

**SEQUENTIAL EXTRACTION OF Pb, Zn, Fe, Cd AND Cu, IN SOIL FROM
SELECTED ARTISANAL MINING SITES IN TALATA MARAFA LOCAL
GOVERNMENT AREA OF ZAMFARA STATE, NIGERIA**

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ABSTRACT

This study aimed to establish the forms of heavy metals in soils around artisanal mining sites in Talata Marafa Local Government Area, Zamfara State, Nigeria, using sequential extraction methods. Samples were collected from Kadauri, Hura and Gebawa. Soil physicochemical parameters (particle size distribution, pH, Electrical conductivity (EC) and cation exchange capacity) were determined using standard methods. The speciation of heavy metals (Pb, Zn, Cd, Fe, and Cu) in the soil was determined using standard sequential extraction method. The results of physiochemical parameters revealed that for the soil particle size distribution, the percentage ranges of the sandy fraction across the site were 65 (Kadauri) to 75% (Gebawa) while the silt and clay fractions were 15 (Gebawa) to 20% (Kadauri, Hura) and 10 (Gebawa, Hura) to 15% (Kadauri), respectively. With a mean range value of 9.10 (Gebawa) - 7.40, the pH values at the mining and control site soils were alkaline to slight alkaline (Kadauri). The cation exchange capacity across the sites ranged from 10.22 (Hura) to 11.39 Mol/kg and the electrical conductivity ranged from 98.00 (Kadauri) to 120.00 μ S/cm (Hura). The organic matter content ranged from 5.55 (Gebawa) to 9.36% (Hura). The results of the soil sequential extraction showed highest concentrations for the metals: Pb in exchangeable fraction (F1) (250 mg/kg), Cd, Fe and Cu in organic bound fractions (F4) are 150, 100 and 198 mg/kg and Zn in the oxidizable phase (F3) is 206 mg/kg. Availability of metals in exchangeable (F1), carbonate (F2) and oxidizable (F3) fractions of the samples indicates that they may be environmentally bioavailable and hazardous to human health.

Keywords: Mining sites; heavy metals; pollution; soils, heavy metals

INTRODUCTION

In Talata Marafa area of Zamfara State, Nigeria, abundant mineral resources are luring individuals to engage in artisanal mining of ore in pursuit of gold for profit, which has led to much harm, particularly to youngsters. Environmental contamination also results by mining,

metal corrosion, atmospheric deposition, heavy metal leaching from mining sites, metal evaporation, and metal suspension into groundwater and soil from water resources [1].

The removal and doling out of gold, which include, heap leaching carbon-in-leach with cyanide, oxidation, and roasting, are where the majority of mining pollution is produced. Nevertheless, the gold mining sectors are inadequately taken care by the laws in existence, a very common phenomenon in poor African countries, which is detrimental to the environmental [2, 3].

Researchers have established that gold mining and doling out can have an unconstructive crash on the environmental qualities and ultimately and way of life [4]. Artesian gold miners frequently release harmful compounds into water bodies, such as mercury, cyanide and arsenic, exposing workers and residents to a variety of health problems [5]. Processing gold ores results in the emission of hazardous heavy metal compounds into the environment, including oxides and sulfides [6-8].

The number of mining sites has expanded in Talata Marafa metropolis due to population growth and the need for means of subsistence [6]. Tons of heavy metals dusts are released into the atmosphere during the processing of contaminated gold ore due to the competitive struggle to make more money while engaging in risky mining activities [6, 9-10]. There has been copious information of heightened lead (Pb) poisoning in recent past among populace of some villages in Zamfara State, Nigeria [11]. The majority of the inhabitants of these remote communities, who make less than fifty cents per day, have connected this to the illegal mining operations [11].

Heavy metals in both soil and water must be thoroughly examined because even slight changes in their concentrations above acceptable levels, whether caused by natural or anthropogenic factors, can have serious environmental and subsequent health effects [12]. In view of the fact that there has been diminutive research on the presence of heavy metal pollution in environmental samples (soil samples) from the study area, the effects of heavy metal contagion on the environment should therefore be of great concern. As a result, the objective of this study was to evaluate the concentrations of heavy metals (Pb, Cd, Fe, Zn and Cu) in the soils and waters near a few artisanal mining sites in the Talata Marafa Local Government Area of Zamfara State in Nigeria.

MATERIALS AND METHODS

Description of Study Area

Three mining sites - Gebawa, Hura, and Kadauri in Talata Marafa Local Government Area of Zamfara State, Nigeria, were studied in this investigation. Approximately inhabited areas and agricultural lands are the mining sites. The investigated area, Talata Marafa, is positioned in the core of Zamfara State between latitudes $12^{\circ} 00'$ and $13^{\circ} 15'$ North and longitudes $5^{\circ} 00'$ and $7^{\circ} 15'$ East as shown in Figure 1 with yearly temperature ranging from 28 to 37.6°C . Zamfara is $38,962 \text{ km}^2$ in size, well-designed urban area with a few commercial hubs. 3,278,873 people were counted in the population in 1991 [13].

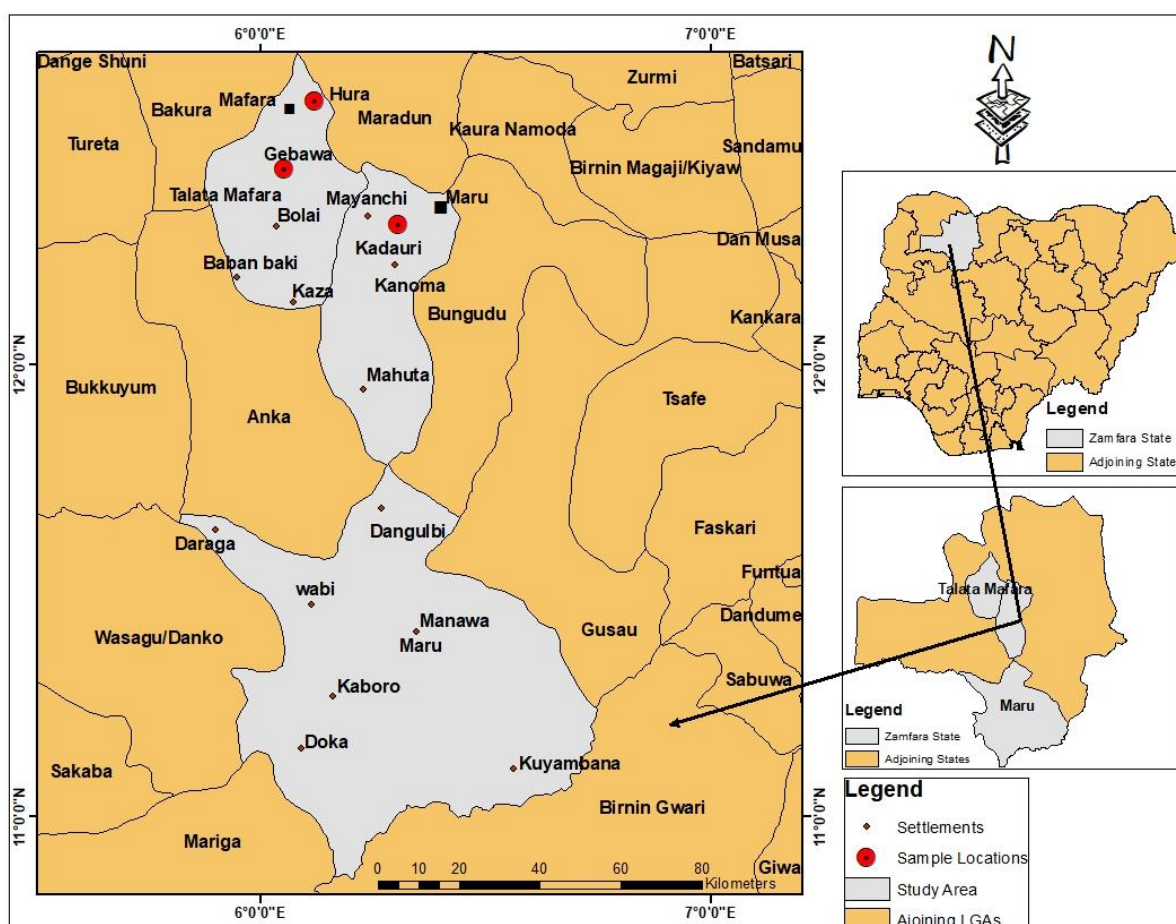


Figure 1: Map of Zamfara State Showing Sampling Sites in Talata Marafa Local Government Area

Soil Samples Collection and Treatment

Sampling was done in the hot and dry season of 2021, between March and April. Using a suitable auger and measuring tape, five (5) soil samples each were taken around the mining sites in Kadauri, Hura and Gebawa of Talata Marafa LGA, Zamfara State. The crest 0 to 15 cm of the soil was where the soil samples were taken. To avoid contaminating the samples,

care was taken to wash and clean the auger before sampling each location. As almost immediately as possible, the sample was taken to the laboratory for processing and preservation [14].

Three days at room temperature were spent air-drying the collected soil samples. For more analysis, the soil samples were beached and sieved by the use of a 2 mm sieve before being stored in disinfected polythene bags. Using standard techniques, the physicochemical characteristics of the soil, including pH, particle-size distribution, cation exchange capacities, and organic matter content, were measured [15]. To identify the bioavailable metals and those bound to various fractions, the soil samples were subjected to sequential extractions using a modified Tessier's procedure as reported [16].

Sequential extraction

According to Kumar *et al.* [16], sequential extraction was performed using a modified Tessier's method based on the principle of selective extraction: the exchangeable fraction was first extracted (F1) which was extracted using $Mg(NO_3)_2$. Furthermore, the carbonate fraction (F2) was extraction, followed by the reducible fraction (Fe-Mn oxide) (F3) extraction. The oxidizable which is the organic bound fraction (F4) using mixture OF HNO_3 and H_2O_2 . For the residual fraction (F5), aqua regia, hydrofluoric acid, and $HCl/HNO_3/HF$ were combined. The concentrations of Pb, Zn, Fe, Cd and Cu in the extracts were determined using Varian model AA240FS atomic absorption spectrophotometer (AAS).

Quality Assurance

In order to assure the quality of results, spiking experiment was conducted to ascertain the accuracy and reliability of the analytical procedure. Hence, two pre-digested soil samples were spiked with 20 ml of multi-element standard solution (0.5 mg/l of Pb, Zn, Fe, Cd and Cu) prepared from nitrate salts of the metals [5]. The samples were digested for total heavy metal concentration using the method described by Awode *et al.* [8]. The filtrate was measured for metal concentrations using the AAS and the metal concentrations in the corresponding unspiked samples and the spiked samples were used to evaluate the percentage recovery of the metals in the sample. Statistical analysis of data were done using IBM SPSS version 22. All mean recorded were determined at 95% confidence level.

RESULTS AND DISCUSSION

Validation Experiment

The percentage recoveries obtained for the metals under investigation are shown in Table 1. The pattern of recovery for soils was found to follow the decreasing orders: Pb > Fe > Cd > Cu > Zn. High percentage recoveries obtained in these samples validate the experimental protocol.

Table 1: Percentage recovery of heavy metal in studied samples

Metal	Percentage (%) Recovery
Cd	101.00
Cu	100.00
Zn	99.20
Fe	101.60
Pb	110.00

Physicochemical Parameters of the soil

The analysis of the soil physicochemical parameters is shown in Table 2. The pH (H₂O) and pH (CaCl₂) of the soils falls within the ranges of 7.40±0.50 to 9.10±0.15 and 7.90±1.11 to 8.20±0.15, respectively. The control soil, on the other hand had a pH of 6.50 and 5.90 in H₂O and CaCl₂, respectively which is slightly acidic than the study sites. The bioavailability of metals in soils decreases above pH 5.5 to 6.0 [17]. Metals in the soil solution are more or less bioavailable depending on the pH of the soil. Also as shown in Table 2, the soils were predominantly sandy loamy across the sampling sites. The sand composition in the area ranges from 65 to 75% and 50% at the control site. This finding corroborated with Shehu *et al.* that the soils around mining sites are usually sandy loamy [18]. This indicates poor retention of heavy metals in the soils.

The percentage of organic matter (% OM) varied from 5.55 for Gebawa to 9.36 for Hura. The values recorded for OM (%) across the studied area were 9.36% to 5.55% and the control site was 0.88% as shown in Table 2 sites. In the organic matter portion of the soil, positive ions (cations) are adsorbed and held by electrostatic force (OM). Preceding studies have established that higher OM (>3.0%) levels are typically associated with fine soils and lower OM levels with coarse soils [5].

CEC in soils typically ranges from 3 Cmol/kg for sandy soils low in OM to > 25 Cmol/kg for soils high in particular types of clay or organic matter (OM) [5]. The present study showed CEC range of 10.99 - 11.39 Cmol/kg. The CEC measures the soils capacity to absorb or release cations which is crucial to the availability of heavy metal in contaminated

soils. Clay minerals and organic matter both contribute to the CEC and this electric charge is what determines how many cations are present in the water [18].

Table 2: Physicochemical parameters of the soil samples

Parameter	Sampling Sites			
	Gebawa	Hura	Kadauri	Control
Sandy (%)	75.00±3.48	70.00±0.60	65.00±2.30	58.00±0.66
Silt (%)	15.00±2.99	20.00±8.00	20.00±7.84	22.00±3.44
Clay (%)	10.00±9.99	10.00±4.50	15.00±3.33	20.00±5.00
Soil Textures	Sandy Loamy	Sandy Loamy	Sandy Loamy	Sandy Loamy
pH (H ₂ O)	9.10±0.15	7.50±0.10	7.40±0.50	6.50±0.40
pH (CaCl ₂)	8.20±0.15	9.10±0.10	7.90±1.11	5.90±0.40
CEC(Mol/kg)	11.39±4.00	10.20±0.45	10.99±0.30	2.00±0.66
EC(μS/cm)	105.00±2.00	120.00±5.00	98.00±0.10	15.50±5.55
OM (%)	5.55±0.09	9.36±0.14	8.26±0.12	0.88±1.20

A near-neutral pH will affect CEC in soil than an acidic pH [19, 20]. The concentration of clays has less of effect on soil CEC than organic matters, so soil CEC is typically higher in study sites than in control sites. At control site, a location that is not a mining site, CEC and OM recorded the lowest mean values (0.88±1.20). Additionally, the mean values of the CEC across the sites did not significantly different. The results were similar to that obtained by Moses [21] and lower than values reported by Mohammad. and Abdullah [14].

Sequential Extractions

The concentrations of chemical fractionation of Zn, Cr, Cd, Pb, and Fe in the soil across the sampling sites are shown graphically in Figures 2 - 6. The exchangeable fraction (F1), carbonate fraction (F2), Fe-Mn oxide fraction (F3), organic bound fraction (F4), and residual fraction (F5) are the five chemical fractions.

LEAD (Pb)

The results of chemical fractionation of Pb across the mining site soils is shown in Figure 2 in different fractions which ranges from 250 -50 mg/kg for F1 and F5 respectively across the whole mining sites and fractions, the chemical associations of lead (Pb) were dominated by the exchangeable phase (F1), carbonate phase (F2) and oxide phase (F3) fractions respectively with a total (F1+F2+F3) which by implication will be available for uptake plant and leached into water [23]. The residual fraction (F1) has the highest level of (250 mg/kg) and while the F5 (50 mg/kg) was lowest in organic fraction (F5). All of the locations had significant Pb concentrations in the exchangeable fraction with Gebawa having the highest

concentration (250 mg/kg). The Pb distribution fractionation follows this pattern: $F1 > F4 > F5 > F2 > F3$. This contradicts the conclusions reached by a number of authors [19, 24]. The F2 fraction was found to be the predominant form of Pb in the Kocani paddy soil, accounting for 12.7% of the total soil Pb [23]. Pb levels in the soils of all mining sites exceeded the Federal Environmental Protection Agency's (FEPA) maximum allowable level of 300 mg/kg [24].

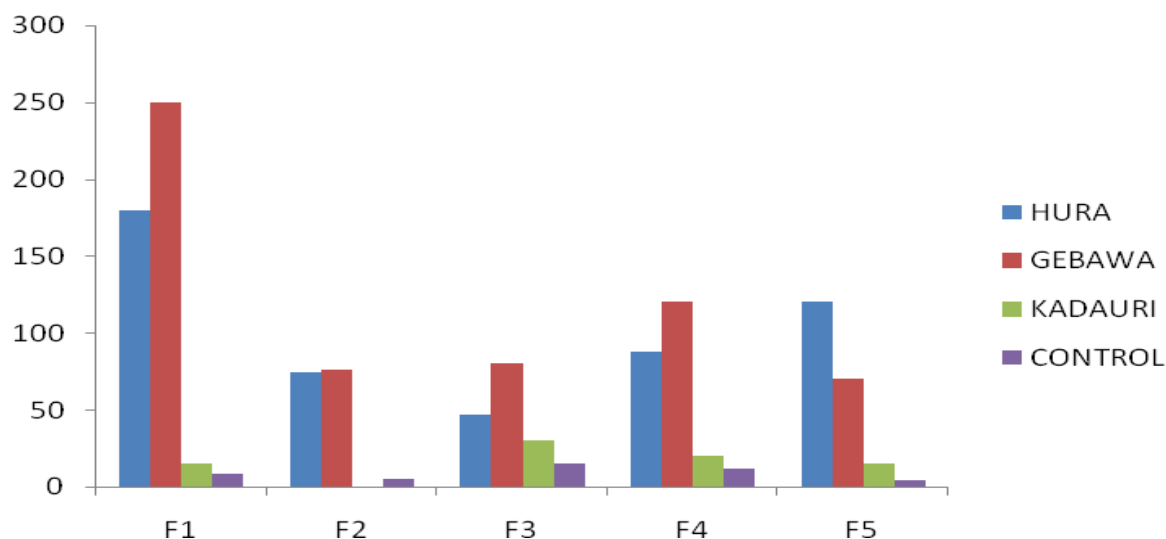


Figure 2: Concentrations (mg/kg) of Pb in different soil fractions

Cadmium (Cd)

The highest contents of Cd are associated with the F4 fraction with a mean of 150 mg/kg, F4 and F1 with a mean of 98 and 30 mg/kg, respectively (Figure 3) and Soil Cd in the F1, F2 and F3 fractions accounted for > 79.42 % of total soil Cd. According to the outcome of the sequential extraction, up to 90% of the Cd found in soil samples was linked to high stable fraction like oxide, organic, and residual fraction. In general, the order oxide was followed by metal distribution in soil samples [21-23]. The total extractable fractions (F1+F2+F3+F4+f5) contained Cd in amounts that were above the critical level which is 300 mg/kg for soil recommended by FEPA [24].

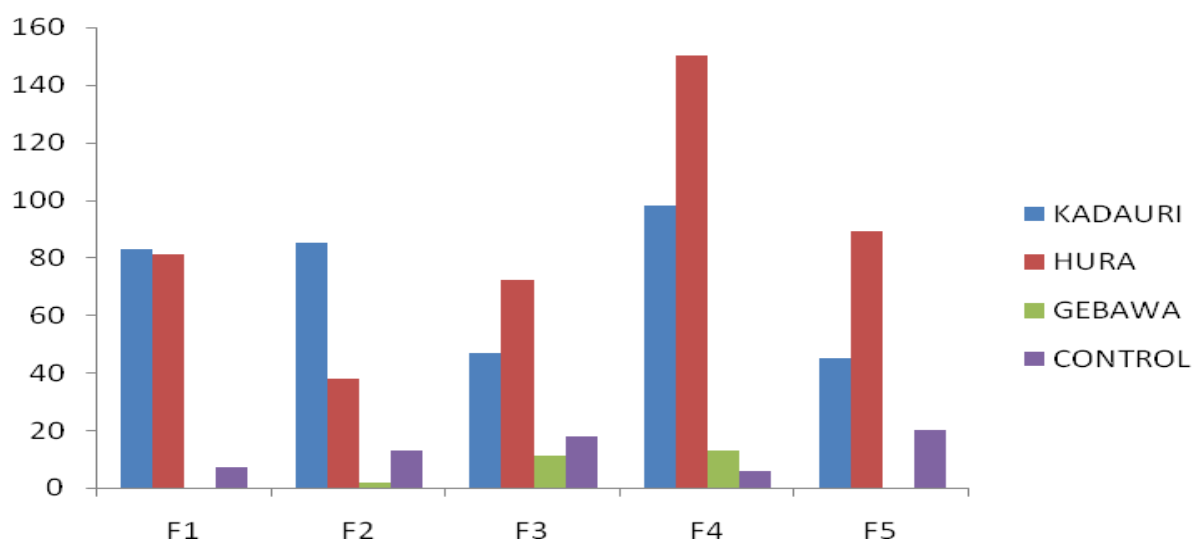


Figure 3: Cd concentrations (mg/kg) in different soil fractions

Iron (Fe)

The amount of iron present in the extractable fractions is depicted in Figure 4 (F1, F2, F3, F4 and F5). The F1, F4, and F5 fractions had the highest concentrations of Fe (85, 100, and 140 mg/kg, respectively), which indicates that the F4 fraction has a higher tendency for Fe to be highly mobile in the soil. The presence of a metal in these fractions suggests that it is largely incorporated for plant uptake in the soil's crystal lattice [27, 28, and 29]. Soil Fe in the F1 fraction accounted for 51.00 % of total soil Fe and remainder was distributed between other (F2, F3, F4 and F5) fractions at Kduri mining sites. Results indicated that F5 was mainly held with 26.00 % at Hura and 30.00 % F5 fractions, with other forms of fractions contributing 70 % of total soil Fe at Gebawa mining sites.

F4 (100 mg/kg) was discovered to be the dominant fraction in the soil sample when compared to other fractions, and the highly mobile exchangeable phase and pH-sensitive carbonate phase indicate an increase in anthropogenic Fe input into the environment. Since the highly mobile exchangeable phase is so high, Fe can be easily released to other environmental components like crop water [28, 30]. Due to the high concentration of Fe associated with the non-residual fraction (associated with 72% of the total Fe content), and the ease with which Fe can enter the food chain via water reservoirs, uptake by plants growing in the soils of mining sites could potentially have a negative impact on the environment and, consequently, on human health. All of the mining soils had total Fe concentrations that were greater than the 200 mg/kg toxic limit established [4, 24].

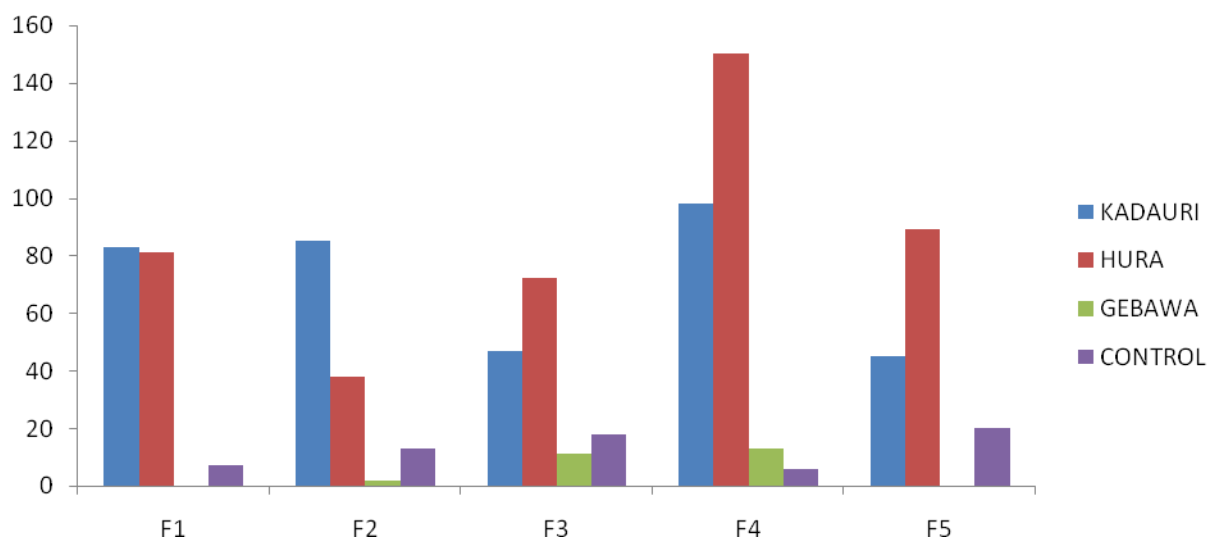


Figure 4: Fe concentrations (mg/kg) in different soil fractions'

COPPER (Cu)

The distribution of copper obtained in the five fractions by the extraction of sediment across all the three locations showed that copper was mostly concentrated in the Organic Phase (F4) with the highest concentrations of 198 mg/kg in Kadauri mining sites and the least at oxide phase (24 mg/kg) at Gebawa as shown Figure 5. The outcome of the result showed that Cu was largely bonded in F4 fractions 198 and 114 mg/kg for Kadauri and Hura respectively, with other forms contributing the total soil Cu. More so the results of Cu fractionation in mining soils of Gebawa showed that Cu was principally bonded in F5 fractions (75 mg/kg) fractions accounting for the highest fractions. The total extractable copper (F1+F2+F3+F4+F5) was found to be above the 300 mg/kg limit for agricultural soils suggested by the Federal Environmental Protection [24] and [15, 25-26] based on the findings presented in Figures 4. These studies' findings concur with those of [29, 27] who also noted a similar Cu concentration from the Ado Ekiti Metropolis in southern western Nigeria. A mining operation's soil may contain copper that is bioavailable to plants because the percentages of bio-available copper at each site were relatively high (70%) [31-35].

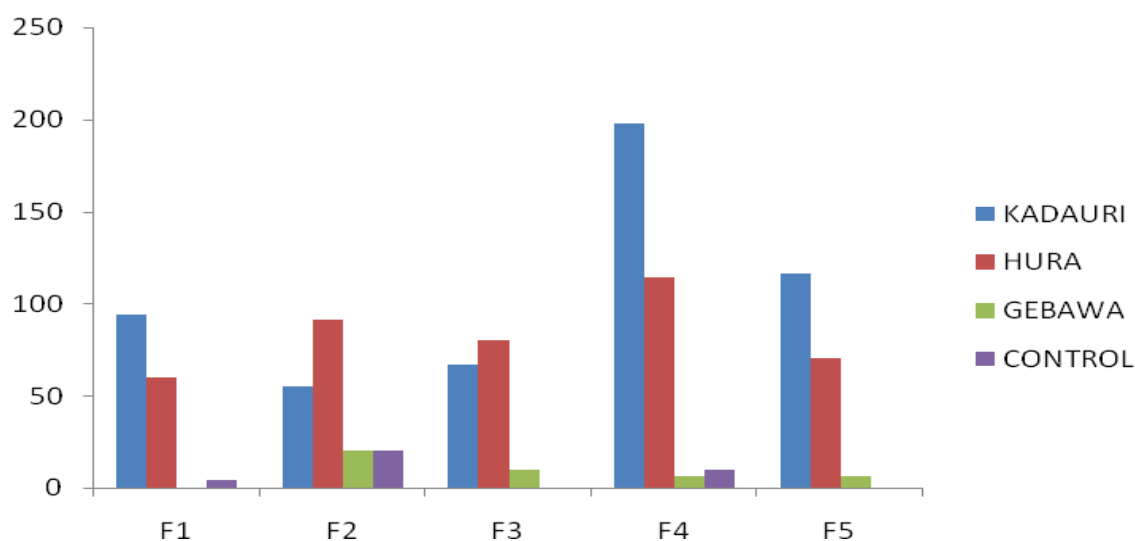


Figure 5: Cu concentrations (mg/kg) in different soil fractions'

Zinc (Zn)

Zn recorded the highest percentage level in the organic fraction across all the locations with exception of control sites. The lowest concentrations were generally recorded in the exchangeable fraction across all the three locations. This suggests that zinc was mostly concentrated in the oxides bound fraction (206 mg/kg) more than its concentration in exchangeable fraction (13 mg/kg). The residual fraction has concentration of 161 mg/kg while exchangeable fraction has the least value. Contrary to an earlier report in a related study, this stated that the level of the studied metals was highest in the residual fraction, is this statement [16, 30-32]. While the high concentration of Zn in the residual and exchangeable fractions was probably brought on by the mineral's high affinity for association or retention, such as with resistant sulfides and detrital silicates, the high percentage of Zn in the non-residual fractions may be related to the high cation exchange capacity and pH characteristics of the soil samples [20, 32-33]. The low content of metals in the organic fraction is likely due to either a low level of organic matter in and of itself or the organic matter's poor ability to retain metals due to the weak bonds between humic and fulvic acids [17,34].

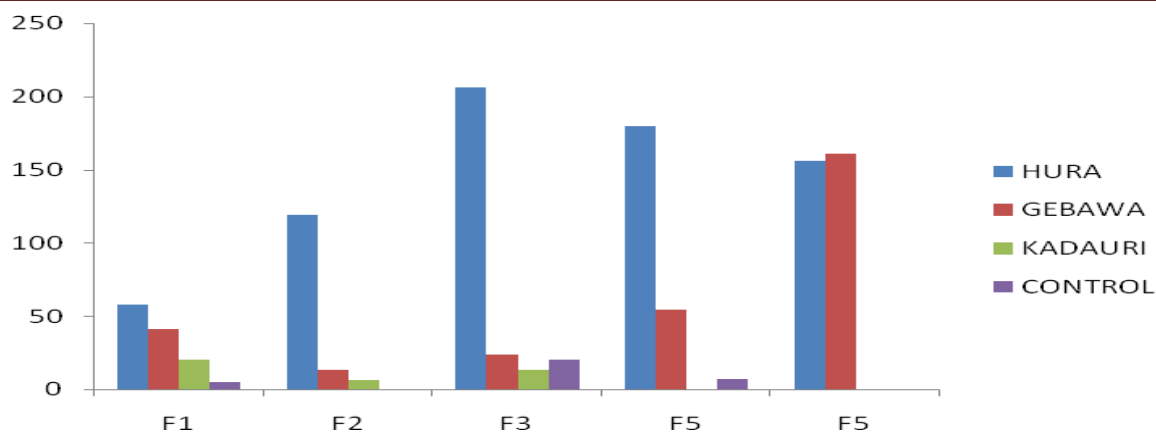


Figure 6: Zn concentrations (mg/kg) in different soil fractions

CONCLUSION

According to the physicochemical analysis, the soils were slightly neutral to alkaline. Each metal's discharge from or adsorption into each fraction is influenced by the pH variation in soil samples. Despite a noticeable amount of organic matter to balance the transfer and bioavailability of heavy metal improvement from waste soil, EC values reveal that there is a significant amount of inorganic salt obtainable in the soil. It is clear that there are differences in the strength of the bonds between the metals and the different soil fractions when comparing the methods by which the metals were bonded to them. Inputs of Cd and Pb were primarily in the exchangeable fraction and carbonate phase, while inputs of Zn and Fe were primarily in the form of residuals (F2). Cd inputs were present in both the Oxide Phase (F3) and Organic Phase (F4) fractions. The distribution of the five studied metals in the various fractions supports the various metal mobilities. Of the five elements under study, Cd and Pb appeared to be the most readily soluble, making them the most potentially bioavailable. Due to Cd and Pb, this possibly will result to harmful health effects.

Recommendations

To control these toxic wastes in the environment, there should be phytoremediation on heavy metals. It is furthermore advised that speciation of toxic metals be carried out across the seasons and at various depths in more mining sites in the town. It has been established that mining operations at Talata Marafa directly contribute to the soil and water pollution there. The illegal site should therefore be properly closed and mining activities within the site should cease.

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