Walisongo Journal of Chemistry Vol. 6 Issue 1 (2023), 69-79
ISSN: 2621-5985 (online); 2549-385X (print)
DOI: https://doi.org/10.21580/wjc.v6i1.16097

Speciation of Potentially Toxic Metals from the Mine Impacted soils: A Case Study of Riruwai Mining Area, Kano State, Northern Nigeria

***Hamza Badamasi*[1]**, *Umar Faruk Hassan*[2]*, *Harami Malgwi Adamu*[2]*, *Nasirudeen Mohammed Baba*[3]*, *Dahiru Ajiya Adamu*[2]*, *Haruna Baba*[4]**

[1]Department of Chemistry, Federal University Dutse, Dutse, Jigawa State, Nigeria
[2]Department of Chemistry, Abubakar Tafawa Balewa University Bauchi, Bauchi State, Nigeria
[3]Department of Chemistry, Federal University of Lafia, Nasarawa State, Nigeria
[4]Department of Chemistry, College of Education Minna, Niger State, Nigeria

*Corresponding author: hamza.badamasi@fud.edu.ng

Received: 5 May 2023; Accepted: 20 June 2023; Published: 25 July 2023

Abstract

*Mining and smelting sectors contribute significantly to global growth on a regional and local scale. However, the operations are causing significant environmental damage, particularly pollution of the soil with potentially toxic metals (PTMs). In this study, the speciation of PTMs (*arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc*) from the mine impacted soils of Riruwai mining area was investigated using a modified Tessier sequential extraction method. The findings of the study revealed that all the PTMs examined are considerably associated with non-residual fractions in all the sampling locations. This indicates that all the PTMs investigated in the study area may be highly mobile in the soils and hence potentially toxic. The concentrations of PTMs in the soil's geochemical fractions were found to vary with the sampling locations, with active mining sites significantly ($p \leq 0.05$) recording the highest value, followed by farmland, while the lowest value was reported at the control site. Therefore, to protect the environment and the health of the local populace, PTMs in the soils of the study area should be regularly monitored and a treatment program should be put in place.*

Keywords: *Mining; toxic metals; fractions; Riruwai; Speciation*

Introduction

Mining is contributing substantially to the world economic growth. The activities however, have resulted in environmental deterioration, notably soil contamination with potentially toxic metals, PTMs (Aliu *et al*., 2016; Jiménez-Oyola *et al*., 2021). Arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc are examples of PTMs that are known to be hazardous and harmful to humans and animals as well as the environment (Fazekašová & Fazekaš, 2020; Focus et al., 2021). These PTMs are frequently found in industrial waste, including mining waste, electronic waste, and other hazardous waste. When these wastes are not properly handled, PTMs can leach into the soil, groundwater and subsequent accumulation in the biota, causing serious threats to both the environment and public health (Focus *et al*., 2021; Wang *et al*., 2022). The transfer of PTMs from soils to other media such as air and water, and then to biological systems, as well as their potential hazards, is dependent on their speciation patterns in the soils (Liu *et al*., 2013).

A common technique of determining the speciation of PTMs in environmental samples is sequential method. This method involves the sequential separation of metal species based on their chemical association with different soil fractions (Li *et al*., 2022). By analyzing the metal concentrations in each of the fractions, it is possible to determine the speciation of the PTMs and their potential mobility and bioavailability in the environment (Meng *et al*., 2018; Li *et al*., 2022). The different fractions that PTMs exist in soil include organic matter-bound, exchangeable, reducible, and residual fractions (N'goran *et al*., 2022).

The distribution of these fractions determines the potential movement and availability of the metals in the soil and, hence their toxicity. If they are predominantly in non-residual fractions (organic matter-bound, exchangeable, reducible), they may be leached down to the soil profile and reach groundwater or they may be taken up and accumulated by plants, invertebrates, humans and other animals (Sinduja *et al*., 2022). PTMs that exist primarily in residual forms pose little to no risk to living organisms or the environment (Nevidomskaya *et al*., 2021). Therefore, measuring total PTMs contents in soils cannot provide an accurate assessment of the negative effects of mining activities (Jahromi *et al*., 2020). It is therefore necessary to identify the geochemical fractions of metals in soils in order to evaluate the risks of metal contamination and propose viable remediation approaches. For this reason, this study was aimed at studying the speciation of PTMs from the mine-impacted soils of Riruwai Zn-Sn Mine in Kano State, Northern Nigeria. To the best of our knowledge, no similar studies were carried out in the study area.

Methods

Description of the Study Area

Riruwai mining area is located between latitudes 10°43'97" and 10°45'01" N and longitudes 8°43'3" and 8°47'39" E (Fig. 1). The area has a total area of 129 km^2 (Alhaji *et al*., 2017; Lambu, 2019). The climate was classified as tropical savanna by the Köppen climatic classification system. The mean annual rainfall varied between 400 and 1,200 mm each year, with a minimum temperature of 14.02 °C and a maximum temperature of 32.03 °C (Yakubu, 2016). In terms of geology, Riruwai is one of the new granite complexes in Nigeria. The complex is an excellent example of decayed alkaline volcano roots that formed in the early Jurassic as part of a sequence of anorogenic centers that formed sequentially over time. It is surrounded by a collection of calc-alkaline meta-igneous and metamorphic rocks that have undergone metamorphism and a Cambrian age modification (Olasehinde et al., 2012).

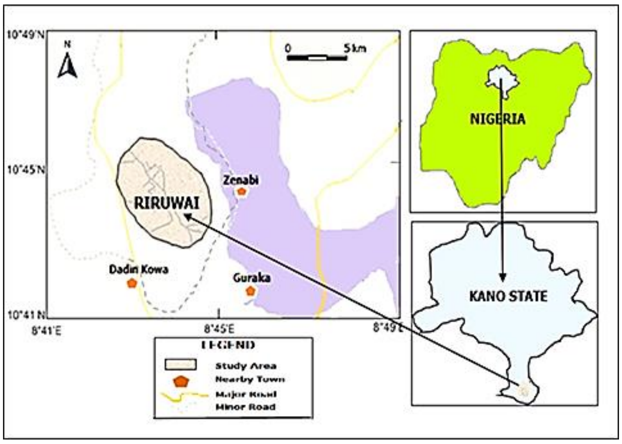

Figure 1. Geographical map of the study area

Soil Sampling and Collection

Forty-eight (48) soil samples were collected at a depth of 0–20 cm from three (3) sampling locations, including 18 from active mine sites, 21 from farmlands, and 9 from control sites using a systematic sampling strategy with the help of a steel soil auger. A grid of equal space lines was constructed, sampling sites were partitioned into equal sub-areas, and an equal distance of 10.00 meters was measured at intervals between each sampling site. Top layers were collected because, when soils are contaminated with heavy metals, the highest levels of metals are usually found at the surface layer of the soil profile (Mazurek *et al*., 2017). Control soil samples were collected 6.00 km distant from other sampling locations in the area with the same lithology, but with little or no human intervention as reported by Ngole-Jeme & Fantke (2017). At each sampling location, three sub-samples were collected within a distance of 5 m surrounding the location and mixed together to form a composite sample. A 1.00 kg from the mixed samples was selected by quartering method, stored in a polyethylene bag, labelled and transported to laboratory for analyses (Fan & Wang, 2017; Yang *et al*., 2017). Samples of soil were air-dried in the laboratory for five (5) days at room temperature. The large fragments, stones and gravels were removed. The homogenized soil was pulverized, sieved through a 2 mm polyethylene sieve, stored in polyethene bags and labelled appropriately for further analyses.

Determination of PTMs Speciation in Soil

A modified Tessier sequential extraction technique adopted by Uba *et al*. (2008) and Zhang *et al*. (2020) was used for soil partitioning. As part of the modification, ammonium ethanoate was used instead of magnesium chloride to prevent the re-adsorption or precipitation of the leached metals on to the surface of the soil substrate due to the metal complexing power of ethanoate (Sagagi, 2013).

Determination of Exchangeable Phase (F1)

A 1.00 g of air-dried soil was shaken in a 50 cm3 polypropylene centrifuge tube at room temperature with 10.00 cm3 of 3.5 mol/dm3 ammonium ethanoate at a pH of 7.00 for 1 hour, centrifuged and the supernatant was decanted and made up to 100.00 cm3 with deionized water. The residue was reserved for further analyses (Zhang *et al*. 2020).

Determination of Oxidizable Phase/Bound to Organic Matter (F2)

A 10.00 cm^3 of 8.80 mol/dm^3 hydrogen peroxide and 6.00 cm^3 of 0.02 mol/dm^3 trioxonitrate (V) acid were added to residue from F1 and agitated for 5 hours at 98 °C. 10.00 cm^3 of 1.00 mol/dm^3 ammonium ethanoate was added centrifuged and supernatant made up to 100.00 cm^3 with deionized water. The residue was reserved for further analyses (Uba *et al*., 2008; Anju *et al*., 2010)

Determination of Acid Soluble Phase /Bound to Carbonate (F3)

A 25.00 cm^3 0.05 mol/dm^3 of disodium ethylenediaminetetraethanoate solution was added to the residue from F2, agitated for 6 hours and centrifuged. The supernatant was decanted into a 100 cm^3 volumetric flask and made up to 100.00 cm^3 with deionized water. The residue was reserved for further analyses (Sut-Lohmann *et al*., 2022).

Determination of Acid Reducible Phase /Bound to Fe-Mn Oxides (F4)

A 17.50 cm^3 of 0.10 mol/dm^3 hydroxylamine hydrochloride and 17.50 cm^3 of 3.50 mol/dm^3 ammonium ethanoate were added to the residue from F3, agitated for l hour and centrifuged. The supernatant was into a 100 cm^3 volumetric flask decanted and made up to 100.00 cm^3 with deionized water. The residue was reserved for the determination of residual phase /bound to silicates (F5)

Determination of Residual Phase /Bound to Silicates (F5)

A 5.00 cm^3 of concentrated hydrochloric acid, 15.00 cm^3 of concentrated trioxonitrate (V) acid and 5.00 cm^3 of concentrated hydrofluoric acid were added to the residue from F4 and digested in an acid Teflon cup. The mixture was heated using electric hot plate at 180 °C until the solution was dried. The beaker was removed and cooled to room temperature. The dried solution was diluted to 100.00 cm^3 with deionized water (Vuong *et al*. 2022).

The extract from each extraction step was used for the determination of arsenic, cadmium, chromium, mercury, nickel, manganese, lead and zinc at their respective wavelengths using Microwave Plasma Atomic

Emission Spectrometer (Model Number 4200, Agilent, USA).

Quality Control and Statistical Analysis

Appropriate quality control/assurance procedures and precautions were taken to ensure the reliability of the analytical results. To prevent cross-contamination, samples were handled with extreme caution. Throughout the study, analytical grade chemicals were used. All glass and plastic wares were immersed in 10.00% (v/v) trioxonitrate (V) acid overnight before being thoroughly washed three times with deionized water and dried in an oven. The wares were dried for 20 minutes in a desiccator before analysis (Ashraf *et al.*, 2011). Reagent blanks were determined to minimize the errors caused by reagent contaminants. Each sample was analyzed in triplicate, and the results were expressed as the mean ± standard deviation. An analysis of variance (ANOVA) was used to establish whether there was a significant difference between the sampling locations. Tables and graphs were plotted using Microsoft Excel 2010.

Result and Discussion

As presented in Table 1, the speciation patterns of arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc at the active mining site in exchangeable fraction (F1) are 7.49, 4.31, 3.90, 0.29, 90.61, 1.05, 21.23 and 18.23 mg/kg respectively. The values of all the PTMs are within the WHO/FAO (2001) limits of 20.00, 3.00, 100.00, 2.00, 2000.00, 50.00, 50.00, and 300.00 for agricultural soils. Manganese was found to be the highest in the exchangeable fraction, while mercury was found to be the lowest. In the oxidizable phase/bound to organic matter (F2), the concentrations of arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc are 3.55, 1.09, 23.22, 0.17, 104.07, 5.44, 104.0 and 882.05 mg/kg respectively. In this fraction, zinc was recorded as the highest metal bound to oxidizable phase, while mercury was found to be the lowest.

This indicates that zinc is the highest heavy metal bound to organic matter among the studied PTMs. PTMs that are bonded to the organic matter may become available because some of them are water soluble (Elijah *et al.*, 2020; Ogunwale *et al.*, 2021). The levels of PTMs in acid soluble fraction/bound to carbonates (F3) are: arsenic (6.38 mg/kg), cadmium (2.01 mg/kg), chromium (6.51 mg/kg), mercury (0.12 mg/kg), manganese (18.11 mg/kg), nickel (9.37 mg/kg), lead (34.31 mg/kg) and zinc (398.01 mg/kg). Zinc had the highest level, while mercury had the lowest. This suggests that in active mining site, considerable amount of zinc was bound to carbonates and very small fractions of mercury were bound to carbonates.

The levels of PTMs (mg/kg) in acid reducible fraction/bound to Fe-Mn oxides (F4) are as follows: arsenic (2.10), cadmium (0.09), chromium (11.28), mercury (0.07), manganese (47.91), nickel (3.07), lead (10. 40) and zinc (58.43). In this fraction, zinc was the highest metal bound to Fe and its oxides, while mercury was least recorded. The levels of arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc in residual fraction are 1.05, 0.07, 12.77, 0.05, 23.29, 2.06, 15.08 and 42.40 mg/kg respectively. Similar to other fractions, zinc is the highest heavy metal in the residual fraction, while mercury is the lowest. In this sampling site, very considerable amounts of heavy metals are found in non-residual fraction. The percentage contributions of PTMs to non-residual fraction as shown in Figure 2 are 1.04, 0.40, 2.40, 0.03, 13.95, 1.01, 8.54 and 72.61 % for arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc respectively.

The high percentage (%) association of PTMs with non-residual fraction is a reflection of their high mobility and hence bioavailability. The rate of mobility decreases in the following order: zinc > manganese > lead > chromium > arsenic > nickel > cadmium > mercury. Rodrı´guez *et al.* (2009) reported similar observation that PTMs are associated with non-residual fractions when they investigated PTMs distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain. Yiika *et al.* (2023) observed significant mobility of PTMs in artisanal gold mine tailings in eastern Cameroon.

In the farmland, the levels of arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc in exchangeable fraction are 4.46, 0.36, 5.33, 0.13, 37.79, 1.34, 11.57 and 92.34 mg/kg respectively. Zinc is observed to be the highest contributor to this fraction while mercury is the lowest contributor. The concentrations of PTMs (mg/kg) in oxidizable fraction are: arsenic (3.12), cadmium (0.09), chromium (9.89), mercury (0.10), manganese (61.82), nickel (8.59), lead (25.10) and zinc (158.50). This fraction contains highest amount of zinc and lowest amount cadmium. The levels of arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc in acid soluble fraction are 3.9, 0.10, 15.34, 0.07, 15.38, 0.71, 16.06 and 78.45 mg/kg respectively.

Zinc and mercury were the highest and lowest contributors respectively. The concentrations of arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc in acid reducible fraction are 3.58, 0.25, 8.00, 0.04, 11.20, 1.47, 10.80, 48.47 mg/kg respectively. Zinc had the largest share of this fraction, while mercury had lowest share. The levels of PTMs (mg/kg) in the residual fraction are 0.41, 0.07, 7.70, 0.11, 9.01, 0.98, 9.45, 31.67 for arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc respectively. Zinc is the largest contributor to this fraction, while cadmium is the least. Non-residual fraction takes very significant part of this fraction with individual PTM contributions of: arsenic (2.37 %), cadmium (0.13 %), chromium (6.08 %), mercury (0.05 %), manganese (19.89 %), nickel (1.91 %), lead (10.02 %) and zinc (59.55 %) as presented in Figure 2. All PTMs levels fall within the ranges of limits set by WHO/FAO (2001).

In the control site, the concentrations of arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc in the exchangeable fraction are 2.37, 0.18, 8.92, 0.003, 29.17, 2.80, 14.09 and 34.04 mg/kg respectively with highest contribution from zinc and lowest from mercury. The levels of arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc in the oxidizable fraction are 5.04, 0.15, 5.23, 0.002, 20.5, 3.46, 6.18 and 8.83 mg/kg respectively. Manganese is the largest contributor to this fraction while mercury is the lowest. The levels of PTMs (mg/kg) in the acid soluble fraction are: arsenic (2.24), cadmium (0.07), chromium (5.42), mercury (0.002), manganese (13.38), nickel (0.46) lead (1.57) and zinc (23.98). Zinc had the highest, while mercury had the lowest. In acid reducible fraction, the levels of PTMs (mg/kg) are 1.57, 0.05, 3.93, 0.001, 9.40, 0.29, 0.88 and 8.20 with highest contribution from zinc while the lowest from mercury. The levels of PTMs in residual fractions are: arsenic (0.34 mg/kg), cadmium (0.09 mg/kg), chromium (1.09 mg/kg), mercury (0.001 mg/kg), manganese (3.40 mg/kg), nickel (1.45 mg/kg), lead (0.31 mg/kg) and zinc (10.42 mg/kg). Zinc had the highest level in the residual fraction, while mercury was had lowest. Very significant amount of heavy metals are associated with non-residual fraction. The values of each PTM are within the WHO/FAO (2001) limits of 20.00, 3.00, 100.00, 2.00, 2000.00, 50.00, 50.00, and 300.00 for agricultural soils. The percentage contributions of each metal are 5.28, 0.21, 11.06, 0.004, 34.11, 3.30, 10.70 and 35.33 % for arsenic, cadmium, chromium, mercury, manganese, nickel, lead and zinc respectively (Figure 2)

Generally, the sequential extraction showed that all the PTMs examined are considerably associated with non-residual fractions in all the sampling locations. This implies that all the PTMs investigated in the study area are highly mobile in the soils. It has also been reported that PTMs released by anthropogenic sources, such as mining operations, are highly mobile in the soil environment and have a greater potential to harm the environment and humans than those released from geogenic sources (Kaasalainen & Yli-Halla, 2003; Kumar *et al.*, 2011; Hu & Cheng). The levels of all PTMs in both residual and non-residual fractions were found to be significantly (p ≤ 0.05) higher than the rest of the locations. This is followed by farmland, while the lowest value was recorded at the control site. High values of PTMs in the active mining and farmland sites compared to the control site could be due to the fact that mining activities and farming involve the excavation of deep soil, which exposes previously undisturbed PTMs that were already buried beneath the ground to the soil's surface, increasing their concentration level in the soil (Aliu *et al*., 2016; Ling *et al*., 2019; Adewumi & Laniyan, 2020; Hai *et al*., 2021).

Moreover, the variation of PTM concentrations across the sampling locations could be due to a number of factors, including changes in physico-chemical parameters, soil mineralization, and the application of fertilizer (Sungur *et al*., 2020; Jalali *et al*., 2023). Based on this findings, it is evident that that all the PTMs investigated in the study area are highly mobile in the soil and can be bioavailable and hence toxic in the environment. Rodrı´guez *et al.* (2009), Liu *et al.* (2016) and Vuong *et al*. (2022) reported similar observations that PTMs from mining areas are associated with non-residual fractions. The speciation of PTMs in soil is regulated by soil pH, organic matter level, redox potential, and the presence of other elements. For example, in acidic soils such as those found in this study area (pH 6.05-6.26), as reported in our previous studies (Badamasi *et al*., 2022), heavy metals tend to be more soluble and mobile, which can increase their bioavailability and toxicity to plants and animals (Elijah *et al*., 2020: Ogunwale *et al*., 2021).

Therefore, understanding the speciation of PTMs is important because it affects their mobility, bioavailability and toxicity in the environment (Chu *et al*., 2010; Vuong *et al*., 2022). By identifying the mineral components in which each metal has the greatest affinity, speciation assists in understanding the behavior of the metals in relation to their environment (Monterroso *et al*., 2014; Ogunwale *et al*., 2021). Mobility and bioavailability are regulated by dynamic equilibrium between the concentrations of these fractions instead of total metal concentrations. Therefore, measuring total PTMs levels in soil samples is inadequate for evaluating probable mobility, bioavailability and consequently, the toxicity of PTMs in the soil (Ahn *et al*., 2020; Kaninga *et al*., 2020).

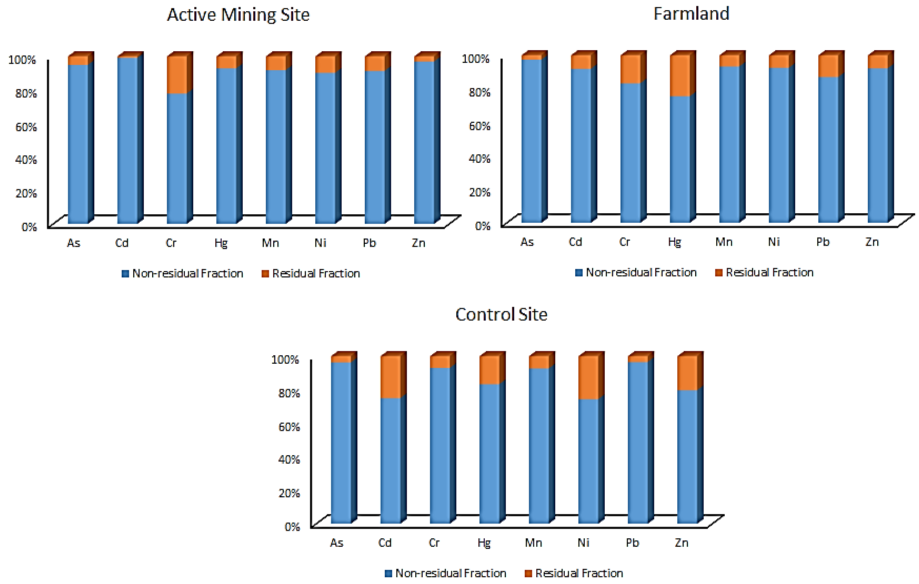

Figure 2. Distribution (%) of PTMs in residual and non-residual fractions in the soils of Riruwai mining area

Table 1. Speciation Pattern of Some Heavy Metals (mg/kg) in Soil

Metals fractions	**Active Mining site**							
	As	**Cd**	**Cr**	**Hg**	**Mn**	**Ni**	**Pb**	**Zn**
F1	7.49 ± 1.55	4.31 ± 0.23	3.90 ± 0.09	0.29 ± 0.15	90.61 ± 9.55	1.05 ± 0.02	21.23 ± 4.23	18.23 ± 5.66
F2	3.55 ± 0.23	1.09 ± 0.31	23.22 ± 7.11	0.17 ± 0.05	104.07 ± 10.00	5.44 ± 1.23	104.01 ± 17.04	882.05 ± 21.10
F3	6.38 ± 1.61	2.01 ± 0.01	6.51 ± 1.02	0.12 ± 0.08	18.11 ± 2.37	9.37 ± 2.77	34.31 ± 9.51	398.01 ± 16.23
F4	2.10 ± 0.15	0.09 ± 0.04	11.28 ± 5.19	0.07 ± 0.02	47.91 ± 15.50	3.07 ± 0.86	10. 40 ± 4.00	58.43 ± 9.02
F5	1.05 ± 0.15	0.07 ± 0.02	12.77 ± 6 .31	0.05 ± 0.03	23.29 ± 7.96	2.06 ± 0.25	15.08 ± 6.11	42.40 ± 7.00
Metals fractions	**Farmland**							
	As	**Cd**	**Cr**	**Hg**	**Mn**	**Ni**	**Pb**	**Zn**
F1	4.46 ± 1.56	0.36 ± 0.07	5.33 ± 0.17	0.13 ± 0.05	37.79 ± 9.05	1.34 ± 0.55	11.57 ± 4.35	92.34 ± 20.27
F2	3.12 ± 0.52	0.09 ± 0.02	9.89 ± 1.15	0.10 ± 0.03	61.82 ± 12.96	8.59 ± 2.04	25.10 ± 6.75	158.50 ± 17.46
F3	3.90 ± 0.38	0.10 ± 0.03	15.34 ± 5.55	0.07 ± 0.05	15.38 ± 8.47	0.71 ± 0.07	16.06 ± 9.00	78.45 ± 12.39
F4	3.58 ± 1.98	0.25 ± 0.10	8.00 ± 2.02	0.04 ± 0.01	11.20 ± 5.10	1.47 ± 0.18	10.80 ± 3.70	48.47 ± 10.43
F5	0.41 ± 0.06	0.07 ± 0.02	7.70 ± 1.55	0.11 ± 0.06	9.01 ± 6.39	0.98 ± 0. 15	9.45 ± 1.05	31.67 ± 8.51
Metals fractions	**Control Site**							
	As	**Cd**	**Cr**	**Hg**	**Mn**	**Ni**	**Pb**	**Zn**
F1	2.37 ± 0.33	0.18 ± 0.03	8.92 ± 3.17	0.003 ± 0.001	29.17 ± 7.48	2.80 ± 0.35	14.09 ± 3.77	34.04 ± 6.30
F2	5.04 ± 1.81	0.15 ± 0.07	5.23 ± 2.08	0.002 ± 0.001	20.5 ± 5.20	3.46 ± 1.01	6.18 ± 2.77	8.83 ± 2.95
F3	2.24 ± 0.90	0.07 ± 0.03	5.42 ± 1.97	0.002 ± 0.000	13.38 ± 5.37	0.46 ± 0.15	1.57 ± 0.09	23.98 ± 9.36
F4	1.57 ± 0.37	0.05 ± 0.03	3.93 ± 1.05	0.001 ± 0.000	9.40 ± 2.92	0.29 ± 0.09	0.88 ± 0.06	8.20 ± 2.19
F5	0.34 ± 0.07	0.09 ± 0.05	1.09 ± 0.08	0.001 ± 0.000	3.40 ± 1.74	1.45 ± 0.35	0.31 ± 0.09	10.42 ± 8.00

Values are mean ± standard deviation (n = 3). **F1**= Exchangeable fraction, **F2** = Oxidizable fraction/ bound to organic matter, **F3** = Acid soluble fraction/bound to carbonate, **F4** = Acid reducible fraction/bound to Fe-Mn oxides, **F5** = Residual fraction/ bound to silicates.

Conclusion

In this study, the speciation of PTMs from the mine-impacted soils of the Riruwai mining area of Kano State, Northern Nigeria, was investigated. The findings of the study revealed that all PTMs studied in all locations were found to be considerably associated with non-residual fractions and hence highly mobile and potentially toxic. The values of PTMs were found to vary with the sampling locations, with active mining sites significantly ($p \leq 0.05$) recording the highest value, followed by farmland, while the lowest value was reported at the control site. Therefore, a human biomonitoring study should be carried out on the residents of the mining area in order to evaluate the degree of PTMs transfer to humans.

Acknowledgement

The authors would like to thank Tertiary Education Trust Fund (TETfund) Nigeria for providing funding for this study. The authors are grateful to Mal. Mansir Muhammad Riruwai, Mal. Yaro Jinjiri, and Musa Shu'aibu for their invaluable assistance during sample collections and reconnaissance surveys.

Reference

Adewumi, A. J. and Laniyan, T. A.D. (2020). Contamination, sources and risk assessments of metals in media from Anka artisanal gold mining area, Northwest Nigeria. *Science of the Total Environment, 718*, 1-14.

Ahn, Y., Yun, H. S., Pandi, K., Park, S., Ji, M., & Choi, J. (2020). Heavy metal speciation with prediction model for heavy metal mobility and risk assessment in mine-affected soils. *Environmental Science and Pollution Research*, *27*, 3213-3223.

Alhaji, M., Adamu, S. & Buba, L.F. (2017). Assessment of summer heat stress condition for tourism development in Riruwai ring complex, Doguwa local government, Kano State, *Dutse Journal of Pure and Applied Sciences*, *3*(2), 288-299.

Aliu, M., Šajn, R. & Stafilov, T. (2016). Spatial distribution of lead in soils of Pb-Zn mining and smelting area of the Mitrovica region, Republic of Kosovos. *Journal Environmental Science Health, 51*(7), 588-608.

Anju, M., & Banerjee, D. K. (2010). Comparison of two sequential extraction procedures for heavy metal partitioning in mine tailings. *Chemosphere*, *78*(11), 1393-1402.

Ashraf, M.A., Maah, M.J. & Yusoff, I. (2011). Heavy metals accumulation in plants growing in ex-tin mining catchment. *International Journal of Environmental Science and Technology*, *8*(2), 40-416.

Badamasi, H., Hassan, U.F, Adamu, H.M., Baba NM, Adamu, D.A (2022). Physico-chemical Properties and Heavy Metal Contamination Levels of Soils from Riruwai Mining Area, North-western Nigeria. *Malaysian Journal of Applied Sciences*, *7*(2), 29-45.

Chu, N.K., Nguyen, V., Noi, L.T., Son, H.M., Ngoc, S.T., Takuro, N. et al. (2010). Heavy metal contamination of agricultural soils around a chromite mine in Vietnam. *Soil Science & Plant Nutrition*, *56*(2), 344-356.

Elijah, L. Horsfall, J. & spiff, A.I. (2020). Speciation of some heavy metals in sediments of Pennington River, Bayelsa State, Nigeria. *American Chemical Science Journal*, *5*(3), 238-246.

Fan, S. & Wang, X. (2017). Analysis and assessment of heavy metals pollution in soils around a Pb and Zn smelter in Baoji city, Northwest China. *Human and Ecological Risk Assessment: An International Journal*, *23*(5), 1099-1120.

Fazekašová, D. & Fazekaš, J. (2020). Soil quality and heavy metal pollution assessment of iron ore mines in Nizna Slana (Slovakia), *Sustainability*, 12(6), 1-15.

Focus, E., Rwiza, M. J., Mohammed, N. K. & Banzi, F. P. (2021). Health risk assessment of trace elements in soil for people living and working in a mining area. *Journal of Environmental and Public Health*, 2021, 1-12.

Hai, D., Rui, W., Mingshu, Y., Jiao, Z., Zhongmin, J., Shaobiao, L., *et al*. (2021). Risk

Hu, Y., & Cheng, H. (2016). A method for apportionment of natural and anthropogenic contributions to heavy metal loadings in the surface soils across large-scale regions. *Environmental Pollution*, *214*, 400-409.

Jahromi, M.A., Jamshidi Zanjani1, A. & Darban, A.K. (2020). Heavy metal pollution and human health risk assessment for exposure to surface soil of mining area: a comprehensive study*. Environmental Earth Sciences*, *79*, 365-375.

Jalali, M., Farahani, E. A., & Jalali, M. (2023). The impact of organic and inorganic fertilizers on availability and speciation of phosphorus and heavy metals in calcareous soils. *Environmental Earth Sciences*, *82*(6), 142.

Jiménez-Oyola, S., Chavez, E., García-Martínez, M., Ortega, M.F., Bolonio, D. & Guzmán-Martínez, F., et al. (2021). Probabilistic multi-pathway human health risk assessment due to heavy metal(loid)s in a traditional gold mining area in Ecuador. *Ecotoxicology and Environmental Safety*, *224*, 1-11.

Kaasalainen, M. & Yli-Halla, M. (2003). Use of sequential extraction to assess metal partitioning in soils. *Environmental Pollution*, *126*(2), 225-233.

Kaninga, B. K., Chishala, B. H., Maseka, K. K., Sakala, G. M., Lark, M. R., Tye, A., & Watts, M. J. (2020). Review: mine tailings in an African tropical environment-mechanisms for the bioavailability of heavy metals in soils. *Environmental Geochemistry and Health*, *42*(4), 1069–1094.

Kumar, B., Kumar, S., Mishra, M., Singh, S. K., Prakash, D., Sharma, C. S., & Mukherjee, D. P. (2011). Geochemical fractionation of some heavy metals in soils in the vicinity of sukinda mining Area, Orissa. *Advances in Applied Science Research*, *2*(5), 263-72.

Lambu, I.B. (2019). Forgetting to remember: the fate of Riruwai old Tin mining communities in Kano State Nigeria. *African Journal of Earth and Environmental Sciences*, *1*(2), 265–280.

Li, Q., Wang, Y., Li, Y., Li, L., Tang, M., Hu, W., Chen, L., & Ai, S. (2022). Speciation of heavy metals in soils and their immobilization at micro-scale interfaces among diverse soil components. *The Science of the Total Environment*, *825*, 153862.

Li, Q., Wang, Y., Li, Y., Li, L., Tang, M., Hu, W., *et al*. (2022). Speciation of heavy metals in soils and their immobilization at micro-scale interfaces among diverse soil components. *Science of the Total Environment,* 153862.

Ling, Q., Dong, F., Yang, G., Han Y, Nie, X, Zhang, W. et al. (2019). Spatial distribution and environmental risk assessment of heavy metals identified in soils of decommissioned mining area. *Human and Ecological Risk: An International Journal*, *16*, 1-15.

Liu, X., Song, Q., Tang, Y., Li, W., Xu, J., Wu, J. et al. (2013). Human health risk assessment of heavy metals in soils–vegetable system: a multi-medium analysis. *Science of the Total Environment*, *464*, 530–540.

Mazurek, R., Kowalska, J. & Siorek, M. (2017). Assessment of heavy metals contamination in surface layers of Roztocze national park forest soils (SE Poland) by indices of pollution. *Chemosphere*, 168, 839–50.

Meng, J., Tao, M., Wang, L., Liu, X., & Xu, J. (2018). Changes in heavy metal bioavailability and speciation from a Pb-Zn mining soil amended with biochars from co-pyrolysis of rice straw and swine manure. *Science of the Total Environment*, *633*, 300-307.

Monterroso, C., Rodríguez, F., Chaves, R., Diez, J., Becerra-Castro, C., Kidd, P.S. et al. (2014). Heavy metal distribution in mine-soils and plants growing in a Pb/Zn mining area in NW Spain. *Applied Geochemistry*, *44*, 3-11.

N’goran, K. P. D. A., Diabate, D., Kouassi, N. G. L. B., Yao, K. M., Kinimo, K. C., Ouattara, A. A., & Trokourey, A. (2022). Geochemical speciation and distribution of trace metals in sediments around industrial and artisanal gold mining areas in northern Côte d'Ivoire. *Environmental Earth Sciences*, *81*(12), 333.

Nevidomskaya, D.G., Minkina, T.M., Soldatov, A.V., Bauer, T.V., Shuvaeva, V.A., Zubavichus, Y.V. *et al*. (2021). Speciation of Zn and Cu in Technosol and evaluation of a sequential extraction procedure using XAS, XRD and SEM–EDX analyses. *Environmental Geochemistry and Health*, *43*, 2301-2315.

Ngole-Jeme, V.M. & Fantke, P. (2017). Ecological and human health risks associated with abandoned gold mine tailings contaminated soils. *PLoS ONE* , *12*(2), 1-24.

Ogunwale, T. O., Oyekunle, J. A. O., Ogunfowokan, A. O. & Oluwalana, A. I. (2021). Seasonal chemical speciation and potential mobility of heavy metals in the surface soil of some poultry farm establishments of Osun State, South-western Nigeria. *International Journal of Environment and Pollution Research*, *9*(2), 1-24.

Olasehinde, A., Ashano, E.C. & Singh, G.P. (2012). Analysis of magnetic anomaly over the Riruwai younger granite ring complex: a geodynamic implication. *Continental Journal of Earth Sciences*, *7*(1), 9-18.

Parvin, A., Moniruzzaman, M., Hossain, M.K., Saha, B., Parvin, A., Suchi, P.D. & Hoque, S, (2022). Chemical Speciation and Potential Mobility of Heavy Metals in Organic Matter Amended Soil. *Applied and Environmental Soil Science*, 2022.

Rodrı´guez, L., Ruiz, E., Alonso-Azca´rate, J. & Rinco´n, J. (2009). Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn Mine in Spain. *Journal of Environmental Management*, 90(2), 1106–1116.

Sagagi, B. S. (2013). *Determination and Fractionation of Potentially Toxic Element in Urban Particulates* [University of Strathclyde]. https://stax.strath.ac.uk/concern/theses/3r074v07c

Sinduja, M., Sathya, V., Maheswari, M., Dhevagi, P., Kalpana, P., Dinesh, G. K., & Prasad, S. (2022). Evaluation and speciation of heavy metals in the soil of the Sub Urban Region of Southern India. *Soil and Sediment Contamination: An International Journal*, *31*(8), 974-993.

Sungur, A., Vural, A., Gundogdu, A., & Soylak, M. (2020). Effect of antimonite mineralization area on heavy metal contents and geochemical fractions of agricultural soils in Gümüşhane Province, Turkey. *Catena*, *184*, 104255.

Sut-Lohmann, M., Ramezany, S., Kästner, F., Raab, T., Heinrich, M., & Grimm, M. (2022). Using modified Tessier sequential extraction to specify potentially toxic metals at a former sewage farm. *Journal of Environmental Management*, *304*, 114229.

Uba, S., Uzairu, A., Harrison, G.F.S., Balarabe, M.L. & Okunola, O.J. (2008). Assessment of heavy metals bioavailability in dumpsites of Zaria metropolis, Nigeria. *African Journal of Biotechnology*, *7*(2), 122-130.

Vuong, X. T., Vu, L. D., Duong, A. T. T., Duong, H. T., Hoang, T. H. T., Luu, M. N. et al. (2022). Speciation and environmental risk assessment of heavy metals in soil from a lead/zinc mining site in Vietnam. *International Journal of Environmental Science and Technology*, *1*, 1-16.

Wang, R., Chen, N., & Zhang, E. X. (2022). Ecological and health risk assessments based on the total amount and speciation of heavy metals in soils around mining areas. *Huan Jing ke Xue= Huanjing Kexue*, 43(3), 1546-1557.

WHO/FAO (2001). Food additives and contaminants. Joint FAO. *WHO Food Standards Programme, ALINORM*, *1*, 1-28.

Yakubu, A., Oladimeji, Y.U. & Hassan, A.A. (2019). Technical efficiency of maize farmers in Kano State of Nigeria using a data envelopment analysis approach. *Ethiopian Journal of Environmental Studies & Management, 12*(2), 136 – 147.

Yang, S., Danek., T., Chend, X. & Huang, Q. (2017). Risk Assessment of heavy metal pollution in soils of Gejiu tin ore and other metal deposits of Yunnan province. *IOP Publication Conference Series: Earth and Environmental Science*, *24*(3), 351-359.

Yiika, L. P., Tita, M. A., Suh, C. E., Mimba, M. E., & Jean-Lavenir, N. M. (2023). Heavy Metal speciation by Tessier sequential extraction applied to artisanal gold mine tailings in eastern Cameroon. *Chemistry Africa*, 1-19.

Zhang, Z., Wu, X., Wu, Q., Huang, X., Zhang, J., & Fang, H. (2020). Speciation and accumulation pattern of heavy metals from soil to rice at different growth stages in farmland of southwestern China. *Environmental Science and Pollution Research*, *27*, 35675-35691.