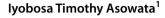
Geophagic clay around Uteh-Uzalla near Benin: mineral and trace elements compositions and possible health implications



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Abstract

Geophagic clay consumption, which is an age-long cultural practice by humans and animals in many parts of the world, and particularly in Nigeria, may have long time health effects on the consumers. This is particularly so because of the relatively high concentration of harmful minerals and toxic elements. This study sought to determine the mineralogical and trace element compositions of geophagic clay in Uteh-Uzalla area, which is underlain by the Benin Formation of Oligocene to Miocene age, in order to evaluate the potential health risk associated with the consumption of the clay. Sixteen clay samples were collected from mine face profiles of an open pit, analysed for mineral and trace element compositions, using x-ray diffraction technique and ultra-trace inductively coupled plasma mass spectrometry (ICP-MS) methods, respectively. The mean mineral concentration in % includes kaolinite, quartz and smectite (64.88, 19.98, and 9.54), respectively, among other minerals. And the mean concentrations in mg/kg for Cu (15.0), Pb (14.4), Zn (30.9), Co (8.9), Mn (39.4) and Th (10.5) among other elements were found in the clay. From the trace elements results when compared with health risk indices by Agency for Toxic Substances and Diseases Registry (ATSDR): Minimum Risk Level, recommended daily intake and estimated daily intake, it was found that the elements are far above the daily oral intake requirement. Also, considering the relatively low pH (acidic) values that were exhibited by the clays, harmful minerals and elements contained in the clay may be bioavailable in the internal system among those who are frequently involved in the consumption of the clay.

Keyword ICP-MS · Quartz · Clay profile · Health risk · X-ray diffraction

1 Introduction

The act of consumption of earth or soil-like materials such as clay is referred to as Geophagia or Geophagy, and such clay is referred to as geophagic clay. It occurs in animals where it may be a normal or abnormal behaviour, and also in humans, most often in rural or preindustrial societies among children and pregnant women [1, 2]. Sometimes the practice can also be seen among urban residences, as seen in the sale of the produced clay in many urban markets in Nigeria, [1–5]. Geophagic clay consumption has been reported to be age long, since four hundred (400) years back, and the act had been practiced by different cultures, [2, 6–8]. Human geophagia may be related to pica, a psychological disorder characterized by an appetite for substances that are largely nonnutritive, such as ice (pagophagia); hair (trichophagia); paper (xylophagia); stones (lithophagia) or soil (geophagia); and chalk. [9,

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10], pointed out that geophagic constituents could act as a lubricant for fibrous forages, provide extra minerals and stimulate the flow of saliva, which contain high concentration of sodium (Na) and phosphorus (P) and could thus relieve a mineral shortage in the rumen, which is also supported by [11]. Historically, and today in Nigeria, geophagia is almost synonymous with clay consumption and some pregnant women patronise those who sell the commodity, [1, 5]. Areas in Africa where such practices are in existence include; South Africa, Nigeria, Cameron, Uganda, Tanzania, Ghana, [9, 11–13], among many other areas of the continent.

Many research works have been carried out on the evaluation of essential elements in geophagic clay for effective curative of both skin and intestinal disorder among pregnant women, and recommended pharmaceutical regulatory agency to effectively put control on its consumption, [1, 14–16]. The metal and mineralogical characteristics of clay in many parts of Nigeria such as Ibadan, Benin, Calabar and other Southern parts of Nigeria, [2, 4, 5, 9] as well as some of the other parts of Africa have been carried out with a view to finding the total metal content and possible health implications on their consumer [17–19]. Result showed that for the Calabar clay, it was relatively enriched with Zn, Pb and other potentially harmful elements, using inductively coupled plasma mass spectroscopy (ICP-MS) and the findings showed that these elements may probably be the cause of high prevalence of hypertension, cardiac failures and gastrointestinal problems within the study areas, [5]. Similar results have been observed and recommendations were given for communities in Free State province of South Africa, [20]. The works of [21–25], have reported the possible presence of high concentration of potentially harmful elements such as Pb, Cu, As, Zn and Hg and radionuclides such as Th, La and U in the clays and emphasized the need for more gualitative scientific investigation to avoid possible consumption of toxic elements. Recently, [16] carried out in detail the mineralogical, geochemical and health impacts of that earth materials consumed by humans in Vhembe district in Limpopo province, South Africa and found out that there are essential elements like selenium in them that could be extracted for immune booster for HIV patents, [16]. It was therefore recommended that pregnant women and children that consume this clay material without control should seek protection against gastrointestinal problem and toxin because of the possible high bioaccessibility of some potentially harmful elements like Hg, As, Pb and Zn found to be high in both in their intestine and stomach, [16]. The works of [22, 26-29] further reported the relevance of carrying out bioaccessibility and bioavailability of geophagic clay in the human internal system in order to know the relative health risk that such clay consumption

SN Applied Sciences A SPRINGER NATURE journal poses to the human beings. Issues relating to frequency of consumption, which brings about gradual build-up over time of these elements in the vital organs of the body, the nature of the chemical species and oxidation state of these harmful elements, soil pH, stomach and intestinal pH, soil-to-solution ratio and fasting condition can increase health risk. The causes and consequences of geophagic clay consumption were studied by [30], using in vivo type of bioaccessibility, to check for Fe content enrichment in the hemoglobin, duodenal cytochrome and ferroportin of the internal system. And it was analysed, using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES). It was observed that there were low (minimal) impacts of Fe in those parts of the internal systems studied. These findings were also in agreement with the in vitro study that was carried out with smectite of Ugandan geophagic clay using Caco-2 model by [31]. This finding showed that in consuming the clay, there was no significant increase of bioavailability of Fe in the internal system; hence, there was no significant health effect of the consumption of the clay [31]. Similarly, the bioavailability studies of trace elements such as lead (Pb), cadmium (Cd) and mercury (Hg) were carried out by [32]. The study showed that bioaccessibility of Pb intake by person (pregnant women) weighing 60 kg exceeds the provisional tolerable daily intake (PTDI) of 0.0036 mg/kg body weight when more than 10 g of the clay are consumed per day as well as when bioavailability of Pb is relatively high, say > 10%. The study also showed that newborn babies (3 kg body weight) are at higher risk of exceeding the provisional tolerable daily intake of Pb. Low quantity of Hg and Cd was also recorded in the internal system, suggesting that the daily ingestion of geophagic clay does not contribute to unsafe mercury and Cadmium intake for both adult and newborn babies for that particular study. Exposure of lead to pregnant and breast-feeding women is of higher risk, as reported by [33, 34]. This is because it was observed that the metal easily crosses the placenta and migrate (absorbed) into breast milk even at a relatively low exposure, causing adverse effects on child's neurodevelopment and physical growth. Similarly, [11] studied some major elements as well as toxic metal concentrations in clay in Volta region of Ghana, using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The elements were iron (Fe), copper (Cu), zinc (Zn), potassium (K), magnesium (Mg), sodium (Na), arsenic (As), manganese (Mn), lead (Pb) and nickel (Ni). This clay was found to be consumed by pregnant women in the study area. The results showed that Fe, Cu, Zn, K, Mg, Na, As, Mn, Pb, and Ni, recorded 1.38, 2.40, 7.74, 4.01, 13.24, 13.76, 1.63, 4.72, 0.53 and 1.85, respectively, in µg/kg. Harmful elements such as As, Mn, Pb and Ni were further compared with World Health Organization [35] threshold recommendation at μ g/kg at 60 kg body weight per day of 3.0, 4.9, 3.0

and 5.0, respectively. From the result, [Kortei el al., 2020] opined that the cumulative effect of the consumption of the clay may cause detrimental effect on the foetus of the unborn child. Hence the need for proper evaluation in other to know the places wher thes clays are mined and sold. In Nigeria, most works that have been carried out, which have only been done by first sampling from the market places where most of the clays are sold [2, 4, 22] as well as determination of total metal content in the evaluated clay. Till date, no known published work has been carried out on the total metal content, mineral composition determination in the deposits where these clays are mined, processed and sold for consumption in this study area. Hence, the aim of this research is to evaluate the mineral composition and trace elements concentration in the geophagic clay in the study area (at Uteh-Uzalla, near Benin City) (Fig. 1) in order to check the possible health risk if any, in the consumption of the geophagic clay.

2 Geology of the area

The study area falls within the Benin Formation, which is of Oligocene to Miocene age, in Fig. 2, which is the youngest in the sequence of formations in the Niger Delta Basin, [36]. The other two formations are Akata and Agbada, [36–38]. The lithologies of the Benin Formation comprise of reddish brown sands, silt, sandstone and clay, which are generally referred to as coastal plain sand, [39, 40]. In some localized areas, the clay thickness, as presented in Fig. 1 of the supplementary Material, is significantly above 30 m, while in some other areas, they appears as thin beds of less than one (1) meter. Their colours also vary from light brown, reddish brown and pale white colours as observed in the field study. The mined clay samples are cut to sizes as seen in Fig. 2 of supplementary material, and loaded in sack bags for firing before sale, in Fig. 3 of supplementary material.

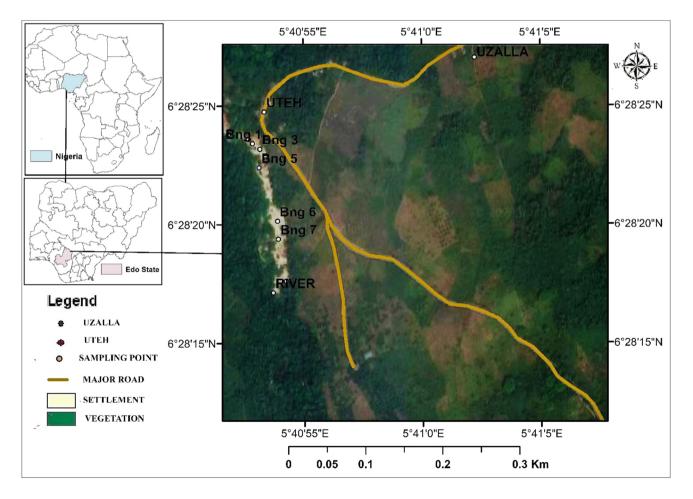


Fig. 1 Study location map

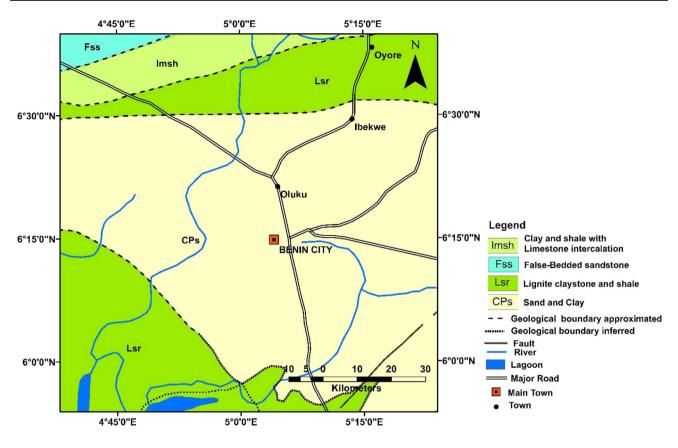


Fig. 2 Geologic Map of Benin area [4]

3 Materials and methods

The clay sample at the study area which is an open pit mining site was identified from the various open pits in the mining site. These open pits were made so because of the ways artisanal miners carry out the mining activities and sixteen (16) clay samples were collected. It was observed at the mining site that the clays were separated by the miners between the consumed type and the one that are not consumed (Fig. 1 of the supplementary material). The variation between the one collected for consumption was observed from their lotho-strata in the mining site. The top layer of the clay sequence were not mined for consumption, hence, the top layer are discarded at the mine site by the miners, while the bottom layer were collected for consumption. This variation was easily identified in the exposed strata based on their colour and grain size variation within the litho-sequence based on field study. The clay samples that were collected were air dried at room temperature of 26 °C based on the average temperature in Akure, Nigeria and after three (3) days, the samples were pulverized and stored in polythene bags for physicochemical, geochemical and mineralogical analyses. For the physicochemical analyses, 120 ml of deionized water were added to 20 g of clay samples in a beaker, and

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were allowed to stay for 48 h at room temperature of 26 °C. Thereafter, pH, electrical conductivity (EC) and total dissolved solid (TDS) were measured using multi-pH meter, at the Geochemistry laboratory of Marine Department, Federal University of Technology, Akure. Similarly, the trace elements concentration of the clay samples was determined, using 0.5 g of sieved clay samples at > 53 μ m mesh fraction from the pulverized (Pulp) samples. Before the geochemical analysis, the clay samples were digested using aqua regia. The process involves gradual adding of 5 ml of nitric acid (Merck Suprapur of 65%), then, addition of 2 ml of hydrochloric acid (Merck Suprapur 36%), and 10 ml of ultrapure water (18 m Ω -cm of specific resistivity) in a clean Pyrex tube. The samples were heated at a temperature of 95 °C for a period of 2 h in a microwave oven. Later the samples were poured into a 50-ml volumetric flask, and the solution filtered, extracted by a disposable syringe and made to be filtered with a 0.45 filter membrane before the analysis was carried out, and subsequently analysed using ultra-trace inductively coupled plasma mass spectrometry method (ICP-MS) (AVIO 200, PerkinElmer, MA, USA). The quality assurance and quality control procedure were carried out; blank samples testing along with the samples analysed were carried out in group, together with reference certified materials according

to ACME laboratory protocol. Also, duplicate samples were analysed simultaneously for 20% of the total clay samples and the standard deviations of the samples were averagely found to be under 10% from the expected values. The minimum detection limits of the analysed trace in mg/kg were Cu (1.0), Pb (3.0), Zn (1.0), Co (1.0), Mn (2.0), Th (2.0), Sr (1.0), V (1.0), La (1.0), Cr (1.0), Ba (1.0), Sc (5.0) and Ni (1.0). The sensitivity of the equipment in terms of the minimum detection limit (MDL) as declared by the laboratory was satisfactory for the determined elements. X-ray diffraction (XRD) technique analysis was also carried out for eight (8) at of the sixteen (16) samples, using 45 g of the clay samples. These include the consumed and the nonconsumed clay samples at the XRD Analytical and Consulting CC, Lynnwood Glenn, South Africa. The clay samples were prepared for XRD analysis using a back loading preparation method. It was analysed with a Malvern Panalytical Aeris diffractometer with PIXcel detector and fixed slits with Fe filtered Co-K a radiation. The phases were identified using X'Pert High score plus software. The relative phase amounts (weights %) were estimated using the Rietveld method.

Similarly, estimation of geophagic clay intake was carried out. The mean daily intake (MDI) of the consumed clay analysed was estimated to be 20 g. This estimation was arrived at as a relatively conservative outcome from published works in some countries in Africa and in Nigeria particularly, [2, 4, 5, 9, 41, 42]. This estimate became appropriate based on anecdotal evidences about consumption pertain in their studies. The probable daily intake (PDI) of the selected elements was calculated by multiplying the mean concentration of the trace elements (T) by the mean daily consumption, under an assumed body weight of 60 kg, which is a major parameter in human health metabolisms [41].

 $PDI = [T \times MDC]$

where MDC = mean daily consumption (μ g).

The results were compared against recommended mean daily intake by the Joint WHO/FAO Committee on Food Additives (JECFA) [35].

4 Results and interpretation

4.1 Physicochemical characteristics

The result of the pH in both the consumed and nonconsumed clays in the study area showed that it ranged from 3.19 as seen in sample Bng4 to 6.01 as observed in Bng2A. The pH of clay samples showed that they are generally slightly to moderately acidic (Table 1). However, the result for the electrical conductivity (EC) ranges in μ S/cm from 11.0 to 1861, indicating a wide range of variation of EC in the clay sample. Similar variation result in the Total Dissolved Solid (TDS) was observed in the clay samples. The TDS values showed that it ranges in mg/l from 5.0 to 935. It was generally observed that there were no clear variations in the physicochemical parameters measured between the consumed clay samples from the nonconsumed clay samples.

Trace elements concentration in the geophagic clay samples (Table 2) showed that Cu (mg/kg) ranges from Below Detection Limit (BDL) (< 1) – 21.0, mean 15.0, standard deviation \pm 7.09). Pb (13.0–18.0; mean 14.4; \pm 1.86) mg/kg, Zn (4.0–76.0, mean 30.9 \pm 27.25) mg/kg, Co (1.0 – 16.0; mean 8.9; standard deviation \pm 5.22) mg/kg, Mn (8.0 – 128.0; mean 39.4, \pm 37.80) mg/kg and Th (6.0 – 14.0; mean 10.5 standard deviation \pm 2.27) mg/kg among other trace elements determined. It was observed that there were relative variations in elemental concentration in both the consumed and nonconsumed clay samples analysed from one sample pit to the other.

The highest concentrations of Cu for the consumed clay were at pit BnG6A and BnG8A with a concentration of 21.00 mg/kg, respectively, while pit BnG1A was below detection limit, as the only sample was Cu was not detected. Pb was found in all the samples analysed, with the highest concentration of Pb, 18.0 mg/kg in BnG3A, while the lowest concentrations of 13.0 mg/kg were found in samples BnG1B, BnG5A, BnG7A and BnG9, respectively. Similarly, Zn was recorded in all the samples analysed. The

Table 1Physicochemicalproperties of the clay in thestudy area

	Consu	med Clay			Nonco	Nonconsumed Clay				
	рН	EC (µs/cm)	TDS (mg/l)		pН	EC (µs/cm)	TDS (mg/l)			
BnG1A	3.74	33	17	BnG1B	4.51	13	6			
BnG2A	3.46	400	199	BnG2B	6.01	11	5			
BnG3A	3.12	1861	935	BnG3B	4.05	25	12			
BnG5A	3.23	745	374	BnG4	3.19	1061	531			
BnG6A	3.37	405	203	Bng5B	5.62	13	7			
BnG7A	6.02	13	6	BnG6B	4.86	22	11			
BnG8A	3.55	322	161	BnG7B	3.31	1479	740			
BnG9	3.86	33	17	BnG8B	3.28	1193	598			

Table 2Trace elementscompositions of the geophagicclay in the study area in mg/kg

Element	Min	Consum	ed Clay (n=	8)		Nonco	nsumed Clay	/ (n=8)
		Max	Mean	Std. Dev	Min	Max	Mean	Std. Dev
Cu	BDL	21.0	15.0	7.09	3.0	26.0	12.75	8.35
Pb	13.0	18.0	14.4	1.85	10.0	17.0	14.25	2.05
Zn	4.0	76.0	30.9	27.25	3.0	56.0	12.00	18.29
Со	1.0	16.0	8.9	5.22	1.0	7.0	2.00	2.14
Mn	8.0	128.0	39.4	37.80	3.0	22.0	9.50	7.35
Th	6.0	14.0	10.5	2.27	9.0	14.0	11.13	1.73
Sr	10.0	19.0	13.5	2.93	5.0	17.0	12.13	4.02
V	23.0	35.0	27.8	4.59	25.0	64.0	38.88	14.42
La	10.0	33.0	16.1	7.45	14.0	26.0	21.38	4.90
Cr	17.0	29.0	24.3	3.65	19.0	38.0	25.38	6.14
Ba	34.0	104.0	60.0	22.49	14.0	98.0	43.38	29.75
Sc	5.0	9.0	7.3	1.28	5.0	10.0	7.38	1.69
Ni	0.5	22.0	14.6	7.69	0.5	15.0	3.44	5.12

highest concentration of Zn, was found in BnG2B, 76 mg/kg, sample BnG5A 64 mg/kg also recorded relatively higher enrichment of Zn. However, BnG1B 4.0 mg/kg, showed the lowest concentration of Zn. Similar variation in concentration was exhibited by the selected trace elements in both the consumed and unconsumed geophagic clays. Comparatively, the mean concentrations in mg/kg of Cu, (12.75), Pb, (14.25), Zn, (30.9) Co, (8.9), among other trace elements were found to be higher in the nonconsumed clay, Cu, (12.75), Pb, (14.25), Zn, (12.00), Co, (2.0) and Mn (9.50) except for V, (27.8), La (16.1) and Cr (24.3) that the mean concentration for the consumed clay is lower than the nonconsumed clay, V (38.88), La (21.88) and Cr (23.38), respectively.

The average elemental concentrations of the selected trace elements in the geophagic clay were compared with some published article's reports published elsewhere. It was observed that the mean concentration of these selected trace elements in the geophagic clay of this study is relatively lower than many of the clay consumed elsewhere and sometime higher, but generally of close similarity in elemental concentrations. For example, the mean concentration in mg/kg for Cu (15.0) in this study is lower than clay studied in Kano (16.1), Asaba (19.88) and Cameroon (42.0), but higher than the clay samples analysed in Katsina (7.6), Calabar (14.3) and Okon-Eket (12.17). The mean concentration for Pb (14.4) is found to be higher than the Pb mean concentration for Kano (11.5) and Katsina (6.3) but lower than the mean concentration for Asaba (46.3), Calabar (36.48), Okon-Eket (33.8) and Cameroon (24.0). Similar trend was observed in Zn, Co among other trace elements (Table 3).

Also, the mean concentrations for Cu, Pb, Zn, Co, Mn, Th, Sr, V, La, Cr, Ba, Sc, and Ni were observed to be lower than the mean result of these same elements in the average shale concentration (ASC) according to [43] (Table 3). This suggests that the consumed clay sample have lower enrichment of these selected trace elements concentration than the average shale concentration. The mean concentration in mg/kg for Cu, Pb, Zn, Co, Mn, Th, Sr, V, La, Cr, Ba, Sc, and Ni were also compared with the average Continental Crust Composition by [44] (Table 3). From the result, it was observed that the mean concentration of these elements in this study were lower than the average Continental Crust concentration except Pb (5.0), Th (2.0) and La (11) when compare to Pb, Th and La of this study with mean concentration of 14.4 and 14.25, 10.5 and 11.13, 16.1 and 21.38, respectively, for both consumed clay and the nonconsumed clay (Table 3). This may have been influenced by the grain size of the clay samples in this study, which may have increased the absorption surface.

Similarly comparison was carried out between the trace elements of this study with the minimum risk level recommended by Agency for Toxic Substances and Diseases Registry (ATSDR), [45] and recommended daily intake of trace elements in the human system [46]. It was revealed that these elements exceeded the minimum risk level as prescribed as well as the expected amount in the body system (Table 3). This was also observed in Table 4, where by the estimated probable daily intake (PDI) was higher that the WHO/FAO, 2011 recommended daily intake in all the available elements that were compared with WHO/FAO daily intake standards as seen in Cu (threefold higher), Pb (6 folds higher), among other elements. This suggests that the continuous consumption of this clay may pose significant health risk, especially with the continues accumulation of these harmful elements over a long period of time as revealed by [32].

The presence of elements such as Pb, Th, La and Sc in the analysed samples may pose some health risk to those

Table 3 Comparison of mean	n concentration of trace e	lements in clavs the stud	v area with other pu	Iblished works in ma/ka

Ele	Mean ^a	Mean ^b	A	В	С	D	E	F	G	Η	I	ATSDR (mg/kg/ day)	Recommended Daily intake mg/ kg/day
Cu	15.0	12.75	16.1	7.6	19.88	14.13	12.17	42	32.25	50	90	0.01	1.0–1.5
Pb	14.4	14.25	11.5	6.3	46.3	36.48	33.8	24	1.53	20	5.0	NST	NST
Zn	30.9	12.00	15.5	3.0	40.4	46.0	41.29	110	32.63	90	83	0.3	10–15
Co	8.9	2.00	5.25	2.8	13.56	6.78	5.77	1.5	29.0	20	33	0.0001	0.002 - 0.1
Mn	39.4	9.50	-	-		76.83	106.43	-	-	850		0.3	2–3
Th	10.5	11.13	18.6	16.3	13.9	-	-	24	8.1	12	2.0	NST	NST
Sr	13.5	12.13	96.8	121.4	80.13	-	-	64	73.9	400	220	2.0	0.5–1.5
V	27.8	38.88	-	-	-	-	-	84	124.0	130	271	0.01	-
La	16.1	21.38	-	-	-	-	-	-	99.85	40	11	NST	NST
Cr	24.3	25.38	-	-	-	-	-	1.5	124.24	100	219	0.0001	NA
Ba	60.0	43.38	-	-	-	-	-	330	-	-	150	0.2	NA
Sc	7.3	7.38	-	-	-	-	-	18	-	-	35	NST	NA
Ni	14.6	3.44	6	1.7	_	23.87	22.6	42	30.7	80	156	0.0002	2–3

NST = No safe Threshold

NA = Not Available A-Kanu—[2] B-Kastina—[4] C-Asaba—[4] D-Calabar—[5] E-Okon-Eket—[5] F- Cameroon—[20] G- Volta (Ghana)—[59] H- Average Shale Concentration [43] I—Average Continental Crust composition [44] ATSDR- Agency for Toxic Substances and Diseases Registry: Minimum Risk Level [45] Recommended Daily intake [46] Mean^a = Consumed Clay (This Study)

Mean^b=Nonconsumed Clay (This Study)

pregnant women who are habitual consumers of this clay, owning to the fact that these trace elements have no recommended guidelines of any quantity for their consumption because of their toxic nature and presented by, [47].

4.2 Mineralogical characteristics

The mineral compositions of the geophagic clay were determined following the obtained X-ray diffractogram patter presented in Figs. 4–11 of the supplementary materials. And the summary results of the mineral found are presented in Table 5. The result showed that kaolinite was the dominant mineral in all the selected eight (8) samples analysed. The highest amount of kaolinite was found in samples BnG5B (76.7%) while the lowest was found in BnG2A (54.2%). Kaolinite mineral abundance was closely followed by quartz, in all the samples. The

highest amount of quartz was found in BnG7B (38.9%) and was closely followed by BnG 1A (33.4%), while the sample with the lowest quartz was found in BnG7A (11.7%). Other minerals present in the analysed samples were muscovite, anatase, pyrite, calcite, gypsum, smectite and rutile which occurred in relatively lower amount. The relative abundance of kaolinite in the eight (8) samples showed that the geophagic clay in the area is essentially rich in kaolin, making the clay a kaolinite rich clay, with relatively fair amount of quartz and as well as other minor/trace amount of other minerals. Also, it was observed that smectite content in the consumed clay samples was found in BnG1A (15.2%), BnG6A (9.7%) and BnG9 (10.4%) which were fairly higher compare to the nonconsumed samples as observed in sample BnG1B (1.5%) and BnG5B (1.2%).

Elements	Mean Conc. (mg/kg)	Estimated daily intake (μg/day)	WHO/FAO PMTDI (µg/ day)		
Cu	15.0	300	100.0		
Pb	14.4	288	50.0		
Zn	30.9	618	110.0		
Co	8.9	178	N/A		
Mn	39.4	788	490.0		
Th	10.5	210	N/A		
Sr	13.5	270	100.0		
V	27.8	556	N/A		
La	16.1	322	100.0		
Cr	24.3	486	N/A		
Ва	60.0	1200	N/A		
Sc	7.3	146	N/A		
Ni	14.6	292	5.0		

PMTDI: Permitted Maximum Tolerable Daily Intake WHO: World Health Organization

FAO: Food and

Agriculture Organization

N/A = Not Available

5 Discussion

The consumed clay mineral composition was also compared with geophagic clays consumed by humans in other parts of the world and geophagic clays of southern part of Nigeria. And from the results, it shows some similarities with those of China, Zimbabwe, Uganda and Indonesia (Table 6) which all have kaolinite as a dominant constituent. The samples studied show marked compositional differences from geophagic materials from other parts of the world; for example, smectite is dominant in some of the geophagic clays of China and Indonesia, while halloysite is the dominant clay mineral in geophagic materials of USA and Indonesia; illite is present in subordinate percentages in geophagic clays of USA and Indonesia, while it is found in southern Nigeria geophagic clays only in trace percentages.

The geophagic clay studied has been found to have been formed through secondary (weathering) processes hence, deposited within Benin Formation, of the Niger delta basin of Nigeria, [36]. Therefore, the process of deposition may have been made possible through activities such as groundwater flow, surface water runoff before deposition. During the period, ionic species are lost or depleted, which gives room for clay mineral purity and accumulation, [48].

The health risk associated with the consumption of clay is largely a function of the pH values of not just the clay itself, but also base on the pH values of the internal organs that directly interact with the consumed clay, [32]. Saliva, gastric juice, duodenal juice and bile have been reported by [30, 32, 49], to range from 1 to 8 pH values within the digestive system. It is on this bases that the bioavailability/ accessibility of these (quartz, pyrite, rutile, muscovite and smectite) minerals and harmful elements (Pb, Cr, Th, La, Cu, Ni, Co and V) are of concern.

Mineralogically, the Uteh-Uzalla geophagic clay is essentially rich in kaolin and quartz with some traces of smectite for the consumed clay. Quartz in the clay may pose health risk to those patronizing and frequently indulging in the consumption of the clay. This is because by hardness scale, quartz is significantly hard and has been reported to be harder than dental enamel in the human system [5]. This may by implication curse damaging effect on the internal system. Again, for the fact that quartz in the clay passes through the gastrointestinal tract, can accumulate in the colon and possibly lead to rupture in the colon as earlier reported by [50].

 Table 5
 Mineralogical Composition of Geophagic Clays in the study area (%)

	Consum	ed Clay						Nonconsumed Clay				
Minerals	BnG1A	BnG2A	BnG6A	BnG7A	BnG9	Range	Mean	BnG1B	BnG5B	BnG7B	Range	Mean
Quartz	12.7	34.3	21.2	11.7	20	11.7–34.3	19.98	33.4	16.9	38.9	16.9–38.9	29.73
Pyrite	0.3	6.9	2.5	3.2	2.1	0.3–6.9	3	0	0	0	0-0	0.00
Kaolinite	69.5	54.2	64.4	71.4	64.9	54.2-71.4	64.88	62.3	76.7	58.9	58.9–76.7	65.97
Anatase	1.4	1.7	1.6	1.8	1.6	1.4–1.8	1.62	2.2	2.9	2.1	2.1-2.9	2.40
Rutile	0.5	0.9	0.6	0.6	0.8	0.5-0.9	0.68	0.2	0.6	0	0–0.6	0.27
Muscovite	0.1	0	0	0	0.2	0–0.1	0.06	0	1.3	0	0–1.3	0.43
Smectite	15.2	1	9.7	11.4	10.4	1–15.2	9.54	1.5	1.2	0	0–1.5	0.90
Calcite	0.4	0	0	0	0	0-0.4	0.08	0.4	0.4	0	0-0.4	0.27
Gypsum	0	1	0	0	0	0–1	0.2	0	0	0	0–0	0.00

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Table 6 Comparison of Geophagic Clay in this study with other parts of Nigeria and the world

	Asaba	Ekiti	Ibadan	This study					
(Study Area)					1	2	3	4	5
Kaolinite	Dorm	Abunt	Abunt	Dorm	Abunt		Abunt	Dorm	Sub
Smectite				Tr	Dorm	Sub		Sub	Dorm
Halloysite		Tr			Sub	Dorm	Sub		Dorm
Nontronite	Abunt								
Palygorskite	Abunt	Sub	Sub						
Illite	Tr		Tr			Sub			
K- Feldspar	Tr		Tr						Sub

Dorm-Dominant (> 50%), Abunt-Abundant (25–50%), Sub-Subordinate (5–25%), Tr-Trace (< 5%)

1-China [58]

2-U SA [61]

3-Zimbabwe [61]

4- Uganda [62]

5- Indonesia [63]

According to [51], kaolin rich clay is chemically inert in nature over a wide range of pH values; the mineral assists as antiacid, and hence inhibits corrosive activities. [48] reported that Cation Exchange Capacity (CEC) of kaolinitic clay is found to be among the lowest of clay minerals, thereby allowing for little exchangeable ions exchanges sites. Beside these, the particle size of clay assists in the formation of coating in and around the gastro-intestinal walls. These properties measured above, is summarily reported to that kaolin serves as protective minerals for intestinal organs [52] which is the reason pharmaceuticals make good use of clay for medicinal active ingredient carriers for gastrointestinal disorder treatments, [5]. The highlighted relevance of kaolin in clay may have been the reasons for the consumption of this clay in many parts of the country. Nevertheless, the mere fact that this clay is consumed may put the consumers at risk healthwise.

Similarly, the presence of some potentially harmful elements in the geophagic clay is of concern. These elements include Pb, Cu, Th, V, Co, La, Sc Ni, V, Cr and Sr. The American Agency for Toxic Substances and Diseases Registry (ATSDR) [45] has reported that oral consumption of Pb, Th, La and Sc is not allowed, no matter how little in quantity that is present. These elements can be extremely toxic to the human internal system. The health toxic effects of Pb oral consumption include hearing loss, reduction in intellectual quotient, for children, [53]. However, for adults, it can cause kidney and fertility systems damage and anaemia, [20, 54, 55]. Cr oral consumption may cause lung cancer and dermatitis just as Ni oral consumption also has ability to cause respiratory diseases, [56, 57]. Th and La have radioactive isotope that causes toxic effect to the lungs, liver, brain and other vital organs of the body, which can degenerate to cancer of those organs, [55, 58]. High oral consumption of Co can lead to asthma and pneumonia, even though low consumption has positive benefits such as stimulation of the red blood cells in the body. Other trace elements determined Zn and Ba have some relatively positive health benefits when consumed. Zn for example is considered nontoxic, when consumed within tolerable dose. However, when the consumption of Zn exceeds acceptable limit, it can lead to electrolyte imbalance, renal failure, abdominal pain, vomiting, impair immune responses, among other health risk, [52, 55].

Since most of these harmful and toxic trace elements are significantly present in the studied clay, in some case more than 200- to 300-fold higher than the recommended threshold for oral consumption by the American Agency for Toxic Substances and Diseases Registry (ATSDR), it can be said that the studied clay may be unsafe for consumption. This is further buttressed by the result of the estimated probable daily intake whose result showed significant effect when compared with the WHO/FAO standards of metal intake per day.

However, it can be said that we cannot satisfactorily estimate the health risk that are scientifically associated with the consumption of geophagic clay. Most of the exposure factors and individual risk factors as expressed by [30–32, 59, 60] are poorly known based on the scope of this research; hence, more scientific information is needed with respect to nature and provenance of the geophagic clay, bioavailability and bioaccessibility of these potentially harmful elements (PHEs) as well as harmful minerals in the clay samples, consumption habits of the pregnant women that are known to consuming this clay, breastfeeding mothers and children. Similarly, the frequency level will further add to knowing the health risk of these PHEs and minerals of this clay as reported by [30–32, 60].

6 Conclusion

The geophagic clay samples collected from Uteh-Uzalla mine site were assessed; the clay is derived from secondary sedimentary environment. The pH of the clay samples showed slightly to moderately acidic with a pH value of between 3.19 and 6.01. The result of x-ray diffraction shows abundance of kaolinite in all the clav samples analysed. The dominance of kaolinite and to a lesser extent smectite may have been the reason for the continuous consumption of this clay because of the antiacid effect that it has on the digestive system. Quartz was also found in all the samples as the second most abundant element. Other minerals that occurred in minor percentage include anatase, pyrite, rutile, muscovite, calcite and gypsum, which by their concentration may not have significant health risk to the human internal system. The relatively high percentage of quartz is of concern because the mineral is hard in physical form and may cause colon rupturing, which is a very serious health risk that calls for concern.

Trace elements contents (Cu, Pb, Zn, Co, Mn, Th, Sr, V, La, Cr, Ba, Sc and Ni) that were analysed showed relatively elevated concentration in all the samples. The trace elements results when compared with American Agency for Toxic Substances and Diseases Registry and recommended daily intake by [Belitz, 2009], it was found that the elements are far above the daily oral intake (Threshold) requirement. The presence of Pb, La, Th and Sc elements in the studied clay possibly poses serious health risk. These elements are referred to as high priority toxic elements that need not be present in what human beings consume especially in it natural form. Since the concentration of essential elements such as Zn, Mn, Ba, among others, is far more than the tolerable limit of intake in the study samples, their continuous consumption of this clay need be discouraged because of the possible health implications. Apparently no doubt, geophagic clay consumption is known to be age-long practices among women and children in both rural and semi urban dwellers, discouraging people who are used to it will be difficult because of some inherent health benefits and habits. Because of the scope of this research, it should be said that studies on the bioaccessibility and bioavailability of this clay will in no small means give more information on the health risk, if any, of the consumption of this clay.

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Declarations

Conflict of interest I hereby state that I am the author of this article; there is no conflict of interest in this article.

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