

LEVELS OF HEAVY METALS IN SOILS AND FOOD CROPS CULTIVATED WITHIN SELECTED MINING SITES IN EBONYI STATE, NIGERIA

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ABSTRACT

The level of heavy metals (Fe, Cu, As, Pb, Cd, Mg, Ca, Hg, Ni, Cr, Zn, Ag, Co, Mo, Se and Al) in soils and food crops (okra, cassava and rice) cultivated within selected mining sites in Ebonyi State, Nigeria were determined using FS240AA Atomic Absorption Spectrophotometer (AAS) according to the method of American Public Health Association (APHA). Soil samples were collected from Enyigba mining site, Ikwo mining site, AmeriAmekamining site, Izza mining site, MkpumeAkwatakwa mining site and MpumeAkwaokuku mining site while the food crop samples (okra, cassava and rice) were collected from the farmlands within the mining sites. Control samples were collected 500m away from the mining destinations where there was no evidence of mining activities on the soils. A total of sixty sub-samples and six control soil samples were collected for this study. Generally, the values of all the heavy metals analyzed for soil and food crop samples were higher than the values recommended by the World Health Organization (WHO), and those from the control site suggesting possible mobility of the metals from mining sites to farmlands through leaching and runoffs. The findings in this study also revealed that the food crops contain heavy metals exceeding the maximum permissible concentration, and could be detrimental to human health when they are consumed.

Keywords: Heavy metals; Physicochemical; Soils; Food crops; Mining site

INTRODUCTION

Anthropogenic activities such as mining and metal smelting have led to increased level of heavy metals in soils and food crops cultivated within industrial areas [1]. The soil quality of arable and cultivated lands near industrial and abandoned multiple metal mine is concerning. As reported by the Ministry of Environment Protection [2], about 16.1% of soils, including 19.4% of the arable lands and 36.3% of enterprise surrounding soils was over the Grade II environment quality standard [3,4]. According to previous studies, mining sites were mainly polluted by anthropogenic activities such as mining exploitation, metal smelting, industrial processes, and traffic emissions [1,5-7]. The soil-plant-human route is a dominant pathway for heavy metals in food crops especially rice, okro and cassava [2,4,8].

So far, many studies have shown that plant roots can uptake and accumulate these contaminants and gradually transfer them to the edible parts, ultimately posing a potential risk to human health through the food chain when consumed [1,7,9]. It is noteworthy to mention that direct consumption of leaf vegetables can cause a severe threat to the health of the local populace [10,11]. Also, consumption of foods containing high level of heavy metals depletion of essential nutrients stored in the body [12]. Frequent exposure to heavy metals such as lead (Pb), cadmium (Cd), and arsenic (As) can lead to kidney dysfunction, liver and nervous system damage, lung and skin cancer, and bone fractures [8,13-15].

In recent years, studies focusing on the level of heavy metals in soils and food crops cultivated within mining sites have been conducted [12,16-22]. However, little study has been reported for most mining sites in Ebonyi State, Nigeria. Therefore, this study was conducted to bridge the knowledge gap. The main objectives of this study are to estimate heavy metals pollution levels in soils and food crops cultivated within selected mining sites in Ebonyi State, Nigeria. The results obtained from this research will provide a scientific basis and theoretical support for environmental management in mining communities.

MATERIALS AND METHODS

2.1 Study area

The study was conducted in six mining sites, namely: Enyigba, Ikwo, Ameri-Ameka, Izza, Mkpume-Akwatakwa, Mpume-Akwaokuku, and the control site (Abakaliki town). The Enyigba mining site is one of the significant communities where mining is vigorously done. It is situated in the south of Abakaliki; 14 km south of Abakaliki town of Ebonyi State [12,18,23]. Previous investigations at the examination area zeroed in on the effect of heavy metal tainting on deserted mine pits, underground water sources, waterways, streams and counterfeit lakes [14,15,24]. The region is a driving producer of rice, sweet potato, potatoes, cocoyam, Okro, maize, plantain and cassava [15,23]. Ikwo is located on the eastern part of the state. The territory is plentiful in mineral assets and progenitors of the present occupants created bronze projecting methods in excess of 500 years prior. The region is a driving producer of rice, sweet potato, potatoes, cocoyam, Okro, maize, plantain and cassava [19,24]. Ameri-Ameka is situated in the south of Abakaliki town. It comprises of cretaceous dregs of the Asu stream bunch, predominantly shales, silty shales, limestone and volcanic rocks. They are one of Africa's most notable lead-zinc mineralized region [14,19,24]. The region is a driving producer of rice, sweet potato, potatoes, cocoyam, Okro, maize, plantain and cassava [15,19,24]. The Izza south mining site is situated in the south of Abakaliki town. There are various kinds of soil around there, specifically: lateritic mud soil, sandy soil with mudstone and clayey shaly soil. The soil is gotten predominantly from the old sedimentary rocks. The territories are driving producers of rice, sweet potato, potatoes, cocoyam, okro, maize, plantain and cassava. The Mkpume-Akwaokuku and Akwatakwa mining sites are situated in the north of Abakaliki town. Exercises completed at the examination destinations incorporate open pit mining. Chinese specialists were engaged with the mining; and the mining done there were mainly shut pit mining. The vegetation is overwhelmed by grasses, bushes and trees such as palm trees, coconut, mango and orange trees [15,19,24]. The territories are driving producers of rice, sweet potato, potatoes, cocoyam, Okro, maize, plantain and cassava. The sampling sites and their coordinates are presented in Table 1.

Table 1. Sampling site and their coordinates

Sampling sites	Coordinates
Enyigba mining site	N: 06° 11.642' E: 008° 08.380' 263.4ft
Ikwo mining site	N: 06° 10.590' E: 008° 07.438' 196.8ft
Ameriamekamining site	N: 06° 11.042' E: 008° 06.110' 149.3ft
Izza mining site	N: 06° 09.929' E: 008° 06.625' 161.9ft
MkpumeAkwaokuku mining site	N: 06° 23.588' E: 008° 09.784' 192.8ft
MpumeAkwaokuku mining site	N: 06° 30.268' E: 008° 16.352' 226.6ft
Control (Abakaliki town)	N: 06° 19.163' E: 008° 06.559' 142.8ft

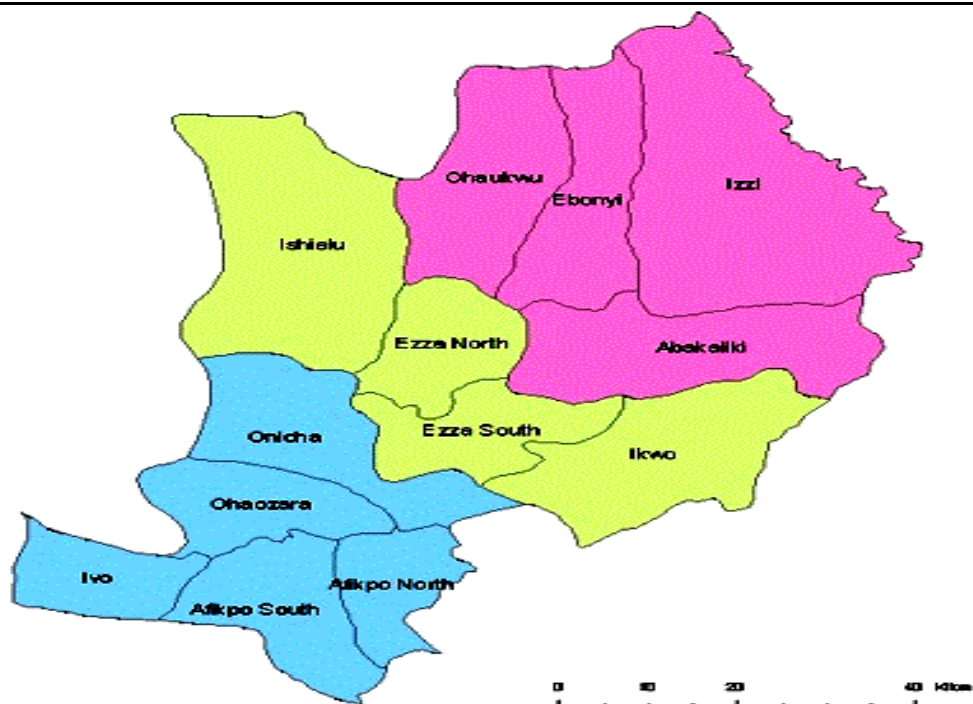


Figure 1. Map of Ebonyi State showing the different local governments

2.2 Samples Collection

Composite soil samples were collected from Enyigba mining site, Ikwo mining site, Ameri-Ameka mining site, Izza mining site, Mkpume-Akwatakwa mining site and Mpume-Akwaokuku mining site. The food crop samples (Okra, Cassava and rice) were collected from the farmlands within the mining sites, 500 metres away from the mining sites. Control samples were collected from destinations where there was no evidence of mining activities on the soils (Abakaliki). A total of sixty sub-samples and six control soil samples were collected for this study. The collected soil samples were air dried, crushed, sieved and thoroughly mixed in a clean plastic bucket, then stored in polythene bags and labeled appropriately prior to analysis.

2.3 Samples Preparation

2.0 g of prepared soil samples were digested with 15.0 ml nitric acid, 20.0 ml perchloric acid and 15.0 ml hydrofluoric acid and placed on a hot plate for 3 hours. On cooling, the digest was filtered into a 100.0 ml volumetric flask and made up to the mark with distilled water [12]. Similarly, dry powdered food crops (okra, cassava and rice) samples were digested with 60% HClO_4 , concentrated HNO_3 and H_2SO_4 [3,25]. Blanks were prepared to check for background contamination by the reagents used.

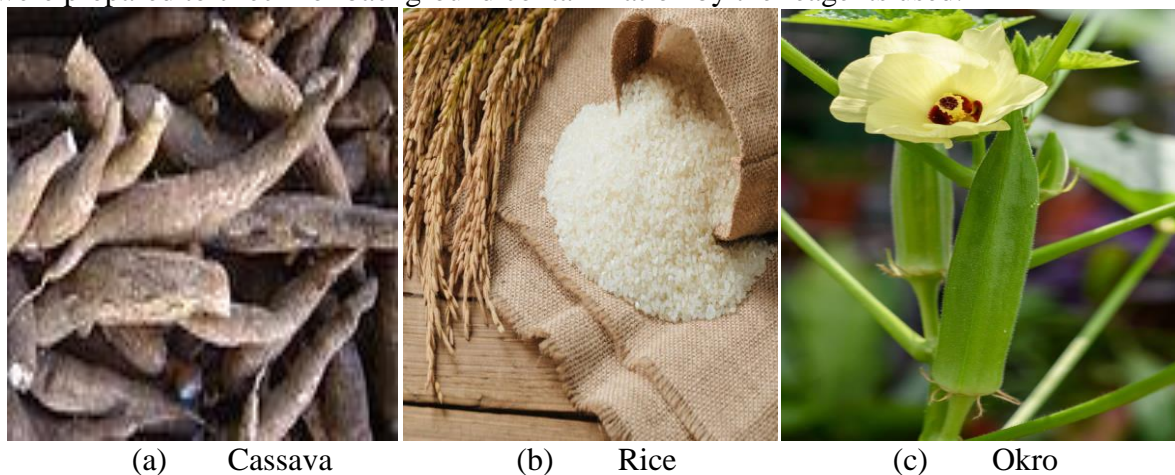


Figure 2. Pictorial representation of the food crop cultivated within the mining sites.

2.4 Assessment of Soil Physicochemical Parameters

The pH of the sample was measured according to the method prescribed by the American Public Health Association [26]. About 10g of the air dried and sieved soil sample was weighed and placed into a beaker, 100ml of water was used to mix thoroughly the sample; after which, the solution was allowed to stand for 1 hour, before the pH was taken. The exchangeable acidity was measured according to method described by [27]. About 5g of dry soil sample was weighed into a clean 50 ml beaker; 25 ml of KCl was added into the solution and stirred thoroughly. It was placed over a 100ml collecting bottle. And the soil suspension was poured through the filter. When the liquid has drained, the soil sample was leached three times with 3 further 25ml portions of KCl, it was allowed to drain before adding the next (total of 100ml leaching solution), using a measuring cylinder, 25ml of the leachate was transferred to a 50ml flask. 5 drops of phenolphthalein indicator was added, and the flask was placed on a magnetic stirrer. The resultant solution was titrated against 0.01M NaOH until the first appearance of a faint pink color. Exchangeable Ca and Mg and Na were analyzed using the method described by APHA (2005). This was done using a measuring cylinder, 25ml of the leachate was transferred to a clean beaker and 1ml of strontium nitrate solution was added, the concentration (mmol l^{-1}) of Ca, Mg and Na in the leachate was determined by Atomic Absorption Spectrophotometer (AAS). The exchangeable Ca, Mg and Na in the soil sample was determined (mmol kg^{-1}) by multiplying the concentration of each by 20. Cation exchange capacity (CEC) (mmol kg^{-1}) and Base Saturation (%) were evaluated using the formula in equation 1 and 2 respectively.

$$CEC (\text{cmol/kg}) = Ca + Mg + K \quad (1)$$

$$\% \text{ Base saturation} = \frac{100 (Ca + Mg)}{CEC} \quad (2)$$

Total Sulphur was determined gravimetrically according to the ASTM 1995 standard method [28]. Approximately 1.0g of the soil sample was mixed with 5.0 g of Na_2CO_3 and NaNO_3 . In a crucible, the mixture was preheated at 400°C for 30mins in an electric muffle furnace, and then fused at 950°C after the fusion, the crucible was allowed to cool and transferred into a 200ml beaker. Enough deionized water barely to cover the content of the crucible was added and the beaker heated at a temperature just below boiling point on a hot plate, until the melt was thoroughly disintegrated. The crucible was then been removed and washed with deionized water. At this point 20cm^3 of 6M HCl was added to neutralize the NaCO_3 and to make the solution slightly acidic. This was filtered into a 100cm^3 volumetric flask and the volume made up to the mark with deionized water. The solution was brought to boiling and 10cm^3 of 10% BaCl_2 slowly added to precipitate the sulphate. The solutions were allowed to cool and were filtered. The residue was washed with deionized water. The ashless filter paper was ignited at low temperature (40°C) and the precipitate weighed. The percentage sulphur in the precipitate was calculated using equation 3.

$$\% \text{ sulphur} = \frac{\text{gmBaSO}_4 \times 13.17}{\text{wt. of sample in gm}} \quad (3)$$

The % Silt, Clay, Sand (Particle size analysis) were determined according to ASTM 1995 (28). About 30g of the soil sample was added into a 250ml measuring cylinder, the container was loaded up with refined water up to the 200ml mark. The soil sample was washed with distilled water. 20ml of 20% sodium hexametaphosphate was added to the solution, and 200ml of distilled water. The resultant solution was allowed to stand for 16hrs. After which, the sample was sieved. The sample that remains on the sieve is the sand while the sample that passes through the sieve is the sediment. The particle sizes were calculated using Equations 4,5,6.

$$\% \text{ sand} = \frac{\text{Residue} \times 100}{\text{sample 1}} \quad (4)$$

$$\% \text{ silt} = \frac{\text{Residue} \times 100}{\text{sample 1}} \quad (5)$$

$$\% \text{ Clay} = 100 - \frac{(\% \text{ Silt} + \% \text{ Sand})}{N} \quad (6)$$

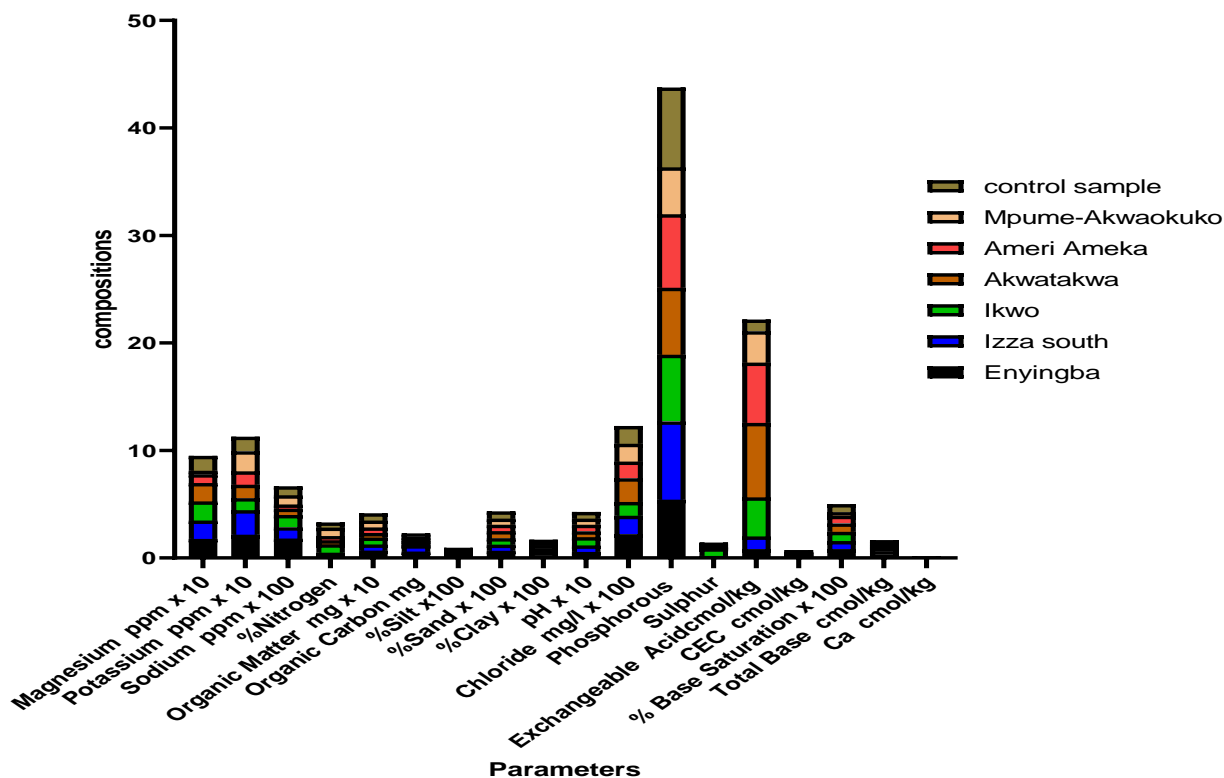


Figure 3 Physicochemical properties of soil samples from the selected mining sites

2.5 Heavy metals analysis

Heavy metal analysis was conducted using FS240AA Atomic Absorption Spectrophotometer according to the method of American Public Health Association (APHA, 1998). The digested samples were analyzed for heavy metals (Fe, Cu, As, Pb, Cd, Mg, Ca, Hg, Ni, Cr, Zn, Ag, Co, Mo, Se and Al). The instrument setting and operational conditions were done in accordance with the manufacturers' specifications. Following the same protocol as the samples, standard reference material (SRM 2783) filter from National Institute of Standards and Technology (NIST) was analysed for elemental concentrations and compared with their certified values to validate the analyses [22] and results were found within $\pm 5\%$ of the certified values.

2.6 Data Analysis

The data analysis for the data reported in this study was done using Ms-Excel and IBM SPSS Statistics Version 20.

RESULTS AND DISCUSSIONS

3.1 Physicochemical properties of soil samples

As shown in Figure 3, the physicochemical properties of soil sample analyzed within the mining sample and the control sample. From the results, it was observed that the soil samples were generally acidic with a pH range of 5.63 – 6.29, while the pH of the control sample was 6.20. All the samples are sandy loamy with %sand ranging from 54.93 – 66.18%; while % clay varied from 15.143 – 29.183%. Akwatakwa and Ameriameka had high exchangeable cation with concentration of 6.93 and 5.60 mg/l respectively compared to other mining samples with low exchangeable cation. Sodium, magnesium and potassium were detected in all the samples with Ameriameka having the least concentration, phosphorus were also detected in all the soil samples which implies the soil sample will be useful for plant growth. The control soil samples were generally acidic with pH ranging from 5.30-6.293, with sandy loamy characteristics and high chloride content. This was as a result of soil excavation going on in the sites. A higher exchangeable cation was

found around the mining sites compared to the control with Ameriameka having the highest concentration. Similar results were reported by [22,29] for dumpsite and floodbasin soils.

3.2 Result of heavy metal concentration

The result of figure 4 showed a high concentration of iron within the mining site and 500m from the mining site. With Akwatakwa having the highest iron concentration of 166.61mg/kg and Izza south 500 metres from the mining site with the least level of iron (55.38mg/kg). Higher level of lead and zinc were also detected within the mining site compared to soil sample 500m from mining site and control. When soil samples from Enyigba and Izza mining site were compared with soil samples collected 500m from mining site respectively, it was observed that lead, zinc, mercury, calcium, arsenic and aluminum did not vary significantly ($P>0.05$) while other heavy metals were significantly higher ($P<0.05$) when samples around the mining site were compared with samples 500 metres from mining site. Soil samples from Ikwo mining site was compared with soil samples 500 metres from mining site; it was observed that arsenic, lead, chromium and silver did not vary significantly ($P>0.05$), while a significant variation was reported for other heavy metals ($P<0.05$). No variation in heavy metals (arsenic, lead and aluminum) was observed in soil samples collected from Akwatakwa mining site and 500 metres away from the mining sites ($P<0.05$). Also, copper, chromium, nickel, cobalt, and calcium did not vary with soil samples collected from Akwatakwa mining site and soil samples collected 500m from mining site while other heavy metals statistically varied ($P<0.05$). Arsenic, lead and calcium did not vary when soil samples collected from Mpumeakwaokuku was compared with samples collected 500 metres from Mpumeakwaokuku mining site. It is of importance to note that the heavy metal concentrations reported in this study was higher than the concentrations reported by [1,2,8,15].

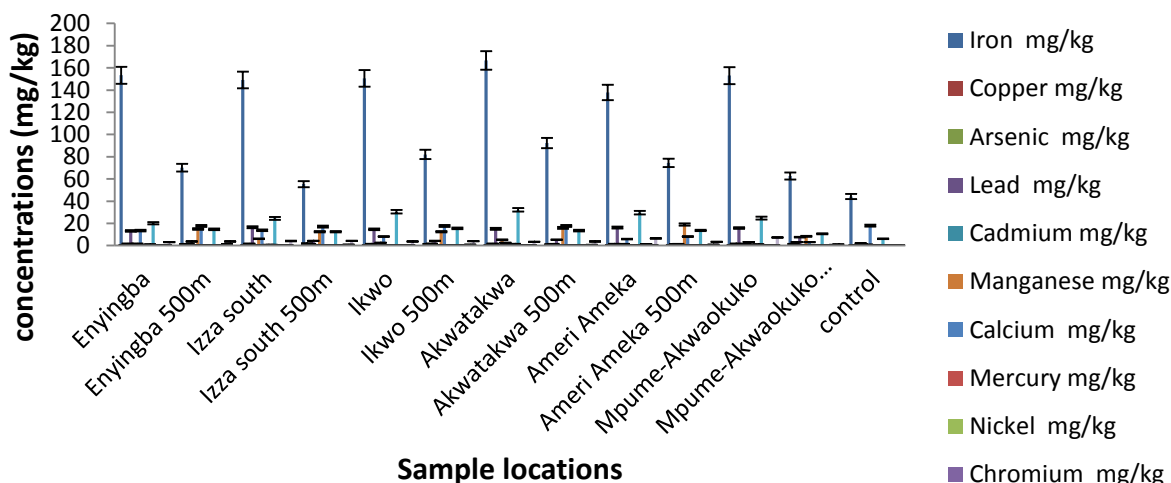


Figure 4 Heavy metal analysis of soil samples within the selected mining sites

3.3 Proximate Analysis of Food Crops

3.3.1 Result of Proximate Analysis of Okro

As shown in Figure 5, the proximate composition of okro grown around mining site and 500 m away from the mining site showed a higher percentage of carbohydrate. The samples collected 500 metres away from the mining site and Izza south had the highest concentration (59.30%) of carbohydrate while the sample collected in Mpume-Akwaokuko had the least carbohydrate concentration (44.32%). High moisture content was detected in all the studied sites with Akwatakwa having the highest concentration (37.67%). Generally, fat and protein recorded low concentrations in the studied mining sites. Worthy of note is that there is no significant difference between the samples collected within the mining sites and 500 metres away from mining sites.

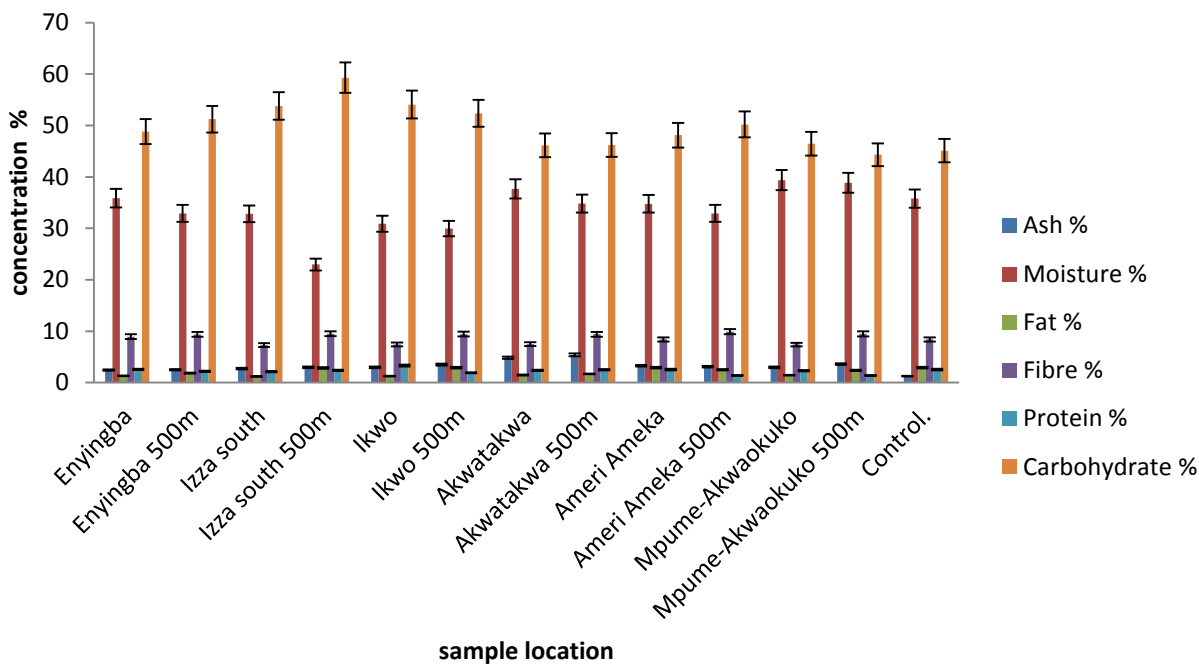


Figure5. Proximate composition of okro grown around mining sites, 500m from mining sites and the control sample

3.3.2 Result of Proximate Analysis of Cassava

The result in figure 6 showed generally a high carbohydrate concentration in the entire studied mining site. The mining site in Mpume-Akwaokuko and 500 m from mining site had the highest concentration of 76.12% and 75.53%. High moisture content was detected in all the studied mining sites while other parameters recorded low to moderately high fat and protein contents. The results showed no significant difference between samples collected within the mining sites and samples collected 500 metres away from mining site.

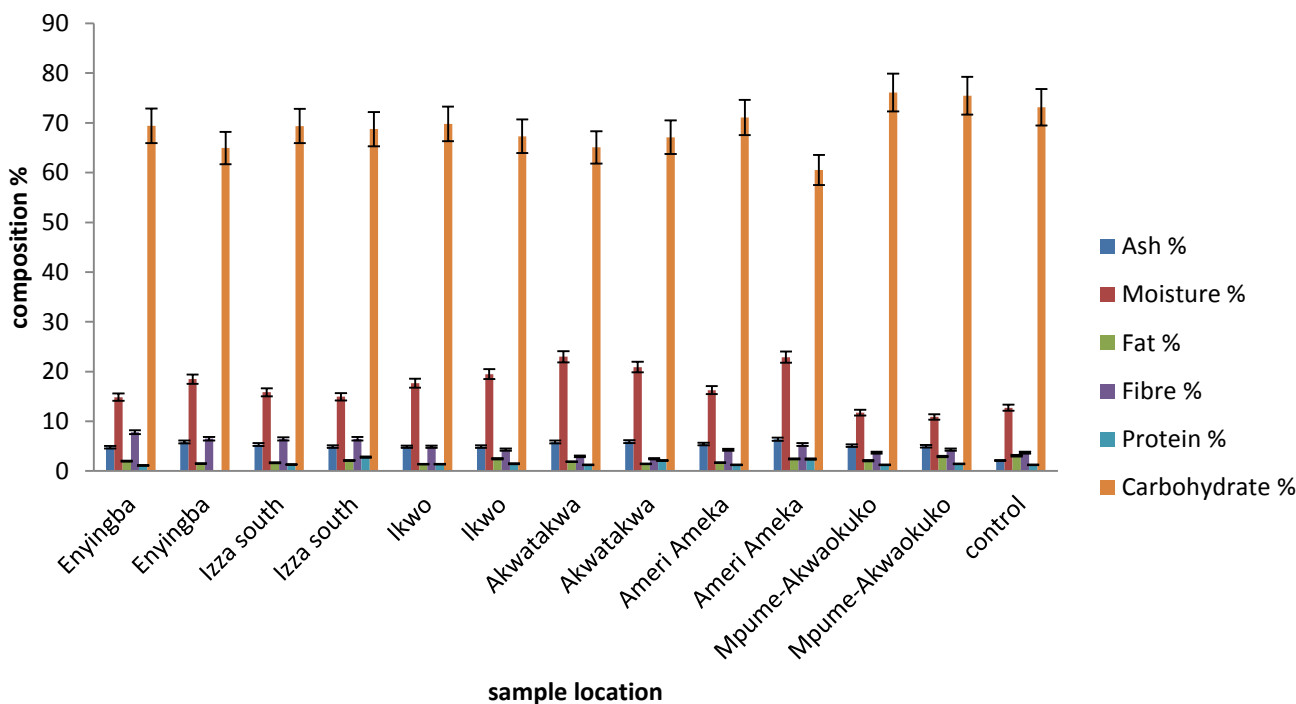


Figure6. Proximate composition of Cassava grown around mining sites, 500m from mining sites and the control sample.

3.3.3 Result of Proximate Analysis of Rice

As shown in Figure 6, the proximate composition of rice grown around mining site and 500m away from mining site showed a high concentration of carbohydrate in all the studied mining sites; with Ameri-Ameka having the highest concentration (85.18%). Moderate to low proximate compositions were found literally in all the studied sites. However, the results showed there was no significant difference between samples collected within the mining sites, 500m from mining sites and control sites.

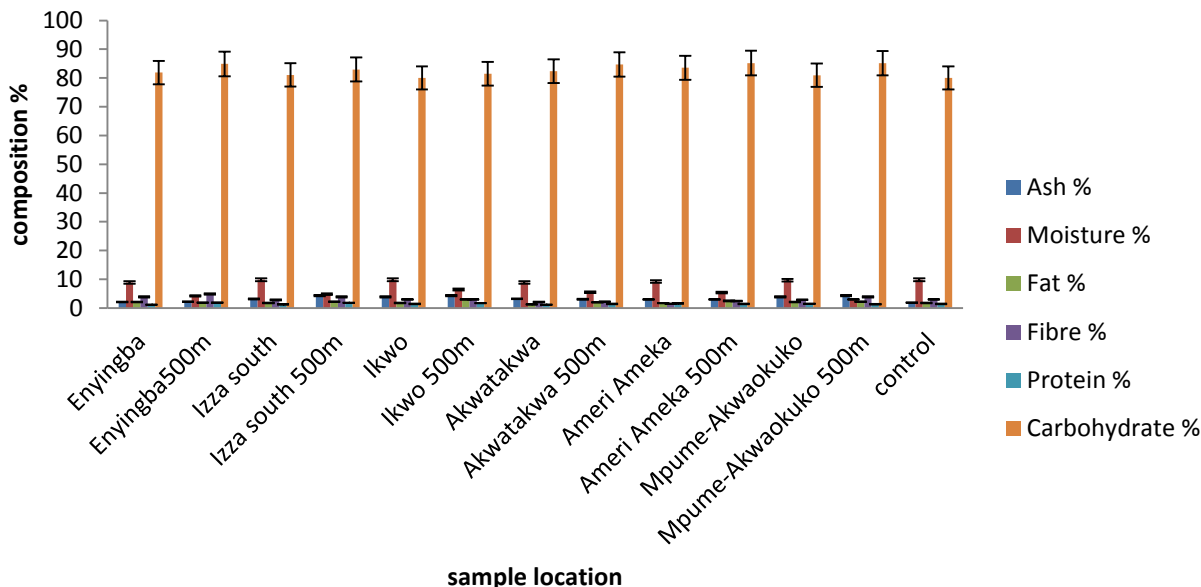


Figure7. Proximate composition of rice grown around mining sites, 500m from mining sites and the control sample.

3.3.4 Minerals in Food Crops

3.3.4.1 Results of mineral composition in Okro

The result in Figure 8 showed generally a high level of zinc in all the studied sites. Enyngba mining site had the highest concentration (43.23mg/kg). Sodium, potassium and magnesium were also detected at considerable high concentration in most of the studied sites while manganese and copper were detected at considerable low concentrations. Furthermore, the result showed that zinc in the mining site varied significantly ($P < 0.05$) with the samples collected 500m from mining site and control samples.

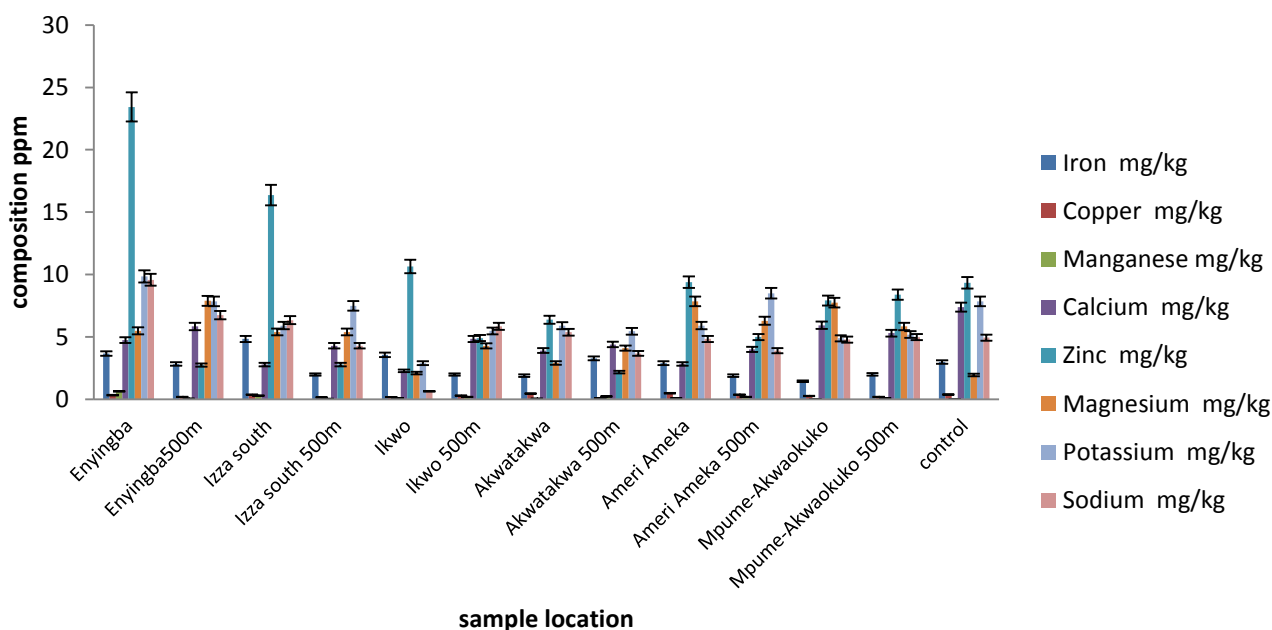


Figure8. Mineral composition of Okro grown around mining sites, about 500m from mining site and control

3.3.4.2 Results of mineral composition in Cassava

As shown in Figure 9, a high zinc level was found within the mining sites. Enyigba mining site had the highest concentration (15.27 mg/kg of sodium). Also, potassium and magnesium were detected at high concentration in most of the studied sites while manganese and copper were detected at low concentration. Statistical analysis showed that zinc in the mining sites varied significantly ($P < 0.05$) from the samples collected 500m away from mining site and control.

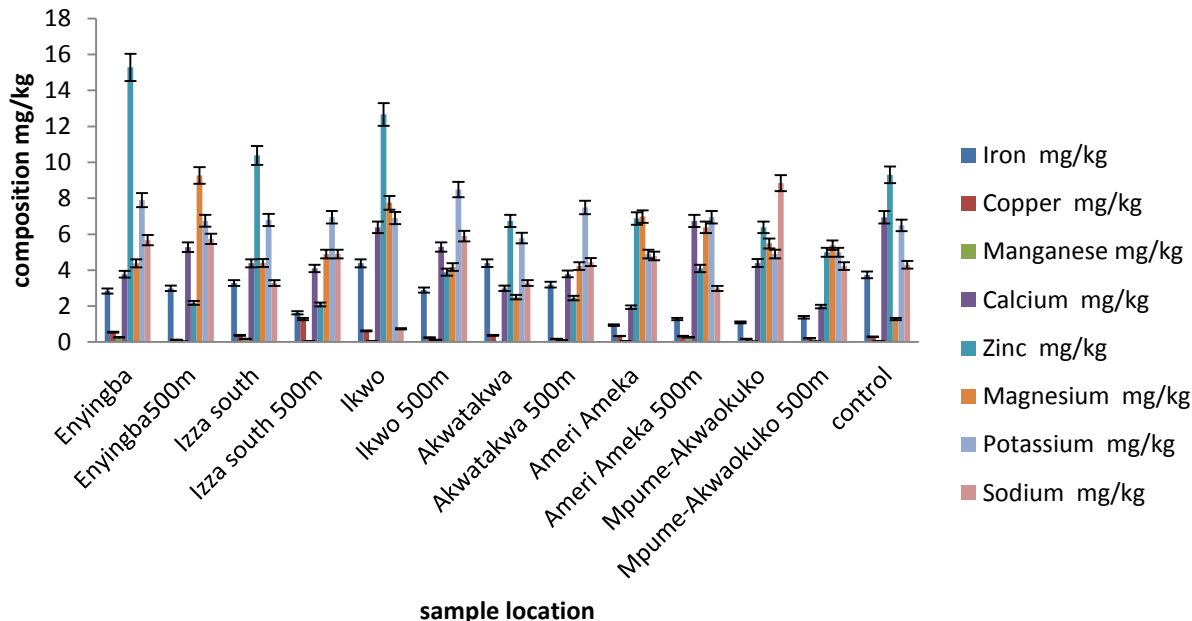


Figure 9 Mineral composition of Cassava grown around mining sites, about 500m from mining site and control

3.3.4.3 Results of mineral composition in Rice

The results obtained in Figure 10 showed a high zinc level in most of the studied sites. Izza mining site had the highest concentration of zinc (16.39 mg/kg); while Izza 500 metres away from mining site had the least concentration (2.09 mg/kg). Magnesium, potassium and sodium were detected at a considerably high concentration in all the studied sites whereas iron, copper and manganese were detected at lower concentrations. The level of zinc in Izza mining site varied significantly with the samples collected 500 metres away from the mining and control sites.

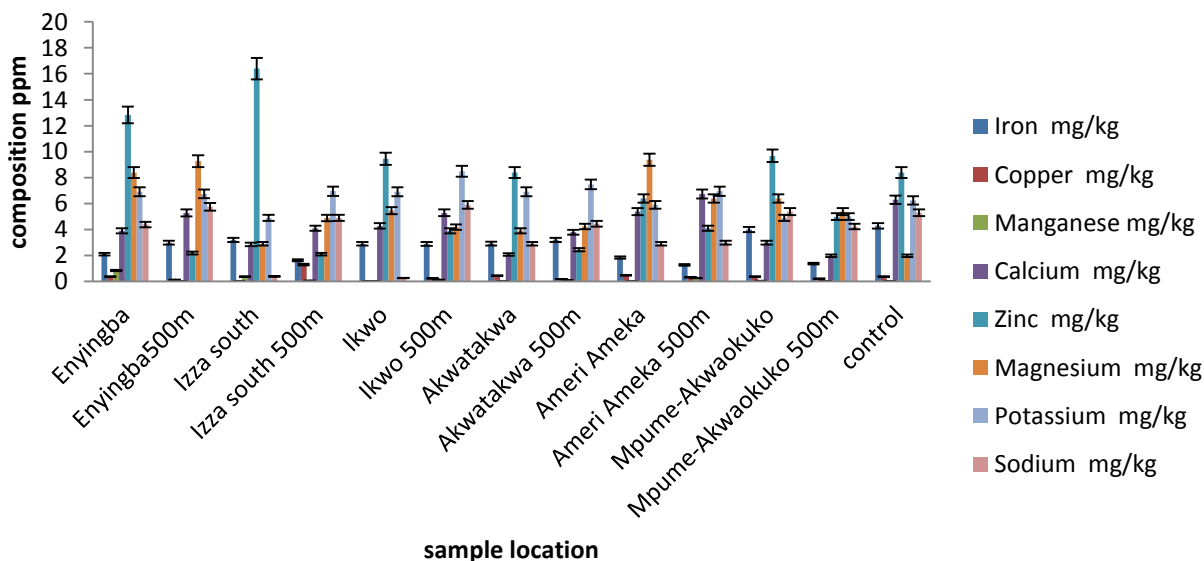


Figure 10. Mineral composition of rice grown around mining sites, about 500m from mining site and control

3.4 Heavy metals in Food Crops

3.4.1 Results of heavy metals in Okro

The results in Figure 11 showed a high level of lead in Enyigba mining site with a concentration of 3.84 mg/kg; followed by Ikwo mining site (3.38 mg/kg), while the least concentration of lead was detected in the control samples (0.07 mg/kg). Similarly, high nickel concentration was detected in Ameri-Ameka (2.81 mg/kg) while the other heavy metals recorded moderate to low concentrations. The result of the statistical analysis showed that the lead concentration within the mining site was significantly higher than the control site as well as samples collected 500m from the mining sites. Nickel concentration in Ameri-Ameka mining site also varied significantly with the control samples and samples collected 500 metres from the mining site. Also, the results showed that the control samples had the least total heavy metal concentration, while Enyigba and Ameri-Ameka recorded the highest heavy metal concentrations. According to Liu *et al.* [25], irrigation of farmlands with metal-contaminated water can lead to high concentrations of trace metals in food crops planted in the farmlands.

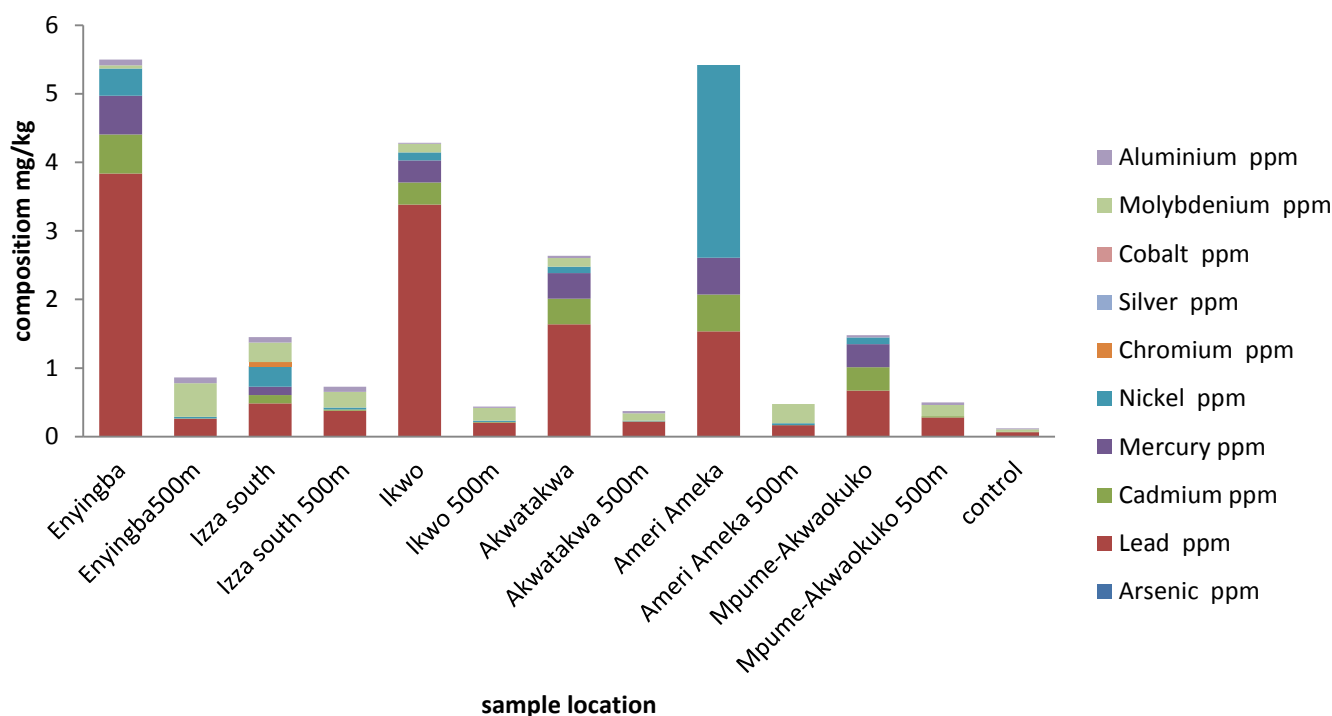


Figure 11. Heavy metal levels in okro grown around mining sites, about 500 metres from mining site and control

3.4.2 Results of heavy metals in Cassava

The result in Figure 12 showed a high level of lead in cassava grown within the mining sites. Enyigba recorded the highest concentration (3.00 mg/kg) followed by Akwatakwa with concentration of 2.88 mg/kg and the control site (Abakaliki) having the least concentration of lead (0.09mg/kg). All other heavy metals recorded a moderately low concentration. Akwatakwa mining site had the highest heavy metal concentration of 3.72 mg/kg; followed by Ikwo with a concentration of 3.59 mg/kg and the control site having the least concentration. Statistically, the result showed that lead within the mining site was significantly higher than the control site and samples collected 500m from mining site. Worthy of note is that plants readily bio-accumulate a significant amount of lead through their roots with no alteration in total yield or appearance [11,29,30]. According to Liu *et al.* [25], metal-contaminated farm irrigation water can lead to high concentrations of trace metals in food crops planted in agricultural soils near mining sites.

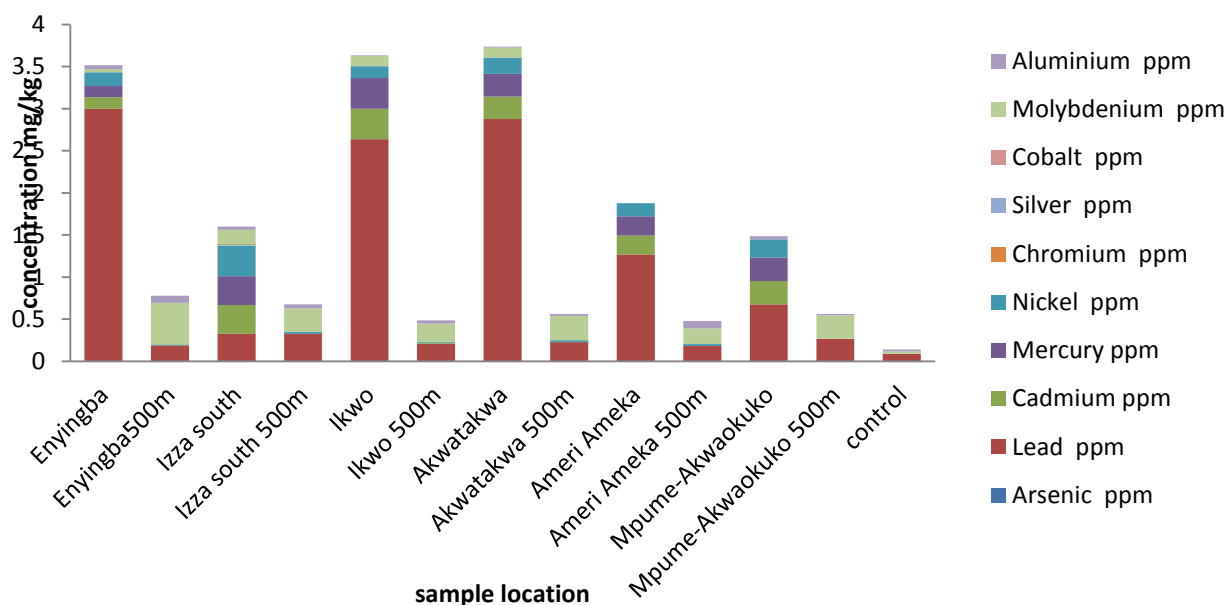


Figure 12. Heavy metal levels in cassava grown around mining sites, about 500m from mining site and control

3.4.3 Results of heavy metals in Rice

As revealed in Figure 13, high concentration of heavy metals in rice samples was recorded within the mining sites compared to rice samples collected 500 metres away from the mining and control site.

Mpumeakwaokuku had the highest heavy metal concentration of 4.10 mg/kg while the control having the least concentration of 0.25 mg/kg. The concentrations of lead in rice samples were highest in Mpumeakwaokuku mining site (2.98 mg/kg) while the least was recorded in the control site. High nickel concentration was detected in Ameriameka mining site with a concentration of 0.94 mg/kg. Statistically, the result showed that lead concentration within the mining site was significantly higher than the control site as well as the samples collected 500 metres from mining site. Nickel in Ameriameka mining site also varied significantly with the control samples and samples collected 500 metres away from Ameriameka mining site. According to Liu *et al.*, [25], metal-contaminated farm irrigation water can lead to high concentrations of trace metals in food crops planted in agricultural soils near mining sites.

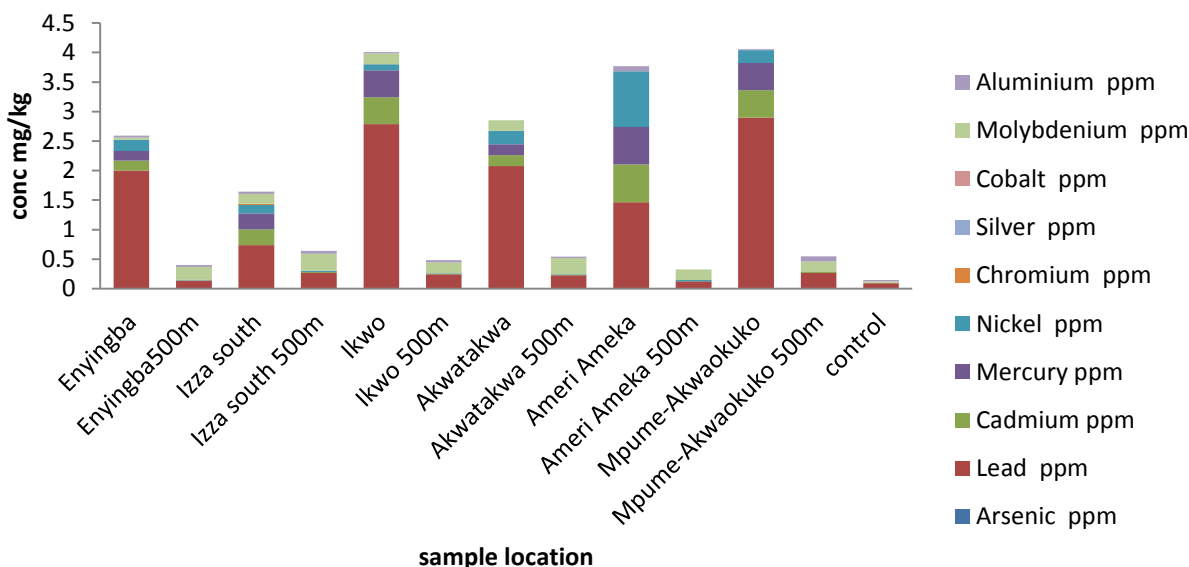


Figure 13. Heavy metal levels in rice grown around mining sites, about 500 metres away from mining site and control

CONCLUSION

This research has revealed that the soils from the mining sites are acidic (low pH). The low pH recorded was due to the influence of mining activities within and around the area. The concentration of heavy metals (Fe, Cu, As, Pb, Cd, Mg, Ca, Hg, Ni, Cr, Zn, Ag, Co, Mo, Se and Al) determined in the mining site revealed that Fe was the metal with the highest concentration in the mining sites. Furthermore, plants grown within and around the mining site recorded high concentration of Pb; while Cr had the lowest concentration. This research concludes that continuous usage of soils with the mining sites for agricultural activities causes the bioaccumulation of these metals and their eventual entry into the food chain with the associated health risks being manifested.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this manuscript

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