Original Research Article

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

ABSTRACT

Determination of heavy metal contents in edible clay (kaolinite) 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 Co, Cu and Ni. This study shows that the levels of Co and Cu are below the permissible limits as established by the regulatory organization (World Health Organization, WHO), but that of Ni didn't compare well (is above WHO daily permissible limit). Thus, the kaolin sample is not suitable for human consumption though there might be lower concentrations of other absorbed heavy metals.

Key words: Heavy Metal, Kaolin, Consumption

INTRODUCTION

Clay minerals are usually formed over a long period of time by systemic chemical weathering of rock (silicate compounds), by low concentrations of carbonic acid and other solvents. These solvents, mostly acidic, migrate through the weathered rocks after leaching through upper layers. In addition to the weathering process, some clay minerals are formed by hydrothermal activity. Clay deposits may be formed as residual deposits in soil, but thick deposits are mostly formed as a result of a secondary sedimentary deposition process after it have been eroded and transported from its original site of formation (Hillier, 1995). Depending on the sources, they are about four major groups of clays namely: *Kaolinite, Montmorillonite-Smectite, Illute, and Chlorite*[1].

Clay consumption is a worldwide practice that has existed since human's evolution from primates, and had continues 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 picture of the clay eater gradually emerges as the various academic disciplines examine culture globally to understand the advantage and the effect of clay consumption[2].The consumption of food 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. Taking into consideration the role of metabolism in some metals and the large use of kaolin, it is imperative to evaluate the presence of heavy metals in locally consumed kaolin[3,4]. In sub-Saharan Africa, the rates of pregnant women eating soil or clay range from 28% - 65%[2,5] (Wiley and Solomon, 1998).

However, clay has been reported to decrease the absorption of drugs that chelate with aluminum salt (e.g. digoxin, clindamycin, lincomycin) and can cause pneumoconiosis as a result of excessive intake[6]. Furthermore, due to levels of heavy metals concentration present in most clay samples, which have been established to be non-biodegradable, it could result in the development of lung cancer, nose cancer, larynx cancer, and prostate cancer[7].

Copper is found in all tissues and organs of human body, at a varying concentrations ranging from few ppm to several hundred ppm[8]. Infants, who show copper deficient as a result of the exclusive consumption of low milk, or non-copper diets, are reported to have hypochromic anaemia, microcytic anaemia, hypoferraemia, and hypoproteinemia[9]. In addition, several central nervous system disorders including ataxia, clome seizure, hypomyelination or demyelination and reduced levels of sphingolipides are symptoms of copper deficiency[10]. However, excess copper in the body can lead to the following health disorder: nausea, vomiting (food or blood), diarrhea, stomach pain, black (tarry) stools, difficulty breathing and irregular heart beat etc[11].

Cobalt is a bio-essential chelating element that is found at the center of vitamin B_{12}. It is important for healthy red blood cell formation and neurological health in humans. Cobalt can stimulate antioxidant and anti-inflammatory biological process. Despite of these advantages, cobalt can bio-accumulated in mammals up-to a toxic levels in the heart, kidney, liver, pancreas and also in the skeleton or skeletal muscle. It has been reported to accelerate the growth of tumor in humans and likely carcinogen as well[12].

Most food stuffs contain small amount of nickel (Ni) especially chocolate and fats. The human body needs nickel as an essential micronutrient mineral. It is a common trace element in multiple vitamins which increases iron absorption, preventing iron-poor blood (anemia), and treatment of weak bones (osteoporosis)[13]. Large uptake of nickel could result in lung embolism, respiratory failure, birth defects, higher chances of development of lung cancer, nose cancer, larynx cancer and prostate cancer, sickness and dizziness. Kaolin that contains nickel have been listed by the National Toxicology Program (NTP) as being carcinogens[14].
In this research, kaolin will be main focus of study which is kaolinite.($A1_2Si_2O_5(OH)_4$) formed by chemical weathering of aluminum Silicate mineral like Feldspar, and these kaolinite, may contain heavy metal (e.g. Cu, Zn, Mg, As, Cl, Cr, Fe, Ni, Mn, Co, Pb, Au, etc.) as investigated by previous studies owing to their absorption capacities[15,25]. The research seeks to investigate some of the heavy metal contained in clay sample (kaolin) from Enyigba lead mining site in Ebonyi State of Nigeria and however, quantity the amount of these heavy metals present and note 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 6^0.09'N and 6^0.14'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

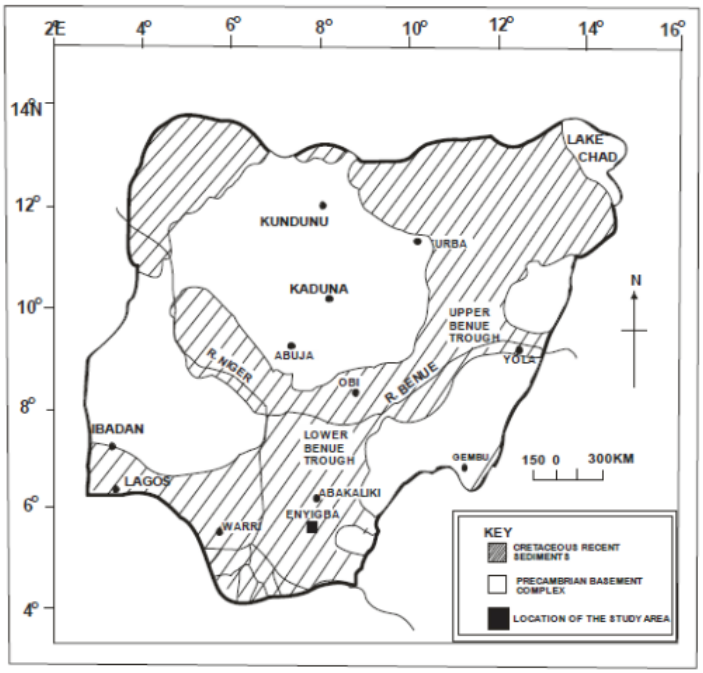

Figure 2: Mapping geological structures controlling mineralization in Enyigba Area South Eastern Nigeria, using Magnetic inversion Technique[25].

Reagent

All chemicals used in the research were of analytical grade. 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).

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	Concentrations of the Clay (Kaolin) mg/ kg
Cu	0.113
Co	0.012
Ni	0.712

Copper is essential in human body but very can cause adverse health problems when taken in large amount. However, too much exposure to copper can cause irritation of the mouth, nose and eyes. It may sometimes cause stomachaches, headaches, vomiting, dizziness and diarrhea[16].Copper poisoning may results in Wilson's disease, characterized by a brain damage, hepatic cirrhosis, demyelination, copper deposition in the cornea and renal disease. Its deficiency may result in leucopenia, hypochromic anemia, and osteoporosis in children[17]. The copper content of the kaolin sample was 0.113mg/kg. The permissible limit of copper for plant is 10mg/kg recommended by WHO[13]. The maximum permissible limit for copper in water is 2mg/l. Thus, the Copper concentration analyzed in the clay sample is within WHO permissible limit[18].

Cobalt is used in the body to ensure the absorption and processing of Vitamin B[12]. In addition, it helps also in the repair of myelin and also used in treatment of some diseases such as anemia. These happens when there are in permissible standard required in the human body as it aid the formation of red blood cells. However, at a substantial level, Cobalt can rise to a distinctive increasingly and reversible depression of cardiac systolic function. The concentration of Co in the analyzed sample is 0.012mg/kg which is within the permissible range as stipulated by WHO[18].

Nickel has been found to be an bio-essential trace element for human and animal health[13]. The permissible limit of Nickel in plants recommended by WHO is 10mg/kg. The maximum permissible limit for Ni in water is 0.2mg/L[13]. However, the concentration of Ni in the analyzed sample is 0.712mg/kg which is above the WHO permissible standard per daily intake[18].

The heavy metal content in the given kaolin from Enyigba lead mining site shown in the table above shows that the levels of Cu, and Co analyzed are within permissible limits and compared well to

standard permissible intake of heavy metals found in a recent study[19]. However, the concentration of Ni is above the recommended permissible limit.

The uptake of elements from food consumption is usually dependent on the element concentrations in food and the quantity of food consumed by individual. Renown world agencies like US Environmental Protection Agency (US EPA), Joint FAO/WHO Expert Committee on Food Additives[20] and Institute of Medicine of the National Academies (IOM) have given regulations on the intake of elements by humans. The IOM of the National Academies recommended the adequate intake (A_I) and the tolerable upper intake level (U_L) values for some essential elements[21,22]; the JECFA recommended permissible tolerable weekly intakes (PTWIs) and acceptable daily intakes as regulations for food additives and certain contaminants in foods[23]. Also, the US EPA provided reference dose (R_fDo) values in ug/kg body weight/day for some elements[24].
Finally, the results of the study supplies valuable information about the heavy metal contents in Kaolinite found in Enyigba mining Site in Ebonyi State of Nigeria. Moreover, these results can be used to improve the chemical quality of Kaolinite (NZU) as regards to the possible health hazards associated with consumption of kaolin by local population.

CONCLUSION

From the study, Copper and Cobalt concentration level are normal for human consumption owing to the international (WHO) permissible standard. However, the concentration value of Ni in the kaolin is above the permissible limit standard. Furthermore, there may be low concentrations of certain heavy metals in an edible clay sample, overdoes intake or long term use can cause disease which may led to cancer[8]. Hence, proper regulation should be applied in the rate of local consumption of this kaolin in Enyigba as its long term risk may led to cancer.

RECOMMENDATION

There are still risk of consumption of this clay since the concentrations of some other heavy metal which were analysed 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 advice and support for the safe and productive use of edible clay.

REFERENCES

1. Huertas F., Fiore S., and Linares J., (1999). Experimental study of the hydrothermal formation of Kaolinite. Chemical Geology pp 171-190.

2. Enviromedica (October 22, 2018): Eating Clay: Lessons and Medicine from worldwide cultures. Retrieved from https://www.environmedica.com/wellness/eating-clay-lessons-on-medicine-from-worldwide-cultures

3. APHA (American Herbal Products Association). Heavy metal analysis and interim recommended limits for botanical dietary supplements: White Paper. *AHPA*: Silver Spring, MD, January (2009).

4. H. Colak, M. Soylak and O. Turkoglu, *Trace Elements and Electrolytes*, **22**, 192 (2005).

5. Wiley, A.S and Solomon H.K. (1998): Geophagy in pregnancy: A test of a Hypothesis. Current Anthropology, 39(4): 532-545

6. World health organization (1996) trace element in Human Nutrition and Health

7. Bowman N.C and Rand, Mj (1980): Textbook of pharmacology 2nd edition: pp 241-261

8. Soma E. (1974). Toxic potential of trace metal in foods, a review journal of food science 39 (2):

9. Graham G.G and Cordano, (1984) a copper deficiency in human health and disease 35:245-254.

10. Sturgeon P. and Boubaker C.(1956): Copper deficiency in infants. Jouranal of syndromes characterized by hypocuremia, iron deficiency and Hypoprotenemia 92(3):254--265

11. https://www.healthline.com/nutrition/copper-deficiency-symptoms

12. https://www.cobaltinstitute.org/about-cobalt.html

13. Zaigham Hassan, Zubair A, Khalid Usman K., Maxhar J, Rizwan Ullan K, Jabar Zaman K.K et al (2012) "civic pollution and its effect on water quality of Rivers Toi at Districk Kohat, NWFP," Research journal of Environmental and Earth Science. Vol 4,5.

14. IARC. 1976 Nickel and Nickel compound in cadmium, Nickel, some epoxides, miscellaneous industrial chemicals and General Considerations on volatile Anaesthetic. IARC Monographs on the Evaluation of Carcinogenic ristk of channels to humans. Vol. Lyon France: International Agency for Research in Cancer pp75-112.

15. Ogah S.P.I and Ikelle I.I. (2015): The determination of the amount of some heavy metals in edible clay of Enyigba village in Abakaliki, Ebonyi State, Nigeria. Der Pharma Chemica, 7(11): 264-267

16. A. Ikem and N. O. Egiebor, *Journal of Food Composition and Analysis*, **18**, 771 (2005).

17. S. Kanumakala, A. Boneh and M. Zacharin, *Journal of Inherited Metabolic Disease*, **25**, 391 (2002).

18. FAO/WHO (1984): List of Maximum levels recommended for Contaminant by the Joint FAO/WHO, Codex Alimentarius Commission, 2nd Edn. FAO/WHO, Rome, Italy, pp 1-8

19. Ruqia Nazir, Muslim K., Muhammad M. Hameed Ur R., Nareed Ur R., surrya Shahab, Nosheen A., Muhammad S., Mohib U., Muhammade R., Zeenat S. (2015). Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water an plants and analysis of physio-chemical parameter of soil and water collected from Tanda Dam Kohat Vol.7(3). Pp 89-97.

20. H. L. Needleman, C. McFarland, R. B. Ness, S. E. Fienberg and M. J. Tobin, *Neurotoxicology Teratol*, **24**, 711 (2002).

21. World Health Organization, (1993) Guidelines for Drinking Water Quality, WHO, Geneva.

22. Institute of Medicine (IOM), (2002) Dietary reference intakes for vitamin A, vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium,and zinc. Washington, DC: Institute of Medicine of the National Academies, *The National Academy Press*, 2001 Constitution Avenue. p.773.

23. JECFA, Summary and conclusions of the 61st meeting of the joint FAO/WHO Expert Committee on Food Additives. JECFA/61/SC, Rome, Italy (2003).

24. Institute of Medicine (IOM), (2003) Dietary reference intakes applications in dietary planning subcommittee on interpretation and uses of dietary reference intakes and the standing committee on the scientific evaluation of dietary reference intakes. Washington, DC: Institute of Medicine of the National Academies, *The National Academies Press.* p. 248.

25. Ema M.A, Daniel A. M and Ndidialmaka N.E (2018). Mapping Geological Structures controlling mineralization in Enyigba Area, South Eastern Nigeria, using magnetic Inversion Technique. International journal of mining Science (IJMS): Vol 4 (3): pp31-39