DETERMINATION OF SOME HEAVY METALS (Cu, Co, Ni) IN EDIBLE CLAY FROM SOUTH EASTERN NIGERIA AND ITS EFFECT DUE TO CONSUMPTION

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ABSTRACT

Determination of heavy metal contents in edible clay (kaolin) from Enyigba in Abakaliki, Ebonyi State of Nigeria was carried out using Atomic absorption Spectrophotometer (AAS). The quantitative analysis of heavy metal analyzed in the edible clay sample were 0.012mg/kg for Co, 0.113mg/kg for Cu and 0.712mg/kg for Ni. This study shows that the levels of these heavy metals (Co, Cu and Ni) in kaolin are below the permissible limits as established by the regulatory organization (World Health Organization, WHO). Compared to the safety intake levels for these heavy metals recommended by US Environmental Protection Agency (US EPA) and Joint FAO/WHO Expert Committee on Food Additives (JECFA), Expert Group on Vitamins and Minerals (EVM), and Agency for toxic substance and disease Registry (ATSDR), the dietary intakes of the three heavy metals from daily consumption of 20g of kaolin should pose no health risk to human.

Key words: Heavy Metal, Kaolin, Consumption

INTRODUCTION

Clay minerals are naturally occurring hydrous aluminum silicates complexes with other mono and divalent metals that contain large percentage of water trapped within the silicate sheets [1]. They are very common in soils, in fine-grained sedimentary rocks, metamorphic slate and phyllite as well as in ultrafine-grained form. Clay minerals are important constituents of soils, and have been useful to humans in agriculture and manufacturing [2].

Clay consumption is a worldwide practice that has existed since human's evolution from primates, and had continued till today among traditional ethnic groups as well as numerous mammal species. Historically, clay eating has been associated with treatments for cholera and bacterial infection. However, a new trend of clay consumption emerges as various academic disciplines investigate to understand the advantage and the effect of clay consumption [3]. Food intake had been identified as the main pathway of human's exposure to toxic metals, when compared with other source of exposure such as dermal contact and inhalation [3,4].

However, clay has been reported to decrease the absorption of drugs that chelate with aluminum salt (e.g. digoxin) and can cause pneumoconiosis as a result of excessive intake [5]. Furthermore, due to the levels of heavy metals concentration present in most clay samples, which is non-biodegradable, its intake could result to the growth of cancerous cells [6].

Clay minerals have similar structural and chemical properties. There are four major group of clay minerals which are Chlorite group, Smectite group, Illite group and Kaolin group [1].

Kaolinite is the major mineral component of kaolin, which usually may contain minor minerals such as quartz and mica. It is widely used for a large number of applications as revealed by previous studies owing to their absorption capacities [7, 8]. Kaolin ($A1_2Si_2O_5(OH)_4$) is formed by chemical weathering of aluminum Silicate mineral which may contain heavy metal (e.g. Cu, Zn, Mg, As, Cd, Cr, Fe, Ni, Mn, Co, Pb, Au, etc.). Heavy metals can be classified as toxic (arsenic, cadmium, lead, etc.), non-essential (vanadium, cobalt) and essential (copper, zinc, iron, manganese, etc.). Heavy metal occurs naturally at various concentrations in the ecosystem. It is necessary to assess their level in food items and report those that would pose health hazard.

Cobalt is a bio-essential chelating element that is found in vitamin B_{12}. It is important for healthy red blood cell formation and neurological health in humans. It can stimulate antioxidant and anti-inflammatory biological process. Despite of these advantages, it can bio-accumulate in mammal up-to a toxic levels in the body organs. Earlier research have report that it accelerates tumor growth in humans and likely carcinogen.

Copper is an essential metal found in human body at a varying concentrations [6]. Infants who tends to show copper deficiency as a result of the exclusive consumption of low milk, or non-copper diets, are reported to have anemia [9]. In addition, several central nervous system disorders and reduced levels of sphingolipids are symptoms of copper deficiency [10]. However, excess copper in the body can lead to the several health disorder: nausea, vomiting (food or blood), diarrhea, stomach pain, black (tarry) stools, difficulty in breathing and irregular heart beat etc.

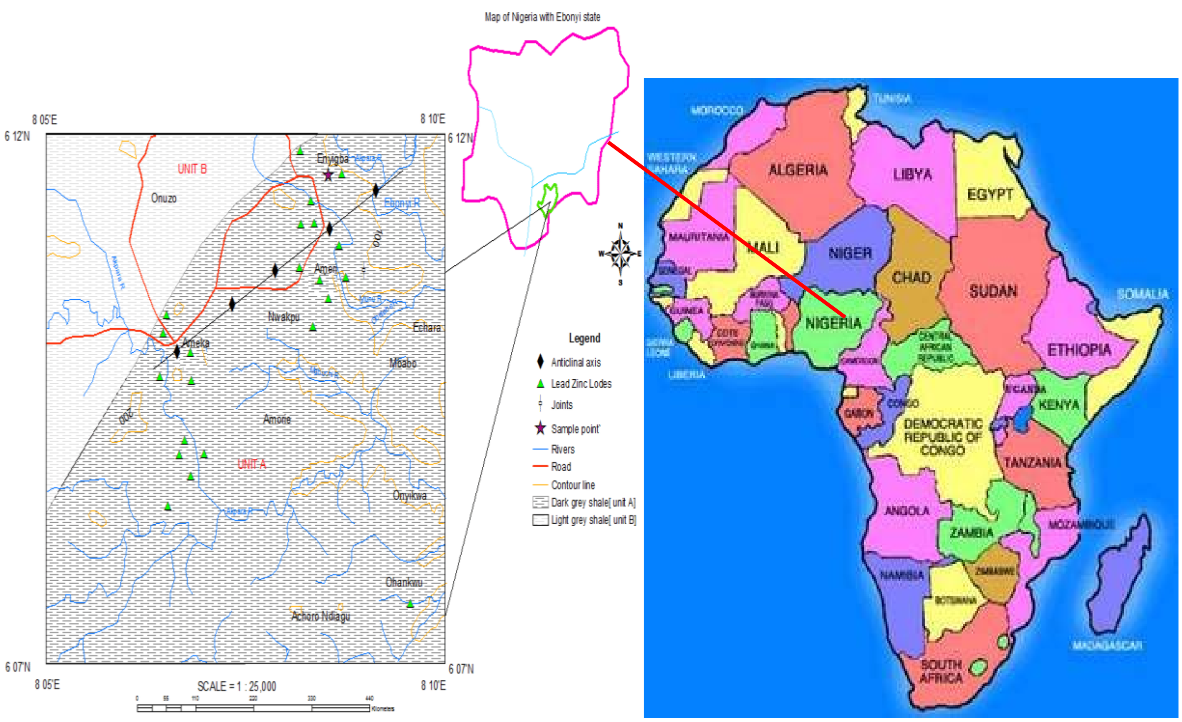
Nickel is an essential micronutrient mineral. It is a common trace element in multiple vitamins which increases iron absorption in blood and osteoporosis treatment [11]. Large uptake of nickel could result in respiratory failure, birth defects and the development of cancerous cells.
Thus, this research seeks to investigate level of some heavy metals contained in clay sample (kaolin) from Enyigba lead mining site in Ebonyi State of Nigeria and their effects on humans due to consumption.

MATERIALS AND METHOD

Sampling and Sample Collection:

Fig. 1 shows a sample of an edible clay (kaolin) also locally known as Nzu in Igbo language which weighs about 16.3g that was collected from a lead mining site at Enyigba in the city of Abikaliki, Ebonyi State of Nigeria. It is worth nothing that the geographical coordinates of Enyigba located within Ikwo and Abakaliki Local Government Area of Ebonyi stat are latitudes 6^0.07'N and 6^0.12'N and longitude 8^0.05'E and 8^o10'E (Fig. 2) and falls within the lower Benue Sedimentary Formation of South Eastern Nigeria. The region is noted for lead/zinc mineral (Pb/Zn) mining activities.

Figure 1: A sample of kaolin from Enyigba, Abakaliki, Ebonyi State of Nigeria



A *B*

Figure 2: A. *Mapping geological structures controlling mineralization in Enyigba Area South Eastern Nigeria, using Magnetic inversion Technique*[25]. B. *Map of Africa indicating Nigeria.*

Reagent

All chemicals used in the research were analytical grade purity. Deionized water was used in the preparation of solutions.

Sample Preparation and Spectroscopic Analysis

The kaolin sample was pulverized. The fine powder was dried in an oven at a temperature of 108^{o}C and then cooled till a constant weight was obtained. It is then transferred into a Teflon Crucible. Digestion mixture (1:3 v/v) of HCl and HNO_3 were added. 1ml of HF and 5ml of the freshly prepared aqua regia was added little at a time to dissolve the material. The mixture was allowed to stand overnight for complete digestion of the clay sample. Then the mixture was diluted with distilled water, and filtered. The filtrate was analyzed for the elements using Atomic Absorption Spectrophotometer (AAS) model VGP, 210.

RESULT AND DISCUSSION

The concentrations of heavy metals (Cu, Ni and Co) in the clay sample taken from Enyigba lead mining site are shown in Table 1 below.

Table 1. Heavy metals content of Kaolin.

METAL	Mean Concentrations in Kaolin (mg/kg)	FAO/ WHO Permissible limit (mg/kg)
Co	0.012 ± 0.005	-
Cu	0.113 ± 0.071	10
Ni	0.712 ± 0.162	10

The heavy metal content in the given kaolin from Enyigba lead mining site in table 1 above shows that the levels of analyzed heavy metals Co, Cu and Ni are 0.012, 0.113 and 0.712mg/kg respectively. These values compared well to standard permissible intake of heavy metals found in food by WHO [12, 13]. However, WHO did not include quality guideline for Co. Comparison of tables 1 and 2 reveals that the levels of heavy metals in the kaolin are well below the maximum permissible limits. Moreover, these results correspond to earlier report on assessment of heavy metal contamination of water sources in different location at Enyigba Pb-Zn district [14]. From his findings, the mean levels of these metals (Co, Cu and Zn) in the water were 2.22, 0.18 and 1.12mg/L respectively. The variation in the heavy metal content of water and kaolin might be attributed to the high dissolution of metallic salts in water run-off across the mining sites. Furthermore, the level of heavy metals in kaolin could be toxic, if they are taken in excess amount.

Cobalt occurs in nature more in minerals associated with other metals, such as arsenic, manganese, nickel, and copper. However, its content in soil is usually in the range 1-40 mg/kg [15, 16]. About 0.012 to 0.02 µg of cobalt are required by human per day and doses up to 1 mg/kg bw of cobalt have been previously used as a treatment for anemia in pregnant women, because it enhances the production of red blood cells [16]. In humans, food intake is the main source of cobalt and its compounds [15]. Although, the estimated permissible daily intake from food varies substantially between countries which might be as a result of large variations in concentrations of cobalt in drinking water [15].

Copper is well absorbed after oral intake. Being an essential element, however, the rate of intestinal absorption of copper in humans depends on numerous physiological and dietary factors. Although, established tolerable dietary intake (TDI) for copper was 140 µg/kg bw/day [17]. According to the WHO standard, a daily copper requirement of 20-80 µg/kg bw/day [5]. Copper deficiency cause effects that are critical to human health and may lead to cancer.

The background of natural occurring nickel in agricultural soil varies between 3 and 1000mg/kg [18]. After intake, nickel is bound to serum proteins that apparently facilitates transport. Nickel is concentrated in kidney, liver, lungs, and lymph nodes [19]. High intake of nickel compounds could cause nausea, vomiting, headache and death [18]. IARC classified nickel compounds as carcinogenic to humans (group 1); metallic nickel and alloys were classified as possibly carcinogenic to humans (group 2B) [20]. WHO estimated the average daily intake of nickel between 100-300 µg/day [5].

Considering this, the current study also estimates daily dietary intake of these heavy metals by children, adolescents and adults with its potential health risks. The daily dietary intake of metals was estimated using the equation given by [21].

$$\text{Daily Intake of Metals} = \frac{C_{metal} \times C_{food}}{B_w}$$

where Cmetal (mg/kg) is the concentration of metals in the samples; C_{food} represents the daily average amount of the kaolin consumed (assumed 0.02 kg/day); B_w is the body weight assuming that samples are consumed by children between the ages of 1-5 years with average body weight of 20 kg, adolescents between the ages of 12-17 years with average body weight 52kg, and adults (especially pregnant women) between the age of 18-48 years with average body weight of 74kg. The estimated daily dietary intake of metal value for the clay studied based on consumption is shown in table 2 below.

Table 2.Estimated intake values of metals based on consumption of edible clay (kaolin)

Metals	**Dietary estimated intake values (µg/kg bw/day)**			**[a]Tolerable daily intake oral exposure (µg/kg bw/day)**	**[a]Background exposure (µg/kg bw/day)**	**[b] Daily intake value estimated from JECFA and EVM (µg/kg bw/day)**
	Children	Adolescents	Adults			
Co	0.012	0.005	0.003	1.4	0.3	0.6
Cu	0.113	0.044	0.031	140	30	1500
Ni	0.712	0.274	0.192	50	4	6.5

[a] RIVM [19] *[b] Anonymous [21,22,23] and EVM [24]*

The uptake of elements from food consumption is usually dependent on the food's elemental concentration and the quantity consumed by individual. Renowned world agencies like US Environmental Protection Agency US-EPA, Joint FAO/WHO Expert Committee on Food Additives [25], ASDR [16], IARC [15] have evaluated and recommends total daily intake of heavy metals in food. The JECFA and EVM recommended permissible tolerable daily intake of heavy metals as shown in table 2. However, these standards compared well with the estimated daily intake of heavy metals for children, adolescents and adults. This shows that the concentration of Co, Cu and Ni in the kaolin sample is within permissible dietary limits compared to the value obtained from international regulatory agencies with reports from Re-evolution of human toxicological maximum permissible risk levels [26]. Therefore, the kaolin sample is edible for consumption. Finally, the results of the study supplies valuable information about the heavy metal contents in Kaolin found in Enyigba mining Site in Ebonyi State of Nigeria. However, these results can be used by food regulatory agencies in Nigeria to check-mate the excessive consumption of kaolin and also monitor the level of heavy metal concentration especially Ni

CONCLUSION

From the study, the levels of Cobalt, Copper and Nickel concentrations are within acceptable standards for human consumption since (WHO), and evaluations by other organization show that the TDI, background exposure and permissible standard of the analyzed metals are at safe limit and will pose no health effect to humans due to consumption. Although, the level of other heavy metals were not analyzed in this study. Proper regulation should be applied to control the rate of local consumption of this kaolin in Enyigba since it is obtained from a lead/zinc mining site to avoid a long term health hazard

RECOMMENDATION

There are still risk of consumption of this clay since the concentrations of other heavy metals were not analyzed in the study. Thus. Urgent attention is needed to devise and implement appropriate means of monitoring and regulating industrial and even domestic effluence thereby providing appropriate sensitization of local populate and support safe use of edible clay.

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