the experimental values of 116.05 mg/kg and 103.37 mg/kg found in active and abandoned mining sites respectively during the dry season.

The levels of mercury in the soils varied from 0.01 (control site) to 1.01 mg/kg (active mining site) with 0.50 mg/kg (farm) and 0.84 (abandoned mining site) fell between the lowest and highest observed values during the dry season. During the rainy season, the mercury concentrations ranged from 0.01 (control site) to 0.35 mg/kg (active mining site). The values of 0.36 mg/kg (farm) and 0.67 mg/kg (abandoned mining site) fell between the lowest and highest concentrations of mercury determined. Focus et al. (2021) reported similar results of 0.05 mg/kg mercury in soil in the mining area of the Rwamagasa gold mine in Tanzania's Geita region. The concentrations of mercury in all the sampling locations are below the threshold value of 2.00 mg/kg set by WHO/FAO (2001) in both dry and rainy seasons, denoting less or no apparent contamination of soil by mercury. Mercury and its compounds effect the nervous system, increased mercury exposure can alter brain functions and cause tremors, irritability, memory problems and changes in hearing or vision (Obasi et al., 2020). The observed concentrations of manganese (mg/kg) during the dry season ranged from 115.19 to 314.49. The active mining site had the highest concentration (314.49), while the control site had the lowest concentration (115.19). The experimental values of 148.11 and 203.04 are between the lowest and highest values of manganese determined in the soils. Manganese observed concentrations during the rainy season are relatively lower than that of the dry season, but not statistically significant. The values are 256.00, 155.03, 96.00 and 114.15 for active mining site, abandoned mining site, farm and control site respectively. The observed manganese concentrations were much lower than the WHO/FAO (2001) background concentrations of 2000.00 mg/kg in both seasons as well as all sampling locations. This could imply that the soils in the study area were not contaminated with manganese. The observed values of manganese in the present study are much lower than reported literature values of 189.00-2007.00 mg/kg determined in soils around the pegmatite mining sites at Olode area, Ibadan southwestern Nigeria (Okonkwo et al., 2021).

The levels of nickel in the soil investigated spread from 11.04 (control site) to 26.04 mg/kg (active mining site) with values of 18.31 mg/kg (farm) and 24.50 mg/kg (abandoned mining site) lying between the extreme experimental values determined during the dry season. During the rainy season, the levels of nickel ranged from 7.34 (control site) to 24.43 mg/kg (active mining site). The observed values of 11.45 mg/kg (farm) and 13.09 mg/kg (abandoned mining site) fell between the lowest and highest concentrations determined. Okonkwo et al. (2021) reported a similar literature value of nickel (22.33 mg/kg) found in Pegmatite mining sites in Olode and its environs in Ibadan, Southwestern Nigeria. In all the seasons and sampling locations, the experimental values of nickel are below the threshold value of 50.00 mg/kg recommended by international standard (WHO/FAO, 2001). This indicates that soils of the Riruwai mining area are

not polluted by nickel. The concentrations of lead ranged from 43.11 to 245.00 mg/kg. The highest concentration of 245.00 mg/kg was observed at the active mining site, while the lowest concentration of 43.11 mg/kg was recorded at the control site. The concentrations of 87.21 mg/kg and 89.30 mg/kg were between the lowest and highest concentrations. The observed values of lead in the present study are substantially lower than reported literature values of 46.00 to 6100.00 mg/kg determined in the soils Pb/Zn mining area of North-western Spain (Monterroso et al., 2014). All the sampling locations and seasons with the exception of the control site had higher lead concentrations above the WHO/FAO (2001) threshold value of 50.00 mg/kg, suggesting soil lead contamination in the study area. The concentrations of zinc during the dry season (mg/kg) spread from 135.09 (control site) to 1653.40 (active mining site) with the concentrations of 426.51 and 1248.90 falling between the observed range. During the rainy season, the levels of zinc (mg/kg) ranged from 115.30 to 1394.56. The concentrations of 367.05 and 731.18 fell between the highest and lowest observed concentration. Similar results of 1035.2 mg/kg of zinc in the surface soil of Irankouh zinc–lead mine, Isfahan, Iran was reported by Jahromi et al. (2020). Ezeh and Chukwu (2011) found a comparable concentration of 1460.5 mg/kg in the soils of the Ishiagu mining district in South Eastern Nigeria. The levels of zinc in all the sampling sites and seasons exceeded the WHO/FAO (2001) recommended value of 300.00 mg/kg, with the active and abandoned mining sites having significantly higher concentrations, while the farm sites had moderately higher concentrations. An exception was found in the control sites.

Generally, the concentrations of arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc in active and abandoned mining sites were significantly higher ($p \leq 0.05$) than in farm and control sites with the control sites having the lowest values. Total heavy metal concentrations in soils decreased in the following order: active mining site > abandoned mining site > farm > control site. This study confirmed previous research that heavy concentrations of active and abandoned mining sites are significantly higher than the rest of the locations (Obasi et al., 2020). High concentrations of Pb, Zn and As observed in the farm area beyond their respective safe limits is indicating the spreading of heavy metal pollution from the mining sites. Acidic drainage and wind transport of dust might be the main effects causing the dispersion of pollution (Rodrı´guez et al., 2009). Heavy metals concentrations in the soils were found to be higher in the dry season than in the rainy season. The high levels of heavy metals in the dry season could be due to dilution, dispersion, high mobility, adsorption, oxidation, hydrolysis and rapid precipitation (Ameh et al., 2021).

Table 3. Heavy Metal Concentrations (mg/kg) in the Soils of Riruwai Mining Area during the Dry Season

Heavy Metals	Sampling Location				WHO/FAO (2001)
(mg/kg)	RSS1	RSS2	RSS3	RSS4	(mg/kg)
As	$35.23^{a} \pm 9.01$	$33.72^{a} \pm 7.43$	$21.54^{b} \pm 8.81$	$13.40^{c} \pm 4.02$	20.00
Cd	$13.50^{b} \pm 3.42$	$5.01^{b} \pm 1.11$	$1.51^{b} \pm 0.06$	$0.91^{b} \pm 0.14$	3.00
Cr	$116.05^{c} \pm 20.13$	$103.37^{c} \pm 17.52$	$96.44^{c} \pm 30.75$	$59.52^{c} \pm 10.71$	100.00
Hg	$1.01^{d} \pm 0.003$	$0.84^{d} \pm 0.09$	$0.50^{e} \pm 0.09$	$0.01^{f} \pm 0.00$	2.00
Mn	$314.49^{e} \pm 16.36$	$203.04^{e} \pm 28.63$	$148.11^{e} \pm 47.56$	$115.19^{e} \pm 27.11$	2000.00
Ni	$26.04^{f} \pm 6.05$	$24.50^{f} \pm 9.05$	$18.31^{f} \pm 5.32$	$11.04^{f} \pm 3.84$	50.00
Pb	$245.00^{g} \pm 31.87$	$89.30^{g} \pm 11.98$	$87.21^{g} \pm 20.15$	$43.11^{g} \pm 13.06$	50.00
Zn	$1653.40^{h} \pm 53.25$	$1248.90^{h} \pm 77.22$	$426.51^{h} \pm 35.69$	$135.09^{h} \pm 19.67$	300.00

Values are mean ± standard deviation (n = 3). The values on the same raw with similar superscript letters are statistically the same ($p < 0.05$), whereas values on the same raw with different superscript letters are statistically different ($p < 0.05$), as revealed by one-way ANOVA and the Tukey HSD post-hoc test. RSS1 = Active mining sites, RSS2 = Abandoned mining sites, RSS3 = farm, RSS4 = Control site.

Table 4. Heavy Metal Concentrations (mg/kg) in the Soils of Riruwai Mining Area during the Rainy Season

Heavy Metals (mg/kg)	Sampling Location				WHO/FAO (2001) (mg/kg)
	RSS1	RSS2	RSS3	RSS4	
As	$29.12^{a} \pm 8.92$	$18.50^{a} \pm 7.79$	$13.09^{a} \pm 6.02$	$7.62^{a} \pm 0.51$	20.00
Cd	$11.61^{b} \pm 5.01$	$2.15^{b} \pm 0.52$	$0.09^{c} \pm 0.02$	$0.07^{c} \pm 0.02$	3.00
Cr	$97.24^{d} \pm 31.44$	$84.73^{d} \pm 25.81$	$71.36^{d} \pm 17.13$	$38.50^{d} \pm 11.45$	100.00
Hg	$0.35^{e} \pm 0.11$	$0.67^{f} \pm 0.10$	$0.36^{e} \pm 0.01$	$0.01^{e} \pm 0.00$	2.00
Mn	$256.00^{g} \pm 37.53$	$155.03^{g} \pm 33.97$	$96.00^{g} \pm 23.04$	$114.15^{g} \pm 18.19$	2000.00
Ni	$24.43^{h} \pm 8.31$	$13.09^{h} \pm 5.04$	$11.45^{h} \pm 4.18$	$7.34^{h} \pm 1.05$	50.00
Pb	$237.00^{i} \pm 30.09$	$82.33^{i} \pm 19.56$	$66.01^{i} \pm 16.14$	$39.07^{i} \pm 11.28$	50.00
Zn	$1394.56^{j} \pm 93.30$	$731.18^{j} \pm 41.15$	$367.05^{j} \pm 55.11$	$115.30^{j} \pm 28.38$	300.00

Pollution Load Index of Heavy Metals (PLI)

Figure 2 shows the values of pollution load index (*PLI*) of studied heavy metals in the active mining site, abandoned mining site, farm and control site in the Riruwai mining area during the dry and rainy seasons. Yu et al. (2014) classified the *PLI* values of heavy metals in the soils. According to their classification, PLI of < 1 indicates unpolluted soil. A *PLI* of 1 to 2 signifies moderately polluted soil. A *PLI* of 2 to 10 denotes strongly polluted soil, while *PLI* of < 10 indicates extremely polluted soil. In this study, the *PLI* values of heavy metals ranged from 0.96 (control site) to 9.71 (active mining site) during the dry season. *PLI* values of 1.97 (farm) and 5.09 (abandoned mining site) fell between the lowest and highest values observed. *PLI* values of heavy metals in the active and abandoned mining sites are in the range of 2-10, which indicates that the soils in these locations are strongly polluted by heavy metals. The *PLI* value of the soil in the farm area is within the range of 1-2. This demonstrates that the soil in the studied farm area is moderately polluted with heavy metals. The *PLI* value of the soil in the control site was however, not polluted by heavy metals (*PLI* < 1). The percentage contribution of the sampling locations to heavy metals pollution loads are 55.00, 29.00, 11.00 and 5.00 % in active mining site, abandoned mining site, farm and control site respectively.

During the rainy season, the *PLI* values of the studied heavy metals varied from 0.58 (control site) to 8.65 (active mining site) with values of 1.19 (farm) and 2.72 (abandoned mining site) falling between the lowest and highest extreme values. The *PLI* value of the soil in the abandoned mining site is greater than 10. This indicates that the soil in the site is extremely polluted with heavy metals. In the active mining site, the *PLI* value of soil is in the range of 2-10, which indicates strong pollution. The *PLI* value of soil from farming area fell within then range of 1-2, signifying moderate pollution. In the control site, the *PLI* value of the soil is less than one, which signifies that the soil in that location was not polluted with heavy metals. Active mining site is the location with the largest pollution, accounting for 66.00 % of the total load. This is followed by abandoned mining site (21.00 %), farm (9.00 %) and the control site had the lowest pollution load (4.00 %). The results corroborate with the findings of Chukwu and Oji (2018) who assessed the level, distribution and the contamination status of Pb, Zn, As, Ni, Cu, Cr and Cd in agricultural soils around the settlements of abandoned Lead-Zinc Mine in Nkpuma Ekwoku, Southeastern, Nigeria. Stephen and Maryann (2020) also made similar observations when they evaluated heavy metals pollution status and risk assessment due to artisanal gold mining activities in Bagega Community, Zamfara State, Northern Nigerian.

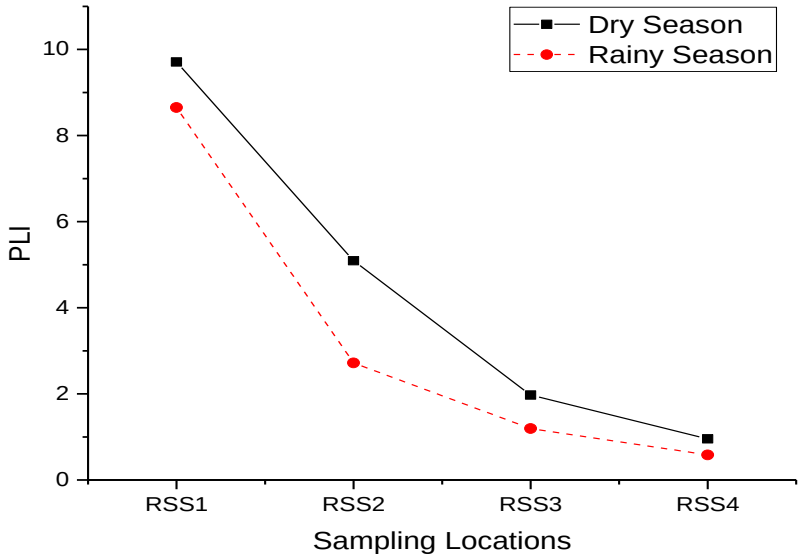

Figure 2. Pollution Load Index of Heavy Metals in soils of Riruwai Mining Area

Conclusion

The concentrations of arsenic, cadmium, lead and zinc in the soils of Riruwai mining area exceeded the threshold value recommended by WHO/FAO (2001) in all the sampling locations and seasons with exception of the control sites. This indicate that the soils, particularly in the active and abandoned mining sites are contaminated by these metals. The contamination had spread to farmland. The pollution load index (*PLI*) results confirmed heavy metal contamination of soils in the study area.

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