QUANTIFICATION OF SELECTED ESSENTIAL AND TOXIC MINERALS IN GEOPHAGIC MATERIALS IN KIAMBU COUNTY, KENYA

BY

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FEBRUARY, 2016
DECLARATION

This thesis is my original work and has not been presented for the award of any degree in any university or any other institution of higher learning.

Signature ..................................................  Date ...........................................

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SUPERVISORS

We confirm that the work reported in this thesis was carried out by the candidate and has been submitted with our approval as university supervisors.

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Signature ..................................................  Date ...........................................

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Department of Chemistry
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DEDICATION

To my lovely sisters: Wairimu, Njeri and Wambui
ACKNOWLEDGEMENTS

I am greatly indebted to the Almighty God for enabling me to pursue this course. May His Name be highly glorified. Many individuals contributed to the success of this work. My sincere gratitude goes to my supervisors, Prof. Nyambaka Hudson and Dr. Nawiri Mildred for their tireless guidance and counsel throughout the process of carrying out this study. Their invaluable suggestions, advice and criticisms contributed to the completion and success of this work. Further gratitude goes to all lecturers and laboratory technicians in the Chemistry department who helped me in the course of my study. I also acknowledge staff at Kenya Geology and Mines where I did my research work. I am also highly indebted to staff at International Journal of Modern Chemistry and Applied Sciences for accepting to publish a paper from this work titled: *Understanding Geophagic Practice as a Source of Mineral Nutrients and Toxicants.*

I also extend my sincere thanks to my colleagues David Muli, Samwel Nyamu, Paul Wafula and David Ywaya for their moral support, encouragement and companionship at every stage of the study. Finally, yet important, deep appreciation is extended to my dear family and friends for their encouragement and support throughout the study period.

MAY GOD BLESS YOU ALL
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ABBREVIATIONS AND ACRONYMS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AAS</td>
<td>Atomic absorption spectroscopy</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of variance</td>
</tr>
<tr>
<td>ATSDR</td>
<td>Agency for toxic substances and disease registry</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>DSP</td>
<td>District strategic plan</td>
</tr>
<tr>
<td>EFSA</td>
<td>European food safety authority</td>
</tr>
<tr>
<td>HEAL</td>
<td>Human ecology action league</td>
</tr>
<tr>
<td>KEBS</td>
<td>Kenya bureau of standards</td>
</tr>
<tr>
<td>ND</td>
<td>Not detected</td>
</tr>
<tr>
<td>RDA</td>
<td>Recommended daily average</td>
</tr>
<tr>
<td>RDI</td>
<td>Recommended daily intake</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SPSS</td>
<td>Statistical package for social sciences</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>WHO</td>
<td>World health organization</td>
</tr>
</tbody>
</table>
Pica is described as the craving and subsequent consumption of non-food substances including earth, charcoal and uncooked rice. Various hypothesis have been fronted to explain pica among them hunger, micronutrient deficiency and protection. Geophagy, a special type of pica applicable to the deliberate consumption of soil and clay deposits cuts across socio-economic, ethnic, religious and racial divides due to cultural, medicinal, physiological and nutritional factors. In sub-Saharan Africa, its popularity has been increasing overtime especially among pregnant women and children under the age of five. Kenya has the highest prevalence rate (89.8%) of the geophagic practice as compared to other African countries. In Kiambu County, an upward trend has been exhibited in the sales made from geophagic materials. With the increase in the geophagic practice in Kiambu County, it is necessary to investigate potential benefits and/or dangers of the materials consumed with respect to their essential and toxic minerals level. The study aimed at examining the levels of essential minerals (Ca, Mg, Fe, Mn and Zn) and toxic minerals (Al, Si and Pb) in geophagic materials from Kiambu County. They were purposively sampled from eight quarry mines, four brands in supermarkets, and yellow and white colours in open-air markets and analyzed using Atomic Absorption Spectroscopy (AAS). The data was analyzed using Analysis of Variance (ANOVA) and t-test. The range was found to be ND - 27.9±0.02 (Ca), ND - 0.18±0.00 (Mg), 0.42±0.00 - 4.83±0.02 (Fe), ND - 0.23±0.03 (Mn) 64.6±0.35 - 233.0±0.89 (Al) and 184.1±0.14 – 291.8±0.34 mg/g (Si). The concentration of Zn and Pb was 10.89±0.32 - 161.67±0.03 and 1.09±0.02 - 79.67±0.04 ppm respectively. Most of the minerals varied significantly (α=0.05) and could be due to differences in their origin. Comparing essential minerals level to Recommended Daily Intakes (RDI) while assuming a 50.0% bioavailability indicated that the minerals were not present in appreciable amounts and therefore have negligible contribution (except for Fe in all the three sources and Mn in some of the sources). For toxic minerals, Al obtained from the three sources was below World Health Organization (WHO) and European Food Safety Authority (EFSA) limits. However, Si and Pb levels were found to be above the WHO/EFSA which has the potential of endangering the health of the individual. With an exception of Fe and Mn, findings point to fears of toxicity. Therefore, there is need to discourage the practice as geophagic individuals expose themselves to health risks associated with toxicity.
CHAPTER ONE

INTRODUCTION

1.1 Background to the study

Pica, the craving and subsequent consumption of non-food substances including earth, charcoal, ice and uncooked rice has researchers hypothesizing various motivations (ATSDR, 2001; Young et al., 2008). They include hunger where individuals consume non-food substances because they have nothing else to eat; micronutrient deficiency which posits that people eat non-food substances because they are deficient in micronutrients and protection hypothesis which states that pica is motivated in an attempt to reduce the harmful effects of plant chemicals or microbes (Wiley and Katz, 1998; Flaxman and Sherman, 2000; Prasad, 2001; Hui et al., 2001; Hooda et al., 2004; Young, 2007). Geophagy is a special type of pica applicable to the deliberate consumption of soil and clay deposits by animals, including humans (Wilson, 2003). It cuts across socio-economic, ethnic, religious and racial divides and has been observed in hundred of cultures on all inhabited continents (Young et al., 2011).

Geophagic tendencies have been postulated to arise from cultural, medicinal, physiological and nutritional factors (Callahan, 2003; Songca et al., 2010). Studies have reported variation in levels of essential and toxic minerals found in geophagic materials obtained from different parts of the world (Ekosse and Jumbam, 2010; Gichuki et al., 2011; Okunlola and Owoyemi, 2011). Since different regions of the earth’s crust vary in levels of minerals because of differences in their physical, mineralogical and chemical properties, there are positive and negative health effects of ingesting soils (Diamond,
Such effects vary depending on the mineralogy and chemical composition of the ingested soils which are largely influenced by the soils pedogenetic development, the quantity of soil ingested and the rate of consumption (Ngole and Ekosse, 2012).

Soil and clay deposits can be significant sources of minerals which are essential to the body. Calcium helps maintain the strength of bones and the internal support structure of the whole body (Shills, 2006). Magnesium works to maintain the $\text{pH}$ balance in the body which is critical for the healthy functioning of nerves and muscles and also helps regulate the heart rhythm (Fox et al., 2004). Zinc is important for the production of enzymes that help our immune system function effectively (Coleman, 2012). Iron is necessary for oxygen transport in the blood from the lungs and carries it to all of the other cells in the body (Casiday and Frey, 2010). After examining sand fractions of geophagic soils, Mahaney et al. (2000) confirmed that they contain mineral constituents and may therefore have a role in mineral supplementation.

Although some soil and clay samples contain essential minerals in appreciable amounts, other samples are reported to be in low levels (Okunlola and Owoyemi, 2011; Ekosse et al., 2011). Geophagic clays from southern Nigeria were reported to have the essential elements that are otherwise not available in appreciable amounts for absorption into the digestive system from consumption of such clays (Okunlola and Owoyemi, 2011). Further, Ekosse et al. (2011) concluded that the percentage of recommended daily
intake (RDI) of nutrients supplied by clay samples to geophagic individuals (persons who practice geophagy) was below average human nutritional needs.

Soils and clay deposits have also been reported to contain toxic minerals such as lead, chromium, arsenic and aluminium that can lead to metal toxicity even in low levels (Ekosse and Jumbam, 2010). High levels of Al in the body can lead to memory loss and dementias with recent investigations having implicated aluminum toxicity in Alzheimer's disease and other brain and senility syndromes (Kawahara and Kato-Negishi, 2011). Lead exposure can result to maternal and fetal kidney damage and impaired cognitive function (Cahnfield et al., 2003). High Pb levels interfere with the production of blood cells and subsequently, the absorption of calcium which is required for healthy and strong bones. World Health Organization (WHO) and European Food Safety Authority (EFSA) group limits Al and Pb to 1 mg/kg and 0.01 ppm respectively (WHO, 1996; EFSA, 2009). Geophagic materials sold in open-air markets in Eastern, Nairobi and Nyanza provinces of Kenya have been reported to contain Pb beyond the WHO recommended levels posing risk of Pb poisoning (Gichuki et al., 2011).

Since geophagic materials have been reported to contain both essential and toxic minerals, studies on the materials that could provide clues on the relationship between soil's mineralogical properties and health effect on geophagic individuals. Determining mineral composition can aid in identifying the motivation behind geophagic practice (Wilson, 2003; Young et al., 2008).
In sub-Saharan Africa, the popularity of the geophagic practice has been increasing overtime especially among pregnant women and children aged below five years (Geissler, 2000). Pregnant women, lactating mothers and children have been reported to ingest soil on a daily basis (Luoba et al., 2004; Kutalek et al., 2010). Selling of geophagic materials is a common phenomenon in many African societies. In Nigeria, clay is mined in large quantities from quarry mines and distributed for sale in open-air markets all over West Africa (Ekosse and Jumbam, 2010). Apart from obtaining geophagic materials from quarry mines, they are sold in open air markets and in supermarkets.

Kenya has the highest prevalence of geophagy at 89.8% as compared to other African countries with about 70% of school-going children in the Western part of the country and 56% of pregnant women in the Coastal region reported to consume soil on a daily basis (Geissler et al., 1997; Geissler et al., 1999; Luoba et al., 2004, Ngozi, 2008). In Kiambu County, an upward trend has been exhibited in sales made from geophagic materials. Geophagic individuals obtain soil and clay from walls of mud houses, termite moulds, quarry mines and hills (Gichumbi et al., 2012). In other instances, they buy them from either open-air markets or branded products found in supermarkets where names such as Udongo and roasted clay soil are used. Geophagic materials present in the open-air markets are mainly yellow or white in colour with the yellow colour being attributed to presence of hematite and goethite minerals (Ngole et al., 2010; Ekosse and Jumbam, 2010).
1.2 Problem statement and justification

In sub-Saharan Africa, the popularity of geophagic practice has been increasing overtime especially among pregnant women and children aged below five years. Different parts of the world have different levels of essential and toxic minerals due to differing mineralogy and chemical composition. These differences result in positive and/or negative health effects of ingesting soils. Positive health effects are due to availability of nutrients in the soil while negative health effects are as a result of presence of toxic minerals. This has led to conflicting views with regards to the suitability of the practice based on RDA and EFSA/WHO limits. While some studies recommend the practice based on nutritional value in the geophagic materials others discourage the practice due to toxic minerals which can endanger the health of the geophagic individual. With the increase in sales made from geophagic materials specifically in Kiambu County, it was therefore necessary to investigate the extent of safety of materials consumed with respect to their essential and toxic minerals level.

1.3 Hypotheses

i. The levels of essential minerals present in geophagic materials found in quarry mines, supermarkets and open-air markets in Kiambu County are below RDI levels.

ii. The levels of toxic minerals present in geophagic materials found in quarry mines, supermarkets and open-air markets in Kiambu County are above the WHO/EFSA limits.
1.4 Objectives

1.4.1 General objective

To determine the levels of essential and toxic minerals in geophagic materials found in quarry mines, supermarkets and open-air markets in Kiambu County so as to identify the extent of their chemical safety.

1.4.2 Specific objectives

i. To determine the levels of essential minerals (Ca, Mg, Fe, Mn and Zn) in geophagic materials found in quarry mines, supermarkets and open-air markets in Kiambu County.

ii. To determine the levels of toxic minerals (Al, Si and Pb) in geophagic materials found in quarry mines, supermarkets and open-air markets in Kiambu County.

1.5 Significance of the study

Consuming geophagic materials, particularly during pregnancy, clearly has substantial and pertinent implications for maternal and child health. The extent of safety of the geophagic materials deserves a closer examination. The results of this study will be useful in providing baseline data on the mineral content of geophagic materials consumed by geophagic individuals in Kiambu County. The data will be used to enhance awareness on potential nutritional and/or the extent of toxicity exposure accruing from consuming geophagic materials.
1.6 Scope and limitation of the study

Although there are over 2000 essential and toxic minerals, this study focused on Ca, Fe, Mg, Zn, Mn, Al, Si and Pb. Only geophagic materials from quarry mines, supermarkets and open-air markets in Kiambu County were investigated. The source of materials sold in supermarkets and open-air markets were not considered. The following branded products available in supermarkets were analyzed leaving out other products: *udongo*, *udongo whole*, *roasted udongo* and *roasted clay soil*. In open-air markets, yellow and white soils were investigated.
CHAPTER TWO
LITERATURE REVIEW

2.1 Geophagy

Pica, defined as the craving and subsequent consumption of non-food substances such as earth, charcoal, uncooked rice, starch, and ice has been investigated for more than 2000 years (ATSDR, 2001; Young et al., 2008). There are three major groups of hypotheses that have been postulated in relation to the physiological causes of pica: hunger, micronutrient deficiency and protection from toxins and pathogens (Wiley and Katz, 1998; Flaxman and Sherman, 2000; Prasad, 2001; Hui et al., 2001; Hooda et al., 2004; Young, 2007). The hunger hypothesis posits that people eat non-food substances because they are have nothing else to eat. The micronutrient deficiency (nutritional) hypothesis posits that people eat non-food substances because they are deficient in micronutrients such as iron, zinc, calcium, or some other micronutrients (Wiley and Katz, 1998; Prasad, 2001). The third hypothesis is the protection hypothesis which states that pica is motivated in an attempt to reduce the harmful effects of plant chemicals or microbes where pica substances protect by either adsorption of pathogens and toxins within the gut lumen, or coating the surface of the intestinal endothelium, in turn rendering it less permeable to toxins and pathogens (Flaxman and Sherman, 2000; Hui et al., 2001).

Geophagy, which is a special type of pica referring to the deliberate consumption of soil/clay was first documented by Hippocrates (460–380 BC) more than 2000 years ago
(Reilly and Henry, 2000; Wilson, 2003). The practice has been ongoing for centuries and cuts across socio-economic, ethnic, religious and racial divides (Songca et al., 2010). Geophagic tendencies have been postulated to arise from cultural, medicinal, physiological and nutritional factors (Callahan, 2003; Songca et al., 2010).

The dietary practice of geophagy still occurs in many parts of the world. It has been reported to be practiced in Africa, America including USA, Asia including India and China, Australia and Europe (Boyle and Mackay, 1999; Reilly and Henry, 2000; Utara, 2002; Woywodt and Kiss, 2002). Previously, geophagy was believed to be common among communities of low social status; however, recent studies have indicated that pregnant females in affluent societies also indulge in geophagic practice (Ngole and Ekosse, 2012). Although the practice is common among pregnant women, women of all ages, irrespective of their educational level and social status engage in the habit (Geissler et al., 1999; Prince et al., 1999; Woywodt and Kiss, 2002; Callahan, 2003; Songca et al., 2010). In sub-Saharan Africa, it is more prevalent among pregnant women, lactating mothers and children under the age of five especially those living in rural areas where culture and indigenous practices remain prevalent and well-established (Kutalek et al., 2010; Ngole and Ekosse, 2012).

Kenya has been reported to have the highest prevalence rate of 89.8% geophagy as compared to South Africa 61%, Namibia 42% and Tanzania 28%, with about 70% of school-going children in the Western part of the country and 56% of pregnant women in the Coastal region reported to consume soil on a daily basis (Geissler et al., 1997;
Thompson, 1997; Geissler et al., 1998; Geissler et al., 1999; Antelman et al., 2000; Luoba et al., 2004; Ekosse and De-Jager, 2011). A study comprising of 827 pregnant women hailing from Bondo County, Kenya found out that geophagy is very common in the region. The study which aimed at investigating the extent and health impact of geophagy in pregnant women and lactating women concluded that the high prevalence of the practice deserves a closer examination. A similar study in Coast province, Kenya revealed that most pregnant women (70%) and young children (56%) ingest soil on a daily basis (Geissler et al., 1999). The study concluded that there is need for more studies to be undertaken on the role of soil eating and its impact on nutritional status.

Many sites are available from which soil/clay can be obtained including the walls of mud houses, termite moulds, quarry mines and hills in rural areas (Luoba et al., 2004; Young et al., 2011). Previous studies have shown that the percentage of RDA of nutrients supplied by clay samples to geophagic individuals vary with the source (Ekosse et al., 2011). The variation is as a result of physico-chemistry, mineralogy and geochemistry of the ingested soils which is mainly influenced by the soils pedogenetic development and the quantity of soil/clay ingested (Ngole and Ekosse, 2012).

In Kiambu County of Kenya, quarry mines where murram is normally mined to construct or repair roads are sources of geophagic materials. Although not previously a common phenomenon, supermarkets in the region are nowadays selling geophagic materials in a variety of sizes at prices ranging from 0.6$ to 2.0$ depending on the size and the packaging company. Udongo, udongo whole, roasted udongo and roasted clay
soil are some of the brand names. Geophagic materials are also sold in open-air markets in varying portions depending on the purchasing power of the consumer (Njoki and Kiprono, 2009). Most preferred colours are yellow and white in colour with the yellow colour being attributed to presence of hematite and goethite minerals (Ngole et al., 2010; Ekosse et al., 2011).

2.2 Essential and toxic minerals

Minerals occur naturally in nonliving things such as rocks and metal ores and can either be classified into essential and toxic minerals; depending on whether they have important functions in the body (essential) or have no known function in the body (toxic) (Vassilev et al., 2009; Rinzler, 2011). Essential minerals are further classified into macrominerals (required in large quantities) and microminerals (needed in small quantities but toxic in excess levels) (Marschallinger, 1997). Some of the essential macrominerals include Ca, Mg, K and Na whereas Fe, Mn, Se, Ti and Zn are some of essential microminerals. Al, As, Si, Po and Pb are some of the minerals that are toxic in the body. The elements considered in this study are discussed in the following subsections.

2.2.1 Calcium

Calcium is the fifth most abundant element of the earth’s crust accounting for 3.6 %. It is not found free in nature since it easily forms compounds present mainly in form of carbonates, sulphates, fluorides, silicates and borates. It is the most abundant element in
our bodies with 99% being found in teeth and bones whereas the rest is distributed in ionic form throughout our system in blood, cells and tissues. It is probably the most important essential mineral needed by the body because it helps maintain the strength of bones, the internal support structure of the whole body (Shills, 2006). Calcium deficiency in children results in short bones, especially in the arms and legs, but also can have a great impact on the bones in the ribcage. In adults, a calcium deficiency leads to brittle bones that break easily. For essential macrominerals, RDI levels are used to identify average requirements needed by individuals to adequately meet nutritional needs. Table 2.1 shows RDI for Calcium.

<table>
<thead>
<tr>
<th>Group</th>
<th>Range in years</th>
<th>RDI in mg/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Childhood</td>
<td>0-8</td>
<td>200-1000</td>
</tr>
<tr>
<td>Adolescent</td>
<td>9-18</td>
<td>1300</td>
</tr>
<tr>
<td>Adult</td>
<td>19-70</td>
<td>1000-1200</td>
</tr>
<tr>
<td>Maturity</td>
<td>&gt;70</td>
<td>1200</td>
</tr>
<tr>
<td>Pregnancy/lactation</td>
<td>-</td>
<td>1000-1300</td>
</tr>
</tbody>
</table>

Source: (Food and Nutrition Board, 2011)

In pregnant women, extra Ca is required for skeletal and bone development of the fetus. In lactating mothers, significant demineralization of maternal bone occurs to meet the increased calcium demand of the neonate (Kalkwarf, 2006). Nutritional sources of Ca include milk, yogurt, cheese, Chinese cabbage, kale, spinach and broccoli (Food and Nutrition Board, 2010).

Calcium-rich clays have diverse benefits among pregnant and lactating women (Wiley and Katz, 1998; Lakudzula and Khonje, 2011). Wiley and Katz (1998) observed that
clay serves as an important Ca supplement as it reduces risk of skeletal problems in the fetus. Contribution of 0.2 % of WHO recommended daily minimum intake of dietary Ca based on an average ingestion of 50 g of Blantyre and Indian ‘edible’ soils sold in Malawi have been reported (Lakudzula and Khonje, 2011). Aufreiter et al. (1997) found out that geophagic soils from China had high content of more than 14 mg/g (2.0 %wt) of Ca mineral and concluded that such soil could be a significant source of Ca. Similar findings were reported by Ekosse and Jumbam (2010). They found Ca to be 0.1 - 0.6 mg/g (0.01 – 2.53 %wt) in clay samples from Cameroon and Nigeria and concluded that geophagic individuals who consumed such clays could possibly benefit from the Ca present.

Contrary to the potential benefits of Ca emanating from consuming geophagic materials, Ngole and Ekosse (2012) found the levels of Ca to range between 0.1 - 18.1 mg/g (0.01 – 2.53 %wt) in geophagic soils from Eastern Cape-South Africa. On assuming a 50 % bioaccessibility rate, they deduced that geophagic individual consuming 5 - 30 g of soil per day would be supplied with less than 1 % of RDI. They concluded that Ca present in the soils could negligibly contribute to the nutrient demands of the geophagic individual irrespective of their age. Gichumbi et al. (2012) reported that samples obtained from open-air markets in Kiambu had Ca content 2.2 - 5.4 mg/g (0.31 - 0.76 %wt). They concluded that the samples were not a significant source of Ca mineral. Further, Ngole et al. (2010) reported that Swaziland and South Africa soil samples had values of Ca content of 7.1 - 18.1 mg/g (1.0 - 2.53 %wt) and could compromise the nutrient supplementing capability of the soils. Okunlola and
Owoyemi (2011) found out that preliminary nutritional value of the southern Nigeria geophagic materials analyzed had minimal nutritional value of Ca (11.4 mg/g) which was low as compared to average human nutritional values. Varied conclusions with regards to geophagic materials being a significant source of Ca mineral necessitated this study.

2.2.2 Magnesium

The abundance of magnesium in the Earth's crust is estimated to be 2.1 % making it the sixth most common element in the earth. Some of the naturally occurring minerals of magnesium are dolomite, magnesite, carnallite and epsomite. Magnesium works to maintain the acid/alkaline balance in the body which is critical for the healthy functioning of nerves and muscles and also helps regulate the heart rhythm to keep it steady, normalizes blood pressure and helps regulate blood sugar levels (Fox et al., 2004). Magnesium is also important for proper metabolism of calcium, phosphorus, sodium, potassium, and vitamin D.

Magnesium has been found to influence the body’s utilization of vitamin D by activating cellular enzymatic activity (Zofková and Kancheva, 1995). Common conditions such as migraines, attention deficit disorder, mitral valve prolapse, fibromyalgia, asthma and allergies have been linked to Mg deficiency (Moshfegh et al., 2005). The RDI levels are used to identify average Mg requirements needed by individuals to adequately meet nutritional needs. Table 2.2 shows recommended daily intake levels for Mg.
Nutritional sources of Mg include legumes, nuts, seeds, fish and whole grains (Canadian Nutrient File 2010). Ekosse and Jumbam (2010) analyzed clay samples from Cameroon and Nigeria and found Mg levels to be 0.1 - 6.0 mg/g (0.02 - 1.00 %wt) with an exception of one sample (195.8 mg/g). They concluded that such clays could be a useful mineral supplement to the geophagic individuals. Ngole et al. (2010) upon analyzing Swaziland and South Africa soil samples reported that the Mg levels (0.1 - 9.1 mg/g) could supplement the nutritional needs of the geophagic individual. Although the materials’ contribution is less than RDI, the authors concluded that geophagic materials could supplement the much-needed nutrients in the body especially for the pregnant women who crave for these materials.

Ngole and Ekosse (2012) analyzed geophagic soils from Eastern Cape-South Africa for Mg content. They found the levels of Mg to be in the range (2.1 - 9.1 mg/g). Assuming a 50 % bioaccessibility rate, they reported that geophagic individual consuming 5 - 30 g of soil per day would be supplied with less than 1 % of RDI. They concluded that the bioaccessible fraction of Mg in the studied geophagic samples makes little contribution to the nutrient demand of a geophagic adult. Lakudzula and Khonje (2011) reported

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**Table 2.2: Recommended Daily Intake (RDI) for Mg**

<table>
<thead>
<tr>
<th>Group</th>
<th>Range in years</th>
<th>RDI in mg/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Childhood</td>
<td>0-8</td>
<td>30-140</td>
</tr>
<tr>
<td>Adolescent</td>
<td>9-18</td>
<td>240-410</td>
</tr>
<tr>
<td>Adult</td>
<td>19-70</td>
<td>310-420</td>
</tr>
<tr>
<td>Maturity</td>
<td>&gt;70</td>
<td>310-420</td>
</tr>
<tr>
<td>Pregnancy/Lactation</td>
<td>-</td>
<td>310-420</td>
</tr>
</tbody>
</table>

*Source: (Food and Nutrition Board, 2011)*
similar observations after analyzing Blantyre and Indian ‘edible’ soils sold in Malawi. Based on an average ingestion of 50 g of soil, they found out that such soils contributed only 0.006% of WHO recommended daily minimum intake of dietary Mg. They concluded that ingesting such soils could not sufficiently contribute to dietary Mg needed by geophagic individuals.

Gichumbi et al. (2012) reported samples obtained from Kiambu County could not be a significant source of the mineral since Mg range was 1.7 - 3.2 mg/g (0.28 - 0.54 %wt). Similarly, Okunlola and Owoyemi (2011) found out Mg was present in low levels (0.2 - 11.5 mg/g) for geophagic materials obtained from southern Nigeria. The low values showed that the essential mineral is not present in appreciable amounts for absorption into the digestive system of the geophagic individual. Data from Mg elemental analyses (0.9 mg/g) of Rwandan soil samples eaten by gorillas led Mahaney et al. (2000) to conclude that mineral supplementation is not an explanation for geophagy. The following study was undertaken to determine the levels of Mg in geophagic materials because there are varied conclusions on whether such materials could be a significant source.

### 2.2.3 Iron

Iron is ranked fourth in abundance comprising nearly 5.6 % of the earth's crust. It rarely occurs in nature as a native metal but in combination with oxygen and sulphur forming oxides and sulphides respectively. In our bodies, iron is necessary for oxygen transport in the blood since it is the central atom of the heme group, a metal complex that binds
molecular oxygen (O$_2$) in the lungs and carries it to all of the other cells in the body that need oxygen to perform their activities. Without iron in the heme group, there would be no site for the oxygen to bind, and thus no oxygen would be delivered to the cells resulting in cells dying (Casiday and Frey, 2010). The RDI levels are used to identify average requirements needed by individuals to adequately meet nutritional needs. Table 2.3 gives the RDI for Fe.

Table 2.3: Recommended Daily Intake (RDI) for Fe

<table>
<thead>
<tr>
<th>Group</th>
<th>Range in years</th>
<th>RDI in mg/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Childhood</td>
<td>0-8</td>
<td>0.27-11.0</td>
</tr>
<tr>
<td>Adolescent</td>
<td>9-18</td>
<td>8.0-15.0</td>
</tr>
<tr>
<td>Adult</td>
<td>19-70</td>
<td>8.0-18.0</td>
</tr>
<tr>
<td>Maturity</td>
<td>&gt;70</td>
<td>9.0</td>
</tr>
<tr>
<td>Pregnancy/Lactation</td>
<td>-</td>
<td>9.0-27.0</td>
</tr>
</tbody>
</table>

Source: (Food and Nutrition Board, 2011)

Nutritional sources of Fe include meat, fish, poultry, dried beans, peas and lentils (Canadian Nutrient File, 2010). Various studies have shown that clay soils contain beneficial amounts of Fe. After XRD examination tests of geophagic samples obtained from Embu, Meru and Chuka town of Eastern Province, Kenya, the levels of Fe were found to be 37.0 - 68.9 mg/g (5.28 - 9.84 %wt) (Mwangi and Ombaka, 2010). The study concluded that geophagic soil obtained from these regions could be a source of Fe supplement. Geophagy was assessed as part of cross-sectional study among 156 primary school children in Western Kenya (Geissler et al., 1997). An analysis of the soil ingested by the children revealed a mean HCl-extractable content of 168.9 mg/kg. Based on the data, the soil could provide an average of 4.7 mg iron which is equivalent to 32 % and 42 % RDI for girls and boys aged 14-48 years respectively. They
concluded that geophagic materials contain beneficial amounts of Fe. However, to fully clarify on the possible impact of the iron present in the soils more studies were suggested.

After analyzing the acid extractable mineral nutrient content of three tropical geophagical soils from Thailand, Uganda, and Zaire soils, in conjunction with an assumed soil ingestion rate, Abrahams and Parsons (1997) concluded that soils could supply a significant proportion of the recommended intake of 17% in the case of Fe. This aspect was further investigated by Abrahams (1997) in a study of a sample set of 13 geophagic soils from Uganda, most of which were being sold as medicines in local markets. Based on geochemical analysis, the author concluded that that daily consumption of 5 g of one soil was capable of contributing 19 - 25% of the daily recommended nutrient intake (RNI) of Fe. However, the bioavailability of Fe in all the other soils examined, as assessed by 0.1 M HCl extraction, contributed less than 1% of RDI.

Another study by Gichumbi et al. (2012) found the levels of Fe in geophagic samples to be 45.1 - 62.2 mg/g (6.43 - 8.88 %wt) and concluded that the high levels of iron may explain why female populations are known to develop exceptional cravings for these materials during pregnancies, when they are more likely to be anemic. On studying weathered tropical soil samples, Fontes et al. (2005) found hematite present since they were brownish and yellowish in colour. This was attributed to the presence of Fe-bearing mineral and Fe-oxides in the soils. The study concluded that such materials may
supply Fe to needy pregnant women. Another study that reported the presence of Fe-containing minerals in geophagic materials (64.4 - 88.9 mg/g) was undertaken by Gichumbi et al. (2012). The study concluded that the presence of Fe-containing minerals could explain the micronutrient hypothesis.

Different findings have been reported in other studies. A pioneering study of geophagic materials from Eastern Cape Province in South Africa which had its preliminary objective as understanding physico-chemistry, mineralogy, geochemistry and inferring on nutrient bioaccessibility found the levels of Fe to be 9.0 - 55.2 mg/g (1.29 - 7.89 %wt) (Ngole and Ekosse, 2012). Based on calculations of nutrient bioaccessibility, the authors concluded that Fe in the soils could not sufficiently contribute to the nutrient demands of the geophagic individuals. Ekosse et al. (2011) undertook a study designed to appraise nutrient properties of geophagic materials obtained from Swaziland and Eastern Cape Province of South Africa and found the level of Fe to be 1.61 - 64.2 mg/g. The study concluded that the nutrient supplementing capability of such soils is compromised by the low levels.

Further, Ngole et al. (2012) reported Fe to be in the range 5.9 - 145.7 mg/g (0.84 - 20.82 %wt) and observed that geophagic materials could negligibly supply the nutrient demands of the geophagic individual. Based on preliminary nutritional value, Okunlola and Owoyemi (2011) observed that geophagic materials have minimal nutritional value. The mean value of Fe (2.0 %) was low as compared to average human nutritional needs. This indicates that essential elements are not available in appreciable amounts for
absorption into the digestive system after consumption of the geophagic clays. The varied findings and conclusions on whether soil could contribute a significant amount of Fe necessitated the following study.

2.2.4 Manganese

Manganese is widely distributed in the terrestrial crust with its percentage abundance being 0.11%. It is usually associated with the iron ores, in relatively small concentrations. The principal manganese ores are in the form of oxides, hydroxides and silicates. Manganese is a trace mineral that helps the body convert protein and fat to energy. It also promotes normal bone growth, helps maintain healthy reproductive, nervous, and immune systems, and is involved in blood sugar regulation. In addition, manganese is involved in blood clotting and the formation of cartilage and lubricating fluid in the joints (Staff, 2008). Rich sources of manganese include whole grains, nuts, leafy vegetables and teas (Institute of Medicine, 2001). The RDI levels are used to identify average requirements needed by individuals to adequately meet nutritional needs. Table 2.4 shows recommended daily intake levels for Mn.

Table 2.4: Recommended Daily Intake (RDI) for Mn

<table>
<thead>
<tr>
<th>Group</th>
<th>Range in years</th>
<th>RDI in mg/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Childhood</td>
<td>0-8</td>
<td>0.003-1.5</td>
</tr>
<tr>
<td>Adolescent</td>
<td>9-18</td>
<td>1.9-2.2</td>
</tr>
<tr>
<td>Adult</td>
<td>19-70</td>
<td>1.8-2.3</td>
</tr>
<tr>
<td>Maturity</td>
<td>&gt;70</td>
<td>1.8-2.3</td>
</tr>
<tr>
<td>Pregnancy/Lactation</td>
<td>-</td>
<td>2.0-2.6</td>
</tr>
</tbody>
</table>

Source: (Food and Nutrition Board, 2011)
Manganese in excess can inhibit proper functioning of the human body resulting to deleterious effects. Elevated levels of manganese in the body may result in multiple neurologic problems (Keen et al., 1999). It is a well-recognized health hazard for people who inhale manganese dust, such as welders and smelters. World Health Organization (1996) limits manganese levels to 2.0 - 5.0 mg/day whereas EFSA (2009) recommends 4 mg manganese/day.

Longo-Mbenza and Ekosse (2011) reported geophagic materials to have high supply of Mn and concluded that clay has high content of Mn than any other soil and therefore could supplement Mn needed in the body. Ekosse and Anyangwe (2012) found out that geophagic materials obtained from Botswana have the potential to provide Mn needed by humans.

Other studies have reported different findings. Ekosse and De-Jager (2011) reported that clay materials contain low levels of Mn in the range 0.0 - 1.1 mg/g (0.0 - 0.14 %wt). The nutrient supplementing ability of the soils is therefore compromised because of the low concentration of Mn in the geophagic materials. In agreement with the findings of Ekosse and De-Jager (2011), Odewumi (2011) reported Mn to be 0.2 - 0.4 mg/g (161 - 403 ppm) in geophagic materials obtained from Share area, Nigeria. The authors concluded that such materials can have adverse effects on the consumer like increasing the gastrointestinal pH and binding points of plant toxins and pathogens. Ngole and Ekosse (2012) reported Mn to be less than 1.0 % present in geophagic materials obtained from Eastern Cape, South Africa and based on nutrient biaccessibility
calculations concluded that the soils could negligibly contribute to the nutrient demands of the geophagic individual. The study suggested that further studies be done to better explain the practice.

2.2.5 Zinc

The abundance of zinc in the Earth's crust is estimated to be about 0.02%. It never occurs as a free element in the earth. Some of its most important ores are smithsonite, sphalerite, zincite, willemite and franklinite. Zinc is an essential mineral our bodies need and is found in just about every cell in our bodies. It is important for the production of enzymes that help our immune system function effectively and in regulating cell division and growth and wound healing (Coleman, 2012).

Zinc in high concentration can result in acute Zn poisoning although only a few occurrences of acute Zn poisoning have been reported after ingestion of 4 - 8 g (60 - 120 mmol) zinc. Long-term higher Zn intakes than the requirements could, however, interact with the metabolism of other trace elements. Prolonged intake of Zn ranging from 100 - 150 mg/day interferes with copper metabolism and causes low copper status, reduced iron function, red blood cell microcytosis, and thus reduced immune function (Nations et al., 2008; Spains et al., 2009). In order to determine average requirements needed by individuals, RDI levels are used. Table 2.5 gives the RDI for Zn.
Rich sources of zinc include seafood, meat, seeds, and cooked dried beans, peas and lentils (Canadian Nutrient File, 2010). Okunlola and Owoyemi (2011) concluded that the geophagic materials’ content for zinc whose range was 43.17 - 200.13 ppm, was in consistent with the human body content and can therefore act as a source of zinc to geophagic individual. Similarly, Gichumbi et al. (2012) reported that geophagic materials can supply zinc supplement since the range was 0.65 - 0.95 ppm. Ekosse et al. (2011) reported Zn to be in the range 9.1 - 85.0 ppm which was above the RDA values and observed that such geophagic materials could supply the nutrient demands of the geophagic individual.

Different findings have been reported by study carried out by Ngole and Ekosse (2012). Based on calculations of nutrient bioaccessibility, the study concluded that the minerals in geophagic materials could not sufficiently contribute to the nutrient demands of the geophagic individuals. They found geophagic materials to contain Zn in the range 23.0 - 127.0 ppm. Hooda et al. (2004) reported the levels of Zn present in geophagic materials to be in the range 24 - 88 mg/kg. The study concluded that although the Zn present was in appreciable amounts, the ingestion of these relatively Zn-rich soils may hinder the
absorption of bioavailable Zn because absorption depends on the dissolution of the gastrointestinal tract. The conflicting conclusions on whether geophagic materials could be a significant source of Zn necessitated this study.

2.2.6 Aluminum

Aluminium is among the most plentiful elements in the earth's crust constituting about 8% of the total mineral components (Verstraeten et al., 2008). It always occurs in combination with other elements most commonly aluminosilicates, oxides and hydroxides in soils and rocks. Aluminium was thought to be one of the least toxic metals but exposure to elevated concentrations of bioavailable aluminium leads to a wide variety of health effects (Kawahara and Kato-Negishi, 2011). High levels of Al in the body can lead to memory loss and dementias with recent investigations have implicated aluminum toxicity in Alzheimer's disease and other brain and senility syndromes (Kawahara and Kato-Negishi, 2011). In some cases, its atomic size and electric charge (0.051 nm and 3+, respectively) makes it a competitive inhibitor of several essential elements of similar characteristics such as Fe (0.064 nm, 3+).

High levels of exchangeable Al have been found in soils derived from granite and sedimentary rocks in North East Victoria, sandy soils in East Gippsland, krasnozems across Victoria and in peaty soils in Western Victoria (Krewski et al., 2009). Following oral exposure, Al distributes itself throughout the organism, with accumulation in bone, kidneys and brain being of concern to humans with evidence of renal dysfunction, anemia or neurobehavioural alterations (Krewski et al., 2009). Highly vulnerable to Al
exposure are infants since their gastrointestinal tract and renal system is immature. Acutely dangerous Al levels range between 302-303 mg/day (Crawford and Bodkin, 2011). On the other hand, EFSA group have set a Total Weekly Intake (TWI) of 1 mg aluminium/kg bw/week (EFSA, 2009).

Majority of soil samples consumed by geophagic individuals have been reported to be mainly alumina in the range 50.8 - 56.7 (9.58 - 10.69 %wt), 31.6-76.1 (5.97 - 14.35 %wt), 43.8-86.4 (8.26 - 16.31 %wt) and 134.6 mg/g (25.4 %wt) (Mwangi and Ombaka, 2010; Okunlola and Owoyemi, 2011; Gichumbi et al., 2012; Tayie et al., 2013). Okunlola and Owoyemi (2011) reported that geophagic materials had high Al content and is the main nutritional value which makes the soils suitable as a traditional antacid. Crawford and Bodkin (2011) reported that consumption of 50 g of geophagic materials contributed Al which is below the acutely dangerous levels.

Contrary to the above findings, Gichumbi et al. (2012) concluded that since geophagic materials are mainly alumina they have no nutritional value and thus have negative health risks on the individual. Similar conclusions were reported by Gichuki et al. (2011). Given that there are varied conclusions on whether soil Al is present in safe levels, there is need to determine its composition in geophagic materials.

2.2.7 Silicon

Silicon makes up 25.7 % of the earth's crust by mass and is the second most abundant element. Pure Si is very reactive and does not occur freely in nature; but it is found in practically all rocks as well as in sand, clays, and soils, combined either with oxygen as
silica (SiO$_2$, silicon dioxide) or with oxygen and other elements for example, aluminum, magnesium, calcium, sodium, potassium, or iron as silicates. The oxidized form of Si in both silica and silicates is also common in the Earth’s crust and is an important component of the Earth’s mantle (Cahn, 2009).

Silicon together with calcium helps grow and maintain strong bones and is important in the formation of connective tissues, like ligaments and tendons and growth of hair, skin and fingernails (MII, 2012). Coarse particles present in geophagic materials as a result of silica have resulted in various medical conditions such as perforation of the sigmoid colon due to the formation of a knot which tightens forming a double loop obstruction (Lohn et al., 2001). In the mouth, quartz particles easily damage dental enamel due to its hardness and lead to destruction of the dental enamel (Ngole et al., 2010). The EFSA group have set a safe Upper Level, referring to the highest average daily nutrient intake level likely to pose no adverse health effects to an individual, for daily consumption of silicon at 12 mg silicon/kg body weight/day for a 60 kg adult (EFSA, 2009).

Majority of soil samples consumed by geophagic individuals have been reported to be mainly siliceous in the range 93.2 - 196.9 mg/g (19.97 - 42.19 %wt) and 96.0 - 157.5mg/g (20.58 - 33.76 %wt) (Ekosse et al., 2011; Ngole and Ekosse, 2012). The samples characterized with high silica content contain high amount of quartz which is mainly composed of sand. This crystalline silica (quartz silica) is not in bioavailable form due to its rigid crystalline nature. Whereas Ekosse et al. (2011) reported that the RDA of nutrients varies with the source, Ngole and Ekosse (2012) concluded that
minerals in the soil could negligibly contribute to the nutrient demands of the geophagic individual. Given that the levels of Si vary depending on the source, there is need to determine its level in different geophagic materials in Kiambu County.

2.2.8 Lead

The abundance of lead in the Earth's crust is estimated to be between 13 and 20 parts per million. It ranks in the upper third among the elements in terms of its abundance. Lead rarely occurs as a pure element in the earth. Its most common ore is galena, or lead sulfide (PbS). Other Pb compounds include sulphates, carbonates and chlorides (Gilbert and Weiss, 2006).

Lead poisoning is a medical condition caused by increased levels of the heavy metal Pb in the body which end up interfering with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems (Patrick, 2006). High Pb levels interfere with the production of blood cells and subsequently, the absorption of calcium which is required for healthy and strong bones. If circulating levels of the hormones in the body are within normal range, Pb alters the bone cell function by interfering with bone cells’ ability to respond to hormonal stimuli (Patrick, 2006). Lead exposure especially when nervous system is being is being formed in the foetus during pregnancy, can result in life-long processes (HEAL, 2012). World Health Organisation (1996) limits lead levels to 1 mg/kg.
Levels of Pb in geophagic materials have been reported to be within the range 0.14 - 0.96 ppm, 0.68 - 1.54 ppm (Mwangi and Ombaka, 2010; Gichumbi et al., 2012). From the reported values, Mwangi and Ombaka (2010) concluded that Pb levels in geophagic materials exceed the WHO limits and thus have deleterious effects on the consumer. Similarly, Ekosse and Jumbam (2010) concluded that the high levels of Pb could pose a health risk as a result of continued use of such contaminated soils. They concluded that consumption of such soils should be discouraged because of the high concentration of Pb. Further, Gichumbi et al. (2012) concluded that the high level of Pb can act as a health risk to the geophagic individual. Given the adverse health effects of high Pb levels being reported, there is need to determine whether the level of Pb in geophagic materials in Kiambu County is above the WHO limits.

2.3 Methods of mineral analysis

There are a number of sensitive and reliable analytical techniques for mineral analysis including Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) Atomic Absorption Spectroscopy (AAS) and Energy Dispersive X-ray Fluorescence (EDXRF) (Shelton, 1999; Tessadri, 2003). Atomic Absorption Spectroscopy (AAS) has the advantages of high accuracy, precision, sensitivity, selectivity and speed (Hou and Jones, 2000; Mester and Sturgeon, 2003).
2.4 Atomic Absorption Spectroscopy

2.4.1 Principle of Atomic Absorption Spectroscopy

Atomic Absorption Spectroscopy (AAS) is an analytical method that is based on the absorption of UV-visible radiation by free atoms in the gaseous state (Boss and Fredeen, 1997; McLaughlin and Glennon, 2011). The sample to be analyzed is ashed and then dissolved in an aqueous solution. The solution is then placed in the instrument where it is heated to vaporize and atomize the minerals. A beam of radiation is passed through the atomized sample, and the absorption of radiation is measured at specific wavelengths corresponding to the mineral of interest. Information about the type and concentration of minerals present is obtained by measuring the location and intensity of the peaks in the absorption spectra. The AAS has successfully been used in analysis of minerals present in geophagic materials (Ndede et al., 2010; Mwangi and Ombaka, 2010; Gichuki et al., 2011).

2.4.2 Instrumentation

Light source

The light source is usually a hollow-cathode lamp of the element that is being measured. Lasers can also be used since they emit enough intensity to excite atoms to higher energy levels. They allow AAS and atomic fluorescence to be measured in a single instrument. The disadvantage of these narrow-band light sources is that only one element is measurable at a time.
**Atomizer**

The AAS requires that the analyte atoms be in the gaseous phase. Ions or atoms in a sample must undergo desolvation and vaporization in a high-temperature source such as a flame or graphite furnace. Flame AAS can only analyze solutions, while graphite furnace AAS can accept solutions, slurries, or solid samples. Flame AAS uses a slot type burner to increase the path length, and therefore to increase the total absorbance. Sample solutions are usually aspirated with the gas flow into a nebulizing/mixing chamber to form small droplets before entering the flame (Skoog and Leary, 1992).

The graphite furnace has several advantages over a flame. It is a much more efficient atomizer than a flame and it can directly accept very small absolute quantities of sample. It also provides a reducing environment for easily oxidized elements. Samples are placed directly in the graphite furnace and the furnace is electrically heated in several steps to dry the sample, ash organic matter, and vaporize the analyte atoms.

**Light separation and detection**

The AAS spectrometers use monochromators and detectors for UV and visible light. The main purpose of the monochromator is to isolate the absorption line from background light due to interferences. Simple dedicated AAS instruments often replace the monochromator with a bandpass interference filter. Photomultiplier tubes are the most common detectors for AAS spectroscopy.
Figure 2.1: Schematic diagram of an AAS (Skoog and Leary, 1992)
CHAPTER THREE
MATERIALS AND METHODS

3.1 Research design

Laboratory procedures were followed where various geophagic materials were sampled from quarry mines, open-air markets and supermarkets in Kiambu County and analyzed for selected essential and toxic minerals using atomic absorption spectroscopy.

3.2 Study area

The study was carried out in Kiambu County which covers an approximate area of 3,284 square kilometers. It borders Nairobi and Kajiado counties to the south, Machakos to the east, Nyandarua and Murang’a to the northwest and Nakuru County to the west. The county lies between latitudes 0°75’ and 1° 20’ south of Equator and longitudes 36° 54’ and 36° 85’ east. The County is divided into several sub-counties namely: Kiambaa, Limuru, Juja, Githunguri, Kikuyu, Lari, Kiambu town, Ruiru, Gatundu South, Thika town and Gatundu North. Kiambu County has three broad categories of soils namely nitisols, andosols and plutonic soils. Nitisols and andosols are generally well-developed, well-drained, deep, high in fertility and are suitable for cultivation of various crops. The plutonic soils found in the semi-arid areas of the district are either sandy or clay soils that are poorly drained (GoK, 2010).
3.3 Sample collection and pretreatment

In quarry mines, samples were collected from 8 out of 13 sub-counties in Kiambu County namely: Gatundu North, Githunguri, Juja, Kiambu, Kikuyu, Lari, Limuru, Thika town and coded QM1-QM8 respectively. Simple random sampling was used to select 3 quarry mines in each constituency and samples obtained mixed to form a representative sample of that constituency. Randomized block design was used to obtain a representative sample on each of the quarry mine sampled by dividing the quarry mine into four portions and two opposite sides randomly selected (Trochim, 2006).
In supermarkets, 4 different brands of geophagic materials (udongo, udongo whole, roasted udongo, and roasted clay soil) identified as SM1, SM2, SM3 and SM4 respectively, were sampled. In open-air markets, the only available 2 coloured samples (yellow and brown) were sampled. The colour of the samples was determined by reference to a Munsell chart which describes colour in order of their hue, quality and chrome (Kuehni, 2002). In total, 14 samples were obtained from the three sources.

Sample preparation followed Balcerzak’s (2002) procedure where they were first dried in an oven at 110 °C for 8 hours and then allowed to cool to room temperature in a desiccator. They were crushed to obtain fine particles and ground into a finer powder of 5 µm size for 6 hours in a ball mill. They were then weighed and stored in labeled sample plastic bottles (Balcerzak, 2002).
3.4 Cleaning of glassware and sample containers

All glassware used was cleaned by soaking overnight in chromic acid followed by further soaking overnight in a detergent and subsequent rinsing with distilled-deionized water. After each analysis, the glassware was rinsed with 50% v/v analytical grade nitric acid followed by distilled-deionized water. The glassware was stored in a closed container. Sample bottles and plastic containers were washed with 50% v/v analytical grade nitric acid followed by a detergent and subsequent rinsing with distilled-deionized water. The glassware was then dried in an oven at 105 °C for 24 hours.

3.5 Chemicals and reagents

All chemicals and reagents used in this study were of analar grade, manufactured by Sigma Aldrich Company and supplied by Kobian Laboratory supplies, Nairobi. Chemical and reagents used were aluminium, iron and silicon standards, calcium carbonate, nitric acid, hydrochloric acid, hydrofluoric acid, boric acid and cesium chloride.
3.6 Instrumentation

The machine model used for analysis was Buck Scientific 210VGP flame AAS. The operating parameters were set according to the manufacturer’s specifications. Air/Acetylene flame and oxidant flow of 4.5 L/min was used for Fe, Mg, Mn, Pb, Si and Zn, while for Al, and Ca, N2O/Acetylene flame was used. Other operating conditions for the instruments are given in Table 3.1.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Wavelength (nm)</th>
<th>Path length (nm)</th>
<th>Detection limit (Mg/L)</th>
<th>Sensitivity check (Mg/L)</th>
<th>Lamp current (mA)</th>
<th>Linear range (Mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>309.3</td>
<td>0.7</td>
<td>0.1</td>
<td>25</td>
<td>12.0</td>
<td>3.75</td>
</tr>
<tr>
<td>Calcium</td>
<td>422.7</td>
<td>0.7</td>
<td>0.01</td>
<td>2</td>
<td>10.0</td>
<td>3.00</td>
</tr>
<tr>
<td>Iron</td>
<td>248.3</td>
<td>0.2</td>
<td>0.03</td>
<td>2.5</td>
<td>15.0</td>
<td>3.75</td>
</tr>
<tr>
<td>Magnesium</td>
<td>285.2</td>
<td>0.7</td>
<td>0.001</td>
<td>0.015</td>
<td>7.0</td>
<td>0.0225</td>
</tr>
<tr>
<td>Manganese</td>
<td>279.5</td>
<td>0.7</td>
<td>0.01</td>
<td>1.25</td>
<td>15.0</td>
<td>1.875</td>
</tr>
<tr>
<td>Lead</td>
<td>283.3</td>
<td>0.7</td>
<td>0.1</td>
<td>10</td>
<td>8.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Silicon</td>
<td>251.6</td>
<td>0.2</td>
<td>0.01</td>
<td>2.5</td>
<td>15.0</td>
<td>0.25</td>
</tr>
<tr>
<td>Zinc</td>
<td>213.9</td>
<td>0.7</td>
<td>0.005</td>
<td>0.50</td>
<td>15.0</td>
<td>0.75</td>
</tr>
</tbody>
</table>

3.7 Preparation of standard solutions

Certified reference materials of aluminium, iron and silicon were used as supplied by Natural Resources, Canada (MO-8). For calcium solution, 2.497 g of dried CaCO₃ was added to a minimum volume of 1:4 nitric acid in a 1 L volumetric flask. The solution was then diluted to the mark using distilled-deionized water to form stock solution of 1000 ppm. In order to prepare standard solution of magnesium, 1.000 g of Mg metal (99.99 % purity) was dissolved in 1:4 nitric acid in a 1 L volumetric flask. The solution was then diluted to the mark using distilled-deionized water to form stock solution of
1000 ppm. For manganese, 1.000 g of Mn metal (99.99 % purity) was dissolved in a minimum volume of 1M nitric acid in a 1 L volumetric flask. The solution was then diluted to the mark using distilled-deionized water to form stock solution of 1000 ppm. For lead, 1.000 g of Pb metal (99.99 % purity) was dissolved in 1:1 nitric acid in a 1 L volumetric flask. The solution was then diluted to the mark using distilled-deionized water to form stock solution of 1000 ppm. In order to prepare standards for zinc, 1.000 g of Zn (99.99% purity) was dissolved in 40 mL of hydrochloric acid in a 1 L volumetric flask. The solution was then diluted to the mark using distilled-deionized water to form stock solution of 1000 ppm. Working solutions were obtained by serial dilution of 1000 ppm stock solution to prepare working standards for each of the elements (Horwitz, 2001).

3.8 Sample preparation for AAS analysis

Two methods were applied in sample preparation: cold digestion for oxide analysis (SiO, Al₂O₃, Fe₂O₃, MgO and CaO) and hot digestion for elemental analysis (Zn and Pb).

3.8.1 Cold digestion procedure

Exactly 0.100 g of the powdered sample was carefully weighed into a 100 mL plastic bottle and using a plastic tipped automatic pipette, 3 L of HCl and 1 mL of HNO₃ added, bottle stoppered loosely and solution allowed to stand overnight. Approximately, 3 mL of HF was added and stoppered immediately to avoid loss of silicon. Using an
automatic dispenser, 50 mL of boric acid solution prepared by dissolving 320 g of H$_3$BO$_3$ and 12.65 g of CsCl in 5 L flask, filling to the mark with distilled-deionized water and heating to near boiling point before allowing it to cool, was added and allowed to stand for at least an hour before adding 46 mL of distilled-deionized water and the solution shaken thoroughly. The solution was allowed to stand for three hours before AAS analysis. Certified reference solutions were treated in the same way as the sample. In order to account for background effect from the acids and to correct for changes resulting from the digestion procedures, a blank was prepared by mixing the acids used in the digestion process in the ratio of 3:1:3:50 (HCl:HNO$_3$:HF:H$_3$BO$_3$) and treated in the same way as the sample (Tessadri, 2003).

3.8.2 Hot digestion procedure

Exactly 1.500 g of the sample in a 50 mL volumetric flask was dissolved with distilled-deionized water to form a slurry before adding 15 mL of concentrated HCl and 5 mL of concentrated HNO$_3$. After the reaction had ceased, the solution was slowly heated in a sand bath to near boiling point for 1 hour with frequent agitation and allowed to cool. After cooling, the solution was filled to the mark with distilled-deionized water before AAS analysis. In order to account for background effect from the acids and to correct for changes resulting from the digestion procedures, a blank was prepared by mixing the acids used in the digestion process in the ratio of 3:1 (HCl:HNO$_3$) and treated in the same way as the sample (Tessadri, 2003).
3.9 Method validation procedures

3.9.1 Calibration curves

The AAS procedure was calibrated using freshly prepared standard solutions. Five working standard solutions of increasing concentration were nebulized into the flame. Calibration curves were obtained by plotting absorbance versus concentration (ppm) for each of the minerals.

3.9.2 Recovery

The degree of recovery of the AAS was investigated by spiking samples with a known amount of standards and triplicate analysis was performed in each case. The concentration of unspiked sample, spiked sample together with that of standard added was recorded.

3.10 Sample analysis

Digested samples together with blanks and standards were analyzed by measuring the absorption atomic spectra at different wavelengths using atomic absorption spectrometer at optimum conditions as specified in Table 3.1. In each of the samples, three readings were obtained. The calibration of the instrument using standards and blank was frequently done between samples to ensure stability of the baseline. The instrument’s detection limit was obtained from the manufacturer’s manual. The actual concentration of minerals in the samples was calculated as shown in eqn 3.1:

Concentration in ppm = \frac{\text{Digested conc (ppm) x Vol of digest (L)}}{\text{Weight of the dried digested sample (Kg)}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots •
In order to determine actual concentration in percentage weight the eqn 3.2 was used.

Concentration in % weight = \( \frac{\text{Concentration in ppm}}{10^4} \) ..............................................Eqn 3.2

In cases of dilution, the actual concentration was obtained by multiplying read-out results with the dilution factor. To calculate the element concentration from oxides in cases of Ca, Mg, Fe, Mn, Al, and Si, eqn 3.3 was used.

\[
\text{Conc. of the element} = \frac{\text{Relative formula mass of the element} \times \text{Conc. of the oxide}}{\text{Relative formula mass of the oxide}}
\]........Eqn 3.3

To calculate the nutritional value derived from consuming the geophagic materials the level of the mineral in mg/g was multiplied by 30 g, (the average daily consumption) and compared with the RDI for that mineral (Brady, 1994).

Nutritional value = Level of the mineral (mg/g) x 30 g ......................... Eqn 3.4

3.11 Statistical data analysis

The data obtained from the various determinations was subjected to statistical analysis and the results expressed as mean±standard error of the minerals in the varieties of geophagic materials. ANOVA was employed in comparison of measurements with p-value \((\alpha<0.05)\) considered significant (Miller and Miller, 1998). Student t-test was used to test whether there was any significant difference between any two values.
CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Introduction

The levels of Ca, Mg, Fe, Mn, Zn, Al, Si and Pb obtained from quarry mines, supermarkets and open-air markets were determined and the results obtained are presented in tables and graphs, and discussed in the following sections. A total of 42 samples were analysed.

4.2 Method validation

Pure standard solutions for each mineral were used to plot calibration curves of absorbance versus concentration (ppm). Figure 4.1 shows the calibration curve for Pb as an example while the rest are presented in Appendix II. The regression equations of the best line of fit, the value of correlation coefficient, percentage recoveries and limits of detection (LOD) are presented in Table 4.1.

![Figure 4.1: Calibration curve for lead standard](image)

\[ y = 0.006x - 0.000 \]
\[ R^2 = 0.999 \]
Table 4.1: Method Validation parameters

<table>
<thead>
<tr>
<th>Metal</th>
<th>Correlation coefficient ($r^2$)</th>
<th>Regression equation</th>
<th>Recoveries (%)</th>
<th>L.O.D (Mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.997</td>
<td>$y = 0.014x + 0.002$</td>
<td>97.50</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca</td>
<td>0.998</td>
<td>$y = 0.078x + 0.017$</td>
<td>99.64</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.999</td>
<td>$y = 0.075x + 0.016$</td>
<td>98.31</td>
<td>0.03</td>
</tr>
<tr>
<td>Mg</td>
<td>0.999</td>
<td>$y = 0.025x + 0.000$</td>
<td>96.00</td>
<td>0.001</td>
</tr>
<tr>
<td>Mn</td>
<td>0.997</td>
<td>$y = 0.060x + 0.009$</td>
<td>96.19</td>
<td>0.01</td>
</tr>
<tr>
<td>Pb</td>
<td>0.999</td>
<td>$y = 0.006x + 0.000$</td>
<td>95.96</td>
<td>0.1</td>
</tr>
<tr>
<td>Si</td>
<td>0.998</td>
<td>$y = 0.077x + 0.013$</td>
<td>98.00</td>
<td>0.01</td>
</tr>
<tr>
<td>Zn</td>
<td>0.996</td>
<td>$y = 0.106x + 0.012$</td>
<td>98.57</td>
<td>0.005</td>
</tr>
</tbody>
</table>

The results showed strong linear positive correlation since the values of correlation coefficient ($r^2$) were above 0.995. This was an indication that over 99% of the responses correlated with concentration. The closer to 1.000 the values are, the more the model approaches a perfect fit (Carl and Praveen, 2002). The positive values of slope in the regression equation indicated that an increase in concentration lead to a subsequent increase in absorbance recorded for each pure standard solution. The y-intercept ranged between 0.000 - 0.017 indicating that the effect of sample matrix was minimal (Hight, and Capar, 2010). The value of percentage recoveries was between 95.00 - 99.64% implying that the method had a conventionally acceptable accuracy (CHMP, 2011).

4.3 Levels of essential minerals

The levels of Ca, Mg, Fe, Mn and Zn determined in geophagic materials are summarized in Table 4.2.
Table 4.2: Levels of Ca, Mg, Fe, Mn and Zn in geophagic materials

<table>
<thead>
<tr>
<th>Soil source</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quarry mines</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QM1</td>
<td>ND</td>
<td>0.12±0.00a</td>
<td>3.57±0.03abc</td>
<td>0.08±0.00b</td>
<td>159.00±0.06d</td>
</tr>
<tr>
<td>QM2</td>
<td>4.5±0.00a</td>
<td>0.18±0.00b</td>
<td>4.83±0.02c</td>
<td>0.23±0.03f</td>
<td>161.67±0.03f</td>
</tr>
<tr>
<td>QM3</td>
<td>4.4±0.00a</td>
<td>ND</td>
<td>3.78±0.03bc</td>
<td>0.15±0.01d</td>
<td>160.00±0.03c</td>
</tr>
<tr>
<td>QM4</td>
<td>ND</td>
<td>0.12±0.00a</td>
<td>3.43±0.03ab</td>
<td>0.23±0.01e</td>
<td>132.67±0.09b</td>
</tr>
<tr>
<td>QM5</td>
<td>12.8±0.00b</td>
<td>ND</td>
<td>4.20±0.03d</td>
<td>0.15±0.02e</td>
<td>127.67±0.03a</td>
</tr>
<tr>
<td>QM6</td>
<td>4.3±0.00a</td>
<td>ND</td>
<td>3.57±0.02abc</td>
<td>0.23±0.01e</td>
<td>133.67±0.03c</td>
</tr>
<tr>
<td>QM7</td>
<td>4.4±0.00a</td>
<td>0.18±0.00b</td>
<td>3.99±0.02ad</td>
<td>0.08±0.01a</td>
<td>159.98±0.09e</td>
</tr>
<tr>
<td>QM8</td>
<td>ND</td>
<td>0.18±0.00b</td>
<td>3.22±0.03a</td>
<td>0.08±0.01b</td>
<td>133.67±0.03c</td>
</tr>
<tr>
<td>p-value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Supermarkets</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SM1</td>
<td>12.8±0.00a</td>
<td>0.24±0.00a</td>
<td>0.63±0.01b</td>
<td>0.03±0.00</td>
<td>11.22±0.33</td>
</tr>
<tr>
<td>SM2</td>
<td>4.4±0.00b</td>
<td>0.96±0.00b</td>
<td>0.42±0.00a</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SM3</td>
<td>4.3±0.00b</td>
<td>0.96±0.00b</td>
<td>0.63±0.00b</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SM4</td>
<td>4.5±0.00b</td>
<td>0.96±0.00b</td>
<td>1.61±0.01c</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>p-value</td>
<td>0.310</td>
<td>&lt;0.01</td>
<td>0.260</td>
<td>ND</td>
<td>0.984</td>
</tr>
<tr>
<td>Open-air markets</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>White</td>
<td>27.9±0.02</td>
<td>1.98±0.01</td>
<td>2.59±0.01</td>
<td>ND</td>
<td>78.66±0.01</td>
</tr>
<tr>
<td>Yellow</td>
<td>15.0±0.01</td>
<td>1.14±0.01</td>
<td>2.66±0.01</td>
<td>ND</td>
<td>70.32±0.01</td>
</tr>
<tr>
<td>p-value^2</td>
<td>0.002</td>
<td>&lt;0.05</td>
<td>0.018</td>
<td>&lt;0.05*</td>
<td></td>
</tr>
</tbody>
</table>

abcd Mean values followed by the same letter in the same source are not significantly different (α=0.05)
ND - Not Detected
1 Zn level expressed in ppm
2 Student t-test

4.3.1 Calcium

The level of Ca was in the range ND - 27.9±0.02 mg/g (Table 4.2). Open-air samples had the highest content with the white variety having a higher content (27.9±0.02 mg/g) than the yellow variety (15.0±0.01 mg/g). Statistical tests showed that there was no significant difference in samples obtained from quarry mines and supermarkets. However, samples obtained from open-air markets were statistically significant at p<0.05.
The findings of this study concur with earlier studies of Ngole and Ekosse (2012) and Gichumbi et al. (2012) who reported Ca weight range of 0.1 – 18 mg/g and 2.2 – 5.4 mg/g respectively. The results show that the geophagic materials in this region are within the range of materials obtained from other regions.

4.3.2 Magnesium

From Table 4.2, the level of Mg in quarry mines was between ND – 0.18±0.00 mg/g. Apart from QM2, Mg weight content within quarry mines was not statistically different (p>0.05). Geophagic materials from supermarkets had Mg in the range 0.24±0.00 – 1.98±0.02 mg/g which was statistically significant (p<0.05). Geophagic materials obtained from open-air markets had Mg ranging between 1.14±0.01 – 1.98±0.01 mg/g with white samples recording higher Mg content (1.98±0.01 mg/g) as compared to the yellow samples (1.14±0.01). Statistical tests showed that there was a significant difference in geophagic materials obtained from open-air markets (p<0.05).

The findings reported in this study are within the range of other studies (Ekosse and Jumbam, 2010; Ngole et al., 2010; Okunlola and Owoyemi, 2011) indicating that the materials are within the range of other geophagic materials obtained from different regions.

4.3.3 Iron

From Table 4.2, the level of Fe was in the range 0.42±0.00 - 4.83±0.02 mg/g with SM2 having the lowest content (0.42±0.01 mg/g) while QM2 had the highest content
(4.83±0.02 mg/g). Samples from quarry mines had Fe in the range 3.22±0.03 - 4.83±0.02 mg/g. Statistical tests showed that the difference was statistically significant (p<0.05). For geophagic materials obtained from supermarkets had Fe range 0.42±0.00 - 1.61±0.01 mg/g. However, statistical tests revealed that the difference was not statistically significant (p>0.05). In open-air markets, Fe was in the range 2.59±0.01 - 2.66±0.01 mg/g with yellow variety having the highest content (2.66±0.01 mg/g) whereas white had the lowest content (2.59±0.01 mg/g). Student t-test showed that the difference was not statistically significant (p>0.05).

The levels of Fe agree with findings reported in earlier studies (Mwangi and Ombaka, 2010; Ngole et al., 2010; Gichumbi et al., 2012; Ngole and Ekosse, 2012). The differences in supermarket samples could be attributed to differences in the way they are handled before selling in addition to differences in their physical and mineralogical characteristics.

### 4.3.4 Manganese

From Table 4.2, Mn was present in geophagic materials obtained from quarry mines with the range being 0.08±0.01 - 0.23±0.03 mg/g. In supermarkets, only SM1 had Mn (0.03±0.00 mg/g) while the other samples had Mn below detection limit. All geophagic materials from open-air markets had Mn below detection limit (0.01 mg/L). Similar results were reported by Ekosse and De-Jager (2011), Odewumi (2011) and Ngole and Ekosse (2012). The level of Mn in geophagic materials obtained from this region is comparable to the levels obtained in other regions.
4.3.5 Zinc

From Table 4.2, Zn was present in the range 10.89±0.32 - 161.67±0.03 ppm. In quarry mines, Zn was present in the range 127.67±0.04 - 161.67±0.19 ppm. Statistical tests showed that the difference was significant (p<0.05). For geophagic materials obtained from supermarkets, Zn level was 11.22±0.23 and 10.89±0.89 ppm for SM₁ and SM₃ respectively with SM₂ and SM₄ recorded below detection levels (0.005 mg/L). Statistical tests showed that the difference was significant (p<0.05). For samples obtained from open-air markets, Zn was present in higher concentration in white (78.66±0.09 ppm) whereas yellow had lower Zn concentration (70.32±0.01 ppm). Student t-test revealed that the difference was significant (p<0.05). The results are within the range reported by Okunlola and Owoyemi (2011), Ekosse et al. (2011) and Ngole and Ekosse (2012) indicating that they are within the range obtained in other regions.

4.4 Nutritional value of essential minerals

The nutritional value derived from consuming geophagic materials was determined to find out whether geophagic individuals could benefit from the minerals present. The level of mineral in each sample was converted to mg/g (in the case of Zn), multiplied by 30 g (average daily consumption) and the value obtained compared with the RDI for that particular mineral (Eqn 4.4). Table 4.3 gives the percentage contribution to RDI respectively.
Table 4.3: RDI contribution

<table>
<thead>
<tr>
<th>Source</th>
<th>Sample</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quarry mines</td>
<td>QM₁</td>
<td>-</td>
<td>3.6</td>
<td>107.1</td>
<td>2.4</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>QM₂</td>
<td>135.0</td>
<td>5.4</td>
<td>144.9</td>
<td>6.9</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>QM₃</td>
<td>132.0</td>
<td>-</td>
<td>113.4</td>
<td>4.5</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>QM₄</td>
<td>-</td>
<td>3.6</td>
<td>102.9</td>
<td>6.9</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>QM₅</td>
<td>384.0</td>
<td>-</td>
<td>126.0</td>
<td>4.5</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>QM₆</td>
<td>129.0</td>
<td>-</td>
<td>107.1</td>
<td>6.9</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>QM₇</td>
<td>132.0</td>
<td>5.4</td>
<td>119.7</td>
<td>2.4</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>QM₈</td>
<td>-</td>
<td>5.4</td>
<td>96.6</td>
<td>2.4</td>
<td>4.0</td>
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<tr>
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<td>SM₁</td>
<td>384.0</td>
<td>7.2</td>
<td>18.9</td>
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<td>0.3</td>
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<tr>
<td></td>
<td>SM₂</td>
<td>132.0</td>
<td>28.8</td>
<td>12.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SM₃</td>
<td>129.0</td>
<td>28.8</td>
<td>18.9</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>SM₄</td>
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<td>-</td>
<td>0.0</td>
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<tr>
<td>Open-air Markets</td>
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<td>59.4</td>
<td>77.7</td>
<td>-</td>
<td>2.4</td>
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<td></td>
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<td>34.2</td>
<td>79.8</td>
<td>-</td>
<td>2.1</td>
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<td>RDI</td>
<td>Adults</td>
<td>1000-1200</td>
<td>310-420</td>
<td>8.0-15.0</td>
<td>1.9-2.2</td>
<td>8.0-11.0</td>
</tr>
<tr>
<td></td>
<td>Pregnant women</td>
<td>1000-1300</td>
<td>310-420</td>
<td>9.0-27.0</td>
<td>2.0-2.6</td>
<td>11.0-12.0</td>
</tr>
</tbody>
</table>

4.4.1 Nutritional value of Ca

The RDI for Ca is 1000 - 1200 mg/day and 1000 - 1200 mg/day for adults and pregnant women respectively (Food and Nutrition Board, 2011). From Table 4.3, the contribution to RDI ranged between 129.0 – 837 mg/30 g for samples which contained Ca. White variety sample had the highest RDI contribution (837 mg/30 g) although it was below the RDI needed for an adult or pregnant women. This clearly shows that Ca in all samples is not in appreciable amounts and therefore cannot act as mineral supplements. Geophagic individuals consuming geophagic materials from these sources do not necessarily benefit from the mineral. Similar conclusions were drawn by Ngole and Ekosse (2012) who deduced that geophagic individual consuming 5 - 30 g of soil per day would be supplied with less than 1 % of RDI. Further, Okunlola and Owoyemi (2011) concluded that southern Nigeria geophagic materials analyzed had minimal
nutritional value of Ca (1.6% weight) which was low as compared to average human nutritional values. Therefore, it can be deduced that geophagic individuals consuming these materials do not necessarily benefit from Ca mineral.

### 4.4.2 Nutritional value of Mg

The RDI range for Mg is 310 - 420 mg/day for both adults and pregnant women (Food and Nutrition Board, 2011). From Table 4.3, the RDI contribution was between 3.6 - 5.4 mg/30 g for samples which had Mg. Although white variety had the highest contribution of RDI (5.5 mg/30 g), it was below the RDI. Therefore, it can be concluded that all the samples had an almost negligible contribution since they account for less than RDI needed by adults and pregnant women. The low levels indicate that Mg is not present in appreciable amounts and therefore geophagic individuals consuming these materials do not necessarily benefit from the mineral. Therefore, it can be concluded that geophagic materials can neither act as a good source of Mg nor as mineral supplement. These findings concur with earlier study of Ngole and Ekosse (2012) who concluded that geophagic individual who consumed 5-30 g of soil per day would be supplied with less than 1 % of RDI. Further, Lakudzula and Khonje (2011) who analyzed Blantyre and Indian ‘edible’ soils reported that such soils could only contribute 0.006 % of RDI. Therefore, it can be concluded that ingesting geophagic materials cannot sufficiently contribute the needed dietary Mg.
4.4.3 Nutritional value of Fe

According to Food and Nutrition Board (2011) the RDI of Fe is 8.0 - 15.0 mg/day and 9.0 - 27.0 mg/day for an adult and pregnant woman respectively. Contribution to RDI ranged between 12.6 – 144.9 mg/30 g. The highest level was present in QM₂ (144.9 mg/30 g) while SM₂ (12.6 mg/30 g) had the lowest. Geophagic materials obtained from quarry mines contributed Fe in the range 96.6 – 144.9 mg/30 g while samples obtained from supermarkets contributed 12.6 – 48.3 mg/30 g of RDI. For samples from open-air markets, yellow variety contributed RDI of 79.8 mg/30 g which was the highest while white variety contributed 77.7 mg/30g of RDI. The results show that all the samples provided Fe which was above the RDI. However, not all the Fe is in bioavailable form. Assuming a 50.0 % bioavailability, the samples would contribute Fe in the range 6.3 – 72.45 mg/30 g. With an exception of SM₂ (6.3 mg/30 g), all the other samples obtained from the three sources had levels which were above the RDI needed for an adult or a pregnant woman on assuming a 50.0 % bioavailability (9.45 – 72.45 mg/30 g). This shows that Fe present is in appreciable amounts and geophagic individuals consuming these materials can benefit from the Fe present. These findings agree with the studies of Abrahams (1997) and Abrahams and Parsons (1997) who found Fe in soils could supply 17-25 % of the RDI needed by an adult. Similarly, Mwangi and Ombaka (2010) found soils to contain high level of Fe and concluded that soils could be a significant source of Fe. Thus, it can be concluded that Fe present in geophagic materials contain appreciable amount for absorption into the digestive tract of the geophagic individual.
4.4.4 Nutritional value of Mn

The RDI for Mn in adult and pregnant women is 1.9 - 2.2 and 2.0 - 2.6 mg/day respectively (Food and Nutrition Board, 2011). As shown in Table 4.3, the RDI contribution to Mn was in the range 2.4 – 6.9 mg/30 g for samples which had Mn. Comparing with RDI showed that all the values were above the RDI levels. Assuming a 50.0% bioavailability had Mn in the range 1.2 – 3.45 mg/30 g. Samples QM1 (1.2 mg/30 g), QM7 (1.2 mg/30 g), QM8 (1.2 mg/30 g) and SM1 (0.9 mg/30 g) had Mn which was below RDI while all the other samples contributed Mn which was above RDI. Whereas some samples had Mn below RDI, majority of the samples had Mn above RDI and could therefore contribute the nutrient demands of the geophagic individual. As a result, presence of Mn in the samples could be used to explain geophagic tendencies. Similar conclusions were reported by Longo-Mbenza and Ekosse (2011) and Ekosse and Anyangwe (2012).

4.4.5 Nutritional value of Zn

According to Food and Nutrition Board (2011), the RDI of Zn for an adult and pregnant women is 8.0 - 11.0 and 11.0 - 12.0 mg/day respectively. The Zn present in the geophagic materials was compared with the required RDI and the results (Table 4.3) showed that Zn was in the range 0.33 - 4.85 mg/30 g. As the findings reveal, all the samples contributed Zn that was below the RDI and therefore it can be concluded that Zn present is not present in appreciable amounts to provide sufficiently for the geophagic individual. Therefore, they cannot act as sources of zinc or mineral supplements. Hooda et al. (2004) and Ngole and Ekosse (2012) had similar conclusion
where they concluded that geophagic materials cannot supply zinc needed by the consumers.

4.5 Levels of toxic minerals

The levels of Al, Si and Pb present in geophagic materials are summarized in the Table 4.4.

**Table 4.4: Levels of Al, Si and Pb in geophagic materials**

<table>
<thead>
<tr>
<th>Soil source</th>
<th>Mean levels (Mean±SE, n=3) in mg/g</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Si</td>
<td>Pb¹</td>
</tr>
<tr>
<td>Quarry mines</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QM₁</td>
<td>126.4±0.15ᵇ</td>
<td>198.4±0.14ᶜ</td>
<td>38.67±0.01ᵃ</td>
</tr>
<tr>
<td>QM₂</td>
<td>166.2±0.45ᵈ</td>
<td>191.5±0.06ᵇ</td>
<td>78.67±0.02ᵍ</td>
</tr>
<tr>
<td>QM₃</td>
<td>166.2±0.35ᵉ</td>
<td>219.5±0.12ᶠ</td>
<td>69.33±0.01ᵉ</td>
</tr>
<tr>
<td>QM₄</td>
<td>140.0±0.26ᵈ</td>
<td>205.3±0.10ᵈ</td>
<td>74.3±0.02ᶠ</td>
</tr>
<tr>
<td>QM₅</td>
<td>121.4±0.35ᵃ</td>
<td>186.7±0.12ᵃ</td>
<td>54.00±0.57ᶜ</td>
</tr>
<tr>
<td>QM₆</td>
<td>159.7±0.15ᶠ</td>
<td>204.3±0.05ᵈ</td>
<td>57.68±0.01ᵈ</td>
</tr>
<tr>
<td>QM₇</td>
<td>167.2±0.19ᵍ</td>
<td>210.8±0.46ᵉ</td>
<td>79.67±0.04ᵇ</td>
</tr>
<tr>
<td>QM₈</td>
<td>156.2±0.76ᶜ</td>
<td>192.9±0.14ᵇ</td>
<td>48.97±0.04ᵇ</td>
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<tr>
<td>Supermarkets</td>
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<td></td>
</tr>
<tr>
<td>SM₁</td>
<td>233.0±0.89ᵃ</td>
<td>190.7±0.46ᵃ</td>
<td>11.00±0.02ᵃ</td>
</tr>
<tr>
<td>SM₂</td>
<td>111.8±0.98ᵇ</td>
<td>184.1±0.14ᵃ</td>
<td>17.33±0.01ᵇ</td>
</tr>
<tr>
<td>SM₃</td>
<td>198.6±0.08ᶜ</td>
<td>189.5±0.07ᵃ</td>
<td>17.34±0.02ᵇ</td>
</tr>
<tr>
<td>SM₄</td>
<td>68.2±0.23ᵃ</td>
<td>291.8±0.34ᵇ</td>
<td>39.00±0.01ᶜ</td>
</tr>
<tr>
<td>Open-air markets</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>White</td>
<td>64.6±0.00</td>
<td>272.5±0.08</td>
<td>1.10±0.02</td>
</tr>
<tr>
<td>Yellow</td>
<td>75.0±0.00</td>
<td>264.1±0.12</td>
<td>1.09±0.03</td>
</tr>
<tr>
<td><strong>p-value</strong>³</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>0.984</td>
</tr>
<tr>
<td><strong>WHO/EFSA limits</strong></td>
<td>302-303 mg/day</td>
<td>12 mg/day</td>
<td>0.01 ppm</td>
</tr>
</tbody>
</table>

abc Mean values followed by the same letter are not significantly different (α = 0.05)

¹ Pb levels expressed in ppm

²Student t-test

4.5.1 Aluminium

From Table 4.4, the range of Al was 64.6±0.35 - 233.0±0.89 mg/g. For geophagic materials obtained from quarry mines, the range was 121.4±0.35 - 167.2±0.19 mg/g.
Statistical tests showed that they were statically significant (p<0.05). Geophagic materials obtained from supermarkets ranged between 68.2±0.23 - 233.0±0.89 mg/g. Statistical tests showed that the difference was significant (p<0.05) while samples obtained from open-air markets, yellow samples had higher Al level (75.0±0.00 mg/g) than white samples (64.6±0.00 mg/g) and the values were statistically significant (p<0.05).

**Toxicity from aluminium**

In all the three sources, Al levels were below the acutely dangerous level (302 - 303 mg/day). Similar findings were reported by Crawford and Bodkin (2011) who found out that consumption of 50 g of geophagic materials contributed Al which is below the acutely dangerous levels. Although consuming geophagic materials obtained from any of these sources are below WHO/EFSA limits, concerns may arise as a result of bioaccumulation over time due to continued consumption. In addition, high concentration of Al in the body inhibits function of other essential minerals such as Mg, Ca and Fe, and results in reduced body immune. Infants are mostly affected by Al exposure since their gastrointestinal tract and renal system has not been fully developed.

**4.5.2 Silicon**

From Table 4.4, the level of Si was in the range 184.1±0.14 - 291.8±0.34 mg/g. The level of Si was 186.7±0.12 - 219.5±0.12, 184.1±0.14 - 291.8±0.34 and 264.1±0.12 - 272.5±0.08 mg/g for samples obtained from quarry mines, supermarkets and open-air markets respectively. Apart from SM₄, samples from supermarkets were not statistically
significant (p>0.05). For samples obtained from quarry mines and open-air markets, statistical tests showed that the difference was significantly different (p<0.05). The findings are within the range of previous work of Ngole and Ekosse (2012) who reported Si to be in the range 93.2-196.9 mg/g.

**Toxicity from silicon**

Silicon level in all the three sources was above the WHO/EFSA safe Upper Limit (12 mg per day). Assuming 50.0 % bioavailability revealed that geophagic materials had Si above WHO/EFSA limits. Therefore, it can be concluded that Si in geophagic materials can have deleterious effects on the individual as it is above the safe Upper Limit. In addition, continued daily consumption could lead to high silica content which could have deleterious effects. Quartz particles present in the samples raises concerns as such particles can easily damage dental enamel due to their hardness and thus destroy dental enamel. In addition, coarse particles have lead to various medical conditions such as perforation of the sigmoid colon and also can easily damage dental enamel due to its hardness and lead to destruction of the dental enamel. Therefore, geophagic individuals consuming such materials are at risk of damaging their colon and dental enamel. Similar results were reported by Lohn *et al.* (2001) and Ngole *et al.* (2010).

**4.5.3 Lead**

From Table 4.4, Pb was present in all the three sources investigated in this study with the range being 1.10±0.02 - 79.67±0.04 ppm. The Pb level was 38.67±0.01 - 79.67±0.04; 11.00±0.02 - 39.00±0.01; 1.10±0.02 - 1.09±0.03 ppm for geophagic
materials from quarry mines, supermarkets and open air markets respectively. For geophagic materials obtained from open air markets, white samples had slightly more Pb level (1.10±0.02 ppm) than yellow (1.09±0.03 ppm). Upon performing statistical tests, it was found out that the difference was statistically significant in quarry mines (p<0.05). However, the difference was not statistically significant for samples obtained from supermarkets and open air markets (p>0.05). Similar findings were reported in earlier studies of Mwangi and Ombaka (2010) and Gichumbi et al. (2012).

Toxicity from lead

World Health Organisation (1996) limits Pb levels to 1.0 ppm. The levels of Pb in all the three sources are above 1.0 ppm clearly showing that geophagic individuals are at risk of lead poisoning with geophagic materials obtained from quarry mines having the highest risk. Assuming a 50.0 % bioavailability shows that only samples from open-air markets have Pb levels below WHO/EFSA limits. All the other samples have Pb levels above WHO/EFSA limits. This shows that geophagic individuals consuming these materials are at risk of lead poisoning. High levels of Pb can interfere with the production of blood cells and the absorption of calcium which is needed for healthy and strong bones. In addition, Pb alters the bone cell function by interfering with bone cells’ ability to respond to hormonal stimuli; even if circulating levels of the hormones in the body are within normal range (Patrick, 2006). Similar results were reported by Ngole and Ekosse (2012) and Gichumbi et al. (2012).
CHAPTER FIVE
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion
The study found out that with an exception of Fe in all samples and Mn in some samples, all the other minerals were below the RDI needed for an adult or pregnant women. Therefore, presence of essential mineral in the samples cannot be used to explain geophagic tendencies. For toxic minerals, although samples from the three sources had Al levels below the acutely dangerous levels, Si and Pb levels exceeded WHO/EFSA limits disclosing the potential risks associated with their toxicity.

5.2 Recommendations

5.2.1 Recommendations from the study
The following are the recommendations suggested from this study:

i. Geophagic materials obtained from the three sources have essential minerals below RDI levels (except for Fe and Mn) and therefore geophagic individuals do not necessarily benefit from the minerals.

ii. Geophagic materials obtained from the three sources have toxic minerals above WHO/EFSA limits (except for Al) exposing geophagic individuals to health risks associated with toxicity.

5.2.2 Recommendations for further study
The following are the recommendations suggested for further study:
i. Since these study concentrated on selected essential and toxic minerals, further geochemical and nutritional investigations can be performed on geophagic materials to identify the levels of other minerals which will help determine the suitability of the practice.

ii. Although this study concentrated on geophagic materials from open-air markets, supermarkets and quarry mines, other sources such as termite moulds, walls of buildings etc should be determined since different sources can have different levels of the minerals.

iii. The findings of this study are from Kiambu County, other studies can be done on geophagic materials obtained from other Counties as the findings cannot be generalized to other counties.

iv. This study assumed that the minerals were 50.0% bioavailable, studies can be performed on specific mineral to determine its bioavailability.
REFERENCES


Food and Nutrition Board. (2011). Institute of Medicine, National Academies.


## APPENDICES

### Appendix I: Sampling stations and sample codes

<table>
<thead>
<tr>
<th>Source</th>
<th>Sampling station</th>
<th>Sample code</th>
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<tbody>
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<td></td>
<td></td>
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<tr>
<td>Quarry mines</td>
<td>Gatundu North</td>
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<td>Githunguri</td>
<td>QM(_2)</td>
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<td></td>
<td>Juja</td>
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<td>QM(_7)</td>
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<tr>
<td></td>
<td>Thika</td>
<td>QM(_8)</td>
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<tr>
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<td></td>
</tr>
<tr>
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<td>SM(_1)</td>
</tr>
<tr>
<td></td>
<td>Udongo whole</td>
<td>SM(_2)</td>
</tr>
<tr>
<td></td>
<td>Roasted udongo</td>
<td>SM(_3)</td>
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<tr>
<td></td>
<td>Roasted clay</td>
<td>SM(_4)</td>
</tr>
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</table>
Appendix II: Calibration curves

Appendix IIa: Calibration curves for calcium

![Graph showing calibration curve for calcium with equation $y = 0.078x + 0.017$ and $R^2 = 0.998$.]
Appendix IIb: Calibration curves for magnesium

\[ y = 0.025x + 0.000 \]
\[ R^2 = 0.999 \]
Appendix IIc: Calibration curves for iron

\[
y = 0.075x + 0.016 \\
R^2 = 0.999
\]
Appendix IIId: Calibration curves for manganese

![Graph showing calibration curve for manganese with equation and R² value]

Equation: $y = 0.06x + 0.009$

$R^2 = 0.997$
Appendix IIe: Calibration curves for silicon

\[ y = 0.077x + 0.013 \]
\[ R^2 = 0.998 \]
Appendix II: Calibration curves for zinc

\[ y = 0.106x + 0.012 \]

\[ R^2 = 0.996 \]
Appendix IIg: Calibration curves for aluminium

\[ y = 0.014x + 0.002 \]

\[ R^2 = 0.997 \]
Appendix IIh: Calibration curves for lead

![Calibration curve for lead](image)

- Equation: $y = 0.006x - 0.000$
- $R^2 = 0.999$
Appendix III: Acceptance letter
Appendix III: Acceptance letter

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Website: www.jicasonline.com E-mail: jicasonline@gmail.com

Date: 11.10.2015

To,
T Kanaa et al.,

Subject: ACCEPTANCE LETTER (jicas-057915)

MS Title: Understanding Geophagic Practice as a Source of Mineral Nutrients and Toxicants

Authors: T Kanaa, HN Nyambaka and MP Nawiti*

Article Type: Review Article

Dear Author,

It gives me immense pleasure to inform you that after review of your manuscript entitled “Understanding Geophagic Practice as a Source of Mineral Nutrients and Toxicants” by in-house reviewers, the editorial board is pleased to publish it in desired International journal of modern chemistry and applied science.

[Signature]
Chief Editor

SJIF Impact Factor (2014) For International Journal of Modern Chemistry and Applied Sciences is 2.467