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Potentially Harmful Element toxicity in Geophagic clays consumed in parts of southeastern Nigeria

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ABSTRACT

An assessment of geophagic clays consumed by adults and children in Calabar and Okon-Eket areas of southeastern Nigeria was done in order to evaluate possible toxicity of Potentially Harmful Elements (PHEs)- Cd, As, Pb, Cu and Zn (CALCZ). Thirteen clay samples obtained from open markets and clay mines were air-dried, pulverized and analysed for their elemental constituents using Inductively Coupled Plasma Mass Spectrometry (ICPMS). Ecological and health risk assessments of the clays were conducted using Index of Geoaccumulation (I_{geo}), Contamination Factor (CF) and Degree (C_{Deg}), Pollution Index (PI), Ecological Risk Factor (Er) and Index (RI), Hazard Index (HI) and Cancer Risk Index (CRI). The clays had PHE concentrations (ppm) in the order: Zn (13.0–148.0) > Pb (16.7–55.6) > Cu (5.7–23.0) > As (BDL-15.0) > Cd (BDL-0.2). I_{geo} values for Cd, As, Cu and Zn in the clays were <0, while Pb had a value of (-1) to 1. The clays from Calabar and Okon-Eket had Pb CF values of 1.8 and 1.7, and PI values of 1.4 and 1.3, respectively. Results of I_{geo}, CF and PI calculations revealed moderate Pb contamination in the clays. Low HQ and HI of the PHEs indicates that they pose no immediate risk of non-carcinogenic nor carcinogenic effects to the geophagic individuals. However, the moderate Pb contamination in the clays is a source of health concern, especially for geophagic children.

Introduction

Geophagy, an age-long practice describing the consumption of soil materials especially of clayey composition, is commonplace particularly among peri-urban, and more recently, urban dwellers. It is a type of *pica*; which is the consumption of non-food substances [2]. Geophagy is practiced in India [3], Asia [4], Europe and America [5,6], and in Africa- South Africa [7,8], Ghana [9], Tanzania [10] and Nigeria [11–13]. It is one of the ways through which metals enter the human system (Fig. 1). Through weathering, trace elements in rocks are released and re-concentrated in soils. The process of leaching affecting the rocks and even soil, leads to the transfer of trace elements into water sources. During mining and rock blasting, these elements become air-borne (especially in dusts) and can be deposited into water, or inhaled directly by humans. From water and soil, there is an uptake of trace elements by plants, which are consumed by animals. Humans consume both plants and animals, and the long-link of trace elements from rocks to plants/animals serves as an indirect means of trace element entry into the human system. The consumption of soil (especially of clayey composition) however, provides a direct link for entry of trace elements into the human system.

Clays are sources of major elements (e.g. Fe, Ca, Mg, Na, etc) which are essential for the regular functioning of the human body. Clays also have adsorbent, emollient and soothing properties; making them suitable as cheap traditional antacids and cosmetic products [12,14]. Their beneficial essential element composition notwithstanding, geophagic clays also contain trace elements such as Cd, Pb, Zn, Hg, As, Co, Cu and Ni; which may be present in concentrations toxic to the human system. Cd, As, Pb and Hg are known carcinogens; responsible for causing damage to several organs in the body. Pb causes increased blood pressure; damage to cardiovascular system, brain and kidney; and affects almost all human system functions [15,16]. Toxicity of Cd causes renal, skeletal, respiratory and reproductive damage [17], it also disturbs calcium metabolism [18]. Hg toxicity results in nervous, digestive, immunity and gastrointestinal system failures [19,20]; while As toxicity induces skin, lung and bladder cancer [21,22]. Excessive quantities of Zn, Co, Cu and Ni in the human system can result in stroke, cardiovascular diseases, dementia and nasal cancer, respectively [23–26]. Assessment of

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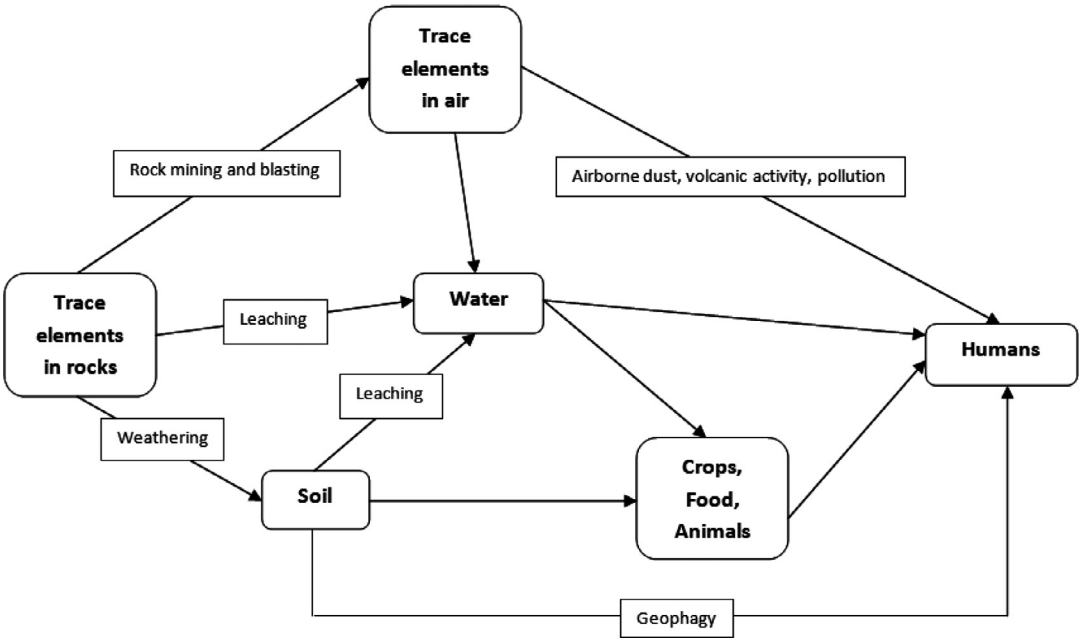


Fig. 1. Element cycling within the environment (modified after [1]).

the risk posed by these elements to the environment and human health are done using ecological and health risk assessment methods. In addition to the trace elemental composition, the geophagic clays could also contain anomalous concentrations of essential elements and harmful microbes [6].

In Nigeria, geophagy is practiced by men, women and children. Traditional, cosmetic and therapeutic justifications have been adduced for the geophagic practice. Pregnant women believe that eating the clays gives the baby a clean, clear skin when it is born; they also believe that it makes their skins radiant and glow. Other women also make the clays into slurry and apply to their skin and that of their children; as cosmetic and skin-smoothening remedies (Supplementary Material 1).

As geophagy is one of the means through which metals are introduced directly into the human system, it is therefore necessary to evaluate the elemental composition of the clays consumed and the possible risks they pose to human health. An ecological and health risk assessment of the geophagic clays consumed in Calabar and Okon-Eket areas of southeastern Nigeria was conducted in this study, by evaluating potential toxicities of Cd, As, Pb, Cu and Zn (CALCZ).

Materials and methods

Site description

The raw clay samples obtained from Calabar (04°57′28.3″, 008°19′22.1″) and Okon-Eket (04°38′28.2″, 007°55′35.3″) were from the Calabar Flank and Niger Delta Complex, respectively (Fig. 2). The sampling sites fall within the sedimentary terrain of Nigeria, which are composed of Tertiary to Recent sediments. The Calabar Flank is part of the Nigerian continental margin, composed of up to 4 km of marine sediments which are Albian to Maastrichtian in age [27]. The formations in the Calabar Flank include Benin sandstone, Nkporo shale, New Netim marl, Ekenkpon shale, Mfamosing limestone and Awi sandstone; all overlying the Basement Complex [28].

On the other hand, the Niger Delta Complex comprises the Benin sands, Agbada formation (alternating sands, silts and shales) and Akata formation (composed of shale, silts and streaks of sand); deposited in continental to marine environments. The Complex is of Paleocene to Holocene age, with maximum combined thickness of ca. 11 km [29]. The formations in both areas are composed predominantly of shale, clay and sand/sandstone, with occasional intercalations of limestone [30–34].

Sample collection, preparation and analyses

Thirteen geophagic clays were obtained from markets (Fig. 3c) and clay mines from Calabar and Okon-Eket areas (Fig. 3b and d). At the clay mines in Calabar, clay layers of thicknesses ranging from 2 to 6 cm within the sandstone formation were sampled, as this is the source of the clays consumed. Samples were obtained by standing on benches (located 10–15 meteres below ground surface) in the walls of the open pit mine (Fig. 3b; after [12]). In Okon-Eket however, the clays were mined from banks of the creeks, at 0.5 to 1 m below water surface level (Fig. 3d). Between 300 and 500 g of clay were collected at each clay mine. The samples collected were denoted using Sample Location, Clay Status, and Clay Source as: CCW- Calabar, Consumed, Watt Market; CCI- Calabar, Consumed, Ikot-Omin mine; CEI- Consumed, Eket, Ikot-Ukpong/Ikot-Obioro Creek; CEU- Consumed, Eket, Udu-Anka Market.

The samples were air-dried, pulverized and sieved using a 75 μm mesh to remove coarse particles before being packed in resealable sachets prior to analysis. They were analysed for physico-chemical properties (pH, EC, TDS) and composition of CALCZ using a Hach Eco 40 Multi pH meter and Inductively Coupled Plasma Mass Spectrometry (ICPMS), respectively.

Analyses for physico-chemical properties were done at the Geochemistry Laboratory of University of Ibadan, Nigeria. About 20 g of each sample was soaked in 120 ml distilled water for 24 h before the physico-chemical parameters were obtained using the multi-meter. Whole rock analysis was conducted at Bureau Veritas Minerals (BVM) Pty. Ltd., Canada. 0.5 g of sample was digested with modified aqua regia (i.e. 1:1:1 HNO_3:HCl:H_2O) and introduced into an argon plasma as aerosol droplets. The plasma dried the aerosol, dissociated the molecules, and removed an electron from the components, thereby forming singly-charged ions, which were directed into the mass spectrometer. Upon exiting the mass spectrometer, the ions struck the first dynode of the electron multiplier, which serves as a detector. The impact of the ions released a cascade of electrons, which were amplified until they became a measurable pulse. The intensities of the measured pulses were compared to those of standards; making up the calibration curve, which was used to determine the concentration of CALCZ. To ensure quality

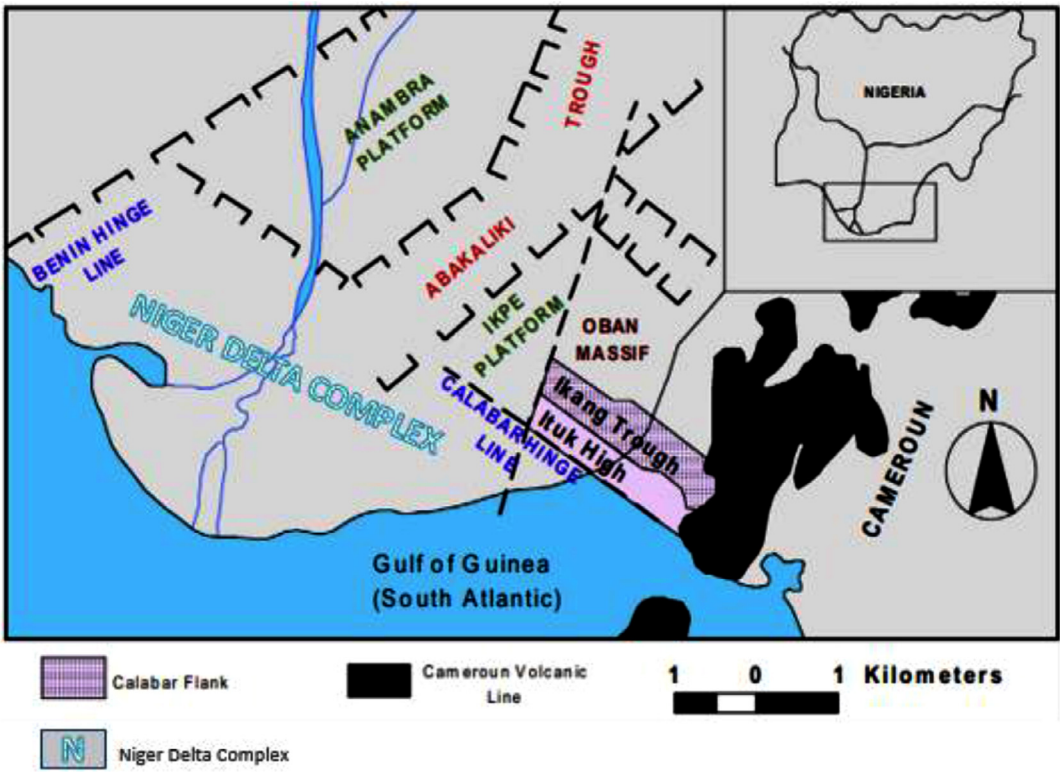


Fig. 2. The Calabar Flank and the Niger Delta Complex of southern Nigeria (modified after [35]).

control, the determination of the equipment precision was done, sample replicates were analysed and standards were used for each element, according to BVM laboratory protocol.

The geochemical results obtained were evaluated to determine the contamination status of the clays, while the estimated daily intakes of CALCZ and their carcinogenic and non-carcinogenic effects were computed.

Ecological assessment of PHEs in the geophagic clays

Index of geoaccumulation (I_{geo})

An assessment of the quality of the clays was done using the index of geoaccumulation proposed by Muller [36] (Table 1) according to the equation:

$$\text{Igeo} = \log_2\left(\frac{\text{Cn}}{1.5 * \text{Bn}}\right) \quad (1)$$

Where C_n is the measured concentration of the metal of interest, B_n is the background concentration of the metal, and 1.5 is a constant introduced to minimize the effect of possible variations in the background values (B_n) attributable to lithogenic variations in clays.

The Average Shale Content (ASC) of Cd, As, Pb, Cu and Zn (0.3 ppm, 13 ppm, 20 ppm, 45 ppm and 95 ppm, respectively) were used as background concentrations in calculating the contamination indices for the clays. The I_{geo} values were used as a basis in evaluating the quality of the Geophagic clays and determining their degree of PHE contamination.

Table 1
Muller's I_{geo} classification.

I_{geo} Values	Class	Quality
$I_{geo} < 0$	0	Uncontaminated
$0 < I_{geo} < 1$	1	Uncontaminated to moderately contaminated
$1 < I_{geo} < 2$	2	Moderately contaminated
$2 < I_{geo} < 3$	3	Moderately to heavily contaminated
$3 < I_{geo} < 4$	4	Heavily contaminated
$4 < I_{geo} < 5$	5	Heavily contaminated to extremely contaminated
$I_{geo} > 5$	6	Extremely contaminated

Contamination factor (CF) and contamination degree (C_{Deg})

To describe the contamination of the clays by CALCZ, the Contamination Factor (CF) and Contamination Degree (C_{Deg}) were calculated using the relations proposed by [37]:

$$\text{CF} = \frac{C^{i}_{(0-1)}}{B_n} \quad (2)$$

$$\text{C}_{\text{Deg}} = \sum_{i=1}^{m} \text{CF} \quad (3)$$

Where CF is the contamination factor,

$C^{i}_{(0-1)}$ is the mean content of metal of interest from at least 5 sampling sites,
B_n is the background concentration of the metal,
C_{Deg} is the degree of contamination in the clays,
$\sum_{i=1}^{m}$ CF is the sum of calculated contamination factors, and
m is the number of PHEs (i.e. 5) (Table 2).

Pollution index (PI)

The Pollution Index was further used to determine the level of pollution of the areas studied by the PHEs using the relation proposed by [38]:

$$PI = \sqrt{\frac{\left(\text{CF}_{Average}\right)^2 + \left(\text{CF}_{Max.}\right)^2}{2}} \quad (4)$$

Table 2
Levels of Contamination Factor and Contamination Degree [37].

Level	CF value	Contamination level	C_{Deg} value	Contamination Degree
1	CF < 1	Low	$C_{Deg} < m$	Low
2	$1 \le CF < 3$	Moderate	$m \le C_{Deg} < 2m$	Moderate
3	$3 \le CF < 6$	Considerable	$2\,m \le C_{Deg} < 4m$	Considerable
4	$CF \ge 6$	Very high	$C_{Deg} > 4m$	Very High

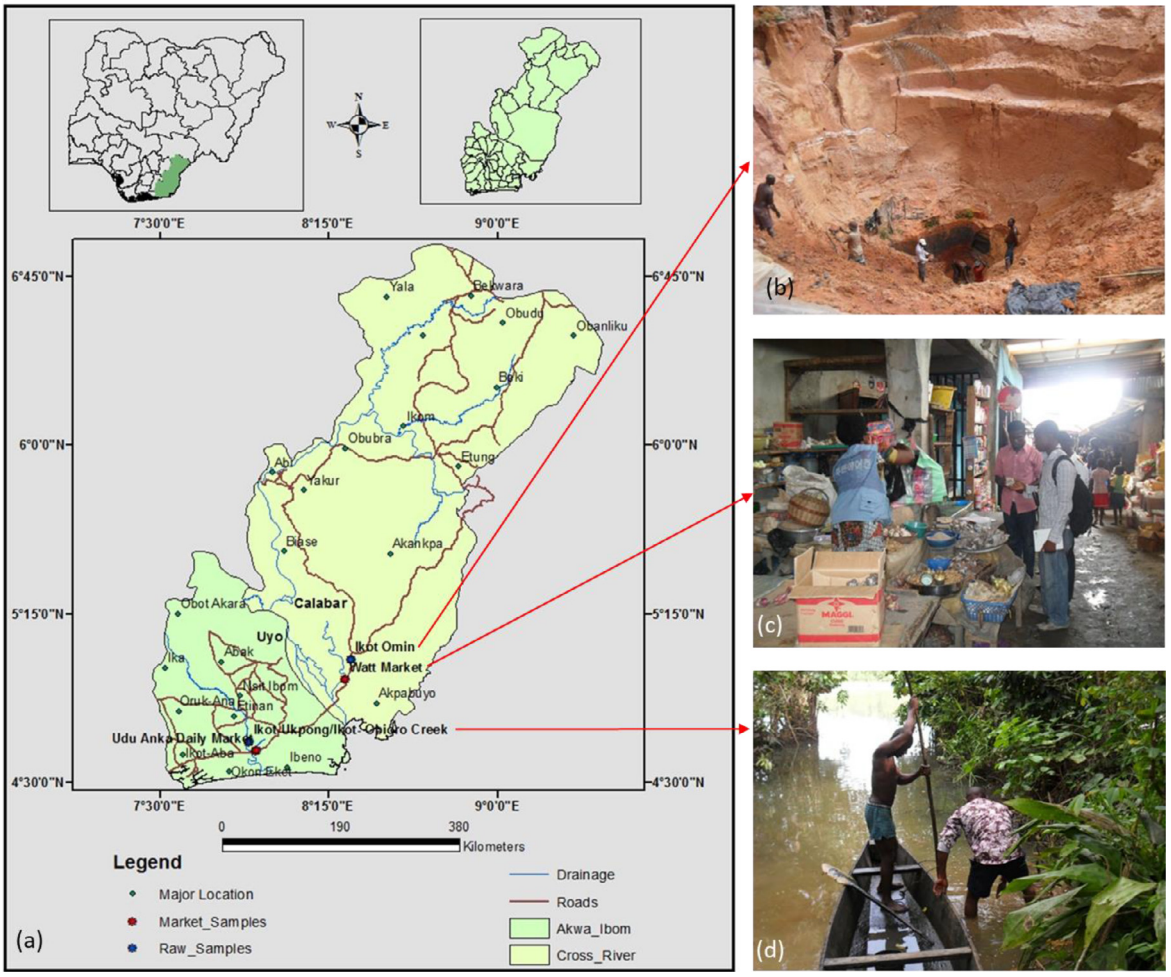


Fig. 3. (a) Sample location map showing clay sample sources: (b) Ikot-Omin Mine after [12], (c) Watt Market and (d) Ikot-Ukpong/Ikot-Obioro creek.

Where

PI is Pollution Index
$CF_{Average}$ is mean value of contamination factors
$CF_{Max.}$ is maximum contamination factor value

And

PI < 0.7: unpolluted
0.7 < PI < 1: slightly polluted
1 < PI < 2: moderately polluted
2 < PI < 3: heavily polluted
PI > 3: severely polluted

Ecological risk factor

The potential ecological risk posed by the PHEs was calculated using Ecological Risk Factor (Er) and Ecological Risk Index (RI) [Eqs. (5) and (6); Table 3] proposed by Hakanson [37]:

$$Er = Tr.CF \quad (5)$$

$$RI = \sum_{i=1}^{5} Er \quad (6)$$

Where

Er is the ecological risk factor,
Tr is the toxicity response of individual metals: Cd (30), As (10), Pb (5), Cu (5), Zn (1),

Table 3
Levels of Ecological Risk Factor and Index [37].

Level	Er value	Potential risk by metal	RI value	Potential risk of environment
1	Er<40	Low	RI<150	Low
2	40≤Er<80	Moderate	150≤RI<300	Moderate
3	80≤Er<160	Considerable	300≤RI<600	Considerable
4	160≤Er<320	High	–	–
5	Er≥320	Very high	RI≥600	Very High

RI is the risk index, and
$\sum_{i=1}^{5}$ Er is the sum of calculated risk factors.

Studies by Odukoya [39] and Ngole-Jeme and Fantke [40] have shown that the ecological risk indices proposed by [37] are also useful in evaluating risks associated with pollutants in soil in spite of their famous use for evaluating risk indices in aquatic environments.

Health risk assessment of PHEs in the geophagic clays

A number of methods have been used by researchers for assessment of health risks associated with the consumption of clay (e.g. [9,13,41] and [42]. Estimated Daily Intake (EDI) aids in the identification of the quantity of metals consumed daily. The risk assessment in this study was based on exposure pathways of ingestion ($DI_{ing.}$) and dermal contact ($DI_{derm.}$), as determined by [43] Model (Tables 4 and 5). The Hazard Quotient (HQ) and Cancer Risk Index (CRI) were used

Table 4
Summary of health risk parameters and values used in Estimated Daily Intake calculations.

Parameters	Unit	Values used		References
		Children	Adult	
Element concentration (C)	mg/kg			
Body Weight (BW)	Kg	15	70	[40,44]
Exposure Frequency (EF)	days/year	350	350	[40,44]
Exposure Duration (ED)	Years	6	30	[40,44]
Ingestion Rate (IR)	kg/day	0.0002	0.0001	[45]
Skin Surface Area (SA)	cm^2	2800	5700	[45]
Adherence Factor (AF)	mg cm^{-2} d^{-1}	0.2	0.07	[45]
Dermal Absorption Factor (ABS)	Unitless	0.001 for all metals		[45]
Conversion Factor (CF_c)	kg/mg	10^{-6}	10^{-6}	[45]
Average time for non-carcinogenic effect (AT)	Days	2190	10,950	[45]
Average time for carcinogenic effect (AT)	Days	25,550	25,550	[45]

Table 5
Toxicological parameters for the PHEs used in health risk assessment [43].

PHE	Reference doses (mg/kg/day)		Slope Factors (mg/kg/day)	
	Ingestion	Dermal	Ingestion	Dermal
Cd	0.001	0.00001	–	–
As	0.0003	0.0009	1.5	3.66
Pb	0.0035	0.00052	0.0085	–
Cu	0.04	0.012	–	–
Zn	0.3	0.06	–	–

to evaluate the non-carcinogenic and carcinogenic risks associated with the PHEs through the aforementioned exposure pathways.

Estimated daily intake (EDI)

The daily intake of metals from the clays depends on both the concentration of metal in them and the amount consumed. In addition, the body weight of geophagic individuals can influence the level of tolerance of elements, especially PHEs [46]. Similarly, the area of the skin exposed determines the amount of elements that can be taken in through dermal contact. The EDI for the respective exposure pathways were computed as follows:

Ingestion of PHEs [47]:

$$EDI_{(ing.)} = C * IR * ED * EF/BW * AT \quad (7)$$

Where $EDI_{(ing.)}$ is the estimated daily intake of PHEs ingested from Geophagic clay in mg/kg/day,

C is the element concentration in mg/kg,
IR represents the ingestion rate in kg/day,
EF is the exposure frequency in days/year,
ED is the exposure duration measured in years,
BW is the body weight of the geophagic individual in kg,
AT is the average period of time in days, and

Dermal exposure to PHEs [42]:

$$EDI_{(derm.)} = C * SA * AF * ABS * EF * ED * CF/BW * AT \quad (8)$$

Where $EDI_{(derm.)}$ is the estimated dose through dermal exposure in mg/kg/day,

C is the element concentration in the sample in mg/kg,
SA is the exposed skin area measured in cm^2,
AF is the adherence factor in mg/cm^2,
ABS represents the fraction of the applied dose adsorbed across the skin,
CF is the conversion factor in kg/mg, and
EF, ED, BW and AT are as defined in Eq. (7).

Non-carcinogenic effect

Utilized to characterize non-carcinogenic effects, Hazard Quotient presents the likelihood of an individual suffering an adverse effect due to consumption of a substance. It is determined using the equation:

$$HQ = EDI/Rfd \quad (9)$$

Where HQ is the hazard quotient, and Rfd is the toxicity baseline value referred to as the chronic reference dose (mg kg^{-1} day^{-1}).

HQ values <1 indicates unlikely adverse health effects and the exposed population is assumed to be safe while HQ values >1 presents a likely adverse health effect. For *n* number of PHEs, the non-carcinogenic effects to the residents due to the summation of all the HQs of individual PHEs is regarded as the Hazard Index (HI) [43]. *HI* is calculated using the equation:

$$HI = \sum_{x=1}^{n} HQx \quad (10)$$

Where HQ_x are the HQs of the PHEs (see Eq. (9)).

If the HI is < 1, the exposed residents are less likely to experience adverse health effects as a result of consumption of all the PHEs through the available pathways. If otherwise, then there is likelihood of potential non-carcinogenic effects [43].

Carcinogenic effect

For carcinogens, the risks are defined by the incremental likelihood of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen (i.e. a contaminant or a combination of contaminants). Lifetime cancer risk is determined by the equation:

$$CRI = EDI * SF \quad (11)$$

Where CRI is Cancer Risk Index, and SF is Slope Factor.

The slope factor converts the estimated daily intake of the heavy metal averaged over a lifetime of exposure directly to incremental risk of an individual developing cancer [43].

Results

Physico-chemical properties and elemental composition

The geophagic clays all had near-neutral pH; ranging from 6.5 - 7.0, and Electrical Conductivity (EC) of 0.30 - 377.71 µS/cm. The Total Dissolved Solids (TDS) ranged from 0.08 - 242.65 mg/l [12]. The concentrations of CALCZ in the geophagic clays from the study areas and the variability in the data are presented in Table 6. There was a 5–8% uncertainty in the measurements of the concentration of the elements and the absolute error of the measurements are also presented in Table 6. While 38.5% of the samples had Cd in concentrations below the detection limit, appreciable concentrations of As, Pb, Cu and Zn were detected in the analysed clays.

Table 6
Elemental concentration, uncertainty measurements and data variability for the Geophagic Clays analysed.

Sample ID	Elemental concentration in mg/kg									
	Cd	Abs. Error	As	Abs. Error	Pb	Abs. Error	Cu	Abs. Error	Zn	Abs. Error
CCW1	BDL	0	BDL	0	27.3	1.911	19.3	1.351	13.0	0.65
CCW2	BDL	0	3	0.24	43.6	3.052	17.5	1.225	36.0	1.80
CCW3	0.1	0.008	2	0.16	16.7	1.169	10.9	0.763	148.0	7.40
CCW4	BDL	0	6	0.48	29.8	2.086	7.6	0.532	14.0	0.70
CCW5	0.2	0.016	6	0.48	45.9	3.213	17.3	1.211	36.0	1.80
CCI1	BDL	0	3	0.24	55.6	3.892	12.2	0.854	29.0	1.45
Mean	0.05		3.33		36.48		14.13		46.00	
Range	BDL-0.2		BDL-6.0		16.7–55.6		7.6–19.3		13.0–148.0	
St. Dev.	0.08		2.34		14.32		4.58		51.00	
CEI1	0.2	0.016	15.0	1.2	40.6	2.842	23.0	1.610	50.0	2.50
CEI2	0.1	0.008	6.0	0.48	21.7	1.519	10.2	0.714	32.0	1.60
CEU1	0.1	0.008	4.0	0.32	45.7	3.199	15.3	1.071	36.0	1.80
CEU2	0.2	0.016	5.0	0.40	31.0	2.17	5.7	0.399	15.0	0.75
CEU3	BDL	0	6.0	0.48	30.7	2.149	9.1	0.637	16.0	0.80
CEU4	0.1	0.008	2.0	0.16	47.5	3.325	10.7	0.749	26.0	1.30
CEU5	BDL	0	4.0	0.32	19.4	1.358	11.2	0.784	114.0	5.70
Mean	0.10		6.00		33.80		12.17		41.29	
Range	BDL-0.2		2.0–15.0		19.4–47.5		5.7–23.0		15.0–114.0	
St. Dev.	0.08		4.20		11.16		5.56		34.26	
ASC [48]	0.3		13		20		45		95	
Target Values [49]	0.8		29.0		85.0		36.0		140.0	

Key: BDL - Below Detection Limit, St. Dev. - Standard Deviation, Abs. Error - Absolute Error.

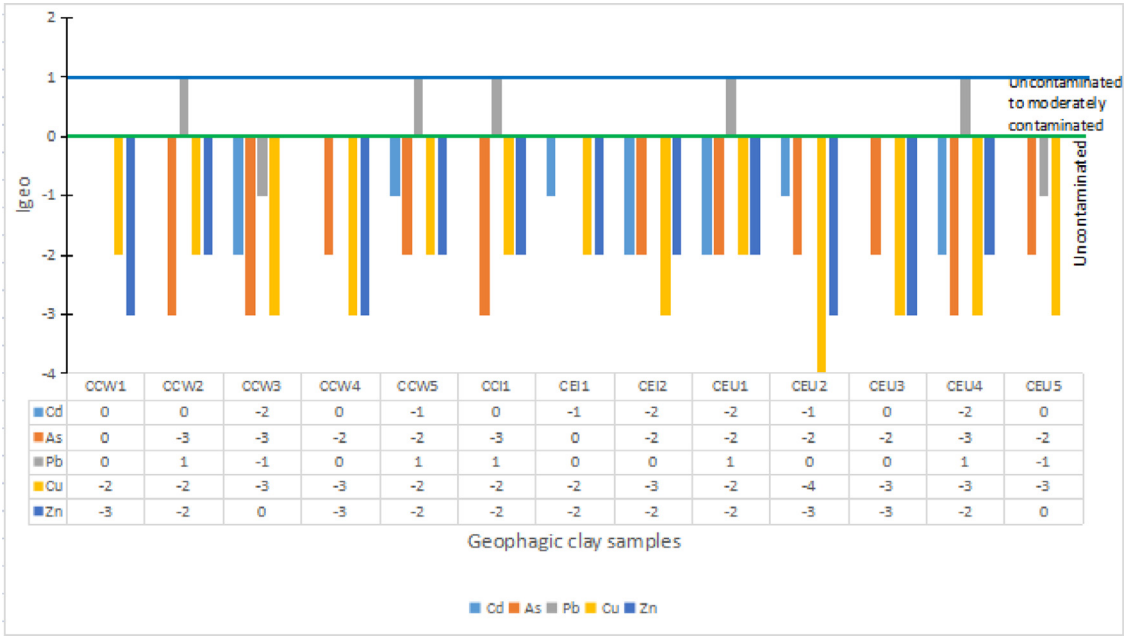


Fig. 4. Index of geoaccumulation of the geophagic clays from Calabar and Okon-Eket revealing moderate Pb contamination.

Index of geoaccumulation (I_{geo})

The calculated I_{geo} values for Calabar geophagic clays were Cd, (−2) – (−1); As, (−3) – (−2); Pb, (−1) – (1); Cu, (−3) – (−2) and Zn, (−3) – (0). The I_{geo} values for Cd in the clays from Okon-Eket were (−2) – (−1); while As, Pb, Cu and Zn had I_{geo} values of (−3) – (0), (−1) – (1), (−4) – (−2), and (−3) – (0), respectively. Fig. 4 presents a summary of the calculated indices of geoaccummulation for the geophagic clays studied.

Contamination factor (CF) and contamination degree (C_{Deg})

The CF values for CALCZ in clays from Calabar and Okon-Eket are presented in Fig. 5. The degrees of contamination of the PHEs in Calabar and Okon-Eket clays were 3.1 and 3.2, respectively.

Pollution index (PI), ecological risk factor (Er) and ecological risk index (RI)

The clays from Calabar and Okon-Eket areas had PI values of 1.4 and 1.3, respectively (Fig. 6). Risk factor (Er) for CALCZ for Calabar geophagic clays were 6.0, 3.0, 9.0, 1.5 and 0.5, respectively while geophagic clays from Okon-Eket had 9.0, 5.0, 8.5, 1.5 and 0.4, respectively. Calabar and Okon-Eket had respective RI of 20.0 and 24.4.

Non-carcinogenic and carcinogenic risk indices

The Estimated Daily Intake (EDI) of the PHEs from the geophagic clays was used in the computation of the non-carcinogenic and carcinogenic indices for the ingestion and dermal contact pathways.

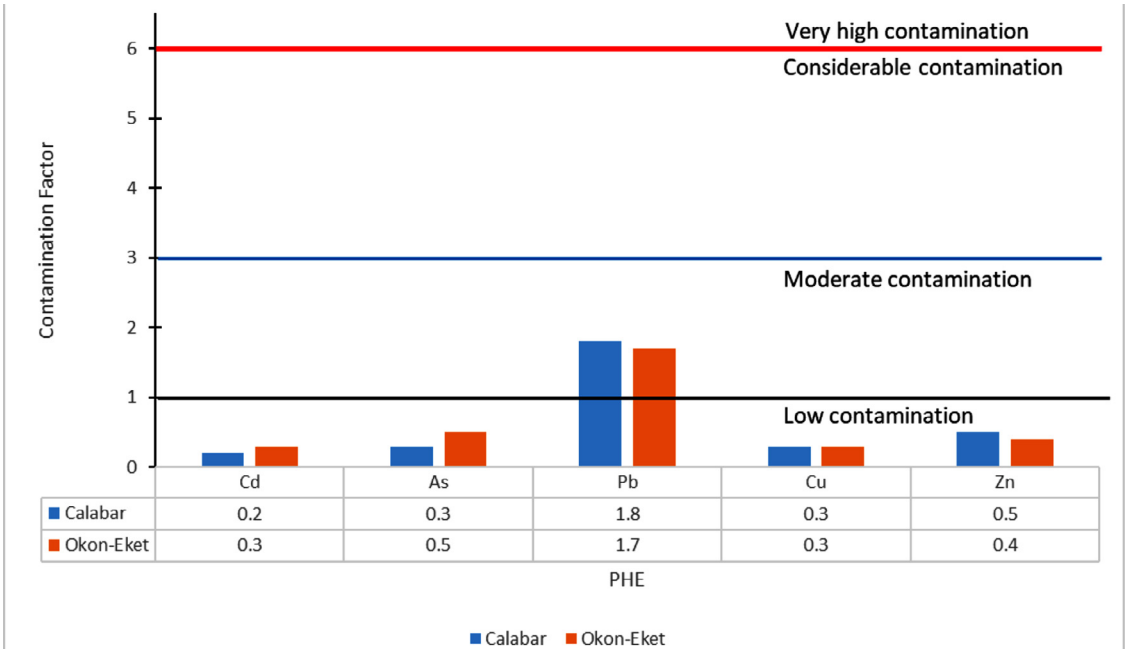


Fig. 5. Contamination Factor for the geophagic clays consumed in Calabar and Okon-Eket.

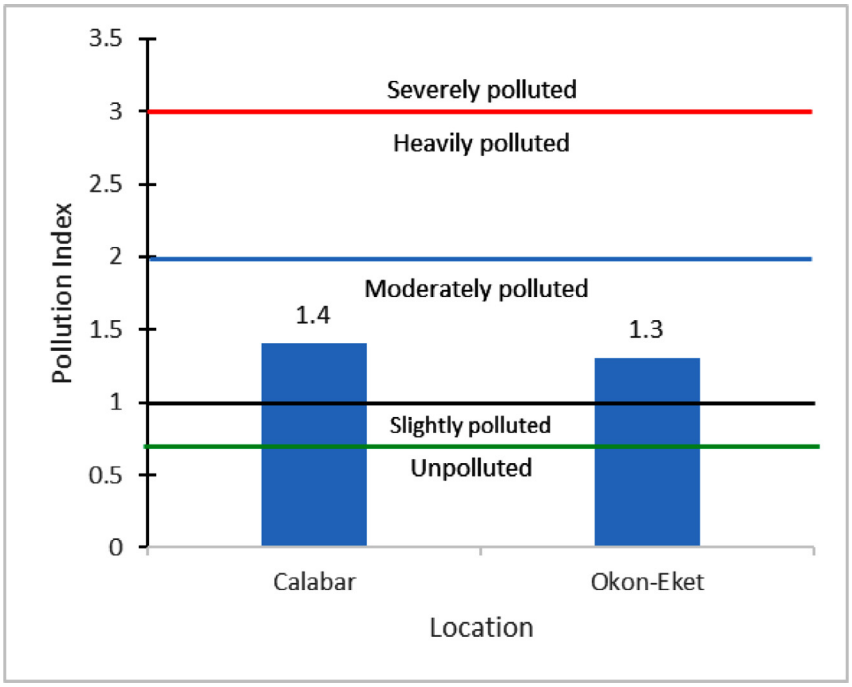


Fig. 6. Pollution index of clays in the studied areas.

The geophagic adults in Calabar had an EDI (mg/kg/day) of 6.85×10^{-8}, 4.57×10^{-6}, 5.00×10^{-5}, 1.94×10^{-5} and 6.30×10^{-5}, respectively of CALCZ from clay ingestion. The children however, had a daily intake (mg/kg/day) of 6.39×10^{-7}, 4.26×10^{-5}, 4.66×10^{-4}, 1.81×10^{-4} and 5.88×10^{-4}, respectively of CALCZ. The adults of Okon-Eket ingested 1.37×10^{-7}, 8.22×10^{-6}, 4.63×10^{-5}, 1.67×10^{-5} and 5.66×10^{-5} mg/kg/day of CALCZ, respectively from the geophagic clays, while the children ingested 1.28×10^{-6}, 7.67×10^{-5}, 4.32×10^{-4}, 1.56×10^{-4} and 5.28×10^{-4} mg/kg/day of CALCZ, respectively.

The amount of PHEs absorbed daily (mg/kg) from dermal contact with the clays by geophagic adults in Calabar was 2.7×10^{-10}, 1.82×10^{-8}, 1.99×10^{-7}, 7.72×10^{-8} and 2.51×10^{-7}, respectively for CALCZ. The children in Calabar absorbed 1.79×10^{-9}, 1.19×10^{-7}, 1.31×10^{-6}, 5.06×10^{-7}, and 1.65×10^{-6} mg/kg/day respectively of CALCZ through their skin. Geophagic adults in Okon-Eket were exposed to 5.47×10^{-10}, 3.28×10^{-8}, 1.85×10^{-7}, 6.65×10^{-8}, and 2.26×10^{-7} mg/kg/day of CALCZ through dermal contact, while the topical application of the geophagic clay slurry on the children in Okon-Eket exposed them to 3.58×10^{-9}, 2.15×10^{-7}, 1.21×10^{-6}, 4.36×10^{-7} and 1.48×10^{-6} mg/kg/day, respectively.

Hazard Index (HI; calculated using Eq. (10)) for adults in Calabar for CALCZ were 9.58×10^{-5}, 1.52×10^{-2}, 1.47×10^{-2}, 4.90×10^{-4} and 2.14×10^{-4}, respectively while that of Okon-Eket was 1.92×10^{-4}, 2.74×10^{-2}, 1.36×10^{-2}, 4.22×10^{-4}, and 1.92×10^{-4}, respectively. The geophagic children in Calabar, had HI of 8.18×10^{-4}, 1.42×10^{-1}, 1.36×10^{-1}, 4.56×10^{-3}, and 1.99×10^{-3}, respectively for CALCZ while

in Okon-Eket, it was 1.64×10^{-3}, 2.56×10^{-1}, 1.26×10^{-1}, 3.93×10^{-3}, and 1.78×10^{-3}, respectively.

For carcinogenic risk, the EDI from ingestion of geophagic clays by adults in Calabar was 2.94×10^{-8}, 1.96×10^{-6}, 2.14×10^{-5}, 8.30×10^{-6} and 2.70×10^{-5}, respectively for CALCZ. Calabar children ingested 5.48×10^{-8}, 3.65×10^{-6}, 4.00×10^{-5}, 1.55×10^{-5}, and 5.04×10^{-5} mg/kg/day, respectively of CALCZ from the geophagic clays. In Okon-Eket, geophagic adults through ingestion, were exposed to CALCZ concentrations of 5.87×10^{-8}, 3.52×10^{-6}, 1.98×10^{-5}, 7.15×10^{-6} and 2.42×10^{-5} mg/kg/day, respectively. The children on the other hand, ingested 1.10×10^{-7}, 6.58×10^{-6}, 3.70×10^{-5}, 1.33×10^{-5}, and 4.52×10^{-5} mg/kg/day of CALCZ, respectively.

Through dermal contact, geophagic adults in Calabar were exposed to 1.17×10^{-10}, 7.81×10^{-9}, 8.55×10^{-8}, 3.31×10^{-8}, and 1.08×10^{-7} mg/kg/day respectively of CALCZ while the children were exposed to 1.53×10^{-10}, 1.02×10^{-8}, 1.12×10^{-7}, 4.34×10^{-8}, and 1.41×10^{-7} mg/kg/day, respectively. In Okon-Eket, adults absorbed 2.34×10^{-10}, 1.41×10^{-8}, 7.92×10^{-8}, 2.85×10^{-8}, and 9.67×10^{-8} mg/kg/day, respectively of CALCZ through dermal contact, while the children were exposed to 3.07×10^{-10}, 1.84×10^{-8}, 1.04×10^{-7}, 3.73×10^{-8}, and 1.27×10^{-7} mg/kg/day, respectively.

As and Pb are the only elements with Slope Factor (Table 5). The Cancer Risk Index (CRI; estimated using Eq. (11)) of As for Adults through the ingestion pathway in Calabar and Okon-Eket is 2.94×10^{-6} and 5.28×10^{-6}, respectively. For Pb, it is 1.82×10^{-7} and 1.68×10^{-7}, respectively. For geophagic children in Calabar and Okon-Eket, the CRI for As through the ingestion pathway is 5.48×10^{-6} and 9.87×10^{-6}, respectively while for Pb, it is 3.40×10^{-7} and 3.15×10^{-7}, respectively. In Calabar and Okon-Eket, the CRI from dermal contact for As for geophagic adults are 2.86×10^{-8} and 5.16×10^{-8}, respectively while for children, the CRI from dermal contact for As are 3.73×10^{-8} and 6.73×10^{-8}, respectively.

Discussion

The geo-environmental and health risks associated with potentially harmful elements such as Cd, As, Pb, Cu and Zn were evaluated due to the importance of these elements to the safety of geophagic individuals.

The concentrations of Pb and Zn were the most elevated in the clays studied. Samples obtained from Ikot-Omin mine had the highest concentration of Pb (55.6 mg/kg) while samples obtained from Watt Market generally had the highest concentration of Zn (148 mg/kg). The slightly acidic nature of the studied clays, means that the PHEs, particularly Pb and Zn, could be more readily bio-available from the clays [51,52]. The concentration of the PHEs in the Geophagic clay from both study locations were in the order: Zn>Pb>Cu>As>Cd (Table 6). However, the PHEs were observed to be within the target values for heavy metals in soils in Nigeria [49], except sample CCW3 which had Zn values that exceeded the target value.

When compared, the concentration of As and Pb in clays from Benue, Bauchi and Osun [13] exceeded the concentrations in the studied clays while clays from Musoma, Kigoma [10] and Volta [9] regions had lower values compared with this study. The Cu and Zn concentration in the studied clays exceeded those of Volta region; Benue, Bauchi and Osun areas (Fig. 7). Comparison of the studied clays with those of Uteh-Uzalla [52] revealed similar Cu concentrations, with Pb and Zn concentrations higher than those of Uteh-Uzalla. While the clays of Calabar and Okon-Eket had Pb concentrations higher than those of Cameroon [54] and East Africa [6], Cu and Zn concentrations in the Cameroon and East Africa clays exceeded those of the studied clays.

Calculated I_{geo} values revealed that the geophagic clays from both Calabar and Okon-Eket are practically uncontaminated with Cd, As, Cu and Zn. They were however, uncontaminated to moderately contaminated with Pb (Fig. 4). Using Contamination Factor, the clays from both Calabar and Okon-Eket areas had low Cd, As, Cu and Zn contamination, but had moderate Pb contamination (with CF values of 1.8 and 1.7, respectively). The degrees of contamination of the PHEs in Calabar and Okon-Eket were however low, with C_{Deg} values of 3.1 and 3.2, respectively (Fig. 5).

The Pb contamination revealed by I_{geo} and CF calculations most likely resulted from burning of the clays using gasoline fuels, which is one of the means of processing the clays prior to ingestion [12]. Artisanal crude oil refining is also a common occurrence in the area and Pb is a known by-product of such activities ([55,56], Supplementary Material 2). Pb is one of the most toxic heavy metals and elevated Pb concentrations in soils has been linked with blood Pb level, especially in children [57]. Pb toxicity affects brain (cognitive) function, affects the nervous system, has a tendency to accumulate in the bones for a long time [57,58] and is the leading cause of autism in children [59]. Exposure to lead during pregnancy significantly increases the likelihood of major physical birth defects [60] and congenital heart defects in offspring [61].

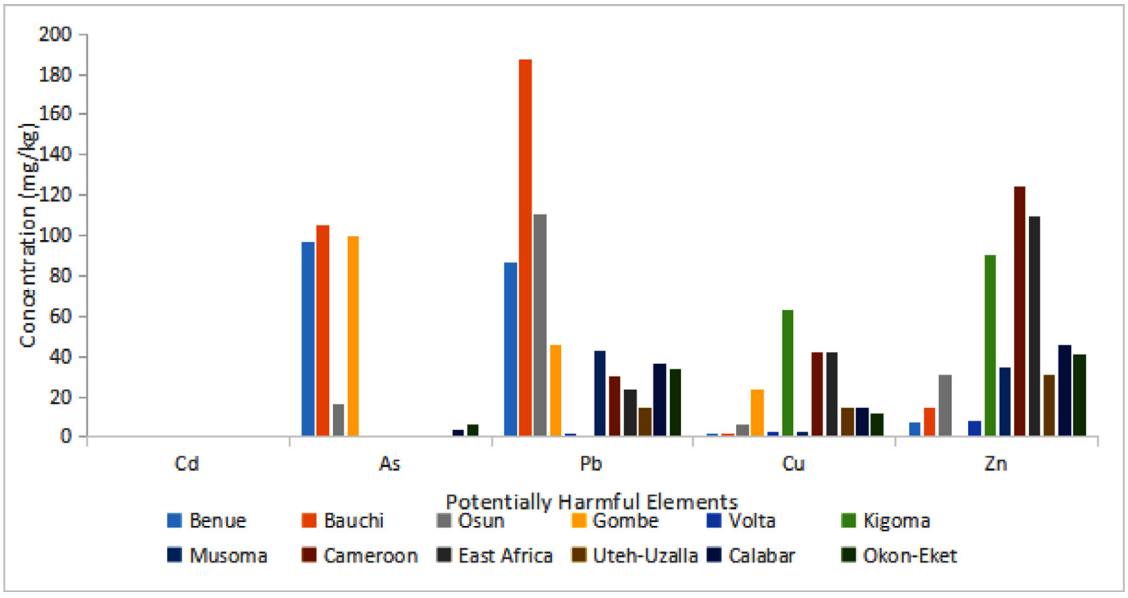


Fig. 7. A comparison of the PHEs in the studied clays (Calabar and Okon-Eket) with other studies.

The clays from Calabar and Okon-Eket rank in the moderately polluted class (with PI values of 1.4 and 1.3, respectively). However, the Er and RI values for the clays (20.0 and 24.4, respectively) revealed that they are of low ecological risk. The moderate pollution of the clays makes them unsuitable for consumption, especially in the long term, considering the cumulative effect of PHEs accumulation, especially Pb, in the human body.

The non-carcinogenic risk associated with the consumption of the geophagic clays for adults and children in Calabar and Okon-Eket were computed based on the toxicity baseline (Rfd) and EDI values (Table 5). The EDI through ingestion of all the PHEs except Pb was lower than the Minimal Risk Level (MRL) prescribed by the Agency for Toxic Substances and Disease Registry [62]. However, as there are no safe ingestion levels for Pb, any quantity consumed has potentially deleterious effect on human health. These effects range from slowed growth, lowered IQ and learning problems in children; to premature birth or miscarriage in pregnant women [63]. Other effects on adults include increased chances of high blood pressure, impairment in kidney function and reproductive malfunctions [64].

The HQ for all PHEs in each pathway, for both adults and children, are < 1. The HI of the PHEs for the geophagic adults and children from ingestion and dermal pathways were also < 1. This indicates that there is no immediate adverse risk of non-carcinogenic effects from the consumption of the clays.

The CRI was computed for As (ingestion and dermal pathways) and Pb (ingestion pathway) using their respective Slope Factors. These elements, considered two of the most carcinogenic elements [65–67], are responsible for a number of debilitating health conditions when in excess within the human system. Examples of these are lung, stomach, bladder, liver and skin cancers; as well as cognitive disorders, [50,68]. The United States Environmental Protection Agency guidelines considers CRI range of 1×10^{-6} to 1×10^{-4} as being acceptable for regulatory purposes. The calculated cancer risk from the As and Pb was observed to be within the requirement for all the samples in both exposure pathways.

A comparison of the geophagic clays of the present study with kaolinitic clays consumed in the Eastern Dahomey and Niger Delta Basins [42] revealed that the HQ values were below the limit in all pathways for children and adults, except the ingestion pathway for children. Like those of the present study, the non-carcinogenic risk for the geophagic clays from Cameroon were also < 1 [53]. For clays eaten by pregnant women in the Volta Region [9], non-carcinogenic risk for As, Pb and Cd were found to be > 1. HQ values for all the metals evaluated in the research by [41] were < 1. However, the cancer risk from As exceeded the allowable limit, having a potential to cause cancer in the individuals consuming the clay.

Conclusion

The study presented new data on the ecological and health indices for the clays consumed in the two areas. The concentration of the PHEs in the Geophagic clays from both study locations were in the order: Zn>Pb>Cu>As>Cd. Results of I_{geo} and CF calculations revealed that the clays from Calabar and Okon-Eket have moderate Pb contamination, which could have resulted from burning during processing prior to consumption, and as a product of artisanal crude oil refining which is a common occurrence in the areas studied. The clays from both locations also rank in the moderately polluted category of the Pollution Index. The calculated HQ and HI values for the geophagic adults and children were < 1 in ingestion and dermal pathways, implying there is no adverse risk of non-carcinogenic effects. The geophagic clays also pose no immediate carcinogenic risk to the geophagic individuals. However, the Pb contamination in the clays is a major source of health concern, especially for geophagic children in the areas, as no quantity of Pb is deemed safe for the human body. The cumulative effect(s) of the continuous consumption of the clays, especially by children in the areas studied, need to be further evaluated.

While the assessment of the health risks associated with the consumption of geophagic clays in the areas studied has been done, a limitation of the current study is that blood/serum and tissue samples of the geophagic individuals were not obtained, in order to evaluate the damage done to their health as a result of the geophagy practice. Further studies need to be conducted in this vein to ascertain the extent of damage geophagic practice has done to the individuals who engage in it.

Ethical statement

No human/animal parts or samples were used in the research.

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Data statement

All inquiries on data availability to be sent to jolugbn@gmail.com.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest on the research or this manuscript.

CRediT authorship contribution statement

Jerry O. Olajide-Kayode: Conceptualization, Investigation, Data curation, Writing – original draft. **Tesleem O. Kolawole:** Data curation. **Opeoluwa O. Oyaniran:** Data curation, Writing – original draft. **Shakirat O. Mustapha:** Writing – review & editing. **Akinade S. Olatunji:** Conceptualization.

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Supplementary materials

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