

Original Research Article

ASSESSMENT OF HEAVY METALS IN EDIBLE CLAYS SOLD IN ONITSHA METROPOLIS OF ANAMBRA STATE, NIGERIA.

ABSTRACT

This study was undertaken to determine and compare the levels of zinc (Zn), lead (Pb), cadmium (Cd), copper (Cu), mercury (Hg), and cobalt (Co) in edible clay samples obtained from four different markets in Onitsha, Nigeria. The research was conducted at the Chemistry Laboratory, Federal College of Education (Technical), Asaba between June and October 2013. Two species of edible clay (Nzu and Ulo) sold commercially, were bought in replicates from four spatially located markets namely Ochanja, Ose, Relief and Okpoko in Onitsha. The samples were prepared for analysis by digestion and the concentrations of heavy metals determined by atomic absorption spectrophotometry. Zn, Cu and Hg were detected in all samples and mean concentrations obtained in ppm in type 1 edible clay were in the range 2.540 to 3.210, 0.116 to 0.205 and 0.145 to 3.004 for Zn, Cu and Hg respectively. For type 11 clay samples, mean concentrations in ppm were in the range 7.911 to 11.719, 0.098 to 0.334 and 0.357 to 1.666 for Zn, Cu and Hg respectively. Pb was detected only in type 11 sample from Ochanja; Cd in both clay types from Ochanja and type 1 from Ose; Co in type 1 sample from Ochanja and all type 11 samples. One-way ANOVA of the mean concentrations of Zn, Pb, Cd, Cu, and Co showed no significant difference [($P = .981$, $.479$, $.335$, $.333$ and $.613$) for Zn, Pb, Cd, Cu, and Co respectively] among markets sampled. The mean concentration of Hg (2.335 ± 0.276) in Ochanja market however, differ significantly ($P = .045$) from those of the other markets, 0.621 ± 0.244 , 0.796 ± 0.280 , and 0.251 ± 0.190 for Ose, Relief and Okpoko respectively. A t test revealed a statistically reliable difference ($P = .000$) between mean concentrations of Zn in type 1 (2.737 ± 0.181) and type 11 (10.332 ± 0.067) edible clays. The trend was observed ($P = .003$) for Co mean concentrations in edible clay types (1 = 0.004 ± 0.004 and 11 = 0.308 ± 0.042). However, mean concentrations of Pb, Cd, Cu and Hg in type 1 and type 11 clays did not differ significantly [($P = .391$, $.288$, $.243$, and $.613$) for Pb, Cd, Cu and Hg respectively]. The essential elements, Zn and Cu were low in the samples whereas there were concentrations of Hg in eventually samples and Cd in few samples. The high levels of Cd, and Hg observed in this study might be due to indiscriminate disposal of waste, agricultural activities and combustion of fossil fuels. There is great need to plan and implement proper waste disposal strategies and to encourage the use of renewable fuels such as biogas and biodiesel in areas where these clays are obtained.

Keywords: Heavy metals, edible clay, potentially toxic, mercury, permissible limit

1.0 INTRODUCTION

Geophagia is defined as deliberate consumption of earth, soil or clay (1, 2). It is related to pica a classified eating disorder characterized by abnormal cravings for non-food substances (1, 2). It exists in humans, most often in rural or pre industrial societies among children and pregnant woman (3). Geophagia is not limited to any particular age group, race, sex, geographic region or time period (2, 3). It is a traditional, cultural or religious activity (4), which has been observed during pregnancy (5), or as a remedy for disease (6, 7). Culturally speaking, the practice amongst many of the kaolin (clay) eaters emanates from having doubtlessly watched their mothers or close relatives eat the clay (8). Many of the studies on geophagia have advanced many more other reasons for this phenomenon around the world. In southern parts of U.S.A, pregnant women who traditionally ate substances like clay, corn starch and baking soda believed that such substances helped to prevent vomiting, helped babies to thrive, cured swollen legs and ensured beautiful children (9). In parts of Africa, rural areas of the United State and villages in India , clay consumption is correlated with pregnancy (3). In Australia, some Aborigines eat white clay for medicinal purposes (8). In Haiti, South Africa, Malawi, Zambia, Zimbabwe and Swaziland, geophagy is widespread (3, 8). In South Africa, the eating of clay is mostly observed among pregnant women. In urban South Africa, young women believe that earth eating will give them a lighter colour (making them supposedly more attractive) and soften their skin (1). Studies have also established that geophagia is rife among the Tanzanians and Kenyans in the eastern part of Africa, as well as, Senegal, Mali and Nigeria in West Africa (8), and South Asia (2).

Clay for consumption in Nigeria is known as calabash chalk. Calabash chalk also known according to language/ locality as Argile, Calabar stone, calabash clay, Ebumba, Lacraie, Mabele, Ndom, Nzu, pote and ulo – is a generic term used for naming these Nigeria, geophagical materials (2). Most of the calabash chalk samples are clay rich soil materials that have been dried and/or baked into blocky or spherical unit (2). Geophagia in Nigeria is noted to be especially associated with pregnant women who consume earth materials to alleviate the symptoms of morning sickness (2). Pregnant women from the Igbo tribe - a large ethnic group of eastern Nigeria were recorded as the main eaters of calabash chalk (clay) (2).

There are obvious risks in the consumption of clay that is contaminated by animal or human faeces, in particular, parasite eggs, such as round worm, that can stay dormant for years, can present a problem. Other dangers associated with geophagia include ingestion of a variety of bacteria, various forms of soil contamination and intestinal obstruction (3, 8). In the traditional societies, there is a widespread practice to heat- treat (bake) the earth before consumption, and this tends to mitigate the risks to some extent (3).

Apart from mineral elements air and water, soil or clay serves as reservoir of chemical and biological agents. Among the chemical agents are heavy metals, radioactive gases and organic chemical (8). Heavy metals (Fe, Mn, N, Cu, Zn, Co, Cr, V, Ti, Cd, Hg, Mo) and trace metals as well as Se and F occur naturally in soil (5). However, concentrations are frequently elevated because of contamination (10, 11).

Minerals such as iron, copper, zinc and manganese are essential and play important roles in biological systems. Meanwhile, mercury, lead and cadmium are toxic, even in trace amounts. However, essential minerals can also produce toxic effects at high concentrations (12).

The sources of contamination in soils are multifarious and include agricultural and industrial pollution (13). Heavy metals are toxic and poisonous in relatively high concentrations. Two factors contribute to the deleterious effects of heavy metals as environmental pollutants. Firstly, they cannot be destroyed through biological degradation as in the case of most organic pollutants. Secondly, they are easily assimilated and can bioaccumulate. Bioaccumulation is the gradual build up over time of a chemical in a living organism. This occurs either because the chemical is taken up faster than it can be used or because the chemical cannot be broken down for use by the organism (12, 14).

The clays (nzu and ulo) are obtained from subsurface area in a local community in Anambra State and sold by its merchants to traders who retail them in the markets. In this local community, there is no proper/organized waste disposal method, hence, the residents engage in indiscriminate dumping of refuse on the land. For instance, lead is used to produce batteries, ammunition, metal products like devices e.t.c. The local residents use batteries a lot to power their torch light and radios and many a times you could see used batteries discarded on the land. Mineral fertilizers contain some cadmium. The farmers make use of fertilizers in farming. Cadmium from the fertilizers can leach into the soil. Mercury occurs naturally in air which eventually settles onto land. It is also emitted into the environment through combustion of coal.

According to Abrahams et al (2013), any ingested geophagical material such as nzu and ulo has the potential to release mineral nutrients and potential hazardous elements (PHE) when they come in contact with digestive fluids. However, the geophagical materials are capable of adsorbing chemical elements, so preventing their absorption.

The edible clays sold in Onitsha metropolis may be poisonous and therefore harmful to the health of consumers because of possible contamination with heavy metals. Moreover, there is insufficient data on the status of edible clays sold in Onitsha. This study was therefore undertaken to ascertain the health implication in terms of heavy metal content in edible clays sold commercially in Onitsha markets.

2.0 SAMPLING/SAMPLE COLLECTION

Two types/varieties of clay popularly known as Nzu and Ulo amongst the Igbo tribe of the Eastern part of Nigeria and sold commercially were purchased from four spatially located markets in Onitsha, Anambra State of Eastern part of Nigeria. These markets were Ochanja, Ose, Relief and Okpoko. In each market, three replicate samples of each clay type were purchased and used for the study.

3.0 MATERIALS AND METHOD

Each variety of clay was ground using a porcelain mortar and pestle and sieved with 5 mm sieve and oven dried at 100 °C to constant weight. 1 g of the dried sample was accurately weighed into a pre-cleaned 250 ml glass beaker and digested with aqua regia (a solution of freshly prepared HNO₃ and HCl in the ratio 1:3) and heated to 100 °C in a water bath until the solute dissolved completely. The solution was left to cool and 15 ml of deionized water was added to the cooled solution to dilute it. The diluted solution was then filtered through whatman 110 mm filter paper previously into a pre - cleaned beaker. The filtrate was transferred into a sterile sample bottle previously washed with 10 % nitric acid, washed

severally with deionized water, and sent for heavy metal analysis using Atomic Absorption Spectrophotometer.

4.0 STATISTICAL ANALYSIS

Results are presented as mean $\pm$ standard deviation; n equals the number of determinations. Data obtained were subjected to One-Way ANOVA and t-test using SPSS 19.0. Results from the different markets were compared using One-Way ANOVA whereas the clay types from the four markets were compared using t-statistics at the 95 % confidence level. $P \leq .05$ was considered to indicate significant difference. Where the means differ in the One-way ANOVA, Least Significant Difference (LSD) was used to determine which means differ.

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5.0 RESULTS AND DISCUSSION

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Fig. 1: Some sample of nzu

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Table 1 shows the mean concentrations of zinc in ppm contained in the calabash chalk obtained from Ochanja, Ose, Relief and Okpoko markets all in Onitsha, Anambra State of Eastern Nigeria. Mean concentration of zinc (ppm) ranged from 2.540 in Relief to 3.210 in Ose in type 1 clay and 7.911 in Relief to 11.719 in Okpoko in type 11. Relief market had the lowest mean concentration of 5.226 ppm while Okpoko had the highest mean concentration of 7.172 ppm. One-way ANOVA of the mean concentrations of samples from the four markets did not show significant difference ($P = .981$). As shown in fig. 3, the mean concentrations in ppm of zinc in both clay types (nzu and ulo) were less than the permissible limit of 100 ug/g i.e 100 ppm of zinc in food substances (FAO/WHO, 2001). There were higher concentrations of zinc in type11 (ulo) clay than type 1 (nzu) clay in all the markets sampled. A t test revealed a statistically reliable difference ($P = .000$) between the mean concentration of type 1 (2.737 ± 0.181) and type 11 (10.332 ± 0.067) edible clays. This may be attributed to the chemical nature/structure of the clays. Nzu is kaolin clay while ulo fits into the description of bentonite clay. Bentonite clays have extremely flat crystals, they are shaped like credit cards or playing cards, and they stack or layer, held together with weak electric bonds (16). Bentonite clays are good at adsorbing heavy metals and other positively

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Fig. 2: Some samples of ulo

charged substances because bentonite is negatively charged, hence, bentonite nanoparticles stick to heavy metals by adsorption. This property is not manifested in other clays like kaolin. The fact that zinc was detected in the two clay types and the concentrations were below the permissible limit for zinc makes them nutritive as zinc is an essential element and non toxic (16). In terms of zinc, type 11 edible clay used in this study has a higher nutritive value compared to type 1 clay.

Table 1: Mean concentration in ppm of zinc in edible clay samples obtained from different markets in Onitsha.

Type/Market	Ochanja	Ose	Relief	Okpoko	Mean
Type 1	2.568±0.146	3.210±0.046	2.540±0.527	2.629±0.007	2.737±0.181 ^a
Type 11	11.582±0.074	10.120±0.086	7.911±0.048	11.716±0.062	10.332±0.067 ^b
Mean	7.075±0.110	6.665±0.066	5.226±0.288	7.172±0.035	

Type 1= Nzu, Type 11= Ulo Means with different superscripts differ significantly at $\alpha = .05$

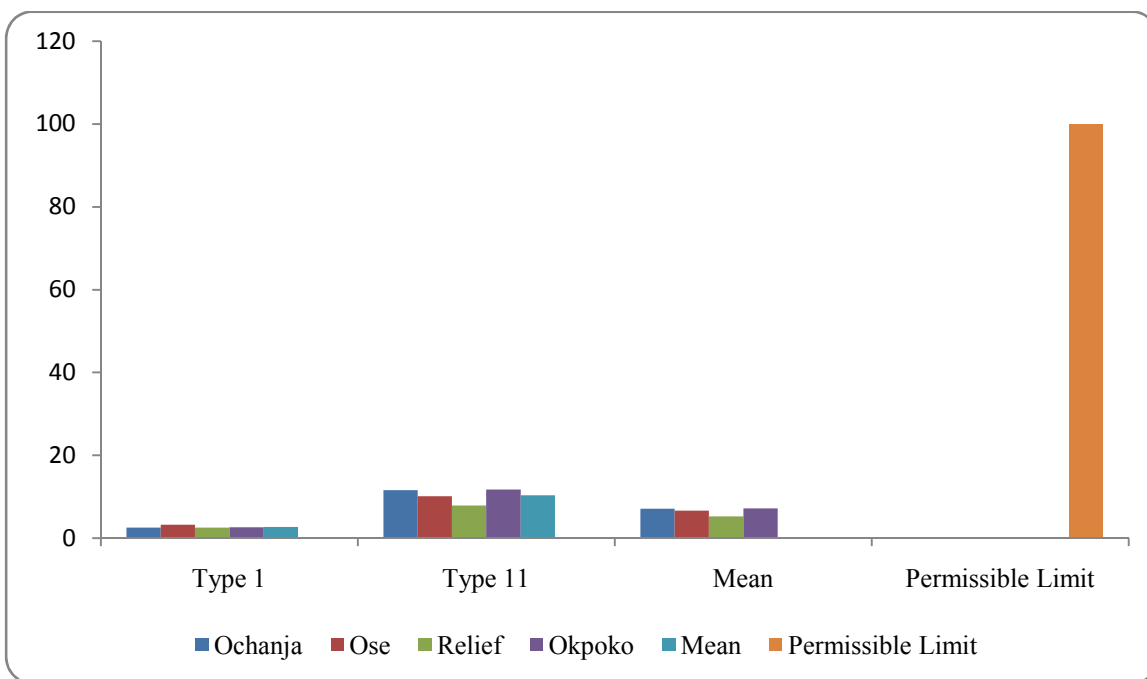


Fig. 3: Mean concentration in ppm of zinc in edible clay types (1 and 11) obtained from different markets in Onitsha and the permissible limit.

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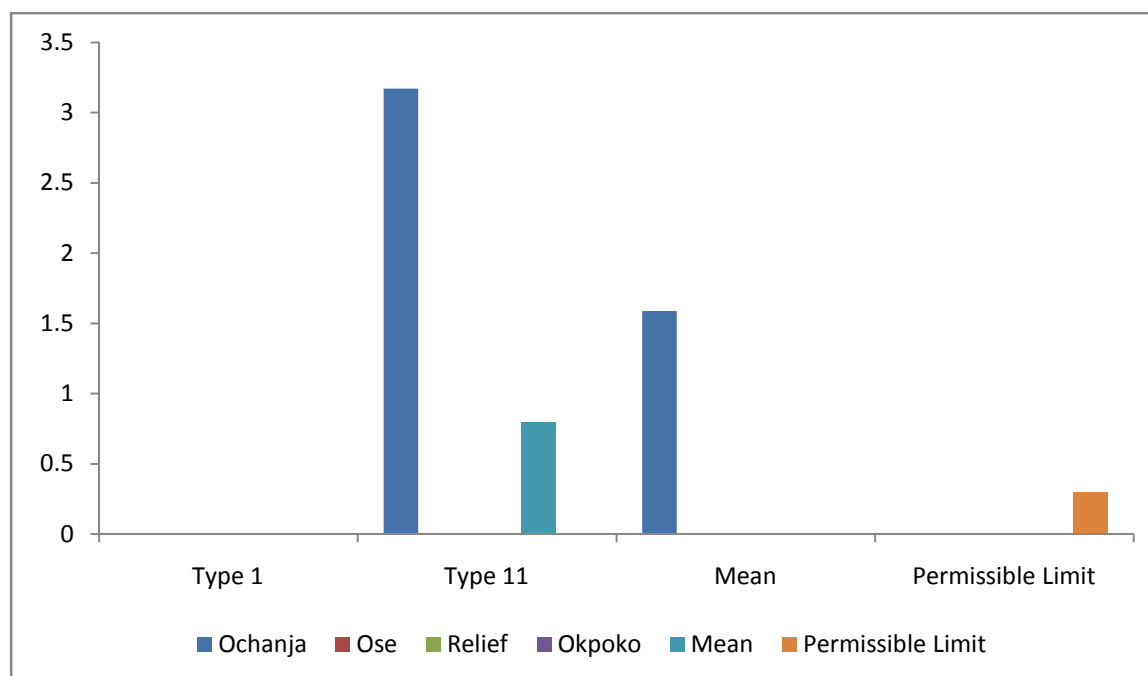
170 The permissible limit for lead in food substances by FAO/WHO (1999) and FAO/WHO, 2001 is 0.2 ug/g
 171 (0.2 ppm) and 0.3 ug/g (0.3 ppm) respectively. The mean concentration of lead in clay obtained from
 172 Ochanja was higher than the permissible limit for lead in food substances. As shown in Table 2, there
 173 was no lead found in type 1 clay obtained from the four different markets used in this study, and type 11
 174 clay obtained from Ose, Relief and Okpoko markets. The mean concentration of type 1 clay did not differ
 175 significantly ($P = .391$) from that of type 11. There was also no significant difference ($P = .479$) among the
 176 mean concentrations of the samples from the sampled markets. The high level of lead above the
 177 permissible limit observed in type 11 clay obtained from Ochanja market makes it unfit for consumption
 178 because lead is toxic even in trace amounts.

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180 **Table 2: Mean concentration in ppm of lead in edible clay samples obtained from**
 181 **different markets in Onitsha.**

Type/Market	Ochanja	Ose	Relief	Okpoko	Mean
Type 1	ND	ND	ND	ND	
Type 11	3.171±0.064	ND	ND	ND	0.793±0.018
Mean	1.598±0.032				

182 *Type 1= Nzu, Type 11= Ulo, ND= Not Detected*



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Fig. 4: Concentration in ppm of lead in edible clay samples obtained from different markets in Onitsha and the permissible limit.

The mean concentration in ppm of cadmium in the analyzed samples is shown in Table 3. The mean concentration Cd in type 1 clay ranged from 0.000 in Relief and Okpoko to 1.027 in Ochanja market. For type 11 clay, cadmium was detected only in the sample obtained from Ochanja market. Relief and Okpoko markets had 0.000 ppm mean concentration while Ochanja had the highest mean concentration of 1.027 ppm. There was no detection of cadmium in both clay types obtained from Relief and Okpoko markets as well as in type 11 clay obtained from Ose. A t test revealed no significant difference ($P = .288$) between the mean concentrations of type 1 and 11 clays sampled. The same trend was observed for the One-way ANOVA of the various markets sampled ($P = .335$). The mean concentration of cadmium in both clay types from Ochanja and type 1 clay from Ose were higher than the permissible limit of 0.1 ppm set for cadmium in food substance by FAO/WHO, (1999) as shown in fig. 5. The presence of cadmium in the clays from Ochanja market and type 1 clay from Ose above the permissible limit makes them unfit for consumption because of the adverse effect of cadmium. Cadmium is not an essential element for humans, animals and plants. Toxicity symptoms induced by cadmium include gastrointestinal disorders, kidney failure, hypertension, reduced pregnancy length and newborn weight and disorders of the endocrine and/ or immune system in children.

Table 3: Mean concentration in ppm of cadmium in edible clay samples obtained from different markets in Onitsha.

Type/Market	Ochanja	Ose	Relief	Okpoko	Mean
Type 1	1.027±0.442	0.282±0.080	ND	ND	0.327±0.130
Type 11	0.163±0.057	ND	ND	ND	0.041±0.130
Mean	0.595±0.249	0.141±0.040			

Type 1= Nzu, type 11= Ulo, ND= Not Detected

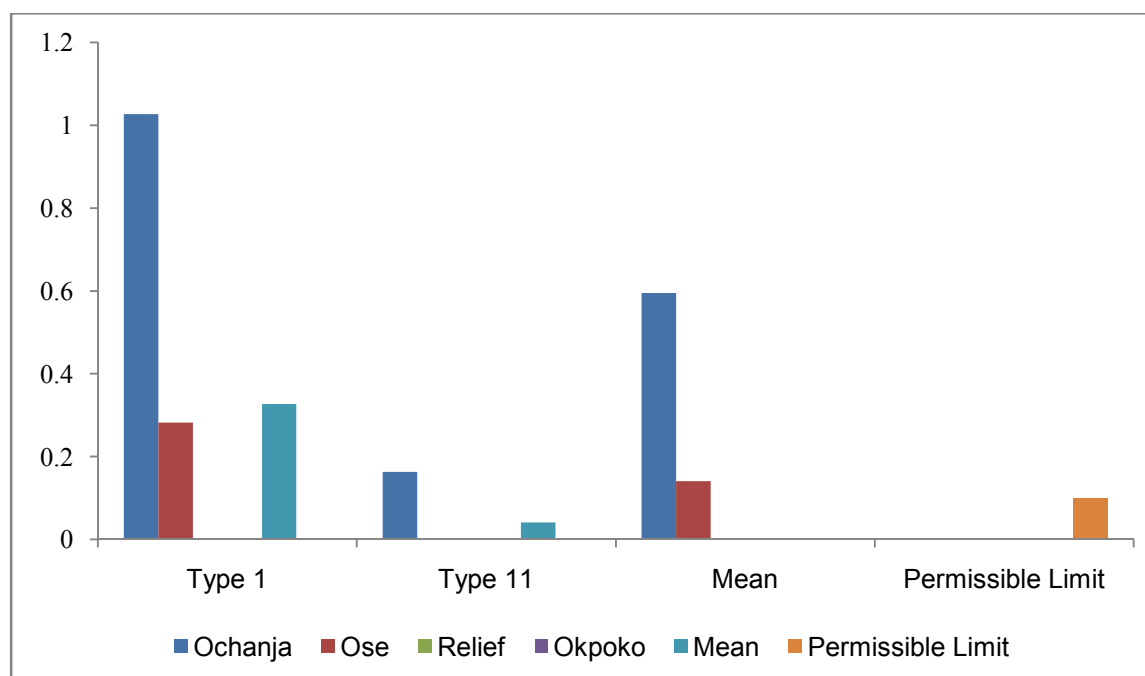


Fig. 5: Concentration in ppm of cadmium in edible clay samples obtained from different markets in Onitsha and the Permissible Limit

Table 4 shows the mean concentrations in ppm of copper in the sampled clays and fig. 6 shows the mean concentration and the permissible limit of copper stipulated by FAO/WHO, (2001). For type 1, the mean concentrations ranged from 0.116 in Relief to 0.220 in Ose while for type 11 the mean concentration ranged from 0.098 in Relief to 0.334 in Ochanja. There was no significant difference ($P = .243$) between the mean concentrations of type 1 and 11 clays used in the study. The same trend was observed among the markets ($P = .333$). The mean concentration in all the samples were lower than the permissible limit of 73 ppm set for copper in food substances by FAO/WHO, (2001)

Table 4: Mean concentration in ppm of copper in edible clay samples obtained from different markets in Onitsha.

Type/Market	Ochanja	Ose	Relief	Okpoko	Mean
Type 1	0.205±0.059	0.220±0.028	0.116±0.054	0.133±0.002	0.119±0.036
Type 11	0.334±0.028	0.235±0.001	0.098±0.078	0.315±0.020	0.245±0.032
Mean	0.270±0.044	0.228±0.015	0.107±0.066	0.224±0.011	

Type 1= Nzu, type 11= Ulo

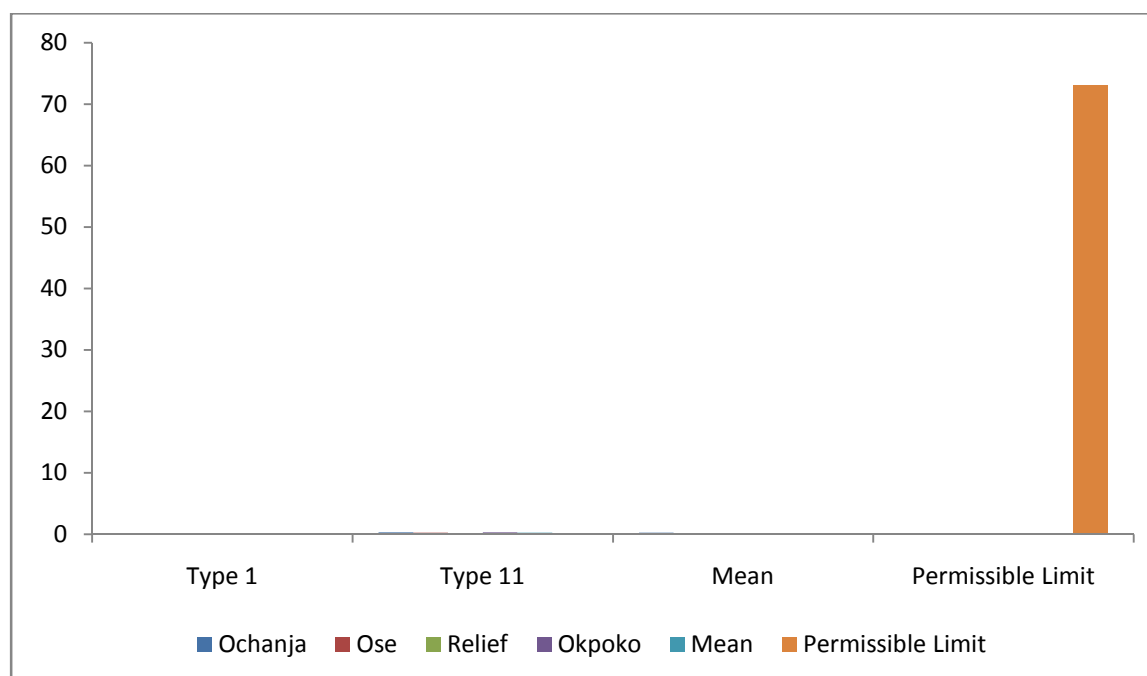


Fig. 6: Concentration in ppm of copper in edible clay samples obtained from different markets in Onitsha and the Permissible Limit

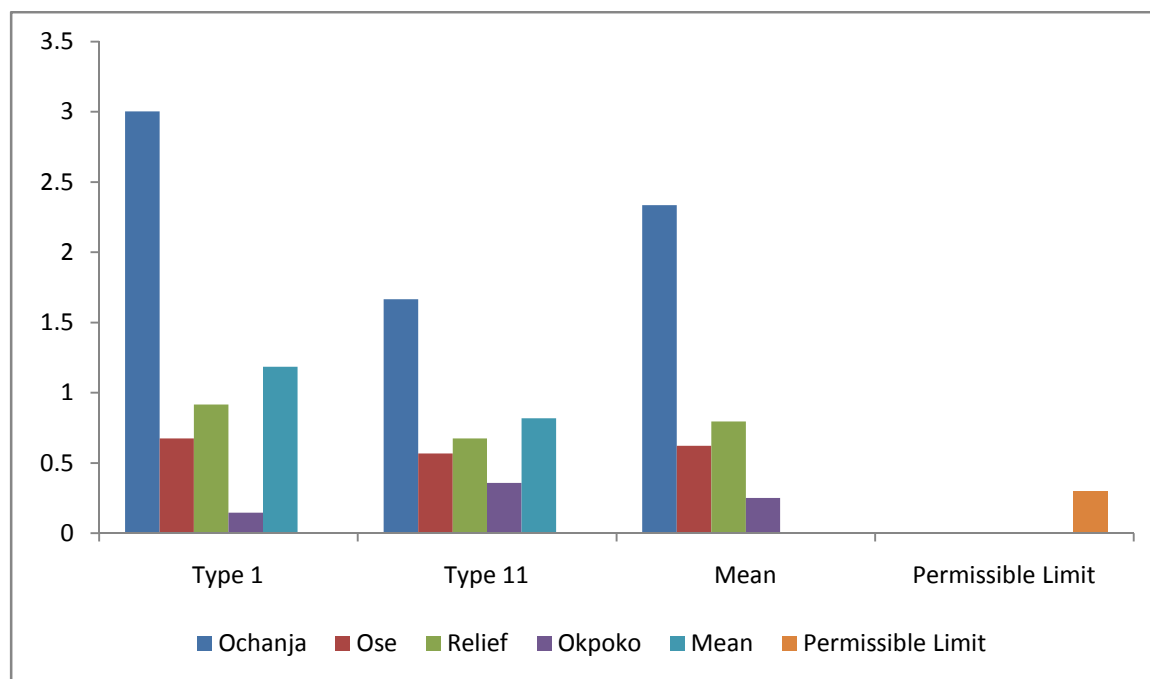
As shown in table 5, the mean concentrations in ppm of mercury were in the range 0.145 to 3.004 for type 1 clay and 0.357 to 1.666 for type 11 clay. Ochanja market had the highest mean concentration 2.335 ppm while Okpoko had the least (0.251 ppm). The mean concentration of edible clay samples obtained from Ochanja Market (2.335 ± 0.276) differs significantly ($P = .045$) from 0.621 ± 0.244 , 0.796 ± 0.280 , and 0.251 ± 0.190 for Ose, Relief and Okpoko markets respectively. The mean concentrations between the clay types ($1 = 1.185 \pm 0.282$ and $11 = 0.817 \pm 0.213$) however, did not differ significantly ($P = .613$).

As shown in fig.7, the mean concentrations of mercury for type I and type 11 clay samples obtained from Ochanja, Ose and Relief markets were higher than the permissible limit of 0.3 ppm set for mercury by FAO/WHO, (1999). For Okpoko market, the mean concentration of mercury in type I clay sample was less than the permissible limit while for type 11 clay sample, it was found to be slightly higher. Mercury is a toxic metal even in trace amounts; therefore, its detection in food or edible substances makes such unfit for consumption.

247 **Table 5: Mean concentration in ppm of mercury in edible clay samples obtained from**
 248 **different markets in Onitsha.**

Type/Market	Ochanja	Ose	Relief	Okpoko	Mean
Type 1	3.004±0.490	0.674±0.222	0.917±0.253	0.145±0.163	1.185±0.282
Type 11	1.666±0.062	0.568±0.267	0.675±0.306	0.357±0.217	0.817±0.213
Mean	2.335±0.276 ^a	0.621±0.244 ^b	0.796±0.280 ^b	0.251±0.190 ^b	

249 *Type 1= Nzu, type 11= Ulo, Means with different superscripts differ significantly at $\alpha = .05$.*



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251 **Fig. 7: Concentration in ppm of mercury in edible clay samples obtained from different**
 252 **markets in Onitsha and the Permissible Limit**

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 255 The mean concentrations in ppm of cobalt were in the range 0.142 to 0.437 for type 11 clay whereas
 256 there was no detection of cobalt in type 1 clay except for the sample from Ochanja market as shown in
 257 Table 6. Okpoko had the highest mean concentration of 0.437 ppm while Relief had the lowest. There
 258 was no significant difference ($P = .921$) in the mean concentrations of samples from the four markets.
 259 Type 1 mean concentration differ significantly ($P = .003$) from that of type 11. However, as shown in fig. 8,

the mean concentrations of all the samples were within the permissible limit of 0.15 – 1.0 ppm set for cobalt by FAO (1983).

Table 6: Mean concentration in ppm of cobalt in edible clay samples obtained from different markets in Onitsha.

Type/Market	Ochanja	Ose	Relief	Okpoko	Mean
Type 1	0.017±0.015	ND	ND	ND	0.004±0.004 ^a
Type 11	0.354±0.039	0.299±0.076	0.142±0.030	0.437±0.025	0.308±0.042 ^b
Mean	0.186±0.027	0.150±0.038	0.071±0.015	0.219±0.012	

Type 1= Nzu, type 11= Ulo, ND= Not Detected, Means with different superscripts differ significantly at $\alpha = .05$.

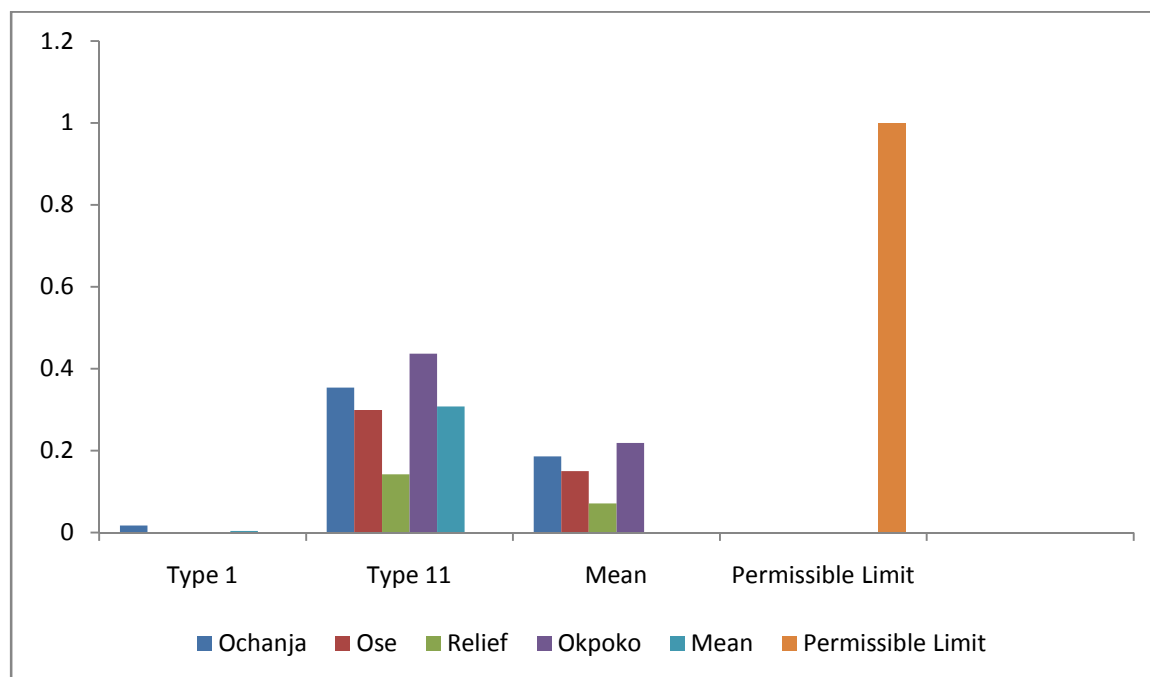


Fig. 8: Concentration in ppm of cobalt in edible clay samples obtained from different markets in Onitsha and the Permissible Limit

CONCLUSION

Based on the results of this study, the concentrations of the essential elements (zinc and copper) in the edible clays were very low compared to the permissible limits stipulated by recognized regulatory body such as FAO and WHO. Therefore, the nutritive values of the clays as estimated from the concentrations of these essential elements were low. On the other hand, the concentrations of the toxic elements mercury and cadmium were relatively high. Heavy metals bioaccumulate, thus, continuous consumption of these clays contaminated with the toxic heavy metals observed in this study pose serious health threat to its consumers. The high concentrations of these toxic heavy metals might be due to indiscriminate waste disposal, burning of hazardous waste and combustion of fossil fuels. There is therefore great need to plan and implement proper waste disposal strategies in areas where these clays are obtained. There is also need to encourage the use of renewable fuels such as biogas biodiesel.

COMPETING INTEREST

The authors declare that there is no competing interest. The research was solely funded by the researchers

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