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Essential and toxic element present in clay obtained from Ghanaian Market

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ABSTRACT

Clay (soil) is a "biologic sink". It contains nutrients, toxic elements, organic matter and microbes among other things. The clay can pose a health threat. It was postulated by Ellis and Schnoes in 2002 that people who eat clay risk psychological abnormalities and health consequences such as lead poisoning and bacterial or parasitic or worm infection. Most spore forming bacteria, such as bacillus and clostridium, like to live in soils [1]. A person can start feeling some abdominal pains when the soil or food contains about 105 colonies of bacillus or clostridium per gram of soil or food in the body [2]. Clostridium in the female genital tract may induce abortion and result in uterine gas gangrene [2].

Introduction

The estimation of health threat associated with intentional clay eating (geophagy) poses a greater challenge [3]. The intentional eating of clay is mostly as a result of pica (the eating of non-food items due to unusual appetite), cultural tradition norms, perceived health benefits and religion beliefs [4]. For example, in line with traditions and culture of people from different part of the world, data is available that indicate the use of clay during food preparation. Specifically, Native Americans who lived in California, Peru and Sardinia (Italy), ate clay with acorn and potatoes or use clay to prepare acorn bread in order to neutralise toxins such as alkaloids in the acorn. Also, in the Philippines, New Guinea, Costa Rica, Guatemala, the Amazon region and Orinoco basins of South America, clay have been used as condiments or spices as well as food during famine [5].

Soil eating (geophagy) is common among pregnant women in Africa and migrants to Africa [3, 6], although it is not always confined to pregnant women. Data available show that geophagy is practiced among all race, social classes, ages and sex in some parts of the world [7]. In sub-Saharan Africa, soils eaten are most sub-surface (60 90 cm) clays, kaolin and montmorillonite [8] that are mostly made in rural areas but available for urban settings. Clays from termite mounds are especially popular among traded clays, perhaps because of their flavour and taste; incidentally these soils are rich in calcium [9]. In Ghana, most of the clay available for consumption is baked before eaten.

Clays have also been used in medication (for example kaolin clay in kaopectate) and for the prevention of nausea in pregnant women. Clays may relieve gastric distress but top soils are not as effective as deep soils at gastric soothing [6]. Wiley and Katz (1998) [8] have proposed that eating clay serves different purposes during different periods of pregnancy, soothing stomach upset during morning sickness in the first trimester and supplementing nutrients (especially Ca) during the second trimester, when the foetal skeleton is forming [8]. Clays eliminate nausea possibly because they coat the gastro intestinal tract and may absorb dangerous toxins. Paraquat poisoning victims were told to promptly swallow soil (clay) because it is deactivated upon contact with soil [4].

It is postulated that regular consumption of soil (clay) by pregnant women might boost the women's secretory immune system. Gut – associated lymphoid tissue is a major site of intense immunologic activity in children and adults.

Although it is not clear why antigens introduced in the gut either promote tolerance of microorganisms or immunize against them, it is clear that immunization through the gut is a major source of immunoglobulin (IgA) [10]. Aluminium salts have been used for sometime as adjuvant (amplifiers of immune response) in human vaccines. For this reason it is believed that aluminium compounds which are contained in soil clay make immunologic adjuvant [6].

The clays might act as vaccines, stimulating the production of antibodies (IgA) against organic antigens such as parasites. In summary eating soil or clay is thought to enhance foetal immunity, increase calcium supply, eliminate gastric upset, detoxify some plant and animal toxins, and possibly boost mother's immunity.

Thus it is of importance to perform elemental analysis on clay mostly consumed by pregnant women, in order to determine whether these elements are still inert and safe for consumption..

Materials and Methods:

Material:

A total of 10 pieces (lumps) of clays were each purchased from 8 different local markets in Ghana, precisely Accra and Kumasi: Madina, Dome, Kaneshie, Nima, Achimota, Nungua, Accra Central and Kumasi (Anloga market). Two colours were observed from the clay bought from Madina: ash, dark-ash. The samples were collected in stomacher bags and transported to the laboratory for analysis

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Method:

Sample preparation:

One each of the 10 pieces (lumps) of clays were first broken into small pieces using mortar and pestle, and then transferred to a blender to obtain fine particles. 0.1 g of the powered samples were weighed from each onto a polyethylene film, wrapped and sealed. This was performed in triplicate. The wrapped samples were then packed into polyethylene capsules for analysis.

Instrumentation:

The samples and the Certified References Materials were irradiated in the Ghana Research Reactor-1 (GHARR-1) at the National Nuclear Research Centre (NNRC), Ghana Atomic Energy Commission. GHARR-1 was operated at half of the full power of 15KW with a neutron flux of $5x10^{11}$n-cm^{-2}s^{-1}. Irradiation time, decay time and counting time all known as irradiation scheme are presented in the table below:

Sample irradiation and counting:

Two separate irradiations were performed; ten seconds irradiation was chosen for short lived radionuclide(s), one hour irradiation for both medium and long lived radionuclide. The decay times were based on the radionuclide of interest and the activity of the sample after irradiation (it was carefully chosen to achieve decreased dead time: less than 5%).

After 10 seconds irradiation, the sample were delayed for a period of 5 minutes and counted for 10 minutes. Medium lived radionuclide were delayed for 24hours after 1hour irradiation and counted for 10 minutes. The same samples were then kept for four weeks and counted for 2 hours to obtain the long lived radionuclide.

Radioactivity measurement of induced radionuclide was performed by a PC-based γ-ray spectrometry set-up. It consisted of an N-type HpGe detector (coaxial type) coupled to a computer based multi-channel analyzer (MCA) via electronic modules. The relative efficiency of the detector is 40%. It energy resolution is 1.8keV at a γ-ray energy of 1332keV of ^{60}Co. The data acquisition and identification of γ-rays of product radionuclide were identified by their γ-ray energy (ies) via ORTEC MAESTRO-32.

Quantitative analysis was done via relative comparator method. The peak area determinations, processing and concentration calculation were done by multipurpose γ-ray spectrum analysis software; winSPAN-2010 version 2.10.

winSPAN calibration

Application of the relative comparator method requires Certified Reference Materials (CRM) or/and Standard Reference Materials for element(s) of interest.

NISTSRM 1646a estuarine sediment a CRM and two IAEA Standard Reference Materials IAEA- SL-1 and IAEA-SL-3 were used for calibration and validated against each other.

Results and Discussion:

The precision and accuracy of the analytical technique was assessed by simultaneous activation of Certified Reference Materials NISTSRM 1646a Estuarine Sediment, IAEA- SL-1 and IAEA-SL-3. The results obtained for the validation are shown in Table 2. Photo peaks of V, Al, Mn, Ti, Ca, Na, and K from estuarine sediment were used to calibrate the winSPAN and validated against both SL-1 and SL-3; while photo peaks of La, As, Ba, Eu, Sc, Fe, Sm, Hg, and Co from SL-1 were used for calibrations and validated against estuarine sediments and SL-3. The purpose of this alternate calibrations and validations was to ensure that, only high photo peaks (well defined peaks and of good statistics) were used for calibrations in order to minimize systematic erros (calibration factors).

Table 2 clearly shows that the values obtained compared favourably with the recommended values. Where the reported values and those obtained are the same, the calibration factor is exactly 1. The element corresponding to these values are used for the winSPAN calibration**.** The experimental samples were within ±5% of the recommended values.

Table 3 gives the concentration of the elements present in the analyzed clay obtained from the different local markets. In the 10 samples analyzed, 16 of the 19 elements investigated were detected: Manganese (Mn), Copper (Cu), and Mercury (Hg). Mg and Cu are known to be Essential Mineral elements.

What are the daily allowable intakes of these elements?

What is the average weight or the weight range of the pellets of the clay that is consumed?

How many pellets are averagely consumed in a day?

Mn is an inorganic cofactor (a non-protein chemical compound that is bound to a protein and is required for the protein's biological activity) in enzyme functions. They can be considered "helper molecules" that assist in biochemical transformations. Cu is a required component of many redox enzymes, including cytochrome c oxidase which is a large transmembrane protein complex found in bacteria and the mitochondrion. It helps establish a transmembrane difference of proton electrochemical potential that the ATP synthase uses to synthesize ATP. The absence of Hg from all 10 samples is good especially for pregnant women who often do take the clay. Mg is detected in sample 4, 7, and 9 only. The absence of this element in sample 1, 2, 3, 5, 6, 8, and 10 may come from the soil mined. Consider looking at the data interms of the markets and also interms of the type of clay (ash and dark ash)

Aluminum (Al), Potassium (K) and Iron (Fe), are present in high quantity. The concentration pattern shown by the essential elements present differs from one sample to another. For example, a concentration pattern of Al> K> Fe> Ti> Ca> Ba> Na> V> Cr> La> Sc> Sm> Co> Eu (As not detected) was seen from sample 1 while in sample 2, rather Fe> K, and Na> Ba. In sample 9, Lanthanum concentration was rather greater than Chromium (Cr). Arsenic (As) was detected from the other 9 samples (i e Sc> As> Sm>Co> Eu; but As> Sc in sample 2).

The changes seen in the elements concentration pattern may be caused by the processing procedures, and the mining sites. As to know how much these contribute to the concentration further studies is needed.

The WHO recommended value of Fe/day is for the ferrous form of iron. Iron in the body is absorbed in the ferrous (Fe^{2+}) form [10]. Iron tablets recommended for pregnant women contain the ferrous form of iron as ferrous sulphate ($FeS0_4$). The iron present in the clay samples demands therefore further investigations. The soils, throughout Ghana, should be characterized to assess the form of iron which is mostly present and to check if the soils contain required iron.

The clay samples may contribute to dietary Ca, Fe, K, Na, and Zn but not Magnesium and Manganese. The variations in the quality of the clays analyzed could be due to differences in the composition of the rocks that weathered to form them. For example rocks with haematite and pyrite would produce iron rich soils, rocks with gypsum, limestone and dolomite would produce calcium rich soils, rocks with zincblende would produce zinc rich soils and rocks with magnesite dolomite would produce

magnesium rich soils. The absence of Magnesium shows that rocks with magnesite dolomite are absent. The topography and climatology conditions also affect element concentrations in soils.

Conclusion:

Out of 10 sample analyzed, 19 elements were investigated from which 3 were not detected: Manganese (Mn), Copper (Cu), and Mercury (Hg). The essential elements present are Na, K, Ca, Zn, and Fe. Higher concentration was seen for Al, K, Fe, Ca, Na, and Ba (in ppm). From the data, it can be said that the clays analyzed have some benefit with respect to the element obtained.

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Table 1: Irradiation Scheme

Element	nuclide	Energy (keV)	Irradiation time	Delay time	Counting time
Mg	^{27}Mg	1014.430	10 seconds	Within 5 minutes	10 minutes
Cu	^{66}Cu	1039.200			
V	^{52}V	1434.080			
Al	^{28}Al	1778.990			
Mn	^{56}Mn	1810.720			
Ti	^{51}Ti	320.080			
Ca	^{49}Ca	3084.540			
Na	^{24}Na	1368.6	1 hour	Within 24 hours	10minutes
K	^{42}K	1524.58			
La	^{140}La	1596.21			
As	^{76}As	559.1			
Hg	^{197}Hg	77.39			
Ba	^{131}Ba	123.77	1 hour	Within 4 weeks	2 hours
Eu	^{152}Eu	964.110			
Sc	^{46}Sc	1120.550			
Cr	^{51}Cr	320.080			
Fe	^{59}Fe	1099.250			
Sm	^{154}Sm	103.18			
Co	^{60}Co	1173.240			

Table 2: Calibration and validation results:

Elements	IAEA-SL3		IAEA-SL1		Estuarine sediment	
	Reported	This work	Reported	This work	Reported	This work
Mg	27000	29150	NR	27610	3880	ND
Cu	NR	ND	30	ND	10.01	ND
V	NR	25020	170	192.1	44.84	44.84
Al	24500	23850	NR	92300	22970	22970
Mn	NR	293.30	3460	2565	234.5	234.5
Ti	2610	2822	5170	3132	4560	4560
Ca	111100	103900	NR	6276	5190	5190
Na	6690	6596	1700	1732	7410	7410
K	8740	9113	14500	12410	8640	8640
La	22.5	23.96	52.6	52.60	17	17.85
As	3.2	BDL	27.6	27.6	6.23	ND
Ba	NR	286.9	639	639.0	210	184.5
Eu	0.66	0.7755	1.6	1.6	NR	0.84
Sc	3.91	4.513	17.3	17.3	5	4.631
Cr	NR	24.86	104	99.96	40.9	48.54
Fe	NR	11780	67400	67400	20080	18920
Sm	3.83	4.485	9.25	9.25	NR	3.384
Hg	NR	ND	0.13	0.13	NR	ND
Co	NR	2.531	19.8	19.80	5	4.642

ND= Not Detected; NR= Not Reported; BDL= Below Detection Limit

Table 3: Concentration of element in clay as ppm (µg/g)

	Concentration (µg/g) of elements in the following samples									
Element	1	2	3	4	5	6	7	8	9	10
Al	78860	80020	101300	83300	79280	106000	79420	85980	73430	84020
K	28684	31009	30827	31066	31058	30268	31866	30648	31941	30846
Fe	15330	39610	29690	27580	39160	28370	23560	38680	20700	25490
Ti	6204	5862	7987	5839	6834	5966	4153	6843	4284	5408
Ca	4525	2894	7165	5986	5280	5246	3684	6315	4510	6505
Na	523.75	654.41	809.61	626.51	554.99	520.78	606.63	673.16	617.64	678.5
Ba	556.91	428.28	607.05	582.76	632.23	332.44	567.38	429.81	621.05	14.94
V	133.2	187.9	200.7	182.4	152.8	186.7	144.4	176.2	91.17	170.8
Cr	63.49	169.1	87.45	120.3	129.9	123.6	77.75	143.9	50.59	142.6
La	51.895	49.682	51.649	53.532	53.532	45.818	48.515	50.152	86.232	43.88
As	ND	22.742	15.151	11.2	14.018	10.297	5.0871	9.801	2.7631	9.315
Sc	16.63	21.1	21.72	24.29	23.37	21.25	20.8	22.32	18.75	21.35
Sm	9.6282	9.8173	9.8088	9.3345	10.304	7.9446	8.0448	8.9896	10.68	7.141
Co	1.34	3.594	3.274	2.088	3.551	3.504	1.997	2.455	1.036	3.095
Eu	1.1182	0.8688	1.2881	1.239	1.1712	0.7227	1.0961	0.8694	1.2775	1.084
Mg	ND	ND	ND	13050	BDL	BDL	19860	BDL	22530	BDL
Cu	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Mn	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hg	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND= not detected; BLD= Below Detection Limit