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Assessing the Bioavailability of some Trace and Major Elements in Geophagical Clays of South-Western and Eastern Nigeria: An *Invitro* Study

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INFORMATION

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ABSTRACT

Geophagy is the deliberate ingestion of soil. This study aims to assess the bioavailability of some trace and major elements in the edible clays of southern parts of Nigeria; in order to ascertain the essential elements and possible potential harmful elements that is bio-accessible and bioavailable to the geophagists. Raw and roasted samples were collected at the mining sites and from market vendors in Aforwa, Ohordua, Uzalla and Nteje. Physiochemical, geochemical and mineralogical compositions were quantified using various analytical equipment. The bio-accessible contents of some trace and major elements were determined by *invitro* bio-accessibility tests that mimic the conditions of the human gastrointestinal environments. The colour of the clays ranges from whitish, to grey; the materials are dominantly clayey size particles. The pH is acidic with moderate to low CEC in all the samples (2.84 meq/100g). A range of elements was identified. The geophagic materials are majorly kaolinite, with other range of minerals like quartz, goethite, hematite. The concentration of the bio-accessible elements in the 2-part acid-alkaline *invitro* physiologically based test at 5g dose shows low bio-accessibility of most elements but at higher dose of 20 g, the concentrations of the bio-accessible elements in the roasted samples were increased supplying 0.07-80% (Fe>Cu>Zn>Mn>Ca>Mg>P>K) nutrients based on the reference nutrients intake required by the geophagists. The Nteje clays are the highest supplier while, the Ohordua is the least supplier of both the trace and major elements, hence the edible clays are a moderate source of mineral nutrients and potential source of potential harmful elements (V, Ni, Cr, and Pb), and if consumed in excess or even at lower concentration may pose toxic effects to the consumers. Moderate dose of this material that is within and/or below the Safe Upper levels should be consume since geophagy has become inherent to human.

1. Introduction

Geophagy is the habit of eating clay or earthy materials, it has been practiced by humans for a long period of time, with the suggested earliest evidence being found at the prehistoric site in the local basin in the Kalambo River valley above the famous Falls on the border between Tanzania and Zambia. Recent reports also, indicate the continuing high prevalence of geophagy among certain human groups (Geissler et al., 1997; Thomson, 1997), although during the middle of the 20th century the practice was described as rare in Europeanised society (Gelfand, 1945). Earlier, (Foster, 1927) recorded pica (of which geophagy is a form) in the United Kingdom as being very uncommon, confined to the cravings of pregnant women and the soil eating propensities of children. Several reasons why some people eat soils, includes to supplement essential minerals, such as Fe, Zn, Cu, Mn, Ca and Mg (Johns and Duquette, 1991a). There are reports, however, that geophagy might increase anemia because it reduces the uptake of Fe (Minnich et al., 1968).

Another reason is to relieve gastric complaints and nausea and to detoxify toxic materials because clay soil can adsorb dietary toxins, such as alkaloids, tannin and other plant constituents (Diamond, 1999; Dominy et al., 2004; Johns and Duquette, 1991a, b). Alternatively, geophagy might be carried out to fill the stomach as a famine food or it might be regarded as a custom or cultural activity. Gelfand (1945) speculated that pregnant women eat soil because of the observed soil's fertility, hoping for the future fertility of their children. The concentration of elements that are bio-accessible to the geophagists is important, as it is not all the concentration of elements of the geophagical materials are biologically available. Thus, following the encounter with digestive fluids, chemical elements can be solubilised from soils and will be potentially available for absorption. Bengali communities in the UK were found by Abrahams et al. (2013) to be a significant source of bio-accessible Fe and other potential elements.

Invitro screening methods have been developed and refined for the determination of nutrient bio-accessibility and bioavailability from foods. These are methods that can provide useful information, especially when one considers the vast number of factors that can affect nutrient absorption. Bioavailability is defined as the amount of an ingested nutrient that is absorbed and available for physiological functions, is dependent on digestion, release from the food matrix, absorption by intestinal cells, and transport to body cells. Bio-accessibility on the other hands is the amount of an ingested nutrient that is potentially available for absorption, its dependent only on digestion and release from the food matrix. Geophagia had been perceived as a means of supplementing essential mineral nutrients, particularly in subsistence communities. This view, however, stems largely either from total elemental contents of the soils or from their partial extractions (Abrahams, 1997; Aufreiter et al., 1997; Smith et al., 2000). Aufreiter et al. (1997) further predicted the dietary/nutritional benefits of geophagic soils collected from the USA, China and Zimbabwe, it however shows a strong acid-soluble (total) nutrient are unlikely to be available for absorption into the body, as a large fraction of the total nutrient content will not be soluble in environments like the gastrointestinal tract (Alloway, 1990), and adsorption of ingested soil can remove food-borne bioavailable nutrients from the intestine. Mineral nutrients released in the stomach (pH 2) may be re-adsorbed through cation exchange and adsorption as the soil enters the intestine (pH range 7 to 10), since the retention of nutrient-ions by these processes tends to increase with pH (Cavallaro et al., 1984). This was further supported by a physiologically-based extraction test (pH range 2 to 7) used by Smith et al. (2000), which showed that only a small fraction of the total contents of elements (e.g. Mg, Fe, Zn) present in the geophagic soils were potentially available for absorption in the intestine. The test however, used a much wider soil to solution ratio (1:100) than expected in the gastrointestinal tract hence the solution contained none of the valuable nutrients.

The aim of this study therefore, is to determine the bio-accessible/bioavailable concentrations of some elements in the edible clays (Eko, Ulo) (Fig. 1a-1b) gotten from South-Western and Eastern parts of Nigeria in order to evaluate the nutritional or toxicity level of this clayey materials using a more recent and faster *invitro* bio-accessibility (IVBA) test according to the modified procedure of the Bio-accessibility Research Group of Europe (BARGE) (Wragg et al., 2003).

2. Geological Setting of the Study Areas

Nteje is in Oyi local government area of Anambra state, it belongs to the Nsugbe Formation of the Ameki group within the Anambra basin. It is one of the seven large sedimentary domains of Nigeria. It shares the singular distinction of belonging exclusively to Nigeria. Anambra Basin is a Cretaceous sedimentary domain partly sandwiched between Niger Delta, Benue Trough and Mid Niger Basin. Edo State is geologically characterized by rocks, whose age ranges from Tertiary to Cretaceous. The study areas, thus is partly within both the Anambra and the Niger Delta basins (Fig. 2a-2b).

Fig. 1. Fresh (a) and smoked (b) samples of edible clays known as "Eko" and "Ulo"

The clays within Uzalla-Benin belong to the Benin Formation. The Ohordua-Ubiaja clays belong to the Ogwashi-Asaba Formation, the formation is mostly continental cross-bedded sandstone and grits, carbonaceous mudstone and shale also occur. The clays are mostly mottled, white, bluish or pink in colour and vary from sandy to plastic in nature. Field relationship suggests that the clays within Auchi-Aforwa belong to the Ajali sandstone formation. Ajali sandstone (Maastrichtian) overlies Mamu Formation (Reyment, 1965; Nwajide, 1990) which is mainly unconsolidated coarse-fine grained, poorly cemented; mudstone and siltstone (Kogbe, 1989).

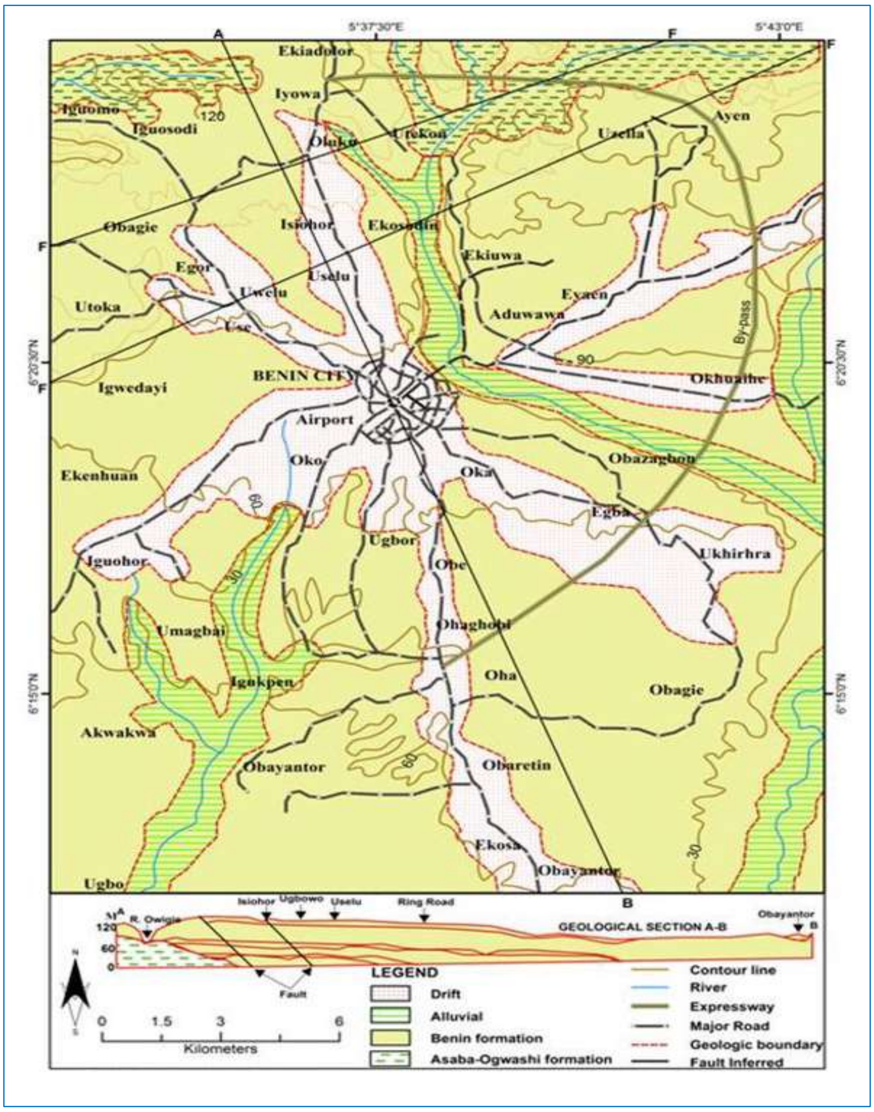

Fig. 2a. Geological map of Benin City and environs (Akujieze, 2004)

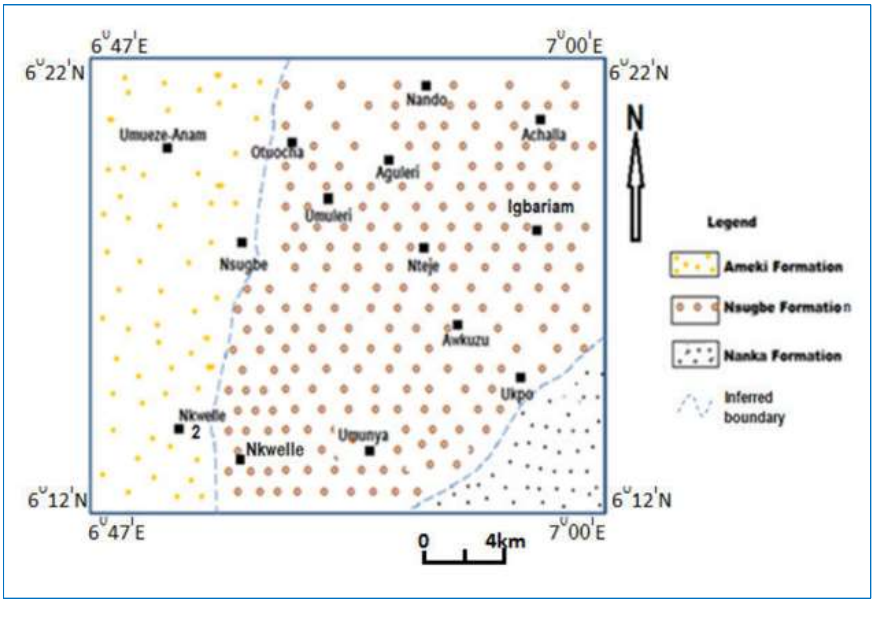

Fig. 2b. Geological map of Anambra Basin showing the study area formations (Modified after Nwajide, 1979)

2. Materials and Methods

2.1. Collection and preparation of samples

With the use of a shovel, and hammer, six samples were collected from the mining sites at (Uzalla, Ohordua and Aforwa) Edo State and (Nteje) Anambra State and also from markets vendors in the communities and towns of both states. Basic laboratory procedure like disaggregation of the soil's samples were carried out with a porcelain mortar and pestle, sieved through a 2 mm nylon mesh. The samples were then packaged in airtight plastic bags labeled and transported to the laboratory for the physico-chemical and mineralogical analyses. Fig. 3 shows a typical mining site at the Njete, Anambra State.

Fig. 3. A typical mining site at Njete, Anambra State

2.2. Physiochemical characterization

The pH of the clayey soil samples was determined both in a 1:2.5 (soil: water) and soil: 1 ml KCl suspension according to the methods advanced by van Reeuwijk (2002) and Palumbo et al. (2000). Electrical conductivity of samples was measured in the saturation paste extract of each sample as described in the Soil Survey Laboratory Manual (1996). The Water Retention Capacity of the soils was determined by percolating an excess amount of water through a known amount of each sample and determining the weight of the percolate after letting the soil stand overnight weight of the percolate after the soil stood overnight was determined (Forster, 1995). The texture of the geophagic soils was determined by the hydrometer method after dispersing with sodium hexametaphosphate (Na_6PO_4) (van Reeuwijk, 2002). Organic matter content of the clayey soil samples was analyzed using the modified Walkley-Black wet combustion method as described by van Reeuwijk (2002). The barium chloride compulsive exchange method of the CEC determination as described by Gilman and Sumpter (1986) employed in the determination of the CEC of all the samples. The clay colour was typically described, using some form of colour reference chart, such as the MSCC (1992).

2.3. Geochemical and mineralogical composition

The bulk elemental compositions of the samples were determined using the PANalytical Axios WDXRF spectrometer in accordance with the method described by the council for Geosciences. X-ray diffraction patterns were obtained with a diffractometer equipped with Ni filtered Cu-kα radiation, with automatic slit and on-line computer control. The samples were scanned from 15° to 72° (2θ). Mineral identification on the diffractograms and a semi quantitative mineralogical composition were processed using EVA software.

2.4. Physiologically based extraction test (PBET)

The samples were subjected to a more recent IVBA, according to the BARGE procedure. This is a PBET that entails mimicking the human gastrointestinal system i.e. (transit times, solution pH, enzyme concentrations and temperature) of the stomach and the small intestine, in a non-fed-state situation. Each soil sample (5.00 g) was mixed with 50 mL of simulated gastric solution (1.25 g pepsin (activity of 800-2500 units/mg), 0.5 g sodium malate, 0.5 g sodium citrate, 420 µL lactic acid and 500 µL of acetic acid to 1L of de-ionized water, adjusted to pH 2.5 with concentrated HCl) in a HDPE (wide-mouthed high-density polyethylene) bottle, placed in a rotary water bath at a constant 37 °C. After 1h, a 5.0 mL aliquot, representing the stomach phase of extraction, was removed and filtered through a Gelman 0.45 µm cellulose filter. Five milliliters of the original gastric solution were then back-flushed through the filter into the HDPE bottle to retain the original solid/solution ratio. The conditions of the bottle were then altered to represent the small intestine by titration to pH 7.0 with saturated $NaHCO_3$ (used to minimize volumetric changes and the solid/solution ratio. 175 mg bile salts and 50mg pancreatin was added.

3. Results and Discussion

3.1. Physiochemical characterization

The pH values of all the samples were generally lower than 7 indicating that they are slightly acidic (Table 1). The pH ranges from 4.67 to 5.50 of the Nteje Fresh and the Ohordua-Ewatto, respectively. Textural analyses results show that the edible clays samples were texturally dominated by clay size particle with grain sizes ranging from 81.05 (Aforwa) - 26.86 (Uzalla Fresh) with some silt and very fine sand particles. Results of the colour analysis show that the samples from the Ohordua-Ewatto are light gray to grayish colour, samples from Auchi-Jattu range from reddish brown to red, while those from Uzalla sample are white to grayish in colour. Those of the Nteje are light grey. The organic matter content in the samples was generally very low ranging from as low as 0.56 to 5.66. The cation exchange capacities of the geophagic clayey soils from the different locations were generally low as compared to those reported by Abrahams and parsons with Nteje Roast has the lowest of 1.78 meq/100 g and Nteje Fresh has the highest of 3.76 meq/100.

3.2. Geochemical and mineralogical composition

Table 2 shows that geophagic clays were dominantly composed of Si content of 46.11 to 56.37 ppm; Al values of

26.78 ppm to 36.38 ppm; Fe_2O_3 values of 22.00 to 50.00 ppm; Mg content of 25.00 ppm to 55.00 ppm; Ca values of 34 .00 to 56.00 ppm; TiO_2 values of 1.30 to 2.30 ppm; K_2O values of 5.12 to 14.08 ppm; Mn values of 20.10 to 50.01 ppm etc. These concentrations suggest that the clays are hydrated siliceous aluminosilicate.

Figs. 4, 5 and 6 show that series of minerals were identified from all of five samples analyzed; the primary minerals are quartz, (SiO_2), Feldspar (orthoclase and Albite) $KAlSi_3O_8$ and $NaAlSi_3O_8$, mica (possibly muscovite), $KAlSiO_3O_8$ several secondary minerals were also available but the most dominant groups were the kaolinite, $Al_2SiO_5(OH)_4$; illite $K,H_3OAl_2Si_3AlO_{10}$; montmorllonitic CaO_2 (Al, Mg) $2Si_4O_{10}(OH)_2.4H_2O$. Another important clay mineral that was identified is halloysite $Al_2Si_2O_5OH)_4.2H_2O$.

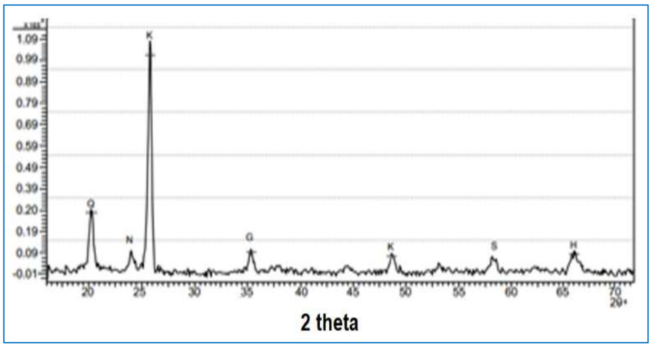

Fig. 4. X-ray diffractogram of Aforwa-Auchi sample (K: kaolinite, Q: quartz, G: gibbsite, N: nacrite, S: sillimanite and H: hematite)

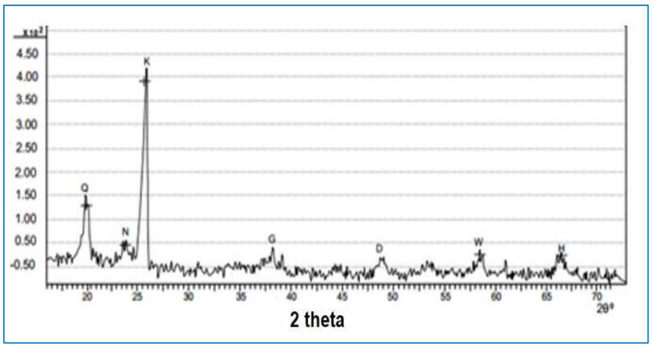

Fig. 5. X-ray diffractogram of Nteje sample (K: kaolinite, D: dickite, N: nacrite, Q: quartz, G: gibbsite, D: dickite, H: hematite and W: wollastonite)

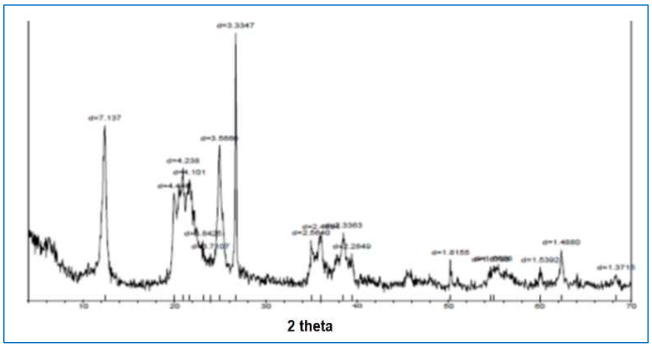

Fig. 6. X-ray diffractogram of Uzalla-Benin sample (K: kaolinite; G: goethite; H: hematite; I: illite, Q: quartz)

3.4. Results of the physiologically-based extraction test

Concentrations (mg/kg1) of elements extracted (leached) from a 5 g edible clay soil sample, from the stomach and small intestinal phases of the PBET system is shown in Table 3, it indicates that large portion of both major and trace elements were soluble in the acidic condition of the stomach (pH 2), provided the nutrients are released from the minerals and exchange sites. The bio-accessible elements associated with the intestinal phase of the PBET system were lower or slightly similar in some cases to those in the stomach phase, this is a combination of binding capacity of the soils and the neutral to alkaline conditions (pH 7-10) in the intestine as these may Pb to their re-adsorption and precipitation, rendering them low or unavailable for absorption in the intestine. Absorption of elements mainly occurs in the intestines (Daugherty and Mrsny, 1999; Plumlee and Ziegler, 2003), hence, to evaluate the importance of the geophagical materials in supplying chemicals elements to humans; the Maximum Absorption Potentials (MAP) values otherwise known as the intake value was therefore calculated by assuming that a 20 g of these edible clays should be consumed.

Table 4 shows the intake MAP of elements following the consumption of 20 g of clayey soil, and a comparison with the Reference Nutrient Intake (RNI) values and Safe Upper Levels (SULs) and Guidance Levels (GLs), for pregnant and lactating age. In order to typically quantify the potential importance of edible clays in supplying significant amounts of elements to the geophagists, the MAP concentrations of elements were compared with the RNI, being the daily dietary values of nutrients above which the amounts will almost certainly be adequate for everybody (actually about 97% of people in a group; Department of Health (1991) and SULs/GLs. The percentage of various bioavailable trace and major is shown in the Figs. 7-17.

4. Discussion

Colour and other physiochemical properties of the edible materials could be indicative of mineralogy or presence of organic matter in the geophagic material, the most common shades employed to infer kaolin mineralogy are; white-cream, red, yellow-brown, grey, and green suggesting the presence of kaolinite, hematite, goethite, and chlorite respectively. Most of the samples were white to grey, yellow, and reddish in color (10YR), suggesting the presence of kaolinite, hematite goethite FeO (OH).

Ngole et al. (2010) asserted that preference for reddish or brownish soils is based on the assumption that the materials are rich in Fe. In general, Fe in heam form (Fe^{2+}) is easily absorbed by the body unlike the nonheme form (Fe^{3+}), with optimal uptake occurring in the duodenum. Given that the color of the geophagic samples from the various locations suggests enrichment in a minor to a major amount of goethite; their ingestion for Fe supplementation may be justified to some extent.

The studied samples were predominantly clayey-soft, apart from the Uzalla, which is imparted by a gritty feel on the materials. Geophagic soils that are gritty contain fine sand particles of quartz and feldspars which may negatively affect the dental enamel of geophagic individuals. Quartz for example, with a higher degree of hardness of 7 on the Mohr scale compared to dental enamel (5 on Mohr scale), can grind, crack and break dental enamel during mastication. (Ekosse and Anyangwe, 2012). Besides, quartz particles in geophagic soils can erode the gastro-intestinal lining of geophagic individuals with the possibility of perforating the sigmoid colon (Barker, 2005).

Table 3. Concentrations (mg/kg1) of elements extracted (leached) from a 5 g edible clay soil sample, from the stomach and small intestinal phases of the PBET system

No	Elements (mg/kg)	Nteje Fresh	Nteje Roast	Uzalla Fresh	Uzalla Roast	Ohoruda	Aforwa
1	Fe	(8.34) 3.17	(10.01) 3.80	(3.75 1.43)	(6.09) 2.31	(2.50) 0.95	(5.17) 1.96
2	Cr	(1.05) 0.40	(1.26) 0.48	(0.47) 0.18	(0.77) 0.29	(0.32) 0.12	(0.65) 0.25
3	Mn	(0.43) 0.16	(0.52) 0.20	(0.19) 0.07	(0.31) 0.12	(0.13) 0.05	(0.27) 0.10
4	Zn	(1.98) 0.75	(2.38) 0.90	(0.89) 0.34	(1.45) 0.55	(0.59) 0.23	(1.23) 0.47
5	Ni	(0.67) 0.25	(0.80) 0.31	(0.30) 0.37	(0.49) 0.44	(0.20) 0.33	(0.42) 0.16
6	Pb	(0.07) 0.03	(0.08) 0.05	(0.03) 0.04	(0.05) 0.05	(0.02) 0.01	(0.04) 0.02
7	V	(0.32) 0.12	(0.38) 0.15	(0.14) 0.05	(0.23) 0.09	(0.10) 0.04	(0.20) 0.08
8	Cu	(0.73) 0.56	(1.22) 0.93	(0.34) 0.26	(0.13) 0.11	(0.07) 0.04	(0.15) 0.12
9	Mg	(0.24) 0.94	(0.40) 0.53	(0.11) 0.43	(0.04) 0.08	(0.02) 0.04	(0.05) 0.20
10	K	(1.06) 1.40	(1.77) 2.34	(0.49) 0.64	(0.19) 0.25	(0.10) 0.13	(0.22) 0.29
11	Ca	(28.54) 37.67	(47.66) 62.91	(13.13) 17.33	(5.14) 6.78	(2.57) 3.39	(5.99) 7.91
12	Na	(94.87)125.23	(158.43)209.13	(43.64) 57.61	(17.08) 22.54	(8.54) 11.27	(19.92) 26.30
13	P	(3.89) 5.13	(6.50) 8.58	(1.79) 2.36	(0.70) 0.92	(0.35) 0.46	(0.82) 1.08

Table 4. The intake MAP of elements following the consumption of 20 g of clayey soil, and a comparison with the RNI values and SULs and GLs, for pregnant and lactating Age

No	Elements mg/kg	Nteje Fresh	Nteje Roast	Uzalla Fresh	Uzalla Roast	Ohodua	Aforwa	RNI	SULs/GLs
1	Fe	12.68	15.20	5.92	9.23	3.80	7.84	14.8	17
2	Cr	1.60	1.92	0.72	1.16	0.48	1.00	30	*10,000 ug*
3	Mn	0.64	0.80	0.28	0.48	0.20	0.40	2.00	11
4	Zn	3.00	3.60	1.36	2.20	0.92	1.88	7.0	42
5	Ni	1.00	1.24	1.48	1.76	1.32	0.64	No RNI	0.26
6	Pb	0.12	0.20	0.16	0.20	0.04	0.08	No RNI	No SUL
7	V	0.48	0.60	0.20	0.36	0.16	0.32	-	1.8
8	Cu	2.24	3.72	1.04	0.44	0.16	0.48	1.2	10
9	Ca	150.68	251.64	69.32	27.12	13.56	31.64	800	1500
10	Mg	3.76	2.12	1.76	0.32	0.16	0.80	300	400
11	K	5.60	9.36	2.56	1.00	0.52	1.16	3500	3700
12	P	20.52	34.32	9.44	3.68	1.84	4.32	250	2400

The pH and dissolved salt content (EC) of geophagic soils influence their taste. Generally, the more acidic soils tend to impart a sour taste. Ibeanu et al. (1997) reported the consumption of clay to control the excessive secretion of saliva during pregnancy among women in Kenya and Nigeria. The use of soil to control the secretion of saliva during pregnancy as reported by some women could be linked to the sour taste of the soil (Diko and Siewe, 2014).

The pH values of all the samples were in the acidic range and thus would impart a sour taste. The sour taste may be beneficial during pregnancy to prevent excessive secretion of saliva and reduce nausea. The geophagic soils all exhibited low EC, indicating that the number of dissolved salts contained in them was low. The taste of these samples is therefore not likely to have been influenced by the salt content.

The clay mineralogy of these edible materials indicates that kaolinite was the dominant clay, with illite, goethite, and hematite as minor components, reflecting the highly weathered conditions in these areas. The samples exhibited OH stretching and bending vibrations similar to that of theoretical kaolinite (Vaculikova et al., 2011). Results from XRD data inferred low to moderate kaolinite crystallinities associated with quartz and Fe oxide contamination. Interactions between these associated minerals and the structure of the predominant clay mineral (say kaolin for example), may reduce its degree of crystallinity and surface area (Oliveira et al., 2013).

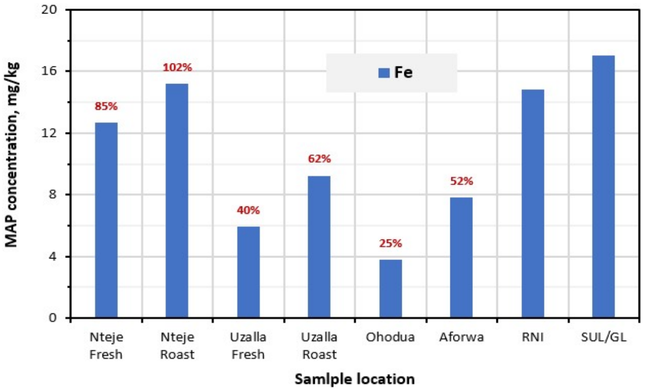

Fig. 7. Percentage of bioavailable Fe against the RNI, SULs and GLs

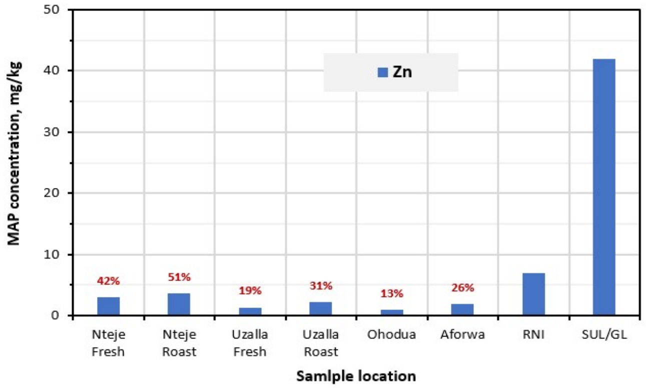

Fig. 8. Percentage of bioavailable Zn against the RNI, SULs and GLs

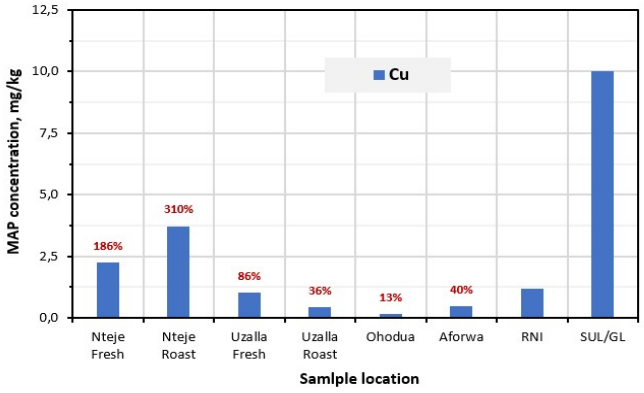

Fig. 9. Percentage of bioavailable Cu against the RNI, SULs and GLs

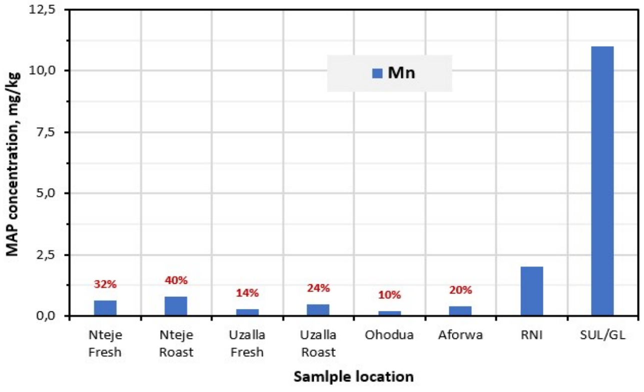

Fig. 10. Percentage of bioavailable Mn against the RNI, SULs and GLs

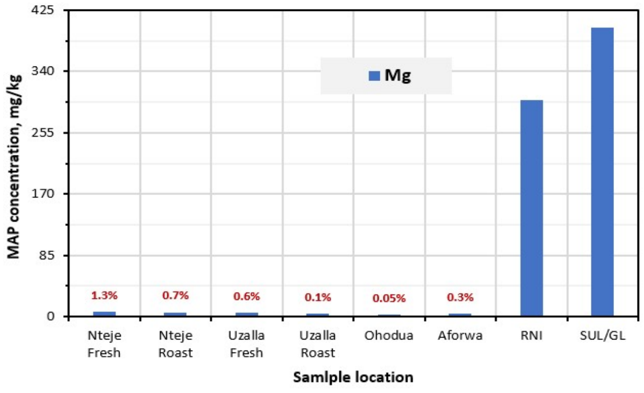

Fig. 11. Percentage of bioavailable Mg against the RNI, SULs and GLs

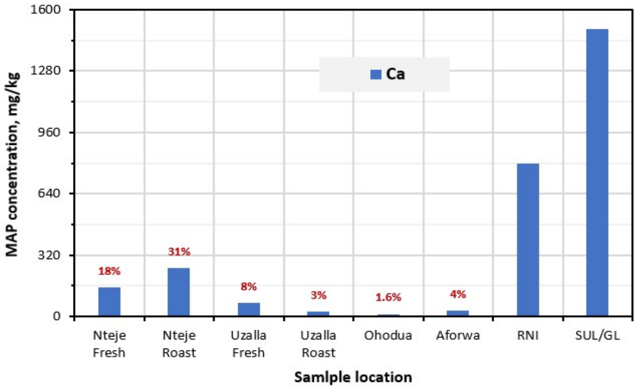

Fig. 12. Percentage of bioavailable Ca against the RNI, SULs and GLs

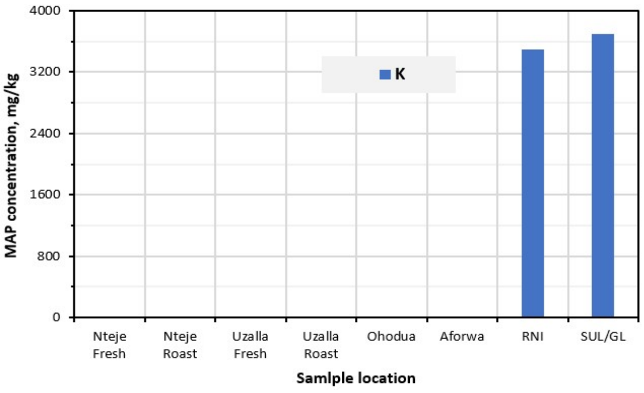

Fig. 13. Percentage of bioavailable K against the RNI, SULs and GLs

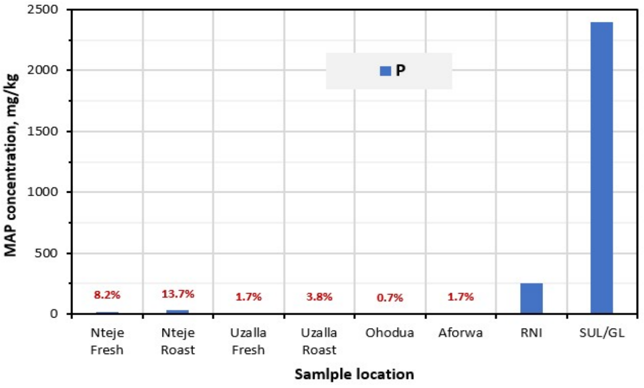

Fig. 14. Percentage of bioavailable P against the RNI, SULs and GLs

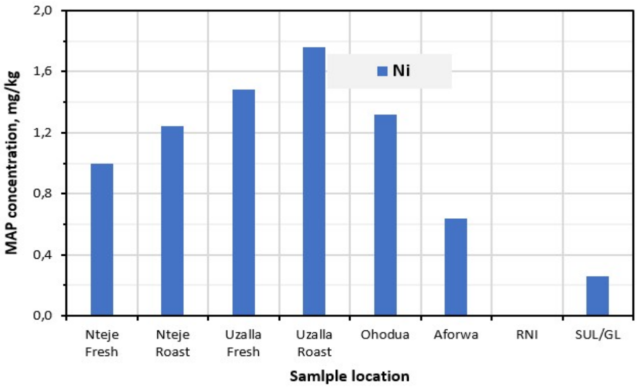

Fig. 15. Percentage of bioavailable Ni against the RNI, SULs and GLs

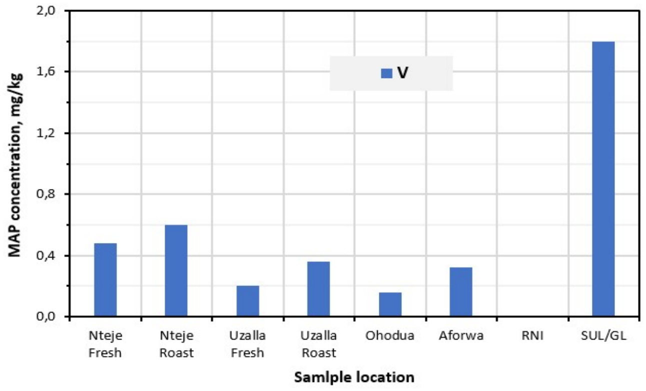

Fig. 16. Percentage of bioavailable V against the RNI, SULs and GLs

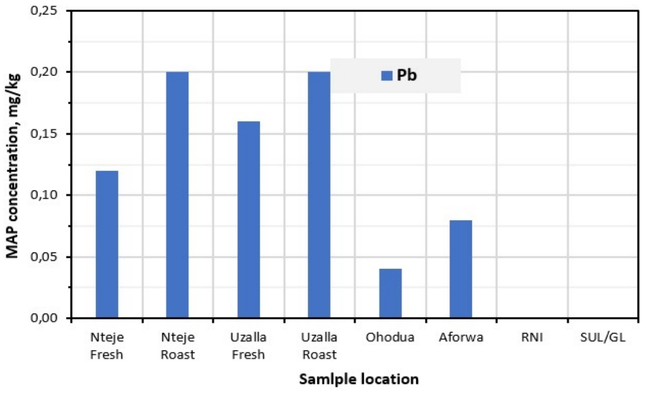

Fig. 17. Percentage of bioavailable Pb against the RNI, SULs and GLs

A decrease in the surface area implies restriction in structural channels available for reactions such as adsorption and isomorphic substitution. As such, the ability of geophagic soils with poorly crystallized clay mineral constituents to be used for nutrient supplementation, detoxification, or as an antidiarrheal remedy will be significantly compromised. Reactions such as isomorphic substitution occurring in the octahedral sheet of kaolinite are usually 67% filled, providing vacant sites for other ionic reactions. Isomorphic substitution is a process whereby an atom is replaced by another (for example, Al^{3+} for Si^{4+} in the tetrahedral and Mg^{2+}, Fe^{2+} and Fe^{3+} for Al^{3+}, in octahedral sheet) within the clay mineral structure, leading to a permanent negative charge (Ekosse et al., 2010). This reaction is particularly important in geophagic soils given that, the net negative charge readily accommodates cations that may be subsequently available for nutrient supplementation or assist with detoxification by forming complexes with toxins. Concerning the studied samples, Fe from goethite and hematite could be supplied from the geophagic soils and absorbed as possible nutritional supplements (Abrahams et al., 2013).

The results of total elemental analysis (Table 2) show that, if all the elements are available for absorption in the gastrointestinal tract, the soils could be significant sources of nutrient supplementation. Whether eating or not eating these relatively nutrient-rich soils becomes a source of nutrient supplementation will however be dependent largely on two factors: The solubility of soil minerals in the gastrointestinal tract, and the nutrient binding capacity of the soils. Large proportions of both transition metals (e.g., Cu, Zn, Mn) and alkaline earth and alkali metals (e.g., Ca, Mg, Na) in the soils (Table 3) became soluble in conditions (pH 2) like the stomach (Alloway, 1990), as some of the nutrients were released from soluble minerals and exchange sites. A combination of the binding capacity of the soils, and the neutral to alkaline conditions (pH 7-10) in the intestine may, however, Pb to their re-adsorption and precipitation, thereby rendering them slightly available or unavailable for absorption in the GI tract.

This research basically described the potential of Edible Clays in supplying significant amounts of Fe, as well as Ca, Cu, Mn, and other nutritional and non-nutritional elements to the geophagists Figs. 7-17. In coming to this conclusion, it is appreciated that the use of the in vitro PBET extraction system only estimates bio-accessibility, and it is not known if this fraction is absorbed by the geophagists. Though, Fe and other elements were relatively low in bio-accessibility as indicated in Table 3. But a significantly small amount of some elements could still be supplied to the geophagists following ingestion.

Table 4 and Figs. 7-17 therefore, show the intake of elements supplied in a bio-accessible form via the consumption of 20 g (i.e., the median mass of all the edible soil tablets). The data are compared against the RNI values, the latter being the daily dietary values of nutrients above which the amounts will almost certainly be adequate for everybody (actually about 97% of people in a group (Department of Health, 1991). The comparison shown in Table 4 demonstrates the potential importance of edible clay in supplying significant amounts ranging from 0.06% to greater than 300% of the RNI of Ca, Cu, Fe, and Mn to the geophagists (note: the Department of Health (1991), set no RNI for Mn, but a safe intake is believed to be greater than 1.4 mg d_1 for adults). It is important to note here also, that when the amount of element absorbed is greater than immediate requirements; the excess is stored in the body (e.g., Fe in the liver), excreted in the urine (e.g., Ca) or excreted via gastrointestinal secretions or intestinal mucosal cells (e.g., Zn, Cu).

The Expert Group on Vitamins and Minerals (2003) has recommended SULs or GLs for nutrients with limited data, of mineral nutrients. Such levels, allow the determination of doses of mineral nutrients that potentially susceptible individuals could take daily on a life-long basis, without medical supervision in reasonable safety. The SULs/GLs for the mineral nutrients considered in this study are presented in Table 4. Should the geophagists be consuming some 20g of soil (equivalent to a soil tablet of average mass) per day, then the GLs for Fe, Ni and other elements can be exceeded provided all the bio-accessible fractions are absorbed in the body.

5. Conclusion

This work therefore, shows that the colours of the clays are whitish, brownish to grey; the geophagic materials are dominantly clayey size particle (56.42%). The pH of the materials is basically acidic with an average of 5.17. A moderate to low CEC was observed from all of the samples (2.84 meq/100g). A wide range of elements were identified, these includes Si, Al, Ti, Fe, K, Mg Na, Mn, V, Ni, Zn, Cr, and Ca. It also indicates that the materials are majorly kaolinite, quartz, goethite, hematite, and traces of other minerals such as mica; microcline; smectite; illite and gibbsite. It further indicates the potential of the edible clays in supplying significant amounts of Fe, Cu, Mn, Zn, Ca, Mg and P to the geophagists to their individual RNI even a low dose of 5g. But at higher dose of about 20 g, a reasonable percent of some trace and major mineral nutrients can supplement to the required daily nutrient of the geophagists. Most of the elements were however within and/or below the SULs/GLs for the age and body weight (60 kg) understudy as recommended by the Expert Group on Vitamins and Minerals (2003), could hence they could be seen as a good source of mineral nutrients but it however shows that Ni and some few other trace elements exceeded the SULs/GLs that is needed.

Remarkably, baking and/or roasting the clayey materials were observed to have increased the concentrations of Pb, Ni, V, Fe, Zn and all the other elements of the Nteje and Uzalla samples. On a whole, the Nteje Roast is the highest supplementation of all the elements, except for Ni, where Uzalla roast supplies more while Ohordua is the least supplier of all the elements to the consumers except for Ni. The Aforwa therefore, seems to be moderate supplier of elements. More research is needed to determine the prevalence of geophagy within the ethnic groups of Nigeria, and provide an understanding of the actual use of ingested soils.

Furthermore, bearing in mind the continuing importance of this practice in a number of societies throughout the world, further geochemical and nutritional investigations into the supply of beneficial and potentially harmful elements to the geophagists would seem to be justified. It is appreciated that the use of the PBET extraction system only estimates bio-accessibility hence other scientists like the nutritionist, biochemist etc, must come to together to carry out further study.

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