Intake of Lead, Cadmium and Mercury in Kaolin-eating: A Quality Assessment

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Clay-eating or kaolin-eating (geophagy or geophagia) is a global practice that exists among humans as well as numerous animal species. Geophagy has been studied by anthropologists, geologists, nutritionists and ecologists in present and traditional cultures from areas across continents, including present-day Arizona and California, Central and South America, Sweden and Sardinia, sub-Saharan Africa, Indonesia and Australia. In 2002, the European Union alerted the Cameroon Ministry of Public Health that kaolin carried from Cameroon to Europe had abnormally high amount of lead (Pb) at levels a 100 times higher than the maximum permissible level. This kaolin that is sold on the several markets is mined from different sources, some locally and others from Nigeria. To investigate this, markets of wholesale dealers in kaolin were visited in five districts selected in a manner to represent the entire territory. Six samples of 1 kg each were then randomly selected and bought. A total of 30 kg was collected from all the districts. The sources of procurement were also visited and 24 samples of approximately 300 g each were collected from all the harvesting sites. Analytical methods for flame spectroscopy were used and stastiticalgraphic for data analysis. The results show that all kaolin is contaminated not only with Pb but Cd and Hg as well. The differences in Pb content at district levels is statistically significant p = 0.02 (p<0.05) while no significant difference exist as regards the origin of kaolin or source of procurement (p = 0.53).

Key words: Kaolin, metal contents, toxic, geophagy
INTRODUCTION

The eating of clays or kaolin occurs among cultural groups on every inhabited continent. Geophagy is prevalent in Asia, the Middle East, parts of Latin America and in the rural South of the United States. In Sub-Saharan Africa hundreds of cultures including both farmers and nomads consume dirt, mainly clay (kaolin) but in some cases sand. Clay consumption is nearly everywhere most common among pregnant women, perhaps because of its antiantiscia effects, experts hypothesize. The limited data indicate that from 30% to 50% of pregnant women in large areas of Africa and among rural blacks in parts of the American South consume clay and that hundreds of millions of women worldwide do it during pregnancy (Vermoe and Ferrell, 1985).

Kaolin is a broad name given to a range of clay-compound substances made up of Kaolinite (predominately) and several other minerals produced by the alteration of felspathic rock. As a compound, the composition of Kaolinite and other minerals and substances varies from sample to sample. Depending on its chemical composition it can be white, green, pink, grey, yellow or red in colour and has a soft plastic nature. Like all other clay it is a hydrated silicate that is very stable during natural conditions. It is ranked as one of the top seven industrial minerals in the world (DME, 2005). Depending on its individual chemical characteristics and the extent to which it is processed, Kaolin is used as filler and input in the manufacture and production of several goods including: Ceramics, bricks, tiles, pottery, cement, paper, fibre glass, refractories, plastic, pharmaceuticals, mineral wool, cosmetics, paint, rubber, industrial products, light bulbs, food additives, toothpaste etc. (DME, 2005).

Physiologically, some nutritionists and other observers have tended to view geophagia and pica in general as a compulsive craving and as a medicine to alleviate discomfort in some respects. Kaolin or clay could absorb dietary toxins and bacterial toxins associated with gastro-intestinal disturbance (Walker et al., 1997). The presence of aluminium, magnesium and benzoic groups has made Kaolin to possess antacids properties and can be a therapeutic food for people suffering from gastric upsets or ulcers. Further, because of its covering properties, it has a bandaging role in gastro-enterology (Banenzoue, 1992).

In a hot and humid milieu, kaolin develops negative charges between its layers and will attract positive charges (such as heavy metals) resulting to contamination (Gumie et al., 1988). Lead, a naturally occurring metal, has always been present in soils, surface waters and ground waters. Lead content of agricultural soils ranges from 1 to 135 mg kg⁻¹ with a median value of 11 mg kg⁻¹ (Holmgren et al., 1993) and will certainly through leaching or washing by rain reach kaolin deposits especially those deposits that are along or within streams/rivers or on slopes below cultivated farm fields. The situation is more serious when the stream/river that is reaching kaolin deposits has passed through a city or industry (Nwewe et al., 2008; Danazumi and Bichi, 2010). Inner-city neighbourhoods in most of our major cities have mean or median soil Pb concentrations in excess of 1000 mg kg⁻¹ (Angie et al., 1974; Johnson et al., 1975; Bornschein, 1986; Mielle et al., 1989; Madhaven et al., 1989; Usman et al., 2007) with values as high as 50,000 mg kg⁻¹ being reported (Chaney et al., 1989). Most of these elevated lead concentrations observed in the urban soils are assumed to come from various anthropogenic sources: industrial emissions, vehicular emissions and exterior lead paint (EDF, 1990; Madakosiri and Dressman, 2010). Additionally, lead is also added to soil as the insecticide lead arsenate, impurity in fertilizers as well as from mining and smelting activities (Davies, 1990).

In 1999, the German authorities came out with information of the presence of dioxin in some portions of kaolin (clay) from mines of the Westerwald region that was used to improve flow during pumping when moving the animal feed from one store to another. This came to add to the medical fear that extreme overindulgence in clay eating can block the colon, which can lead to perforation of the colon and death. A more common problem is the geophagic syndrome seen over the last three decades among scores of clay eaters in Portugal, Iran, Turkey, Egypt and other Middle Eastern countries. The syndrome involves anaemia and zinc deficiencies (Virginia et al., 1968; Hooja et al., 2002), growth retardation, delayed sexual maturity and liver and spleen enlargement (Danford and Huber, 1982). Also, in 2002, the European Union alerted the Cameroon Ministry of Public Health that kaolin carried from Cameroon to Europe had abnormally high amount of lead (Pb) at levels a 100 times higher than the maximum permissible level. In 2003, the national Ministry of Public Health then prohibited the consumption of kaolin within the confines of its jurisdiction. This ban has not stop kaolin dealers from importing or exporting their product or industries from exploiting or using kaolin as a raw material.

Lead is a poisonous metal that can damage nervous connections (especially in young children) and cause blood and brain disorders. Lead poisoning typically results from ingestion of food or water contaminated with lead; but may also occur after accidental ingestion of
contaminated soil, dust, or lead based paint (ATSDR/DETR, 2006). It is probable that lead poisoning may also occur in the case of pica or geophagia which is deliberate ingestion of earth or dirt since lead occurs naturally in them at levels above the required threshold for edible matter. Heavy metal toxicity which is frequently the result of long-term, low-level exposure to pollutants has often been investigated in air, water, food and numerous consumer products (Eleni et al., 2006; EPA, 2006) but hardly investigation is carried out in the case of pica (or geophagia as in this case), or to check the validity of industrial products with clay or kaolin as raw material.

Since, it is established that lead can contaminate kaolin it is important to investigate and confirm or infirm the minister’s assertion that kaolin is toxic. The investigation has assumed that lead was associated with other toxic heavy metals particularly cadmium and mercury. The latter together with lead constitute the three most pollutant heavy metals (FAO/WHO, 1993) and as such contamination of kaolin could be attributed to all the three.

MATERIALS AND METHODS

A pilot study justifying the reason for the study was carried out in the Bamenda region (North Western Cameroon). An investigation was carried on a total of 40 consumers (32 women and 8 children) two months before we started with our market visits. Kaolin vendors gave information regarding the market situation of kaolin and consumption rate. Daily consumption was evaluated by asking consumers to state the amount of money in CFA they use in purchasing kaolin each day. Samples of kaolin were then purchased in varied amounts of money stipulated and weighed.

Sampling: We then visited the popular markets of Douala, Yaounde, Bafoussam, Bamenda, Ngaoundere and Limbe/Tiko (one market each for wholesale and retail was chosen in each district). In each market, we met wholesale dealers and asked for their sources of procurement and at the same time six samples of 1 kg each were randomly selected and paid for. A total of 30 kg carefully labelled and numbered was collected from all the sites. They were then carried to the laboratories where they were stored at ordinary temperature in waterproof papers. Kaolin harvesting sites that supply kaolin into the market (Balengoum and Mbangwi in Western and North Western Cameroon, respectively, and one harvesting site in Nigeria) were revealed by wholesale dealers as their sources of procurement. They were subsequently visited to appreciate the sites and observe local conditioning. Four samples of approximately 300 g each were picked from four cardinal points (N, S, E and W) of each harvesting sites. Conditioning that varied from direct incubation at the harvesting sites (in Bangangté) via direct sun-drying and smoking of the blocks in basins, transforming them into a substance known locally as eko (in Nigeria) to simple sun drying or placing of kaolin above the fire sites (in Mbangwi) was observed. Four samples were then purchased after each kind of conditioning. A total of 24 samples were collected.

Reagents: Standard solutions of Lead (Pb), Cadmium (Cd) and Mercury (Hg) were prepared from stock solutions of 1000 μg L⁻¹ (ppm) by following appropriate dilutions using 10% nitric acid. Glassware was cleaned by overnight soaking in HNO₃:H₂O (1:1) followed by repeated rinsing with water. Only de-ionized water was used throughout this work and acids were all of analytical grade.

Sample preparation and procedure: Samples wereground using a mortar and sieve with the USA Standard Testing sieve No120, opening in micrometer 125 (Tyler Equivalent 115Mesh). Mineralization was carried out in a humid medium. About 1.0 g of the pulverized kaolin samples were digested for 30 min in a mixture of hot perchloric acid (2 mL), nitric acid (10 mL) and sulphuric acid (2 mL) (AOAC, 1984). This was filtered through acid washed filter paper (Whatman 42) into 25 mL flask and made to mark with de-ionized water. The contents were each transferred into 30 mL test tubes (decontaminated initially by steeping in 10% nitric acid) The samples were thus ready for reading at the atomic absorption spectrometer.

Atomic absorption spectrophotometer analysis of samples: The heavy metal analysis was done using Perkin 311 model Atomic Absorption Spectrophotometer, as described by Burtis and Ashwood (2001). From the stock solution of each element containing 1000 parts per million (1000 ppm), four different standard solutions were prepared. A blank was prepared using water and acid mixture (perchloric, nitric and sulphuric acids) only. The blank was first aspirated into the flame to give a reading of zero absorbance. Thereafter each of the four standards was aspirated in-turn, starting from the solution with the lowest concentration. Each standard gave an absorbance value that corresponded to its concentration. With the standard curve the unknown concentration of the particular cation in the sample was obtained. Air-acetylene gas was used as fuel, while the following
wavelengths were used for the cationic estimations—lead 283.3 nm, cadmium 228.8 nm and mercury 253.65 nm (with special attention for Hg, using nasal masks). The absorption signals were evaluated by subtracting the value of blank from the signal of the sample.

**Statistical analysis:** All determinations were done in duplicates and stratigraphic (Statigraphic 5.0) used for statistical analysis—the Duncan test used to compare the different dependent variables.

**RESULTS AND DISCUSSION**

A descriptive analysis of the questionnaire is as follows; Kaolin procurement included three sources; Mbengwi (2.5%), Bangante (15%) and Nigeria (82.5%). 62.5% of the vendors met in the market consumed kaolin while 37.5% were only vendors and never consumed kaolin. Vendors revealed that the rate of purchase of kaolin was high. At consumption level, the reasons for consumption varied from the appreciation of taste, flavour, to therapeutic or beliefs or simply no reasons at all. The health problem encountered mostly was constipation. Ninety percent of those who filled the questionnaire were aware of the ban passed by the Ministry of Public Health on kaolin consumption. 42.5% consumed kaolin in pregnancy, 35% could not remember while 22.5% never consumed kaolin in pregnancy. Estimated average consumption per day stood at 59.2±17.7 g.

These results reveal that kaolin is contaminated with Pb, Cd and Hg. The difference between Pb contents at district levels (Table 1) is statistically significant p < 0.05 while no significant difference exist in Cd and Hg (p = 0.22 and 0.5, respectively). Also, differences in Pb, Cd and Hg contents as regards the origin (Nigeria, Bangante or Mbengwi) of kaolin (p = 0.53, 0.25 and 0.92, respectively) are statistically insignificant.

It is clear that heating during conditioning reduces a bit of Pb, Cd and Hg (Table 2) but the reduction is not statistically significant (p = 0.25, 0.33 and 0.91, respectively). Ranges illustrate that heavy metals are not evenly distributed at the harvesting sites and in kaolin samples (Table 1, 2). This could result from differential contamination from running rain water with varying concentrations of heavy metals due to human activities at the upstream of the harvesting sites or variation in leaching, or contamination by running rain waters or streams that are on and off during the rainy and dry season, respectively (the case in Southern Nigeria near Onitsha, at Nneje, Achala-Agu village). Whatever the source of kaolin may be, the differences in the levels of Pb, Cd and Hg (p = 0.45, 0.74 and 0.79, respectively) are not statistically significant.

Since kaolin is directly consumed by humans—following the pathway of food, exposure to these heavy metals is oral and the exposure limits have been compared to those of Food and Agricultural, FAO/WHO (1999) set at 0.2, 0.1 and 0.3 µg g⁻¹ for Pb, Cd and Hg, respectively. This thus indicates that kaolin in the market is contaminated only with Pb but also with Cd and Hg.

**Health risk and hazards of exposure:** The possibility and the danger of lead or heavy metals getting into human food chain through eating contaminated clay (by birds, animals etc.) should be dreaded. In children for example, such an exposure would lead to adverse health consequences against the developing brain, which may result in long-term cognitive deficits as evidenced in

<p>| Table 1: Pb, Cd and Hg contents in Kaolin samples in various districts |
|---------------------------------|---------------|---------------|-------------------|</p>
<table>
<thead>
<tr>
<th><strong>District</strong></th>
<th><strong>Pb (µg g⁻¹ Kaolin)</strong></th>
<th><strong>Cd (µg g⁻¹ Kaolin)</strong></th>
<th><strong>Hg (µg g⁻¹ Kaolin)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Yaunde</td>
<td>79±51.13</td>
<td>11.18±4.69</td>
<td>386.8±379.31</td>
</tr>
<tr>
<td>Bamenda</td>
<td>110±78.06</td>
<td>12.63±4.87</td>
<td>241.4±80.92</td>
</tr>
<tr>
<td>Douala/Limbe</td>
<td>96±50.98</td>
<td>15.88±5.44</td>
<td>362.3±249.86</td>
</tr>
<tr>
<td>Bafousam</td>
<td>137±26.47</td>
<td>11.37±3.79</td>
<td>519.7±483.49</td>
</tr>
<tr>
<td>Ngoundere</td>
<td>143±35.18</td>
<td>13.13±3.18</td>
<td>275.4±72.80</td>
</tr>
</tbody>
</table>

Values in the same column having the same superscripts are not significantly different (p<0.05)

| Table 2: Pb, Cd and Hg contents at conditioning and harvest mines levels |
|---------------------------------|---------------|---------------|-------------------|
| **Source** | **Level of procurement** | **Pb (µg g⁻¹ Kaolin)** | **Cd (µg g⁻¹ Kaolin)** | **Hg (µg g⁻¹ Kaolin)** |
|----------------|----------------|----------------|----------------|
| Nigeria | Harvest | 133±88.53 | 14.6±5.88 | 368±376.39 |
| Nigeria | Condition | 37.98±71.23 | 9.28±6.48 | 214.2±235.9 |
| Bangante | Harvest | 21.7±30.69 | 9.6±5.36 | 239.5±161.2 |
| Bangante | Condition | 48.89±38.99 | 9.8±5.06 | 156.6±101.5 |
| Mbengwi | Harvest | 182±151.71 | 7.4±4.81 | 313.2±243.5 |
| Mbengwi | Condition | 113±80.89 | 11.88±8.52 | 165.8±97.5 |

Values in the same column having the same superscripts are not significantly different (p<0.05)
Elevated blood lead is known to damage a child’s central nervous system, kidneys and reproductive system. At higher levels it can even cause comas, seizures or death (Golub, 2005). Kaolin consumers are therefore likely to suffer from these manifestations if we consider the high level of lead found in kaolin on Table 1. Also women of child bearing age, their fetuses and the elderly are susceptible to lead poisoning, given that lead is stored in the bone for 10-20 years after initial exposure and high levels of lead can be released into the blood during bone loss in pregnancy and in old age. There is a strong relation between maternal and umbilical cord blood lead levels, indicating the transfer of lead from mother to fetus (Gardella, 2001). Lead levels in the blood are also known to correlate with the lead level in maternal blood posing an additional risk to the neonate (Li et al., 2000), this situation is tragic to innocent neonates who will be susceptible to lead poisoning because of the nutritional habit of their mothers.

High concentration of cadmium on its part exerts detrimental effects on human health and causes severe diseases such as tubular growth, kidney damage, cancer, diarrhea and incurable vomiting. Cadmium as well can cause damage to all types of body cells. It damages the cell membrane and increases the permeability of the cells, the consequence being that the transfer of the other heavy metal elements into the cells is facilitated. In acute stage, cadmium intoxication causes enteritis (Bhattacharya, 1983). As oral exposure risk level for cadmium becomes high, consumers become susceptible to all the other heavy metal poisoning. Increased concentration of cadmium has been found in the placenta of women who have given birth to children with low birth weight, neural damage and Down’s syndrome. Children who are exposed to large concentrations of cadmium in their environment often have learning disabilities (Massanyi et al., 2007). Women who consume a lot of kaolin especially when they are pregnant (as revealed in our pilot study by questionnaire) are together with their children susceptible to cadmium and other heavy metal poisoning.

The concentrations of mercury exceeding the maximum permissible limit (0.03 μg g⁻¹), oral exposure, cause serious health problems such as loss of vision, hearing and mental retardation and finally death occurs. Mercury is a toxic substance which has no known function in human biochemistry or physiology and does not occur naturally in living organisms. Inorganic mercury poisoning is associated with tremors, gingivitis and/or minor psychological changes, together with spontaneous abortion and congenital malformations (Vermeire et al., 1991). Monomethylmercury causes damage to the brain and the central nervous system, while foetal and postnatal exposure have given rise to abortion, congenital malformation and development changes in young children (Baars et al., 2001). Since the risk level for Hg is very high consumers of kaolin and their subsequent generations will suffer from these manifestations, except for the fact that its major pathway into the body’s blood is by inhalation.

CONCLUSION

This investigation shows that kaolin in is highly consumed by the population and contains high amounts of lead, cadmium and mercury, which are known to be very toxic to humans. It is therefore imperative that further studies be carried out (e.g., blood level of these minerals amongst consumers etc.), so as to determine the exact risk level(s). Since these heavy metals are not easily eliminated by the human system, there is a need for the serum investigation of these heavy metals in those countries where this phenomenon is a habit (Public Health problem that can be controlled with chelating drugs). Because of high amount of lead, cadmium and mercury, there is need for further investigation on other chemical contaminants; arsenic content, copper content iron content etc.

REFERENCES


