Identification of Metals in Geophagic Clays: Investigation of their Behaviour in Simulated Gastric Fluid

Elvis Fosso-Kankeu, Frans Waanders, Thembuluwolona Netshitanini, Eunice Ubomba-Jaswa, and King Abia

Abstract - The occurrence and mobility of metals ingeophagic clays is a serious concern with regard to the health of consumers who are numbered in thousands in our communities. The geophagic clay samples were characterized by XRD and XRF. After exposure of geophagic clay samples to gastric fluid, the concentration of metals in the leachates was determined using inductively coupled plasma optical emission spectrometer (ICP-OES). The metals identified in the geophagic clay samples included As, Cr, Cd, Zn, Pb, Ni, Se, Cu and Mg which exhibited different pace of mobility during leaching. The mobility of the metals decreased in the order Pb > Ni > Co > Fe > Cr > Cu > Zn. These results show that the consumption of geophagic clays without prior treatment is likely to negatively affect the health of the consumer.

Keywords: Geophagia; heavy metals, micro-organism, simulated gastric fluid, health risks

I. INTRODUCTION

GEOPHAGIA is the deliberate consumption of clay, it is common among many communities and is more prevalent in pregnant women [1] and has been categorized as a medical condition by the World Health Organization [2]. The consumption of clays can provide a lot of benefits; these include the ability of clay to absorb toxins such as heavy metals, free radicals and pesticides from the gastrointestinal tract and the ability to alleviate diarrhoea by retaining water into human digestive tract [1, 3]. Geophagic clay can also serve as nutritional supplements by providing Fe from goethite, Ca and Mg from calcite and smectite [4, 5].

Despite these advantages, ingestion of clay may also constitute a health risk for human beings [1] due to the fact that geophagic clay is mostly contaminated with toxic heavy metals and microorganisms. Geophagia exposes consumers to toxic or harmful materials such as heavy metals, pathogenic bacteria, viruses and parasites [6; 7; 8; 9]. Metal contamination in soil and water is an issue that affects a host of people. Source of contamination of heavy metals at the collection sites could be from disposal of solid and hazardous wastes from anthropogenic activities and it can have a potential impact to the health of consumers. Other heavy metals (As, Se, F and other trace metals) occur naturally in soils during geological processes (weathering and alteration). The geophagic clay may introduce metals such as iron (Fe), zinc (Zn), copper (Cu), manganese (Mn), nickel (Ni), aluminum (Al) and lead (Pb) into the body of consumers [10]. Several incidents of diseases caused by the presence of metals in geophagic clays have been reported. When pregnant women consume a highly contaminated soil on a regular basis, the implication may be that the unborn baby will be exposed to a high level of lead and this may have an impact in the brain and renal system [11]. Lead poisoning and other toxicities have been observed in children eating contaminated soils [12]. The effect of heavy metals from contaminated geophagic clay on human health cannot practically be evaluated by only measuring the total concentration of individual metals [13; 14]. However, effect of soil heavy metal contaminants on human health can be evaluated by using synthetic digestive fluids with biochemical composition similar to human saliva, gastric fluid, duodenal fluid and bile at physiological temperature of 37°C for human gastrointestinal tract [15]. Application of in vitro extraction studies also involves using the simulated human gastric fluid to evaluate element bio accessibility in soils; similar study on soils from a transect across the United States and Canada, concluded that the bioaccessibility of the elements decreased in the order Cd > Pb > Ni > As > Cr [16]. The primary objective of the study was to simulate the metal mobility and availability during consumption of geophagic clays.

II. METHODOLOGY

A. Materials

Three geophagic clay samples were bought from two (2) different daily market in Pretoria and Potchefstroom and 3 other geophagic clay samples were also obtained from the collection sites (sources of commercialized clays). Clay samples purchased from the market were packed in the plastic bags by the vendors who also provided information regarding the source of the clays. Geophagic clay samples from collection sites were collected in clean plastic containers. The samples were transported to the laboratory. All samples were labelled and kept in refrigerator until they were analyzed.

B. Leaching of metals using simulated gastric fluid

The simulated gastric fluid was prepared by dissolving 60.06 g glycine in 1.9 L of deionized water and adjusting the
pH to 1.54 by adding concentrated HCl. The solution was then brought to a volume of 2 L and warmed in incubator to a temperature of 37°C. Hundred milliliter of the simulated gastric fluid was added into bottle containing 1 g, the mixture was placed in an incubator with shaker and constantly agitated at a speed of 120 rpm; 5 mL of samples were collected at 30, 60, 90, 120 and 150 mins using a 45 µm nitrocellulose syringe filter. The pH of the mixture was simultaneously determined at each sampling period. The filtered solution was diluted by adding 15 mL of deionized water prior to analysis. The metals concentrations in the leachates were then determined using an inductively coupled plasma optical emission spectrometer (ICP-OES).

C. Characterization of clay

Mineralogical studies of geophagic clay were carried out using X-ray diffractometer (XRD). Samples was ground and homogenized to a fine powder and small amounts of powdered samples were loaded on sample holders and mounted in the Philips PW 3710 XRD X-ray diffractometer system for identification of mineral phases. The XRD equipment, which operated at 40 kV and 45 mA, was equipped with Cu-Kα radiation and a graphite monochromator. Samples were scanned at a speed of 1°/2/min; at covering range of 2° to 70°. A PW 1877 automated powder diffraction (APD) XPERT Data Collector software package was employed to capture raw data and a Philips XPERT Graphics and Identity software package was used for qualitative identification and semi quantitative analyses of the minerals from both the data and patterns. X-ray fluorescence spectrometer was used to determined concentration of major and trace element oxides in all the samples of geophagic clays.

III. RESULTS AND DISCUSSION

A. Chemical composition of clays

Results of major oxides (Table 1) show the average SiO₂ values range from 15.56% - 55.62% with the highest value recorded from samples collected at Ikageng field while the samples from Phelandavha field exhibited the lowest value. The concentrations of Al₂O₃ ranged from 5.17% - 33.15% in the clay samples. Geophagic clay samples were generally characterized by relatively high concentrations of SiO₂, Al₂O₃ and Fe₂O₃.Oxides of Si, Al, and Fe made up the greatest values from major and trace elements oxides in all geophagic clay samples(Table 1). Results presented in Table 1 indicate that the concentration of aluminum oxide was lower in sample E than other samples. The concentrations of oxides of Ca, Mg, and Na, were relatively low in all geophagic clay samples, less than 0.6%. Low abundance of MgO and K₂O shows lack of expandable clays [6]. High ratio of SiO₂/Al₂O₃ is related to quartz content.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Minerals</th>
<th>Quartz</th>
<th>Kaolinite</th>
<th>Muscovite</th>
<th>Bentonite</th>
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<td>Ikageng source</td>
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<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ikageng market</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
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</tr>
<tr>
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<td>X</td>
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<td></td>
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<td>Pherialmini market</td>
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</table>

Results show that kaolinite is a dominant clay mineral in geophagic clay samples (except sample from Ikageng), reaching 100%. Kaolin minerals are used as medicines to treat...
the causes and the symptoms of gastrointestinal distress [1]. Others minerals present in the samples were muscovite, gypsum, anatase and illite with few percent.

C. The pH of extraction fluid over specified time

The mobility of metals can be affected by certain factors such pH, soil physical properties, mineralogical and chemical composition, fluid composition [16], however, pH is the most essential parameter affecting the mobility of heavy metal in the soils. Constant shaking was used to simulate movement within stomach. The leached pH increased over the leaching period in samples (Table 3) from Phelandavha and Pheramindi. A slight decrease of pH was recorded in samples from Ikageng market and source as well as Pheramindi market. The cause of variation of leachate pH between 1.32 and 1.67 observed in this experiment is still unknown. When there is a decrease in soil pH, metal solubility and availability increases [16].

D. Dissolution of geophagic clays in gastric fluid and behavior of metals

Previous studies [17; 18] showed that the metals bioaccessibility under low pH (acidic conditions) is consistent with increased metal mobility in soils at low pH. Metals such as Pb, Ni, Co and Fe showed high bioaccessibility with increase mobility. The mobility of the metals was at different pace during the leaching period, it decreased in the order Pb>Ni>Co>Fe>Cu>Zn (Fig 1a, 1b, 2a, 2b, 3a and 3b). Metals are released in various concentrations at different time period of leaching. Iron (Fe) in all samples is released in higher amount as time increases. The effect of time on the release of metals from geophagic clays shows that there is a relative increase in the release overtime. Most metals were released from the first 30 minutes while chromium was initially released after an hour in Pheramindi samples.

Metals were more likely to be released from Phelandavha samples and Pheramindi samples than from the Ikageng samples. For example, from the Phelandavha samples an average of Fe 5.13 mg/L and Cu 0.51 mg/L were released, while from the Pheramindi samples an average of Fe 5.20 mg/L and Cu 0.60 mg/L were released respectively. Comparatively lower amount of metal was released from the Ikageng samples, this is likely due to the presence of bentonite which has high binding affinity for the metals.

### Table III

<table>
<thead>
<tr>
<th>Samples</th>
<th>Initial pH</th>
<th>30 min</th>
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<th>90 min</th>
<th>120 min</th>
<th>150 min</th>
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<td>1.38</td>
<td>1.39</td>
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<td>1.45</td>
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<tr>
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<td>1.4</td>
<td>1.44</td>
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<td>1.43</td>
<td>1.44</td>
</tr>
<tr>
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<td>1.36</td>
<td>1.4</td>
<td>1.41</td>
<td>1.39</td>
<td>1.41</td>
<td>1.4</td>
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<tr>
<td>SP2B</td>
<td>1.34</td>
<td>1.34</td>
<td>1.42</td>
<td>1.42</td>
<td>1.43</td>
<td>1.48</td>
</tr>
</tbody>
</table>

Results are expressed as mean ±SE (n=2). I1A=Ikageng market; S11A=Ikageng source; M1A=Phelandavha market; S1A=Phelandavha source; P1A=Pheramindi market; SP1A=Phelandavha source; 1g; 2g

D. Dissolution of geophagic clays in gastric fluid and behavior of metals

Previous studies [17; 18] showed that the metals bioaccessibility under low pH (acidic conditions) is consistent with increased metal mobility in soils at low pH. Metals such as Pb, Ni, Co and Fe showed high bioaccessibility with increase mobility. The mobility of the metals was at different pace during the leaching period, it decreased in the order Pb>Ni>Co>Fe>Cr>Cu>Zn (Fig 1a, 1b, 2a, 2b, 3a and 3b). Metals are released in various concentrations at different time period of leaching. Iron (Fe) in all samples is released in higher amount as time increases. The effect of time on the
When compared to the adequate daily intake of trace elements in the human body, the amounts of element released from all geophagic clays samples are relatively high (Figure 1a – Figure 3d). The standard limit required for body function of trace elements compared to Pb content that was leached over the leaching period from Pheramindi samples it is significantly high (Figure 3a), in the range of 0.06 - 1.5 mg/L, higher than 20 µg/L set as standard limit for body function. Copper content leached in all geophagic clays samples was in the range of 0.15 mg/L-0.85 mg/L, less than the standard limit required for body function 1000 µg/L (Figure 1a, Figure 3b). The amounts of Zn leached from all the geophagic clays were below 3.81 mg/L which is within the standard limit required for body function 5.0 mg/L.

Average concentration of leached Ni was in the range of 0.06 - 1.5 mg/L, but only 0.025 – 0.03 mg/kg/day is required for body functions. The average Co content in these geophagic clays was in the range of 0.001 – 0.60 mg/L, while the body requirement for this element daily is 0.002 – 0.1 mg/kg. Pb, Ni, Co and Fe were released in concentrations exceeding the value required for the proper functioning of the human body.

IV. CONCLUSION

The amount of leached metals (Pb, Ni, Co and Fe) exceeded the levels recommended, this indicate that these geophagic clay samples may not be safe for human consumption, especially regarding lead as it accumulation in the human body may cause lead poisoning and is associated with damage of central nervous system[9]. The mobility of the metals decreased in the order Pb>Ni>Co>Fe>Cu>Zn. Extraction of metals using simulated gastric fluid suggest that ingestion of contaminated geophagic clay into human gastrointestinal system will be potentially harmfully. The consumers should be educated about the need to process the geophagic clay in the safe way to minimize the amount of contaminants such as metals and microorganisms.

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REFERENCES


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Dr Elvis Fosso-Kankeu has been the recipient of several merit awards.