Evaluation and Speciation of Heavy Metals
Contamination of Selected Artisanal Mining Sites in Mangu Local Government Area of Plateau State, Nigeria

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ABSTRACT

Artisanal (illegal) mining has been reported to have environmental and health effects on the surrounding communities due to heavy metals pollution. The determination of total heavy metal concentration does not reflect the toxicity and bioavailability of the metals. Toxicity and bioavailability of the metals can be achieved by determining the form in which the metal exist in the environment (speciation). This present work evaluated the heavy metals’ (cadmium (Cd), copper (Cu), manganese (Mn), lead (Pb), zinc (Zn) & nickel (Ni)) contamination and the form in which they exist at some mining sites in Mangu LGC, Plateau state, Nigeria. Aqua regia ((HCl + HNO3, 3:1 v/v) was used for total metal concentration while sequential extraction method was used to orderly determine the speciation of the heavy metals. The level of the heavy metals in the digested solutions were determined using Buck Scientific model 210VGP Atomic Absorption Spectrophotometer (AAS). The results divulged that the concentrations of the heavy metals were within the FEPA and WHO recommended permissible limit except Cd and Ni. The values of the metals at Mangu Halle mining site followed the sequence: Mn > Zn > Ni > Pb > Cu > Cd whereas the sequence at Alogwom was Mn > Zn > Pb > Ni > Cu > Cd. The results of the speciation indicated that all metals were bound to the five fractions with the residual fraction dominating except Cd which was bound mostly to the soluble and exchangeable fractions. It could be concluded that the presence of these heavy metals in the mobile fractions, indicate that they could be easily released to the environment from soil. Thus, they are also likely to cause toxicity in the environment. Proper monitoring of the mining activities in the communities was recommended.

Keywords: Artisanal, contamination, Heavy Metals, Mining, Speciation.

I. INTRODUCTION

Mining has contributed greatly to the economy of many low- and middle-income countries that are rich in non-fuel mineral resources [1]. However, when not properly monitor, indiscriminate and unorganized mining can mar the benefits because of its potential for environmental and health impacts [2], [3]. Today, there are widespread artisanal (illegal) mining taking place in Jos South, Barkin Ladi, Riyom, Jos North and Mangu Local Government Areas of Plateau State. Most of the mining activities are undertaken by artisanal miners which are seen as surface or artisanal mining. These are done with little or no technology adaptation to handle the damages of the mining activities [4]. The mining activities have led to mining ponds, dams, and alluvial deposits, which have been abandoned due to the unprofessional handling of the mining [5]. These have immediate and long term environmental and health implications to the communities’ concern [6], [7].

Currently, most of the mining communities have taken to dry season irrigation farming of vegetables using the abandoned mining ponds/dams as their source of water. Also, mining heaps and sands/tailings are used for construction purposes [8]. Most of the mining activities are undertaken by artisanal miners which are seen as surface or artisanal mining. These are done with little or no technology adaptation to handle the damages of the mining activities [9]. Mustafa and Ezeamaka [9] also posited that increasing impact witness over the years was as a result of the fact that most of the miners undertake the activities in mining areas not known to the government and its agencies responsible for the regulation of mining activities. They further said, this in turn makes it difficult for the government to monitor their operations in order to inflict environmental regulations on them. All these have health implications to the society as heavy metals would be introduced into the environment. Many researchers have expressed fears that high and excessive amount of heavy
metals in the soil may eventually contaminate both human and animal food chain [10], [11]. This is because unlike some of the organic pollutants, metals have the tendency to remain in the environment for a long time. They cannot be biodegradable and their residence time in the soil can be thousands of years [12]. The determination of total heavy metal concentrations can only be used to assess heavy metal pollution but cannot be used to assess the mobility and bioavailability of the heavy metals [13], [14]. To determine or assess the toxicity, mobility, reactivity, and bioavailability of heavy metals in the environment, speciation can be an efficient tool to environmentalists [14], [16]. Therefore, heavy metal speciation in soils plays an important role in environmental risk assessment of soil heavy metal pollution. In this assessment, only the soil labile fraction is taken into account because this fraction is often called the bioavailable fraction [11], [15]. According to Huang et al. [17], “the concentration of heavy metal’s solution in the soil, their form of association with other soluble species and the ability of the soil to release them from the solid-phase to the soil solution determine the mobility, bioavailability and the potential toxicity of these metals in the soil.” They further stated that the knowledge of the chemical forms in which those metals are found reveals their behaviour within the environment. The simplest method to identify the speciation of heavy metals in the environment is sequential extraction. In this method, the components that are loosely held in the soil are extracted first, followed by those that are more tightly bonded [12]. The sequential extraction method consists of five different fractions as proposed by Tessier et al. [18] and modified by other researchers. Therefore, the main objectives of the present study are to evaluate the heavy metals contamination of selected artisanal mining sites in Mangu LGA of Plateau State and determine the speciation of the heavy metals in the environment.

II. MATERIALS AND METHODS

A. Description of Study Area

Mangu is a Local Government Area in Plateau State, Nigeria. Its headquarters is in the town of Mangu at 9°31′00″N 9°06′00″E. It has an area of 1,653 km² and a population of 29,4931 at the 2006 census. Mechanized mining has stopped in Mangu but artisanal (illegal) mining is still going at the time of this research leaving behind so many abandoned mining ponds, dams, alluvial deposits, and mining wells scattered all over.

B. Sample Collection

Samples for this study were collected majorly through qualitative techniques during the fieldwork that took place in the study area between September and December 2019. Soil samples were collected randomly from Mangu Halle and Alogwom mining sites in Mangu LGA. The soil samples from five sites in Mangu Halle and four soil samples from Alogwom were collected for this study. The soil samples were air-dried, crushed, and sieved to 2 mm, then stored prior to analysis of heavy metals.

C. Analysis of Heavy Metals in Soil

Three grams (3.0 g) of the sieved soil sample was weight in a Pyrex conical flask and digested with 25 ml of aqua regia (HCl + HNO₃, 3:1 v/v) at 120 °C on a water bath in a fume cupboard. The digested sample was cooled and filtered into a 100 ml volumetric flask and made up to the mark with distilled/deionised water [13], [18]. This process was repeated. The concentration of the heavy metals in the digested soil sample solutions were determined using Buck Scientific model 210VGP Atomic Absorption Spectrophotometer (AAS) at wavelengths and slits specific to each metal. The metals analysed were lead (Pb), copper (Cu), nickel (Ni), zinc (Zn), cadmium (Cd) and manganese (Mn).

D. Sequential Extraction of Metals

The method reported by Asagba et al. [19] was used for the sequential extraction of the heavy metals with slight modification.

1) Soluble fraction [F1]

The soluble fraction was extracted with 10 mL of distilled/deionized water for 16 hours on a mechanical shaker. After each extraction process, liquid-solid separation was affected by centrifuging the mixture at 1,500 rpm for 15 minutes. The supernatant was decanted into a plastic sample bottle for metal analysis while the residue was kept for step II.

2) Exchangeable fractions [F2]

The exchangeable fraction was extracted using 1M BeCl₂, (instead of MgCl₂), pH7, in stoppered polyethylene bottles at room temperature [13]. To the residue from F1, 10 mL of 1 M BeCl₂ was added, and this was agitated for 10 hours on a mechanical shaker. The supernatant was decanted into a plastic sample bottle for metal analysis while the residue was kept for step III.

3) Carbonate fraction [F3]

To the residue from F2, 8 mL of 1 M NaOAc was added, and this was adjusted to pH 5.0 with acetic acid (HOAc). The mixture was agitated for 5 hours

4) Fe/Mn bound fraction [F4]

This fraction was extracted from the residue of [F3] with a mixture of hydroxylamine hydrochloride (NH₂OH.HCl) and 0.2M trioxonitrate (V) acid (HNO₃) and agitated at room temperature for 1 hour [13].

5) The residual fractions (bound to Silicates) [F5]

The residual fraction was extracted with 25 ml of aqua regia (HCl + HNO₃, 3:1 v/v) at 120 °C on water bath in fume cupboard. Metal levels in each fraction were determined using the calibrated Buck Scientific model VGP 210.

III. RESULTS AND DISCUSSION

A. Concentration of Heavy Metals at the Mining Sites

The results of the analyses of soil samples from Mangu Halle and Alogwom mining sites are presented in Tables I & II. From Table I, the concentration of Mn ranged from 40.03-94.85 mg/kg with an average of 60.07 mg/kg whereas Cu ranged from 17.48 to 25.85 mg/kg. Ni ranged from 52.17 to 84.64 mg/kg, Cd ranged from 1.85-6.75 mg/kg, Pb ranged...
from 15.4-45.4 mg/kg whereas Zn ranged from 109.91-157.34 mg/kg. Similarly, from Table II, the concentrations of the heavy metals at Alogwom, Mn ranged from 135.11-359.11 mg/kg with an average of 237.70 mg/kg whereas Cu ranged from 11.56-12.96 mg/kg with an average of 12.18. Ni ranged from 20.56-22.43 mg/kg. Cd ranged from 0.44-0.56 mg/kg. Pb ranged from 33.83-43.77 mg/kg with an average of 4.15 mg/kg whereas Zn ranged from 44.55-65.23 mg/kg.

1) Manganese (Mn)

In this study as can be seen in Tables II and III, Mn had the highest value of 194.85 mg/kg at Mangu mining site and 359.11 mg/kg at Alogwom. The concentration of Mn in this study is similar to the report of Shibdawa et al. [20] in Dorowa Mining Areas of Barkin Ladi, Plateau State, Nigeria. The results also revealed that the concentrations of Mn at all the sites were within the permissible limit of 2000 mg/kg recommended by FAO/WHO. [21]. Shibdawa et al. [20] reported that manganese (Mn) is frequently an abundant constituent of soils, but its low solubility at neutral and alkaline pH prevents excessive uptake by plants. He further asserted that manganese toxicity is nearly always associated with acid soils.

2) Copper (Cu)

Similarly, copper was one of the heavy metals detected in all the soil samples from the areas around the Mangu Halle and Alogwom artisanal mining sites (see Tables II and III). It has a mean concentration ranging from 17.48-25.58 mg/kg and 11.56-12.96 mg/kg at Mangu and Alogwom respectively. The concentration of Cu suggested that there could be anthropogenic contribution since artisanal mining is taking place in the vicinity of these areas. The results also revealed that the concentrations of Cu are within the permissible limit of 30 mg/kg recommended by WHO [22]. Similar results were reported by Singh et al. [23] at 1.5 km distance from the active mining sources and Ali et al. [24] but lower values were reported by Sanusi et al. [25]. The low values of Cu as postulated by other researchers, could be due to its mobility in weathering environment and its ability to adsorb onto soil constituents surfaces through ion exchange process [25], [26].

3) Nickel (Ni)

The results of Ni as can be seen in Tables II and III, revealed that the highest value of 84.64 mg/kg was recorded at Mangu while the highest value of 22.43 mg/kg was recorded at Alogwom. The concentrations of Ni in this study are also similar to the report of Shibdawa et al. [20] but higher than those reported by other researchers [27], [28]. The values obtained from these studies are higher than the FAO/WHO maximum permissible level of 40 mg/kg in soil at Mangu Halle but the values are within the permissible limit at Alogwom. According to Alshaebi et al. [29] in Shibdawa et al. [20] Ni contaminates the soil when the concentration of Ni is higher than 40 mg/kg. Hence, these results show that the soil is contaminated by Ni at Mangu Halle. This could be due to the source of mining. They further asserted that the highest concentration of Ni is usually found at the top layer of the soil that is rich in organic matter or with relatively high content of clay.

4) Lead (Pb)

Similar, Pb was also found in all the soil samples investigated. It had mean concentrations ranging from 15.40-45.40 mg/kg at Mangu and 33.83-43.75 mg/kg at Alogwom. The results of Pb revealed that the concentrations are within the permissible limit of 85 mg/kg recommended by WHO [22] and FAO/WHO maximum permissible level of 100 mg/kg in soil. The values of Pb in this study are lower compared to those reported by other researchers [25], [30], [31] but conforms to the findings of other researchers [20], [24]. The low levels of Pb in the soil as observed from the results could be due to its mobility in weathering environment and the ability to adsorb onto soil constituent surfaces through ion exchange process [25], [26].

5) Zinc (Zn)

Zn was also detected in all the soil samples investigated (Tables II &III). The mean concentrations of Zn ranged from 109.16-157.34 mg/kg at Mangu Halle and 144.55-165.23 mg/kg at Alogwom mining area. Mangu had the highest values of 157.34 mg/kg at site E while Alogwom had the highest value of 165.23 at site A. The results revealed that the concentrations of Zn were above the permissible limit of 50 mg/kg recommended by WHO [22]. The high values of Zn in the soils suggest that there could be anthropogenic contribution. Since local mining have taken place around these areas which no doubt may have contributed to high concentration of Zn metal in the soils. The concentrations of Zn in this study are however lower than the values reported by Sanusi et al. [25] but higher than the values reported by Ali et al. [24].

6) Cadmium (Cd)

Likewise, the results showed that Cd was detected in all the soil samples investigated with an average concentration of 3.37 mg/kg and 0.51 mg/kg at Mangu and Alogwom respectively. This is contrary to what was reported by Ali et al. [24] where Cd was detected only in one sample. The concentrations of Cd in this study were higher than those reported by Ali et al. [24] and Sudan and Ako et al. [32]. The results also revealed that the concentration of Cd varies with sites in the study area with the highest concentration obtained at site C (6.75±0.16 mg/kg) for Mangu mining area and highest at A (0.56±0.04 mg/kg) for Alogwom mining area. From these results, it could be seen that all the values were above the WHO [22] recommended maximum limit of cadmium in the soil (0.35 mg/kg).

Generally, the average concentrations of all the heavy metals at Mangu Halle and Alogwom mining sites were within the WHO [22] and FAO/WHO maximum permissible level except Ni at Mangu Halle and Cd which had concentrations above their maximum recommended limits. Generally, the concentrations of Cd at Mangu Halle were higher than the values at Alogwom village. The concentrations of the metals at mangu Halle mining site decreased in the order Mn > Zn > Ni > Pb > Cu > Cd while the sequence at Alogwom was Mn > Zn > Pb > Ni > Cu > Cd.
TABLE I: AVERAGE CONCENTRATION OF HEAVY METALS IN SOIL AT MANGU HALLE MINING SITE

| Sample | Mn  | Cu  | Ni  | Cd  | Pb  | Zn  |
|--------|-----|-----|-----|-----|-----|-----|
| A      | 59.99 | 17.48 | 52.17 | 3.23 | 27.10 | 132.35 |
| B      | 59.65 | 25.85 | 84.64 | 2.61 | 20.60 | 109.16 |
| C      | ±3.15 | ±3.26 | ±8.15 | ±0.01 | ±5.63 | ±20.18 |
| D      | 45.81 | 23.18 | 67.02 | 6.75 | 15.40 | 154.13 |
| E      | ±5.99 | ±6.19 | ±8.01 | ±0.16 | ±3.33 | ±22.25 |
| Av.    | 40.03 | 18.55 | 40.68 | 1.85 | 45.40 | 157.34 |
| ±4.44 | ±2.25 | ±7.22 | ±0.04 | ±1.58 | ±22.10 |
| Control| 18.11 | 5.30 | 1.12 | 0.11 | 0.25 | 26.00 |

TABLE II: AVERAGE CONCENTRATION OF HEAVY METALS IN SOIL AT ALOGWOM MINING SITE

| Sample | Mn | Cu | Ni | Cd | Pb | Zn |
|--------|----|----|----|----|----|----|
| A      | 135.11 | 12.96 | 22.43 | 0.56 | 33.83 | 165.23 |
| B      | 285.54 | 11.56 | 20.66 | 0.44 | 34.32 | 156.15 |
| C      | ±55.8 | ±2.22 | ±0.15 | ±0.08 | ±1.10 | ±2.10 |
| D      | 171.23 | 11.57 | 20.56 | 0.55 | 43.75 | 162.34 |
| E      | ±18.15 | ±1.50 | ±0.11 | ±0.12 | ±0.55 | ±2.13 |
| Av.    | 359.11 | 12.64 | 20.60 | 0.49 | 35.70 | 144.55 |
| ±24.1 | ±3.44 | ±0.04 | ±0.01 | ±0.22 | ±5.86 |
| Control| 237.70 | 12.18 | 21.06 | 0.51 | 36.90 | 157.07 |
| ±89.3 | ±6.33 | ±0.79 | ±0.05 | ±3.97 | ±9.94 |
| ±18.11 | 5.30 | 1.12 | 0.25 | 26.00 |
| ±0.01 | ±0.01 | ±0.01 | ±0.01 | ±0.01 | ±0.44 |

IV. SPECIATION OF HEAVY METALS AT THE MINING SITES

The speciation study was conducted to ascertain the forms of the heavy metals in the soil. The concentrations of the five chemical fractions for six heavy metals (Cd, Zn, Cu, Ni, Pb) are presented in Tables III & IV while the percentages of the metals in the different fractions are presented in Tables IV & VI. From these tables, the results showed that cadmium (Cd) was associated with all the fractions with the exchangeable fraction having 32.12 % and 35.11% at Mangu and Alogwom respectively (Tables III & IV). The predominance of Cd in the mobile fractions (soluble and exchangeable fractions) has been reported [13, 33]. The high percentage of Cd in the mobile fractions (62.78%) poses serious potential threat to the ecosystem and enhance potential bioavailability [14, 34]. The association of Cd follows the order: exchangeable fractions > soluble fraction > carbonate fraction > Fe/Mn bound fraction > residual fraction at Mangu Halle while at Alogwom, the distribution follows the pattern: exchangeable fractions > soluble fraction > residual fraction > Fe/Mn bound fraction > carbonate fraction. Zinc on the order hand was predominantly bound to the non-mobile fractions (residual fraction & Fe/Mn bound fraction) accounting for 69.27 % at Mangu Halle and 68.75% at Alogwom. This is similar to the reports of other researchers [13]. Hussain [34] and Ochiagha et al. [12] reported that heavy metals that are mostly bound to the residual fraction are not easily bioavailable to plants in the environment. The distribution of Zn on the order hand at Mangu Halle and Alogwom follows the pattern: residual fraction > Fe/Mn bound fraction > carbonate fraction > soluble fraction > exchangeable fraction. Similarly, copper (Cu) was found in all the fractions at the two mining sites with the residual fraction having the highest percent. This is in agreement with Ochiagha et al. [12] but in contrast with the report of Shivaswekumar et al. [35] where Cu was found in only two fractions. The association of Cu in the fractions at the two mining sites follow the order: residual fraction > carbonate fraction > exchangeable fraction > Fe/Mn bound fraction > soluble fraction.

The results also revealed that nickel (Ni) at Mangu Halle was found predominantly in the residual fraction with 50.00% while at Alogwom it was found predominantly with the Fe/Mn bound fraction with 71.78%. This agrees with Omuku et al. in Ochiagha et al. [12]. The high association of Ni in the non-mobile fraction may be attributed to the alkaline stabilization process of the soil [13]. The association of nickel (Ni) follows the pattern: residual fraction > exchangeable fraction > Fe/Mn bound fraction > carbonate fraction > soluble fraction while at Alogwom the pattern was slightly different: Fe/Mn bound fraction > residual fraction > exchangeable fraction > carbonate fraction > soluble fraction.

TABLE III: HEAVY METAL SPECIATION IN SOIL OBTAIN FROM MANGU HALLE MINING SITE

| Heavy Metal | Cu | Ni | Zn | Cd | Pb |
|-------------|----|----|----|----|----|
| F1 | 1.26 | 13.44 | 23.36 | 5.60 | 8.27 |
| F2 | 0.02 | 10.14 | 12.17 | 19.46 | 45.32 |
| F3 | 0.04 | 0.04 | 0.15 | 0.01 | 0.01 |
| F4 | 0.25 | 5.12 | 1.37 | 6.08 | 22.43 |
| F5 | 0.06 | 10.84 | 14.06 | 22.26 | 48.46 |

TABLE IV: PERCENT OF HEAVY METALS SPECIATION AT MANGU HALLE MINING SITE

| Heavy Metal | Concentration (mg/kg) |
|-------------|-----------------------|
| Cd | 30.66 | 32.12 | 23.36 | 5.60 | 8.27 |
| Zn | 10.84 | 6.89 | 13.01 | 20.81 | 48.46 |
| Cu | 5.12 | 13.73 | 15.37 | 11.07 | 54.71 |
| Ni | 10.63 | 14.06 | 11.88 | 13.44 | 50.00 |
| Pb | 2.38 | 16.33 | 9.52 | 15.31 | 54.42 |
| Mn | 16.32 | 2.53 | 0.17 | 6.08 | 73.10 |

TABLE V: HEAVY METAL SPECIATION IN SOIL OBTAIN FROM ALOGWOM MINING SITE

| Heavy Metal | Concentration (mg/kg) |
|-------------|-----------------------|
| Cd | 0.28 | 0.33 | 0.06 | 0.13 | 0.14 |
| Zn | 0.35 | 1.44 | 2.14 | 10.46 | 20.14 |
| Cu | 0.04 | 0.15 | 0.01 | 0.05 | 0.01 |
| Ni | 0.34 | 0.45 | 0.38 | 6.60 | 1.43 |
| Pb | 1.37 | 0.49 | 0.78 | 10.45 | 20.60 |
| Mn | 1.18 | 11.24 | 10.29 | 27.32 | 124.35 |

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The presence of these heavy metals in the mobile fraction indicates that they could be easily released to the environment from soil. Therefore, they are likely to cause toxicity in the environment because, toxicity of heavy metals does not depend on its total concentration but depends on different forms in which metals are present.

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**COMPETING INTERESTS**

Even though this research was sponsored by Tertiary Education Trust Fund (TETFund) in Nigeria. Authors do declare that no competing interests exist.

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**TABLE VI: PERCENT OF HEAVY METALS SPECIATION AT ALOGWOM MINING SITE**

| Heavy Metal | F1 | F2 | F3 | F4 | F5 |
|-------------|----|----|----|----|----|
| Cd          | 29.78 | 35.11 | 6.38 | 13.83 | 14.89 |
| Zn          | 23.21 | 3.23 | 4.81 | 23.50 | 45.25 |
| Cu          | 6.70 | 4.11 | 5.21 | 37.33 | 46.65 |
| Ni          | 3.70 | 4.89 | 4.13 | 71.74 | 15.54 |
| Pb          | 3.45 | 1.23 | 1.97 | 26.33 | 51.90 |
| Mn          | 0.67 | 6.45 | 5.90 | 15.67 | 71.31 |

F1= Soluble fraction; F2 = Exchangeable fraction; F3 = Carbonate fraction; F4 = Fe/Mn bound fraction; F5 = Residual fraction.
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