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CHARACTERIZATION OF SELECTED GYPSITES OF TANZANIA AND ASSESSMENT OF THEIR EFFECTIVENESS AS PLANT NUTRIENT SOURCE AND SOIL AMENDMENT

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ABSTRACT

This study was carried out to assess the suitability and effectiveness of gypsite as soil amendment in release of Ca and S. This is because besides the high potential of gypsite in improving crop yields in some countries, its use in Tanzanian agricultural soils is limited. This is attributed largely to few researches on their agricultural potentials. The gypsite samples used in this study were collected from Pindiro, Makanya, Itigi and Msagali sites. The X-ray fluorescence (XRF) method was employed to analyze the chemical compositions of the composite samples. Using maize as a test crop, pot experiment was conducted to assess crop response to gypsite application at different rates. In addition, incubation study was conducted for 56 days on the solubility of gypsite in release of S in soil solution. The XRF results showed that the gypsites from the four sites varied in amounts of gypsum content from 35.76 to 82.36% for gypsite from Itigi and Pindiro respectively. The contents of S were 15.32, 13.26, 10.52 and 6.65 % for Pindiro, Msagali, Makanya and Itigi gypsites respectively. Calcium contents was 11, 9.5, 7.6 and 4.8% for Pindiro, Msagali, Makanya and Itigi gypsites, respectively. Pindiro and Msagali gypsite sources were selected for pot experiment due to having high S and Ca percentage. Results from pot experiment indicated that maize plant height and shoot dry matter were significantly higher by 22% and 27.2%, respectively for soil amended with Pindiro and Msagali gypsites compared to maize grown in none amended soil. After pot experiment, the postharvest soil analysis indicated that on the average residual S increased by 5 for soil amended with Pindiro and 2 times for soil amended with

Msagali gypsite while Ca increased by 19.6 and 21.7% for soil amended with Pindiro and Msagali gypsites, respectively, compared to control. In addition, incubation results revealed that solubility of gypsites for Pindiro and Msagali were high (178 to 579 and 165.1 to 492.2 mg S kg^{-1}) respectively. Gypsites from Pindiro and Msagali are effective in improving Ca and S availability for plant growth, also gypsite application has acidifying effect to the soils. In this study gypsite application reduced the pH by 0.4 units. However, field trials using different soil types and various crops are recommended in order to make concrete recommendations on use of these soil amendments.

DECLARATION

I, Primitiva Andrea, do hereby declare to the Senate of Sokoine University of Agriculture that this dissertation is my own original work and that it has neither been submitted nor concurrently being submitted for a degree award in any other university.

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Stay blessed by God!

DEDICATION

This dissertation is dedicated to Almighty God Farther of Our Lord Jesus Christ to Him be all Honour and Glory. Let all men know your forbearance. To my dear father Andrea Antony Mboyerwa and my mother Generoza Fidelis, what I am today is a product of their efforts and focus. This also coins in my beloved husband Wolfram Kipengele and our son Rousseau.

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LIST OF SYMBOLS AND ABBREVIATIONS

˚C	Celsius Centigrade
AAS	Atomic Absorption Spectrophotometer
ANOVA	Analysis of Variance
CEC	Cation exchange capacity
cmol (+) /kg	Centimol charge per kilogram
CRBD	Completely randomized block design
DAP	Di-ammonium phosphate
DAS	Days after sowing
DM	Dry mater
DMRT	Duncan's Multiple Range Test
DMY	Dry mater yield
DTPA	Diethylene triamine pentacetic acid
FGD	Flue gas desulfurization
GNP	Gross National Product
H	hour
LOI	Loss on ignition
M	Molar mass
NH_4OAc	Ammonium acetate
pH	negative logarithm of hydrogen ion activity
PTEs	Potentially toxic elements
SO_4-S	Sulphate Sulphur
SUA	Sokoine University of Agriculture
USDA	United States Department of Agriculture
yr	years

CHAPTER ONE

1.0 INTRODUCTION

Tanzania is an agricultural country and the livelihoods of nearly 80% of Tanzanians depend directly or indirectly on subsistence rain-fed agriculture (Mkapa, 2005). Agriculture contributes about half of Tanzania's gross national product (GNP) and provides about 90% of the rural employment (Mmbaga and Lyamchai, 2001). Although agriculture is the backbone of the Tanzanian economy, crop productivity is generally low as a result of a number of factors; among them salinity, drought, pest and disease infections, genetic variability, poor soil management and inadequate macro- and micro-nutrients in the soils (Ley *et al*., 2002).

Increasing the productivity of agricultural soils is important to sustainably supply food, feed, fuel, and fiber for a growing human population. The demand for increased productivity has resulted in the search for alterative soil management practices to increase crop yields, using gypsum as a management tool to improve crop yields and soil is essential. Gypsum's benefits as a plant nutrient source and soil conditioner for agricultural production have been known dating back to the late 18th century (Crocker, 1922). Chen and Dick (2011) reviewed the use of a soft calcium sulfate dihydrate mineral ($CaSO_4 \cdot 2H_2O$), in agriculture and for other land applications.

Gypsite is a rock that contains an abundance of the mineral gypsum ($CaSO_4.2H_2O$) (Mandal and Mandal, 2002). It is naturally occurring as a soft rock in association with limestone, silica, clays and a variety of soluble salts as impurities along with other trace elements, such as copper, zinc, nickel, iron and manganese. These trace elements are not usually found in hard rock gypsum deposits. Under high pressure and temperature gypsum turns into anhydrite ($CaSO_4$) (Dontsova and Norton, 2002). Pure gypsum ($CaSO_4 \bullet 2H_2O$), is Composed of 79% calcium sulfate ($CaSO_4$) and 21% water (H_2O). Pure gypsum contains 23.3% calcium (Ca) and 18.6% sulfur (S) (Dontsova and Norton, 2002). Gypsum is moderately soluble in water (2.5 g per L) or approximately 200 times greater than agricultural lime ($CaCO_3$) (Epri, 2006; Korcak, 1988). This makes the calcium in gypsum more mobile than the calcium in lime and allows it to easily move through the soil profile where it can provide nutrients to deep plant roots and help to alleviate subsoil nutrient availability problems.

Gypsite has various benefits in soil as well as in plants including supplying calcium (Ca) and sulphur (S) for plant nutrition (Bolan *et al*., 1993). Plants require relatively large amounts of calcium and sulphur because Ca is needed at 0.5% shoot dry weight and S is needed in a range of 0.1 to 0.5% dry weights for optimal growth (Brady and Weil, 2008). Gypsum can provide many physical and chemical benefits to soils in addition to nutritional benefits. It increases subsoil Ca (Caires *et al*., 2006), decreases subsoil acidity (Toma *et al*., 1999) and reduces exchangeable aluminium (Al) (Ritchey and Snuffer, 2002; Hue, 2005).

With respect to soil physical properties, the benefits of gypsum when used as soil amendment include increased water infiltration (Sahin *et al*., 2003; Chen *et al*., 2009), increased soil aggregation (Chen *et al*., 2009), decreased Na adsorption, improved or increased root development (Takahashi *et al.*, 2006) and decreased soil compaction. Other benefits are an increase in the hydraulic conductivity of soil after consecutive gypsum applications (Sahin *et al*., 2003), and a reduction in metal toxicities has also been documented (Campbell *et al.,* 2006; Sumner, 2007).

Most farmers in Tanzania do not use sulphate fertilizers as a source of nutrients in soils. In a long run this is causing deficiency of sulphur in soils. Introduction of high yielding crop varieties, intensive and multiple cropping, the decreased use of farmyard manures, removal of crop residues for feed and fuel, leaching, burning, erosion, microbial and plant uptake, a larger proportion of S may be unavailable to plant. The above processes seem to have led to a wide occurrence of S deficiency in soils for plant uptake (Brady and Weil, 2002; Hall, 2008; Sakal and Singh, 1997; Tandon, 1984).

Sulphur (S) deficiencies in soils of tropical and subtropical regions have been recognized for many years (Pasricha and Fox, 1993). Sulphur deficiency has been reported from over 70 countries, including Tanzania (Tandon, 1991). For instance, corn (*Zea mays* L.) removes approximately 18 kg ha^{-1} to 40 kg ha^{-1} for silage and 12 Mg ha^{-1} grain harvest (Murrell, 2005). The combination of reduced inputs and increased S removal from soil has sparked interest in evaluating responses of crops to gypsum additions. In S deficient conditions, the efficiency of applied N, P_2O_5 and K_2O, may be seriously affected and high yields may not be sustained (Ahmad *et al*., 1994). The consequence of this trend in most parts of the country is a decrease in crop production. Inorganic fertilizers in Tanzania are not obtained at the right time and are at higher costs, which are not affordable to smallholder farmers who are basically producing for subsistence (Kisetu and Teveli, 2013). This also was reported by Kimbi *et al.* (1996) that water soluble fertilizers are expensive to resource poor farmers, so farmers could benefit more by using agro minerals, namely gypsite rocks as sources of S and Ca because the country is endowed with large quantities of gypsite deposits (Harris, 1981), these could be used as alternative sources of nutrients in crop production.

1.1 Justification

Low soil fertility and high nutrient mining are among the main factors limiting crop yields in Sub-Saharan Africa (Adu-Gyamfi *et al.,* 2007), Tanzania inclusive (Nyasasi and Kisetu, 2014). Some soil fertility management technologies being used to address low soil fertility in Tanzania include use of organic soil amendments (e.g., crop residues, animal manures, agroforestry tree pruning) and inorganic (fertilizers, agro-minerals) resources (Kwesiga and Coe, 1994) and commercial products such as bio-fertilizers and chemical products. Agro-minerals have improved crop yields in some countries, but in Tanzania the use of gypsites in agriculture as a source of plant nutrients is limited, and this could be due to lack of enough research on their potential suitability. Duarah *et al*. (2011) reported that excessive and improper application of industrial fertilizers imposes residual impact to soils, so the use of agro minerals such as gypsite rock in agriculture can be one of the alternative means of assisting farmers in Tanzania to replenish the soils with sulphur without causing harm to plants. Apart from adding sulphur in the soil, gypsite rocks could also supplement the soil with calcium.

However, gypsite rocks cannot be used without knowing their chemical properties and chemical composition so as to make recommendations for use of gypsite in agriculture, it is important to understanding of its composition and properties. Also characterization of gypsite rocks from Tanzania is necessary because some deposits may occur with a varying amount of potentially toxic elements (PTEs) (Dontsova *et al*., 2005) which may cause toxicity or may affect the availability and uptake of essential plant nutrients in soils. Gypsite rocks contain substantial amounts of chromium (Cr), nickel (Ni), copper (Cu) and zinc (Zn) but their availability for plant uptake is unknown, thus, characterization is essential. The optimum rate of applying S and its influence on crops such as maize performance is critical because of the economic and industrial importance of maize and availability of gypsum as affordable source of S.

1.2 Objectives of the Study

1.2.1 Overall objective

The overall objective of this study was to characterize selected gypsite rocks commonly found in Tanzania and determine their potentials as soil amendment and as sources of plant nutrients in agricultural soils with low levels of S.

1.2.2 Specific objectives

The specific objectives of this study were to:

i) Determine the chemical composition of the selected gypsite rocks of Tanzania.
ii) Determine the extractability of Sulphur, Calcium and selected potentially toxic elements found in the selected gypsite rocks.
iii) Study solubility trends of sulphur release from selected gypsite rocks.
iv) Study the response of maize as a test crop on soil amended with selected gypsite rocks.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Gypsum Deposits in Tanzania

Tanzania is endowed with vast deposits of gypsum. Major rock gypsum and anhydrite resources are found in remote areas, at Pindiro and Mandawa in south-eastern Tanzania, at about 100 km north of Lindi (Harris, 1981). Low-grade and low-volume gypsum resources are also found in seasonal swamp environments (*mbugas*) at Msagali and Itigi in Central Tanzania and at Mkomazi in Lushoto District in the north-eastern Tanzania (Harris, 1981). As so-called 'gypsite' occurs in crystal form in nodules and as finely distributed crystals in a sandy, silt and clay-rich groundmass. Small-scale mining of gypsum from the low-grade gypsite deposit of Mkomazi in north-eastern Tanzania started in 1952. The ore is hand-sorted to produce a concentrate of 60 to 80% gypsum. Since 1953, annual production has been in the range of 4,000 to 9,000 tonnes with a maximum annual production in the late 1970s of 22,000 tons (Richardson, 1982). Another commercial deposit is located at Makanya in Same District.

2.2 Formation of Gypsum

In nature, gypsum and anhydrite occur as beds or nodular masses up to a few metres thick and gypsum is formed by the hydration of anhydrite. In addition, gypsum occurs geologically as an evaporate mineral associated with sedimentary deposits (Korcak, 1988).

The depth of hydration can range from the surface of the deposit down to three hundred metres, depending on temperature and pressure, topography and the structure of the deposit (Richardson, 1982). Anhydrite is often mined in conjunction with gypsum, but is comparatively limited in its technical applications (Korcak, 1988). The content of gypsum in sedimentary rock varies from 75% to 95%, the rest being clay and chalk (Harber and Kuzvart, 1996).

Gypsum is available in two forms namely mineral gypsum and by-product gypsum (Korcak, 1988). The mineral gypsum is mined from land deposits while by-product gypsum includes marine gypsum, phosphor-gypsum, fluoro-gypsum, boro-gypsum, scrubber gypsum, etc. Marine gypsum is recovered from sea-water as a by-product while producing common salt, whereas the other types are obtained as by-products from different chemical plants.

2.3 Mineralogy of Gypsum

Mineral gypsum is the most common of the naturally occurring sulphate minerals as hydrous calcium sulphate ($CaSO_4.2H_2O$) with a composition of 79% calcium sulphate and 21% water (Dontsova and Norton, 2002). Anhydrite calcium sulphate ($CaSO_4$) is also a naturally occurring sulphate mineral with no water of crystallization. According to Dontsova and Norton (2002), pure gypsum contains 23.3% Ca, 32.6% CaO, 18.6% S, 46.5% SO_3 and 20.9% H_2O. Mineral gypsum and anhydrite are frequently found in close association and it is seldom that a natural calcium sulphate deposit will consist exclusively of one mineral or the other. Gypsum tends to be of greater economic importance because of its chemical properties.

2.4 Gypsum as a Source of Plant Nutrients

Gypsum has been reported to be an excellent soil amendment, supplying readily available Ca^{2+} and SO_4^{2-} for plant nutrition (Shainberg *et al*., 1989; Chen *et al*., 2005; Chen et al., 2008). According to Aylmore *et al. (*1971) and Abrol *et al*. (1979), gypsum is soluble in water to the extent of about one-fourth of one percentage by weight is a direct source of calcium. It represents also an important source of Ca^{2+} and S (Bolan *et al*., 1993) for plant growth and it can improve mineral content in vegetal tissues such as N, P, K, Ca, Mn, S and Zn (Caires *et al*., 2006; Tuna *et al*., 2007).

2.5 Calcium in Soils

All agricultural plants have specific needs for calcium in their tissues to ensure proper growth. Total calcium in soils ranges from 0.1 to 25% by weight. This is equivalent to 2,000 to 500,000 kg Ca ha^{-1} (Tisdale *et al*., 2003). Low levels of calcium are found in highly weathered and strongly acid soils of pH < 5. High levels of calcium are found in alkaline soils (arid and semi-arid areas) with high pH (>7.0) and accumulation of free $CaCO_{3.}$ According to Tisdale *et al*. (2003), any soil with total calcium >3% will contain free $CaCO_{3.}$ Furthermore, the ability of calcium to neutralize excess acid or excess alkaline, amphoteric, in the soil environment is the key to proper root growth of the plants. Without proper root growth plants are susceptible to drought and improper mineral nutrition (Tisdale *et al*., 2003).

2.5.1 Forms of calcium in soils

Calcium occurs in three forms in the soil namely calcium in primary minerals, exchangeable calcium and soluble calcium (Tisdale *et al*., 1990). The fraction of calcium in primary minerals constitutes 99% by weight of total calcium in soils. However, in acid soils the sources of calcium are minerals such as anorthite ($CaAlSiO_8$) and pyroxenes (Ca, Na) mg^{2+}, Fe^{2+}, Al) Si_2O_6 or (Ca, Na) mg^{2+}, Fe^{2+},Fe^{3+})Si_2O_6). On the other hand, in alkaline soils there are minerals such as dolomite ($CaMg (CO_3)_2$), calcite ($CaCO_3$) and gypsum ($CaSO_4.2H_2O$) but A large proportion of calcium is held in available forms (Tisdale *et al.,* 2003). Exchangeable and soluble calcium, these are available form of calcium for plant uptake, it contribute 0.1-1% weight of total calcium in soil per hector (Tisdale *et al*., 2003).

2.6 Sulphur in Soils

The main source of sulphur in soils is through addition of organic matter from plant and animal sources and application of inorganic fertilizers. Sulphur can also enter the atmosphere by both natural processes and human activities, some of which are industrial wastes and fossil fuel burnings which help to contribute to a great amount of sulphur to the atmosphere (Somnath and Ghosh, 2009). Sulphur however, finds its way into the soil system through atmospheric depositions (wet and dry). The wet deposition is dissolved in rain while the dry deposition involves compounds containing sulphur e.g. parent materials. Total sulphur in soils ranges from 0.005-0.04% which is equivalent to 100-800 kg sulphur per hectare (Tisdale *et al*., 1993).

2.6.1 Forms of sulphur in soils

Sulphur exists primarily as organic and inorganic forms in soils (Tisdale *et al*., 1993). Most farmers employ the use of inorganic fertilizers due to its quick release of nutrients and ease of application compared to its organic counterpart, however the organic sulphur is superior to inorganic form. In a well-drained and well aerated soil, most of the inorganic forms of sulphur occur as sulphates and the amounts of reduced sulphur compounds are generally less than 1%. Under anaerobic conditions, particularly in tidal swamps and poorly drained or water logged soils, the main form of inorganic sulphur in soils is sulphide and often elemental sulphur (Zhang *et al*., 1996). Hence, the easily absorbed form of sulphur by plants is the sulphates form and the sulphate-sulphur interaction with the soil solid phase influences not only its availability to plants but also its distribution (Barrow, 1985).

2.7 Roles of Calcium and Sulphur in Plant Nutrition

2.7.1 Calcium

Calcium plays a key role as an essential nutrient element in plants (White and Broadley, 2003). It is a regulator of growth and development (Hepler, 2005) and is indispensable in a number of metabolic functions or pathways (Plieth, 2005). As a divalent cation Ca^{2+} has a structural role in cell walls and cell membranes. It also participates in root and stem elongation (White and Brodley, 2003). Ryan *et al*. (1997) indicated that high quantity of Ca is present in the apoplast, where it maintains cell and tissue viability. Its fundamental role in the structure and rigidity of the cell walls has been reported in previous studies conducted elsewhere in the world (Silva *et al*., 2005; Shukry *et al*., 2007).

Calcium is also used as a second messenger in various signal transduction pathways in eukaryotic cells (Sanders *et al*., 2002; Silva *et al*., 2005), and is modulated at intracellular level in response to many signals such as hormones, light, mechanical disruption, and abiotic and biotic stress (Cheng *et al*., 2002; Sanders *et al*., 2002). In addition, Ca^{2+} is involved in the photosynthetic process as an essential activator of the Mn redox chemistry that culminates in the release of O_2 from photosystem II (PSII) in water photolysis (Hommann, 2002; Yocum, 2008), a process that could be inhibited when substituted by other cations such as K^+, rubidium (Rb^+) and cesium (Cs^+) (Ono *et al*., 2001).

Calcium regulates enzymatic activity (Cheng *et al*., 2002), as well as homeostasis in both the chloroplast and mitochondria-activating ATPkinases and produces electrochemical potential (Ryan *et al*., 1997). Lack of calcium usually shows up as distorted, underdeveloped tips of young leaves and yellowing of the leaf (Mengel and Kirkby, 1987).

Calcium is also important for good root growth, especially where the subsoil has suboptimum pH values (Toma *et al*., 1999). Calcium is important in fruit growth and quality in different crops such as melons (Takasu *et al*., 2006), blueberries (Blatt and Mc Rae, 1997). It is also useful in crop yields of wheat (Caires *et al*., 2002), red clover (Zheljazkov *et al*., 2006), brussels sprouts (Carter and Cutcliffe, 1990). Calcium in improvement of yields is also reported in ryegrass (Mora *et al*., 1999, 2002), soybean (Caires *et al.,* 2006; Bachiega *et al*., 2007), coffee (Hue, 2005) and tomato (Tuna *et al*., 2007).

2.7.2 Sulphur

Sulphur is one of the essential nutrient elements for plant growth. Sulphur has specific functions during plant growth, metabolism, enzymatic reactions and overall development (Mengel and Kirkby, 1987). Plant takes up approximately the same amount of sulphur as that of phosphorus (Tandon, 1991). Sulphur is essential in protein and oil production in plants and seeds and in the successful maturation of plants and fruits. Sulphur is required for the synthesis of sulphur-containing amino acids such as cystine, cysteine, and methionine. Sulphur is also a constituent of S-glycosides (mustard oils), coenzymes-A, vitamins such as biotine and thiamine (Tisdale *et al*., 2003).

Sulphur increases oil, protein and glucosinolate in seeds (Malhi and Gill, 2007); improves nitrogen use efficiency and thus it maintains adequate quality of fatty acids and oil content levels (Fismes *et al*., 2000). Crop yields and quality can be affected with inadequate S supply as S is necessary for the structure of methionine and cystein, protein, certain amino acids and enzyme synthesis (Hearn, 1981). Restorative crops need less amount of S than oilseeds and legumes (Reisenaue and Duke, 1986). It has been reported that yields in sugar producing crops increase at 60 kg S ha^{-1} application in the form of gypsum and observed residual effects on the growth of the ratoon crops (Mathew *et al*., 2003).

Sulphur application of up to 40 kg S ha^{-1} enhanced the average grain yield of maize by 0.99 t ha^{-1} (Sakal *et al*., 2000). Haq *et al.* (1988; 1989) reported 20.5 and 9.8% increase in the yields of maize and wheat respectively, with application of 72 kg S ha^{-1}. Furthermore, additional of 22.4 kg S ha^{-1} in the form of ammonium sulphate ($(NH_4)_2SO_4$)) increased the yield of maize up to 43.4% compared with the no application of S (Singh and Chhibba, 1987). On the other hand, wheat yield increased by 38.8% with application of 30 kg S ha^{-1} (Kushwaha and Prasad, 1998;

Singh and Aggarwal, 1998). An optimum response of soybean to S was observed at an application of 40 kg S ha^{-1} (Ganeshamurthy, 1996). Khan *et al*. (2006) reported the increase of maize yield by application of gypsum up to 60 kg ha^{-1}. Sumner *et al*. (2008), Scott *et al.* (1993) and Shear (1979) reported an improvement of horticultural crops by gypsum application. Also Scott *et al*. (1993) and Shear (1979) reported that gypsum partially controlled root rot of avocado trees caused by *Phytophthora*, blossom-end rot of watermelon and tomatoes, and bitter pit in apples. A field trial with sunflower conducted by Sreemannarayana *et al*. (1998) showed that oil content and seed yields were highest, 0.45 and 1.28 t ha^{-1}, respectively, when N and S were applied together at the rate of 100 kg N and 60 kg S ha^{-1}. In addition, seed yield of sunflower was significantly increased with application of S at a rate of 40 kg ha^{-1} (Aggrawal and Verma, 1998) and at 10-50 kg S ha^{-1} (Subhani *et al*., 2003).

Gypsum also decreases storage rots of cantaloupe and tomato (Sumner and Larri-more, 2006; Scott *et al.*, 1993; Shear, 1979). A study conducted by Sumner and Larrimore (2006) found that application of flue gas desulfurization (FGD) gypsum at a rate of 181.2-543.6 kg per hectare increased cantaloupe growth, fruit yield, skin calcium content, and time of storage .

2.9 Gypsum as a Soil Amendment

Gypsum is the most commonly used amendment for sodic soil reclamation (Amezketa *et al*., 2005). Excessive sodium on the exchange sites of clay particles causes the clay to dispense thereby filling soil pores with clay (Dontsova *et al*., 2004). In sodic soils water infiltration is reduced, root development is restricted, and the soils become compact and hard when dry. Gypsum contains Ca^{2+} as its central cation which is easily displaced by Na^{+} which predominates in sodic soils thereby forming Na_2SO_4 which is highly soluble in water hence releasing free Na^{+} in soil solution. Increase in hydration potential with large amount of water will then leach out Na as Na^{+} and retain Ca^{2+} back in the soil. The reaction is such that:

$$2Na - clay\ micelle + \mathrm{CaSO_4} \rightarrow Ca - clay\ micelle + Na_2SO_4 \text{ (Leachable)}$$

Therefore, gypsum and good internal drainage are both necessary to reclaim the sodic soils as this prevents clay dispersion and swelling and maintains good surface infiltration rate (Dontsova and Norton, 2002).

2.10 Effect of Gypsum on the Physical Properties of Soils

2.10.1 Soil structure

Gypsum helps to reduce the dispersion of the clay that leads to surface crust formation and also slows the rate of surface drying (Norton *et al*., 1993; Norton and Rhoton, 2007). Soil dispersion is mainly caused by highly hydrated ions, such as Na+ or Mg^{2+}, attracted to the surface of clay particles, high levels of single charge ions especially sodium will cause soil particles to disperse this in turn causes poor soil structure, soils erode easily when soil particle don't hold together. Addition of soluble Ca can overcome the dispersion effects of Mg or Na ions and helps to promote flocculation and structure development in dispersed soils. For improvement of soil physical properties gypsum usually should be in the range of 181.2 to 907.2 kg per hectare, in some extreme cases, such as for sodic soils, higher rates may be justified (Brauer *et al*., 2006; Norton and Rhoton, 2007).

2.10.2 Soil crusting

Surface crust strength is largely dependent on clay and moisture content. Gypsum helps reduce the dispersion of the clay that leads to surface crust formation and also slows the rate of surface drying (Norton *et al*., 1993; Norton and Rhoton, 2007).

The rate of crust development and final strength will be affected by gypsum additions leading to improved seedling emergence and plant establishment and in the reduction of modulus of rupture and resistance to penetration (Brauer *et al*., 2006). The expected outcome of reducing formation of soil crust is the improved crop yields. Amezketa *et al.* (2005) reported that gypsum was effective in reducing soil crusting. Farina and Channon (1988), Stehouwer *et al.* (1999) and Toma *et al.* (1999) found that gypsum applications to Ca-deficient soils in humid regions had beneficial effects because of Ca movement into the subsoil, thereby improving root growth and lowering water stress.

2.10.3 Water infiltration

Under conditions of significant soil sodium content, application of gypsum to the soil surface at rates of about 0.8 tons per hectare increased water infiltration and reduced surface runoff and erosion (Keren *et al*., 1983; Morin and Van Winkel, 1996). Generally, if soils are not dispersive, gypsum applications do not help water infiltration. Ben-Hur*et al*. (1992), Endale *et al*. (2014); and Norton *et al*. (1993) reported the effects of using flue gas desulfurization gypsum to reduce P losses and increase water infiltration under simulated rainfall events.

2.11 Effect of Gypsum on Chemical Properties of Soils

2.11.1 Aluminium toxicity in acid soils

In soils with pH below 5, aluminium becomes more soluble (Al^{3+}), which is extremely toxic to plant roots; plant roots bend away from regions of subsoil acidity and end up being restricted to shallow depths. Gypsum corrects this by moving into the subsoil, where its ionic form of calcium (Ca^{2+}) displaces aluminium ions from the soil's exchange sites (Farina *et al*., 2000). Sulphate ions (SO_4^{2-}) supplied by gypsum can also react with the free aluminium ions to produce aluminium sulphate complexes that are not toxic and are capable of being leached beyond the root zone (Sumner *et al*., 1986). Farina *et al*. (2001) reported that gypsum is more effective than lime in correcting subsoil acidity to a depth of 0.75 m.

Gypsum reduced subsurface aluminium toxicity and improved deep rooting for water and nutrient uptake by corn, wheat, soybean, sorghum, and leuceana (a forage legume) were dramatically improved (Ritchey *et al*., 1995). Ritchey *et al*. (1995) also found that the percentage of corn roots which were below 45-cm depth increased by more than 600% with the addition of 1.08 tons per hectare or more of gypsum. Application of gypsum at 1.76 tons per hectare ameliorated subsoil acidity and increased cotton yield and overall cotton quality (Ritchey *et al*., 1995). Farina *et al*. (2000) found that yields of corn were improved when gypsum was applied to help overcome problems of subsoil acidity.

2.11.2 Heavy-metal toxicity

Calcium acts as a regulator of the balance of micronutrients in soils such as iron, zinc, manganese and copper and non-essential trace elements in plants (Brady and

Weil, 2008). Calcium prevents excess uptake of many of these nutrients and once they are in the plants, calcium balances their adverse effects at their high levels (Alva *et al*., 1993).

2.12 Quality of Tanzanian Gypsum

Tanzania is reported to have the best gypsum deposits in the world in terms of percentage purity situated in Pindiro and Mbane, Kilwa in Lindi regions (Tanzania Daily News, 2011). The geological evidence shows that the gypsum has about 90 per cent purity with enough stock to last for several decades, but roads and railway infrastructure poses a challenge to exploit the minerals (Abduel, 2011).

2.13 Uses of Gypsum in Tanzania

Itigi gypsite is good for chalk and plaster powder (now under production). The Kilwa occurrence (2Mt) are likely to have enough gypsum for plaster board production (Godfrey *et al*., 2002). Makoi and Ndakidemi (2007) reported the use of gypsum from Makanya deposit in reclamation of sodic soils in Kilimanjaro of Tanzania. Also Bagarama *et al*. (2012) reported the use of gypsum from Itigi for groundnuts fertilization in Tabora of Tanzania. Aloyce *et al*. (2014) reported the use of gypsum for manufacturing cement for building purposes.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of Gypsite Sampling Sites

3.1.1 Makanya site

Makanya is located in Same District, Same is one among the six districts constituting Kilimanjaro Region and it is located in the semi-arid plains of the Western Pare lowlands with coordinates of latitude 4^0 15’S and longitude 37^0 55’ E. Rainfall distribution is bimodal, with an average annual average of 400-600 mm. The short rainy season *Vuli* is experienced during November to January. Short rain is lower and less reliable than the long rainy season *Masika* experienced from March to May. The mean temperatures range from 16 ^oC (July to August) to 32 ^oC (January) and the potential surface evaporation exceeds rainfall in five to ten months of the year. The topography is characterized by scattered hills at the foot of the Pare Mountains, descending to undulating and rolling plains and flat, wide depressions. The highlands are the source of numerous springs and streams that drain into the permanent River Pangani.

3.1.2 Msagali site

Msagali is a village situated in Mpwapwa District, Dodoma in Tanzania. It is located at latitude 6^0 45' S and longitude 36^0 20' E. It is bordered to the west by the Dodoma Urban district, and to the north by the Kongwa District. The area receives an average of about 700 mm per year of rainfall with a unimodal type of distribution of which 90% falls between December and April, and there is usually a dry spell in February.

Average monthly temperatures ranges from a minimum of 15.8 ^{o}C in August to a maximum of 27.7^{0}C in November (Mboera *et al*., 2001).

3.1.3 Itigi site

Itigi is situated in Manyoni, Singida, Tanzania. Its geographical coordinates are latitude 5° 42' 0" South and longitude 34° 29' 0" East. Singida forms part of the semi-arid central zone of Tanzania, which experiences low rainfall and short rainy seasons which are often erratic, with fairly widespread drought in one year out of four. Total rainfall ranges from 500 mm to 800 mm per annum, with high geographical, seasonal and annual variation. There are two rather well defined seasons, the short rainy season during the months of December to March or sometimes goes to April and the long dry season from April to November.

The wetter areas in Singida region are along the escarpment near Kiomboi in Iramba district and in the south-west of Manyoni district near Rungwa, where the long-term mean annual rainfall exceeds 800 mm. The mean annual rainfall is in the range of 600 mm to 800 mm over large areas of Iramba and Singida districts. On the eastern side of Manyoni district near the Bahi Swamp and the Rift Valley depression of Mgori and Shelui divisions lies the drier area in the region where the mean annual rainfall is less than 550 mm. The regional mean annual average rainfall is 700 mm.

The temperatures in the region vary according to altitude but generally range from about 15 °C in July to 30 °C during the month of October. Moreover, temperature differences are observed between day and night and may be very high, with hot afternoons going up to 35 °C and chilly nights going down to 10 °C.

3.1.4 Pindiro site

Pindiro is located in Kilwa District latitude 9° 29’44” S and longitude 39°18’36” E. Is the most northerly district in the Lindi Region of southern Tanzania. To the east is the Indian Ocean, and to the west is the Selous Game Reserve. The area has high annual average temperature of 30.5°C, annual average low temperature of 22.8°C, average temperature 26.7°C also receive annual precipitation of 936 mm.

3.2 Sampling and Analysis of Gypsite Samples

3.2.1 Sampling

Five composite samples of gypsite were randomly collected from each site including Pindiro, Msagali, Itigi and Makanya. The collected samples, were then placed in labelled polyethylene bags and transported to Soil Science Laboratory at Sokoine University of Agriculture, Morogoro Tanzania where the determination of nutrients extractability, incubation and pot experiment studies were conducted. Some samples were taken to Geological Survey of Tanzania Laboratory in Dodoma, where the determinations of the chemical compositions were carried out.

3.2.2 Laboratory analysis

The samples were processed and prepared for laboratory analysis following standard procedures. Chemical compositions of the collected gypsite rocks were determined by using X-ray Fluorescence (XRF) method by the use of XRF machine model: PW4030 with Rh tube and spinner (Khan and Webster, 1968).

Samples were crushed to reduce the size and then mixed well and ground to pass through 75 microns sieve. The ground samples were put in cup covered with polyesterpetp X-ray film 9430 500 07191 at the bottom and compressed. The samples were then placed into a calibrated XRF machine for analysis. Analysis was done by using *Minipal Analytical Software* at the Geological Survey of Tanzania in Dodoma.

3.2.3 Loss on ignition

Porcelain crucibles were heated in the laboratory furnace for 1 h at 100 ^{0}C and then crucibles were taken out of furnace with tongs and placed into desiccators to cool at room temperature. Weight of crucibles were taken and noted down in the note book. One gram of each sample was weighed into the crucible and put into the cool furnace then heated to 900 ^{0}C for 1 h. The samples were placed in desiccators and cooled at room temperature and thereafter reweighed. Loss on ignition (L.O.I) was calculated by using the formula:

$$\mathrm{L.O.I}\,(\%) = \frac{M_0 - M_1}{M_0 - M_c} \times 100$$

Whereas M_o = original mass of sample + crucible; M_l = mass of ignited sample + crucible; and Mc = mass of ignite crucible

3.2.4 Determination of the Extractability of Sulphur, Calcium, Magnesium and Potentially Toxic Elements (PTEs)

Gypsite rock samples were ground to pass through 0.5 mm sieve to ensure high solubility. Extractable sulphur was determined by using $BaCl_2$ turbidimetric method and measurement was done using UV Spectrophotometer (Moberg, 2001). Calcium and magnesium were determined in the neutral ammonium acetate leachate (NH_4OAc, pH 7) saturation method (Moberg, 2001) and quantified by atomic absorption spectrophotometry. Extractable potentially toxic elements (PTEs) were extracted using buffered 0.05 M DTP A (Diethylenetriamine penta acetic acid) and their concentrations were determined by Atomic Absorption Spectrophotometer (AAS- UNICAM 919 model) (Lindsay and Norvell, 1978). These analyses were conducted at the Sokoine University of Agriculture, in the laboratory of the Department of Soil Science.

3.3 Soil Sampling for Incubation and Pot Experiment

One composite soil sample was randomly collected from three different points at the depth of 0-20 cm. The soil for the experiment was collected from SUA Farm, Magadu site at latitude 06^0 51' 15.0" S and longitude 37^0 38' 33.1" E, and altitude 540 m mean above sea level. The soil at this site is isohyperthermic, very fine, and kaolinitic Kanhaplic Haplustult (Msanya *et al*., 2004). The composite soil sample was air-dried, ground and sieved through 2 mm sieve and analysed for physiochemical properties using standard procedures (Moberg, 2001).

3.4. Soil preparation for Incubation and Pot Experiment

The soil used for incubation and pot experiment was air-dried, ground and sieved through 8 mm sieve.

3.5 Soil Analyses

3.5.1 Physical properties of the soil

Physical property determined was the particle size distribution. This was determined by the hydrometer method after dispersing the soil sample in sodium hexametaphosphate solution (Gee and Bauder, 1986) and the corresponding soil textural class was determined using the USDA textural class triangle (USDA, 1995).

3.5.2 Chemical properties of the soil

Soil pH was determined using a pH electrode meter in 1:2.5 soil: water suspension as described by McLean, (1982). Total nitrogen was determined by micro-Kjeldahl distillation method followed by distillation (Okalebo, 2002). Available P was determined by spectrophotometer using filtrates extracted according to the Bray-1 method and colour development by ascorbic acid method of (Okalebo, 2002).

Cation exchange capacity (CEC) was determined by using the neutral ammonium acetate (NH_4OAc, pH 7) saturation method (Moberg, 2001). Exchangeable Ca and Mg in the ammonium acetate leachates were quantified by atomic absorption spectrophotometry, while exchangeable K and Na were quantified using the flame photometer. Extractable Sulphur was determined by the using $BaCl_2$ turbidimetric method and measurement was done using UV Spectrophotometer (Moberg, 2001).

Extractable micronutrients (Zn, Cu, Fe and Mn) were extracted using buffered 0.005 M DTPA (Diethylene triamine penta acetic acid) and their concentrations determined by an Atomic Absorption Spectrophotometer (AAS - UNICAM 919 model) (Lindsay and Norvell, 1978).

3.6 Incubation study

Incubation study was carried out to assess the release of sulphur from gypsites.

Gypsites from Pindiro and Msagali sites were ground to 600 microns. Different rates as per Table 1 of each gypsite were mixed with 500 g of soil prepared as per section 3.4. The type of soil used this study is Kanhaplic Haplustult (Msanya *et al*. ,2004)

The mixture was incubated at a temperature of 25± $1^{O}C$ for 56 days in plastic containers and moistened to 60% of soil moisture field capacity. Soil moisture content was maintained at 60% by intermittent weighing the containers and compensating weight loss with tape water. Destructive sampling was done at 14-day intervals whereby at each sampling 5 g of wet soil was sampled and analyzed for the extractable sulphur by turbidimetric method described by Moberg (2001). Soil pH was determined at 56 days of incubation at 1:2.5 soil: water suspension as described by McLean (1982).

3.7 Pot Experiment

3.7.1 Preparation

Thirty six 4-kg composite soil samples were weighed into clean five litre plastic pots. Diammonium phosphate (DAP) fertilizer and gypsite were added into each pot according to the treatments and thoroughly mixed with soil before sowing of maize seeds as previously done by Chen *et al*., 2008; DeSutter and Cihacek, 2009. Gypsites were used as a source of S and was ground to pass through 600 microns sieve before mixing with soil as described by Chawla and Abrol (1982).

Gypsites from Msagali and Pindiro sites were used for pot experiment because of their high contents of S (13.26% and 15.32%, respectively) compared to gypsites from other studied sites. A 2 × 6 factorial experiment was laid down in a randomized complete block design. There were two factors in different levels namely: 1. Gypsite deposits: (i) Msagali, and (ii) Pindiro; 2. Application rates of gypsites (kg ha^{-1}). Each gypsite rate was replicated three times making total of 36 pots because of two gypsite deposits.

In order to avoid limitations that might be caused by N and P deficiencies, DAP [$(NH_4)_2HPO_4$] was applied uniformly as source of N and P. This was applied at a rate of 150 kg N ha^{-1} and 75 kg P ha^{-1} equivalent to 0.698 g DAP per 4 kg soil pot, respectively. Urea ($CO(NH_2)_2$) was applied in two splits at 0.356 g per 4-kg soil pot to supplement for the deficit N encountered when DAP was applied. First half of urea was applied two weeks after seedlings emergence and the other half at the 4^{th} week after seedlings emergence. The N and P applications to the study soil were based on the fertilizer application rates used for maize production in Morogoro region by (Kisetu and Mtakimwa, 2013). Potassium containing fertilizers were not applied because based on the routine soil analysis, the soils had adequate K.

Table 1: Treatments used in the pot experiment and incubation study

Treatments	Rate applied gypsite kg ha^{1-}	Application rate(g) of gypsite/pot Msagali	Pindiro
T1	0	0	0
T2	20	0.37	0.32
T3	40	0.73	0.63
T4	80	1.46	1.26
T5	100	1.83	1.58
T6	160	2.20	1.90

3.7.2 Seed sowing

Maize (*Zea mays* L.) variety TMV-1 was used as a test crop in the pot study experiment. Four seeds were sown in the moistened soil and the moisture content of the soils in the pots was maintained at ± 90% field capacity for a week prior to sowing by timely application of tape water to replenish moisture lost due to evapotranspiration.

3.7.3 Management of maize plants in pots

Seedlings were thinned to two plants per pot at 12 days after sowing (DAS) and thereafter fertilizers DAP and Urea were applied.

3.8 Data collection

3.8.1 Plant height

Data on plant height was measured on weekly basis at 7th, 14th, 21st, 28th and 35th days after emergence by using tape measure for the measurement taken from the ground level to the tallest leaf.

3.8.2 Sampling and analysis of plant and soil samples

Plants were harvested at 35 days of age and the shoots and roots were rinsed in distilled water to remove soil particles. Shoots were harvested by cutting at 1 cm above the soil surface then dried in the oven at 65 ˚C for 48 h to constant weight. Dry matter weights of the shoots were determined by using digital electrical balance. The dried shoots were ground by using a cyclone mill to obtain powder and sieved through 1-mm sieve after which it was used for laboratory analysis.

In each sample of plant shoots from each treatment, 0.5 g was digested by using HNO_3-H_2O_2 wet digestion method described by Moberg (2001). The digests were used to determine concentrations of nutrients P, K, S, Mg, Ca, Na, Fe, Zn, Cu and Mn. Similarly, 0.2 g of each plant sample was digested using H_2O_2-$HClO_4$-HF in tubes in a block digester at 200 ^oC for 2 h. Thereafter, each digest was cooled and made up to volume of 50 ml and used for the determination of N content of the plants extract.

The soils used in pots were left for two weeks to dry. The soil samples were taken from each pot using a calibrated knife and thereafter ground, mixed evenly and sieved through a 2 mm sieve for determination of pH (MacLean, 1982), macro and micronutrients (Moberg, 2001).

3.9 Data Analysis

Statistical analysis was performed on soil pH, maize plant height, shoot dry matter yields, sulphur release in incubation study, nutrients concentrations in soil and plant materials after pot experiment. GenStat Discovery computer Software 14th edition was used. Treatment means separation was done using Duncan Multiple Range Test at the 5 % level of significance (Wim *et al.,* 2007).

3.10 Statistical Model

yij = ¹ + ¯*i* + ¿*j* + ²*ij* (5.1)

where

yij is the response of the *j*th treatment in the *i*th block;

¹ is the average response of all experimental units (overall mean);

¯*i* is the additive effect of the *i*th block;

¿*j* is the additive effect of the *j*th treatment; and

²*ij* is the random error of the experimental unit that receives the

*j*th treatment in the *i*th block.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Laboratory Analysis of Elemental Composition of the Gypsite

4.2.1 Chemical composition of gypsite

The data for chemical composition of the gypsites used in this study are presented in Table 2. The results showed that all gypsite samples were not 100% pure gypsum, having 35.76, 56.76, 71.26 and 82.36% of $CaSO_4{\cdot}2H_2O$ for Itigi, Makanya, Msagali and Pindiro deposits, respectively. Pure gypsum that contains 79% $CaSO_4$ and 21% $2H_2O$ with 18.6% S and 23.3% Ca (Dontsova and Norton, 2002). Results also indicated that gypsites from Msagali and Pindiro contain high contents of S of 13.26% and 15.32%, respectively compared to Itigi and Makanya deposit with 6.65% and 10.52% S, respectively. Calcium contents of all gypsites were 7.6%, 9.5%, 4.8% and 11% for Makanya, Msagali, Itigi and Pindiro, respectively. This variation was probably due to the variation in proportion of chemical elemental compositions of each deposit such as P, Mg, K, Na, Al, Si, Mn, As, Ni, Fe, Zn, Ba, Co and Cr. The compositions and concentrations of elements also depend on the chemistry of the host rock and environmental conditions, activating the weathering process (Brady and Weil, 2008).

Gypsum, calcium or magnesium carbonate, chlorides, other sulphate minerals, clay minerals or silica are considered as deleterious constituents of gypsites. As a result in most mines, production of gypsum will have the purity ranging between 70% and 95%. This study indicates that gypsites in Tanzania are very inconsistent and the percentage of calcium sulphate varies even in the same deposit.

Table 2: **The XRF analytical results of the gypsites samples**

						Elemental composition									
	L.O.I	SiO2	K2O	CaO	$CaSO_4$.2H2O	**Al**	**Cr**	**Fe**	**Mn**	**Co**	**P**	**Ni**	**Na**	**Ba**	**Mg**
Location		**(%)**								Mg/kg					
Makanya	21.6	12.96	< 0.01	35.01	56.53	0.18	0.004	0.72	180.78	39.26	11.86	<0.01	43.55	11.11	2062
Msagali	21.28	6.45	0.63	33.17	71.26	0.19	0.008	0.59	120.18	37.61	8.13	<0.01	35.3	12.47	2355.4
Itigi	24.45	24.39	< 0.01	34.7	35.76	0.18	0.005	0.66	137.85	29.62	14.68	40.8	50.61	13.03	2118.6
Pindiro	21.05	0.88	< 0.01	35.88	82.36	0.08	0.002	0.16	105.78	25.84	6.28	<0.01	32.07	11.84	2339.3

4.2.2 Loss on ignition

Loss on ignition implies the weight of gypsum after being heated. It indicates the prehydration or carbonation due to prolonged exposure to air, water and carbon dioxide. By heating gypsum up to 900 ^{0}C, water of crystallization and carbonates were lost. In addition, LOI indicates the quality of analysed samples. Samples with high LOI indicates low quality compared with materials containing low LOI. Results indicated that gypsite sample from Itigi deposit had high LOI (24.45%) hence was considered to have low quality compared to gypsite from Pindiro with 21.05% LOI, which is of the good quality. The results of LOI from the gypsites followed an increasing trend of quality of Itigi (24.45) > Makanya (21.60) > Msagali (21.28) > Pindiro (21.05). These results are in conformity with the findings of Harris (1981) which reported 85% purity of gypsum in Pindiro deposit. In addition, Abduel, (2011) reported that Tanzania has the best gypsum deposits in the world in terms of percentage purity, situated in Pindiro and Mbane, and Kilwa in Lindi region.

4.2.3 Macronutrients concentrations

Results of the concentrations of P, K_2O, CaO, $CaSO_4$, Na and Mg in the gypsite samples are shown in Table 2. The amount of total P in all samples was in medium range with values ranging from 6.28 to 14.68 mgkg^{-1} (Landon, 1991). Caires *et al.* (2003) reported that gypsum contains P as an impurity, and it is important for plant nutrition.

Potassium oxide (K_2O) in Msagali deposit was small (0.63%) while other deposits had K_2O < 0.01%. The amount of sodium was in the increasing trend of 32.07 <

35.30 < 43.55 < 50.61 mg/kg for Pindiro, Msagali, Makanya, and Itigi, respectively. Magnesium was high in all deposits whereas CaO and $CaSO_4$ were variable. However, Pindiro had high amounts of $CaSO_4$ followed by Msagali, Makanya and Itigi, respectively.

Furthermore, results showed that the studied gypsites had siliceous minerals probably quartz (SiO_2) as impurities. The amounts of SiO_2 differed among the deposits but Pindiro had the lowest while Itigi recorded the highest SiO_2. Quartz does not contribute important plant nutrients in soils and thus is regarded as impurities in gypsites.

Results in Table 2 showed that both deposits contain high amounts of Mg with concentration values of 2355.4 mg kg^{-1} and 2339.3 mg kg^{-1} for Msagali and Pindiro gypsites, respectively. However, only 0.69% and 0.73% equivalent to 16.28 and 17.19 mg kg^{-1} can be extracted by plants for metabolism (Table 3). Extractable Ca was 101.97 and 116.05 mg kg^{-1} for Msagali and Pindiro gypsites, respectively. The gypsite from Pindiro deposit had more extractable Ca which makes the difference of 14.08 mg kg^{-1} more than that found in Msagali deposit.

Table 3: Extractable sulphur, calcium, magnesium and some PTEs (mg kg^{-1}) in gypsites from Pindiro and Msagali deposits

Element	Pindiro site	Msagali site
SO_4-S	750.79	501.97
Mg	17.19	16.28
Ca	116.05	101.97
Cu	1.09	0.95
Fe	<0.01	<0.01
Zn	0.05	0.14
Mn	0.62	0.62
Co	<0.01	<0.01
Cd	< 0.01	< 0.01
Cr	< 0.01	< 0.01
Pb	< 0.01	< 0.01
Ni	< 0.01	< 0.01

4.2.4 Micronutrients concentrations

The XRF analytical results in Table 2 indicates that the micronutrients Fe was low in all gypsites while Mn was relatively medium compared to the amounts of these elements when present in soils (Landon, 1991). This shows that gypsite can supply Mn for plants.

4.2.5 Elements of environmental concern

Heavy metals accumulation in soils is of a major concern in agricultural production due to the adverse effects on food safety and marketability, crop growth due to phytotoxicity and environmental health of soil organisms. Metal toxicity has high impact and relevance to plants and consequently it affects the ecosystem, where the plants form an integral component. Table 3 shows that the amounts of extractable Ni, Cr, Co, Ba, and Al were in acceptable ranges. Dontsova *et al*. (2005) reported that the elements of environmental concern when present in high levels may cause toxicity or may affect the availability and uptake of essential plant nutrients in soils.

Nagajyotib *et al.* (2010) and Allaway (1968) reported the range of heavy metals of typical uncontaminated soils as follows;

Cd 0.01–0.7 mg kg^{-1}, Co 1– 40 mg kg^{-1} , Cr 5–3,000 mg kg^{-1}, Cu 2–100 mg kg^{-1}, Fe 7,000 –55,000 mg kg^{-1}, Mn 100 – 4,000 mg kg^{-1}, Mo 0.2–5 mg kg^{-1}, Ni 10 – 100 mg kg^{-1}, Pb 2–200 mg kg^{-1} and Zn 10 –300 mg kg^{-1}. Analysis of extractable fractions (Table 3) showed that none of the PTEs in gypsites can affect nutrients uptake by plant when applied as amendment or as fertilizer (as source of S and Ca).

Extractable fractions of micronutrients Zn and Mn for gypsites from Msagali and Pindiro were relatively small. According to Tisdale *et al.* (2003), the amount of extractable Zn found in gypsites from Pindiro and Msagali deposits are categorized as low while Cu is categorized as high. The amount of extractable Cu is sufficient when applied in soils. Total amount of Mn in gypsites from Msagali and Pindiro (Table 2) were 120.18 and 105.78 mg kg^{-1}, respectively but only 0.62 mg kg^{-1} could be extractable for both deposits (Table 3). The extractable fractions were equivalent to 0.5% and 0.59% for Msagali and Pindiro, respectively. According to Tisdale *et al.* (2003), 0.62 mg Mn kg^{-1} of extractable fractions found in both deposits could be rated as low when present in soils.

Heavy metals are generally toxic to most plants for their metabolism and growth, if their concentrations exceed some maximum permissible limits (Melo *et al.*, 2011). The extractable potentially toxic elements such as extractable Fe, Cd, Cr, Co and Ni found in the studied gypsites were all less than detectable limits and thus, use of these gypsites in soils could not have detrimental effects to plants. Total amount of

Co found in these deposits were 37.61 and 25.84 mg kg^{-1} but not easily extracted by plants. This could be attributed to the Co being strongly held in exchangeable sites of minerals present in gypsites. Msaki and Banzi (2010) reported that natural gypsum and gypsum derived products from Tanzania have traces of radioactivity. However, the associated levels are not detrimental to health.

4.4 Sulphur Release from Gypsite

The S release increased with time of incubation (Tables 4 and 5). Such mineralization is in synchrony with maize plants demand thus do not necessitating top dressing of S fertilizer as supplement for increased maize yields. Results showed that both deposits released significantly ($P<0.05$) substantial quantities at the 56 days of incubation compared to other days of incubation (Table 4 and 5). Out of the total released S during the entire period of incubation by each treatment, T2 to T6 ranged from 178 to 579 and 165.1 to 492.2 mg S kg^{1-} for Pindiro and Msagali respectively. The amount of S released from Pindiro gypsite by each treatment (T2 to T6) is equivalent to 56.5%, 30%, 39.6%, 35% and 30.5%, respectively. Msagali with treatment (T2 to T6) released 45%, 34.5%, 23.3%, 19.6% and 22.4% of S on the 56th days of incubation.

Table 4: Sulphur released from soils treated with gypsite from Msagali deposit under different days of incubation

Days of incubation	0	14	28	42	56
Treatments (g)			S(mgkg^{1-})		
T1	34.2d*	34.7f	35.1f	34.9f	34.5f
T2	35.0c	86.9e	88.4e	109.4e	165.1e
T3	35.2c	158.2d	180.3d	203.9d	289.1d
T4	37.5b	203.1c	239.2c	304.1c	340.1c
T5	37.5b	306.3b	397.7b	403.0b	357.6b
T6	37.7a	375.5a	401.2a	459.7a	492.2a
Mean	36.2	192.12	223.64	252.51	279.78
CV%	0.0	0.1	0.1	0.0	0.0
$LSD_{(0.05)}$	0.14	0.15	0.16	0.33	0.32

*Means in the same column followed by the same letter(s) are not significantly different at 5% level of significance according to Duncan Multiple Range Test

The results also showed that the studied gypsite from Msagali had residual effects that can benefit next seasons since mineralization will continue to release plant nutrients slowly. Sabir *et al*. (2007) also reported residual effect of gypsum on the yield of wheat crop. Previous studies have shown that in comparison to soil amendment with lime, gypsum releases substantial quantities of Ca and S, which are evenly distributed throughout the soil profile due to high solubility gypsum (Carter *et al*., 1986; Evanylo, 1989).

Table 5: Sulphur released from soils treated with gypsite from Pindiro deposit under different days of incubation

Days of incubation	0	14	28	42	56
Treatments(g)			S($mgkg^{-1}$)		
T1	34.41c*	35.3f	35.2f	34.8f	34.5f
T2	35.61b	85.1e	80.0e	173.3e	178.6e
T3	36.10b	138.0d	173.7d	190.0d	180.0d
T4	37.43a	227.3c	360.0c	376.6c	500.2c
T5	37.8a	272.3b	390.0b	469.3b	552.9b
T6	37.95a	363.7a	478.0a	501.7a	579.0a
Mean	36.55	186.97	252.9	290.95	337.54
CV%	0.0	0.3	0.1	0.3	2.7
$LSD_{(0.05)}$	0.12	3.67	2.62	3.59	39.96

*Means in the same column followed by the same letter(s) are not significantly different at 5% level of significance according to Duncan Multiple Range Test

4.5 Physical and Chemical Properties of Soil used for Incubation and Pot Experiment

The results of the physical and chemical properties of the studied soil are presented in Table 6.

4.5.1 Soil pH

Soil pH was 4.8 rated as very strong acid (Landon, 1991). The low value of soil pH at the study site could be due to loss of basic cations such as Ca, Mg and Na down the soil profiles even beyond sampling depth through leaching and surface runoff accelerated by the slant nature of the field where the soil was sampled. The loss of basic cations increases chances for the formation and high solubility of acid contributing cations such as Al^{3+} and H^+ in the soil solution thereby increasing soil acidity (Brady and Weil 2008).

The significance of pH lies in its influence on the availability of soil nutrients, solubility of toxic nutrient elements in the soil (Al – not a nutrient element, Fe, Cu and Mn), physical breakdown of root cells, cation exchange capacity in soils whose colloids (clay/humus) are pH-dependent, and on biological activity (Brady and Weil, 2008). However, despite the fact that texture and pH of this soil promise nutrients availability, it could be the case for most micronutrients including Cu, Zn, Mn, Fe, whose potential solubility increases under acidic soils with border pH ranges (5.0 – 6.0) and B and Cl which are independent of pH ranges (Brady and Weil, 2008).

Table 6: Chemical and physical properties of the experimental soils collected from Magadu SUA Farm

Parameter	SI-unit	Value	Status
pH (H_2O)		4.8	*Very strong acid
Total nitrogen	%	0.1	Low
Available phosphorus	mg/kg	2.72	Low
Extractable SO_4-S	mg/kg	35.24	Medium
Calcium	cmol (+)/kg	3.5	Low
Sodium	cmol (+)/kg	0.1	Low
Magnesium	cmol (+)/kg	1.7	High
Potassium	cmol (+)/kg	0.35	Medium
Cation exchange capacity (CEC)	cmol (+)/kg	16	Medium
Cu	mg/kg	2.4	High
Zn	mg/kg	8.7	High
Fe	mg/kg	85	Very high
Mn	mg/kg	82.2	High
Particle size			
Sand	%	39	
Clay	%	55	
Silt	%	6	
Textural class			Clay

*Status column is based on the ratings compiled by Landon (1991)

6.2.2 Extractable Phosphorus

The available P of the studied soil was 2.72 mg P kg^{-1} which is very low (< 6 mg P kg^{-1}) (Landon, 1991). Therefore, the very low available P implies that the soil is deficient in P calling for supplemental application for optimum crop production. According to Kisetu and Mtakimwa (2013), for optimum maize production in Magadu SUA Farm fields with very low available P, there should be deliberate application of at least 25 kg P ha^{-1}. Kisetu *et al.* (2013) reported that the low levels of available P in the soils of Magadu site of SUA Farm was attributed to the high leaching of basic cations thereby increasing soil acidity by acid forming cations (Al and H) and the hydro-oxides of Fe. These hydrated oxides have high ability of retaining P into forms which are unavailable for plant uptake. In other areas, previous studies have indicated that the low amounts of available P are caused by precipitation by Al, Fe, Mn, and by fixation of both oxides of Al, Fe, Mn and kaolinitic clays (Abrol *et al.,* 1988).

4.5.2 Soil Texture

The clayey nature of the studied soil suggests that the soil is potentially very reactive with numerous nutrients' exchange sites. Soil clay particles have been reported to increase availability of essential nutrient elements through cations and phosphates retention and render them susceptible for plant absorption (Kisetu *et al.,* 2013). According to Mutert and Fairhurst (2002), soil clay particles enhance retention and ease release of large amounts of the essential nutrient elements and increase water retention and availability to plants.

4.5.3 Total nitrogen

According to Landon (1991), the levels of nitrogen are low (0.1 – 0.2%) and this is attributed to the low organic matter and its soil parent material. This shows that the soils from this farm need to be supplied with organic matter and nitrogen in order to improve the N reserve in the soil. The low soil's total N indicates that N is deficient for the crop and this might be associated with N losses or N being not or poorly replenished during cropping cycles. Poor agronomic practices and cultivation systems have effects on the annual depletion of N in cultivated soils (Bekunda *et al.*, 2004).

4.5.4 Cation exchange capacity and exchangeable Cations

The cation exchange capacity (CEC) of the studied soil was medium (Table 6). Soils with CEC below 15 (cmol (+)/kg) are considered to be of low fertility status (Landon, 1991). Despite the high clay content the CEC of this soil is medium and this might be attributed to the clay. It is likely that the soil is dominated by low activity clay minerals such as kaolinite and aluminium and iron oxides (Szilas *et al.*, 2005). London (1991) reported the soil CEC ranges between 15 cmol (+)/kg and 25 cmol (+)/kg to be satisfactory for growth of most plants. Based on the ratings by Landon (1991) and Tisdale (2003) the levels of exchangeable bases (Table 6) are low for Ca^{2+} and Na^{+}, medium for K^{+} and high for Mg^{2+}.

4.5.6 Extractable sulphate

The level of soil's extractable S was medium with value of 35.24 mg kg^{1-} SO_4 (Landon, 1991). This level of S in the soil might be associated with previous application of S containing fertilizers (Johnson Semoka, 2015; Personal communication). Brady and Weil (2002), Hall (2008) and Tandon (1984) reported that several factors contribute to sulphur deficiencies including increased use of S-free high analysis fertilizers, multiple and high intensity cropping, removal of crop residues for feed and fuel, leaching and erosion.

4.5.7 Level of micronutrients

Results in Table 6 indicate that the amount of Cu in the studied soil was above the critical range of (2.4 mg Cu /kg). This level of Cu indicates that the soil has adequate Cu. On the other hand, the extractable Zn in the soil was above the critical levels of 0.2 to 2.0 mg/kg suggesting that the amount of Zn in this soil is very high and does not easily reflect its deficiency to plants under other optimal crop growth conditions (Sims and Johnson, 1991).

Based on the critical ranges of Fe (2.5 to 5.0 mg /kg) and Mn (1.0 to 5.0 mg/kg) (Sims and Johnson, 1991), the quantities of Fe and Mn in the studied soil were below the critical levels. Landon (1991) indicated that the levels of micronutrients, Cu, Fe, Mn and Zn under acidic conditions (pH of 5.0) should be high or reaching the toxic levels. This could be attributed by the parent material having high level of micronutrients; hence, high is released to the soil solution (Landon, 1991).

4.8 Response of maize to the applied gypsites

Results on the response of maize plants to the application of gypsite from Msagali and Pindiro sites are presented in Table 7. The results revealed that plant height was significantly ($P<0.05$) enhanced by applied amendments (gypsites). Plant height increased with increasing S levels, whereas the highest plant heights of 137.3 cm and 141.3 cm were obtained by application of 2.196 g/pot and 1.896 g/pot of gypsites for Msagali and Pindiro, respectively. The increase in plant height is attributed to the applied nitrogen due to its ability to promote plant growth, increases the number and length of internodes which results in progressive increase in plant height (Gasim, 2001). Similar results were reported by Koul (1997), Saigusa *et al*. (1999), Gasim, (2001) and Amin, (2011). This finding shows that the combination of S and N as plant nutrients increased plant height. This is also in agreement with the findings of Sahid *et al*. (1990), Omara (1989), Bindra and Kharwara (1994), Elmar (2001), Abdelnd Gader (2007) and Amin (2011). However, the remarkable increase in maize plant height attained for Pindiro gypsite could be attributed to its purity with S of 15.32% compared with Msagali deposit with S of 13.26 %.

Table 7: Effect of gypsites on plant height and shoot dry matter yields

Treatments	Plant height (cm)		Shoot dry matter (g/pot)	
	Msagali	Pindiro	Msagali	Pindiro
T1 (control)	128.3c*	125.7f	19.81f	18.66d
T2	126.3e	135.0d	20.18e	16.93e
T3	127.0d	136.7c	21.76d	18.64d
T4	131.7b	137.3b	22.68c	25.62a
T5	137.0a	132.7e	24.73b	20.48c
T6	137.3a	141.3a	25.41a	24.16b
Mean	131.3	134.8	22.4	20.7
$LSD_{(0.05)}$	13.98	16.44	8.86	10.36
CV (%)	3.4	2.1	1.6	7.7

*Means in the same column followed by the same letter(s) are not significantly different at 5% level of significance according to Duncan Multiple Range Test

The results showed that for the gypsite from Msagali deposit the lowest shoot dry matter weight (19.81 g/pot) was recorded from the absolute control and differed statistically ($P<0.05$) with the shoot dry matter weight values obtained from other treatments. Gypsite application at 2.2g (Table 6) significantly ($P<0.05$) increased shoot dry matter yield to 25.41 g/pot compared with the absolute control (19.81 g/pot). High dry matter yield with sulphur application was also reported by Kochar *et al*. (1990), Mahmood (1995) and Grobler *et al*. (1999).

Furthermore, results indicated that gypsite from Pindiro deposit showed significant ($P<0.05$) difference in shoot dry matter. The findings of this study suggest that higher rates of S from gypsite could not necessarily increase shoot dry matter yield in maize, and thus the optimum shoot dry matter content of 25.62 g/pot could be achieved at an application of 1.26g of gypsite per pot equivalent to 80 kg/ha of S. Khan *et al*. (2006) reported the increase in maize yield by application of gypsum up to 60 kg ha^{-1}. In two other similar studies Haq *et al*. (1988; 1989), 20.5 and 9.8% increase in the maize yield and wheat, respectively, were recorded with application of 72 kg S ha^{-1}. Furthermore, Sakal *et al.* (2000) reported that S application up to 40 kg ha^{-1} enhanced the average grain yield of maize by 0.99 t ha^{-1}. Ganeshamurthy, (1996) reported the optimum response of soybean to S at 40 kg S $ha^{-1.}$ Subhani (2003) reported that application of different S fertilizers (10-50 kg S ha^{-1}) significantly increased the yield of maize crop.

4.9 Effect of Gypsite on Some Chemical Properties of the Soil

Results of the effect of gypsite application on some soil properties are presented in (Tables 8, 9 and 10), and discussed under this section.

4.9.1 Soil pH

The levels of soil pH were reduced by 3.6% and 3.8% after pot experiment and by 8.79% and 8.74% after incubation using gypsites from Pindiro and Msagali deposits, respectively (Table 8). The pH declined significantly (P<0.05) with the increase in amounts of gypsite compared to the untreated (control) soil. This clearly shows that both sources of sulphur (gypsites) have an acidifying effect on soil pH. This indicates the need for liming along with the application of gypsite to the soils, which is not only to neutralize the soil acidity but favours sulphur availability.

According to Shainberg *et al*. (1989), the magnitude of the soil pH to change with gypsum, when present, can vary from 0.2 to 0.3 units, and these differences usually do not appear in pH as measured in $CaCl_2$. Gypsum can decrease the pH by replacement of exchangeable H and Al by Ca, or increase pH by replacement of exchangeable OH^- by SO_4^{2-}. Results have been reported to have an increase, decrease, or little effect of gypsum on soil pH (Ernani *et al*. 2004; Farina *et al*., 2000; Toma *et al*., 1999; Shainberg *et al*., 1989; Pavan *et al*., 1984). Also Dash *et al*. (2012) reported the changes in soil pH due to gypsum application in acid soils.

Table 8: Effect of gypsites from Msagali and Pindiro deposits on soil pH (water) after 35 and 42 days of pot experiment and incubation study, respectively

	35 days pot experiment		42 days of incubation	
	pH water (1:2.5)		pH water (1:2.5)	
Treatments	Msagali	Pindiro	Msagali	Pindiro
T1	4.8a*	4.8a	4.5a	4.4a
T2	4.7b	4.7b	4.3b	4.3b
T3	4.7b	4.6c	4.2c	4.2c
T4	4.6c	4.7b	4.1d	4.1d
T5	4.6c	4.8a	4.1d	4.1d
T6	4.6c	4.8a	4.1d	4.1d
Mean	4.7	4.71	4.2	4.19
LSD(0.05)	0.07	0.13	0.18	0.14
CV%	0.1	0.9	1.1	0.3

*Means in the same column followed by similar letter(s) are not statistically different at 5% level of significance according to Duncan Multiple Range Test

Verma and Abrol (1980) reported that decrease in soil pH may be due to replacement of Na^+ by Mg^+ and Ca^+ in the exchange sites of clay complex through addition of gypsite that supplied soluble calcium directly to the soil. In the present study, soil pH decreased by more than 0.18 and 0.39 units for pot and incubation experiments, respectively, and these results are similar with those of Soliman *et al.* (1992) where a decrease in soil pH by 0.2, 0.5 and 0.9 units was reported as a result of increasing S applications. The findings of this study are also in line with those of Velarda *et al*. (2005) who observed a small (0.3 units), non-significant reduction in soil pH with application of 125 kg S ha^{-1}. Soaud *et al*. (2011) observed a significant reduction in pH of calcareous soils due to S application during first eight weeks of incubation and after soil pH started to increase over time. Skwierawska *et al*. (2008) recorded a significant reduction in soil pH from 5.3 to 4.36 with application of 120 kg S/ha at the end of a three year experiment. Also unpublished data by Gwasso (2003) indicates that soil pH levels were reduced by 21% due to application of gypsum.

4.9.2 Available phosphorus

The quantity of available P was not affected by the application of gypsites (Tables 9 and 10) from both Msagali and Pindiro deposits. Since DAP was applied uniformly in all pots as P source during sowing of maize, some but insignificant (P<0.05) effects of gypsites on P concentration could be due to applied DAP. The P content in gypsites was 6.28 and 8.13 mg kg^{-1} for Pindiro and Msagali, respectively, compared to the very low amount of available P in untreated soil.

Table 9: Effect of gypsite from Msagali deposit on soil nutrient levels after 35 days of pot experiment

	N	K	Ca	Mg	Na	P	SO_4-S	Fe	Zn	Cu	Mn
Treatment	%	cmol(+)kg^{-1}				mg/kg					
T1	0.14a*	0.21b	3.93c	1.21a	0.12a	16.28ab	36.41a	78.95b	8.3bc	1.87ab	61.2c
T2	0.13a	0.24a	4.38ab	1.16a	0.13a	14.59a	79.78b	78.42b	8.3bc	1.97a	59.2d
T3	0.14a	0.21b	4.12ab	1.08a	0.12a	15.14ab	59.15c	78.68b	7.8ab	1.87ab	59.2d
T4	0.14a	0.20ab	4.63b	1.21a	0.12a	13.06a	64.41ab	79.74b	8.2bc	1.70c	63.1b
T5	0.14a	0.19c	4.69b	1.13a	0.13a	16.32ab	86.88a	77.89b	7.6a	1.78b	62.7ab
T6	0.14a	0.19c	5.02a	1.31a	0.12a	18.80b	80.18b	87.37a	8.4c	1.97a	71.5a
Mean	0.13	0.206	4.49	1.18	0.12	15.7	67.8	80.18	8.1	1.86	62.8
LSD	0.01	0.04	0.72	0.31	0.02	3.6	38.01	5.4	0.5	0.17	8.92
CV (%)	3	2.7	1.1	4	5.1	6	10.6	3.7	0.7	2.8	1.6

*Means in the same column followed by similar letter(s) are not statistically different at 5% level of significance according to Duncan Multiple Range Test

Table 10: Effect of gypsite from Pindiro deposit on soil nutrient levels after 35 days of pot experiment

	N	K	Ca	Mg	Na	P	SO_4-S	Fe	Zn	Cu	Mn
Treatments	%	cmol (+) kg^{-1}				mg kg^{-1}					
T1	0.14a*	0.24a	3.93b	1.13ab	0.12a	21.71a	37.3f	87.37b	8.1bc	1.87a	65.1a
T2	0.13a	0.22b	4.69a	1.22a	0.13a	17.62a	70.6e	80.00c	7.4a	1.77a	65.9a
T3	0.14a	0.20ab	4.89a	1.18ab	0.13a	20.29a	181.5d	80.79c	8.4bcd	1.80a	63.9b
T4	0.13a	0.22b	4.89a	1.21b	0.13a	18.68a	190.5c	90.53a	8.6cd	1.91a	65.5a
T5	0.13a	0.20ab	4.69a	1.10c	0.12a	19.70a	232.1b	82.37bc	8.8d	1.77a	66.3a
T6	0.14a	0.22b	4.23a	1.08c	0.11a	18.92a	318.6a	81.58bc	7.8ab	1.87a	67.9a
Mean	0.13	0.216	4.55	1.151	0.12	19.49	171.8	83.77	8.2	1.83	65.8
LSD(<0.05)	0.01	0.02	0.3	0.12	0.03	7.3	148.1	5.08	0.65	0.17	13.73
CV (%)	0.7	3.2	2.2	2	4.5	5.2	6.6	1.5	1.7	3.8	1.8

*Means in the same column followed by similar letter(s) are not statistically different at 5% level of significance according to Duncan Multiple Range Test

The findings of this study revealed that the post-harvest analysis signifies increase in the available P in the soil. This could be due to addition of high amounts of Ca ions that could have contributed to the decrease in P availability (Elrashidi *et al.,* 2010). Ritche *et al*. (1995) reported a decrease in P concentration in soil due to gypsum application. Caires *et al*. (2003; 2006) reported that P contained in the gypsum as an impurity is important for plant nutrition when high rates of gypsum are applied.

4.9.3 Total nitrogen

The levels of total N did not differ significantly with application of gypsites from both Msagali and Pindiro deposits. Although total N was statistically similar across all treatments, there was a general increase in total N contents in soils from 0.13 to 0.14%.

4.9.4 Exchangeable bases

For the levels of exchangeable bases Ca increased by 19.6 and 21.7% in Pindiro and Msagali deposits compared to untreated/control soil. Similar trend had also been observed by Verma and Abrol (1980), Menzies *et al.* (1994), Ritchey *et al*. 1995), Ernani and Miquelluti (2006), and Ernani and Barber (1993). These findings suggest that gypsum can be beneficial to crops with high calcium requirements in acid (Toma *et al*., 1999) and non-acid soils (Laya *et al*., 1998).

The levels of exchangeable K were also not affected by the application of gypsites from both Msagali and Pindiro deposits. The soil which did not receive gypsite from Pindiro deposit had significantly ($P < 0.05$) higher K compared with the K from the soil treated with different rates of gypsite. The variation was not observed in gypsite from Msagali deposit among gypsite levels and with the absolute control. These observations could be attributed to the fact that gypsite and other treatments used in this study do not contain K, and thus, the K obtained is related to its exchangeable potential in the soil ecosystem. These findings are similar to those of Ernani and Miquelluti (2006) who found that the application of gypsum had no effect on the levels of extractable K.

The levels of exchangeable Mg were affected by the application of gypsites. In the soil treated with gypsites from Pindiro and Msagali deposits Mg increased by 12% and 17% respectively. The results in Tables 9 and 10 showed that there was no systematic trend increase in exchangeable Mg with increase in rates of gypsite application. Also there was no significant (P<0.05) difference in the amounts of Mg among gypsite levels from Msagali deposit. On the other hand, only application of gypsite at 1.26 and 1.9 g from Pindiro deposit showed variations in exchangeable Mg compared with the untreated soil. In comparison between the two gypsites, the gypsite from Msagali deposit was superior to gypsite from Pindiro deposit on increasing exchangeable Mg. Similar findings were reported by Menzies *et al.* (1994) that Mg availability in soil increased with application of gypsum. Results generated for the gypsite from Msagali deposit are in line with those of Ernani and Miquelluti (2006) and Ritchey *et al*. (1995) who reported that the application of gypsum had no effect on extractable Mg.

Results in Table 9 and 10 indicated that the exchangeable Na was not affected by the application of the two gypsites. There was no significant difference in Na for the soils treated with gypsites from both Pindiro and Msagali deposits. However, application of gypsite from Pindiro deposit at 1.9g reduced Na by 0.01 units showing that the application of Pindiro gypsite in rates higher than 160 kg ha^{-1} could result in reduction in Na. Vema and Abrol (1980) and Chauhan (1995) observed the reduction in Na due to the application of gypsum but in unspecified rates and rock-source.

4.9.5 Available SO_4-S

Results in Tables 9 and 10 showed that application of gypsites from both Pindiro and Msagali deposits at all levels resulted into significant (P<0.05) increase in SO_4-S concentration compared with the untreated soil as indicated in (Tables 9 and 10). Maximum SO_4-S concentration of 318.6 and 86.88 mg kg^{-1} in soil was recorded at an application of gypsites at rates equivalent to 160 and 100 kg S ha^{-1} for Pindiro and Msagali, respectively. The SO_4-S build up in soils with increasing application of S has also been reported by Sreemanarayana and Raju (1994), Ritchey *et al*. (1995) and Barbora (1995). Balangoudar *et al*. (1999) also reported that the available sulphur content in soils increased with increase in sulphur levels from 0 to 40 kg S ha^{-1} after harvests of green gram.

4.9.6 Extractable micronutrients

Results in Table 9 and 10 indicates that extractable Cu did not differ significantly (P<0.05) among the gypsite rates from Pindiro deposit (Tables 9 and 10). On the other hand, gypsite from Msagali deposit applied at 0.37 and 2.2 significantly

(*P*<0.05) increased levels of Cu in the soil. The amounts of Cu from the soil treated with gypsites ranged from 1.77 to 1.87 mg kg^{-1} for Pindiro deposit and from 1.70 to1.97 mg kg^{-1} for Msagali deposit. Sims and Johnson (1991) reported that the critical range of Cu is from 0.1 to 0.25 mg kg^{-1} and 0.2 mg kg^{-1} of Cu in soils is adequate for plant growth (Lindsay and Norvell, 1978). Application of gypsite from Pindiro deposit at 1.26g increased the amount of Cu by 2.1% and application of gypsite from Msagali deposit at 0.37 and 2.2 increased the amount of extractable Cu by 5.1%.

The quantities of Zn in the study soils differed significantly (*P*<0.05) with application of gypsites from both Pindiro and Msagali deposits. The quantities of Zn ranged from 7.4 to 8.8 mg kg^{-1} and 7.6 to 8.4 mg kg^{-1} for Pindiro and Msagali deposits, respectively as shown in (Tables 9 and 10). Application of gypsite from Pindiro deposit at 1.26 and 1.9g increased the amounts of Zn by 5.8 and 8%, respectively. With application of gypsite from Msagali deposit at 2.2 g the amount of Zn increased by 1.2%.

The amounts of extractable Mn did not differ significantly (*P*<0.05) with application of gypsite Pindiro deposit (Tables 9 and 10). However, for application of gypsite from Msagali deposit showed variations in the quantities of Mn and a rate of 2.2 g was significantly (*P*<0.05) the highest (71.5 mg kg^{-1}) as indicated in (Tables 9 and 10) .The values of Mn in the soil for all treatments ranged from 63.9 to 67.9 mg kg^{-1} and 59.2 to 71.5 mg kg^{-1} for the application of gypsites from Pindiro and Msagali deposits, respectively.

Moreover, results in Tables 9 and 10 showed that extractable Fe in all treatments regardless of the gypsite sources showed significant ($P<0.05$) difference. However, the amounts of Fe when gypsites were applied at T4 and T6 were higher than the rest of the treatments for the gypsites from both Pindiro and Msagali deposits. The quantities of Fe for all treatments ranged from 80.0 to 90 mg kg^{-1} and 77.89 to 87.37 mg kg^{-1} for Pindiro and Msagali deposits, respectively. These values indicated that application of gypsites from Pindiro and Msagali deposits generally increased the quantities of Fe by 3.5% and 9.6%, respectively, compared with the soil which was not treated with gypsites. Archana and Jitendra (2014) indicated that the application of gypsum significantly influenced the soil's available macronutrients such as N, P, K, and S and micronutrients such as Fe, Cu, Zn and Mn which could be associated with acidification that favours solubility of most micronutrients in soils (Vijay *et al*., 1997).

4.10 Effect of Gypsites on Nutrients Concentrations in Maize Shoots

4.10.1 Nitrogen, phosphorus and potassium

The results of effect of gypsites on N, P and K concentrations in maize plant shoots are presented in Table 11

Nitrogen concentration in maize shoots ranged from 1.2 to 1.5% and 1.4 to 2.6% for the application of gypsite from Msagali and Pindiro deposits, respectively (Table 11). These values are below the sufficiency range of N (3.5 - 5%) established for shoots of maize plants of 24 to 45 days after emergence (Lockman, 1984; Vandamme, 2008). The application of gypsites did not increase the concentration of N in maize shoots. These findings are similar with the findings generated from different studies conducted by Caires *et al*. (1999; 2003; 2004) who did not observe effect of gypsum application on the N concentration in maize tissues.

Table 11: Effect of gypsites from Msagali and Pindiro on nutrients N, P and K concentrations in maize plant shoots

	Msagali deposit			Pindiro deposit		
Treatments	N	P	K	N	P	K
		(%)			(%)	
T1	1.3a	0.10a	1.34b	1.5a	0.14a	1.46c
T2	1.5a	0.12ab	1.36b	1.4a	0.09a	1.49c
T3	1.2a	0.15b	1.49c	2.3c	0.16a	0.82a
T4	1.4a	0.08a	1.06a	2.6d	0.04b	1.11ab
T5	1.3a	0.21c	0.98a	1.9b	0.09a	1.41b
T6	1.3a	0.08a	1.35a	1.5a	0.11a	1.47b
Mean	1.3	0.12	1.26	1.9	0.11	1.29
LSD(0.05)	0.3	0.116	0.625	0.8	0.19	0.3
CV (%)	2	0.124	5.6	9.1	23.1	3.3

*Means in the same column followed by similar letter(s) are not statistically different at 5% level of significance according to Duncan Multiple Range Test

The concentration of P in maize shoots ranged from 0.04 to 0.16 % and 0.08 to 0.21% following applications of gypsites from Pindiro and Msagali deposits, respectively (Table 11). The sufficiency range of P (0.3 - 0.6%) was established for shoots of maize plants of 24 to 45 days after emergence (Lockman, 1984; Vandamme, 2008). These findings indicate that the concentrations of P in maize shoots for all treatments were below the sufficiency range suggesting that application of gypsites from both deposits did not increase P concentrations in maize shoots. This would probably be due to low solubility of gypsite thereby causing slow release of P in soil solution for maize plant uptake. Abrol *et al.* (1988) observed that in soils with low pH (<5) level P is likely to be fixed by hydrous-oxides of Fe, Mn, and Al hence hampering quantities of P released into soil solution. Kordlaghari and Rowell (2006) reported the reduction of P solubility by the application of gypsum.

The findings of the present study are also in agreement with those of Clark *et al*. (2001; 1997) who found that corn shoot P concentration decreased with increasing amounts of gypsum applications. However, in contrary, Stout *et al*. (2000) did not find any effect of agricultural gypsum on P uptake by the plant. Cox *et al.* (2005) found that the addition of gypsum increased the ability of the soils to retain P by the exchange of Ca for Al, Fe, and Mn. In addition, Moore and Miller (1994) and Coale *et al*. (1994) indicated that gypsum reduced P solubility by enhancing Ca-P precipitation.

Gypsites application did not affect K concentrations in the maize shoots. The concentration of K in maize shoots ranged from 0.98 to 1.36% and 0.82 to 1.49% for the application of gypsites from Msagali and Pindiro deposits, respectively (Table11). These results indicated that concentration of K in maize shoots is below the sufficiency range of 2.5 to 5.0% proposed by Steinhilber and Salak (2009) and Tisdale (1993). This low concentration of K in maize shoot could be attributed to the high hydration potential of K in highly weathered soils and its easiness of being leached beyond the root zone (Kisetu *et al.,* 2013).

4.10.3 Calcium, magnesium and sulphur

Results on the effect of gypsites on Ca, Mg and S in maize plant shoots are presented in Table 12**.** Gypsite rates of both deposits caused an increase in Ca concentration in the maize shoots (Table 12). Calcium concentrations ranged from 2.39 to 2.93% and 1.92 to 3.12% for the applications of gypsites from Pindiro and Msagali deposits, respectively. These concentrations are in sufficiency range of 0.5 - 1.6% established for shoot maize plants of 24 to 45 days after emergence based on the ratings given by Lockman (1984) and Vandamme (2008). Caires *et al.* (1999; 2003; 2004) reported increase in Ca concentration in maize leaves due to gypsum application whereas Sanderson and Eaton (2004) reported increase in leaf tissue Ca concentration in low bush blueberry.

Table 12: Effect of gypsites on nutrients Ca, Mg and S concentrations in maize plant shoots

	Msagali deposit			Pindiro deposit		
Treatments	Ca	Mg	S	Ca	Mg	S
		(%)			(%)	
T1	1.92ab	0.12ab	0.14c	2.39a	0.12a	0.14c
T2	3.12a	0.20a	0.18ab	2.53a	0.12a	0.16ab
T3	2.99b	0.18ab	0.20ab	2.93a	0.15a	0.18abc
T4	2.45b	0.13ab	0.22a	2.73a	0.16a	0.22a
T5	1.85c	0.08c	0.19ab	2.86a	0.17a	0.21bc
T6	2.39b	0.12ab	0.22a	2.46a	0.12a	0.20bc
Mean	2.45	0.14	0.20	2.65	0.14	0.18
LSD(0.05)	1.13	0.1033	0.06	0.76	0.05	0.04
CV (%)	6.2	8.6	7.8	2.65	6.7	4.6

*Means in the same column followed by similar letter(s) are not statistically different at 5% level of significance according to Duncan Multiple Range Test.

The concentrations of Mg in maize shoots ranged from 0.12 to 0.17% and 0.08 to 0.20% with the highest values of 0.17% and 0.20% being recorded in application of gypsites at 1.58 and 0.37g from Pindiro and Msagali deposits, respectively (Table 12). The lowest Mg concentrations of 0.12 and 0.08% were recorded in application of gypsites at 1.9 and 1.83g from both deposits. The critical range of Mg in maize shoots is given as 0.15 to 0.6% established for shoots of maize plants at 24 to 45 days after emergence suggested by Lockman (1984), Tisdale (1991) and Steinhilber and Salak (2009). These findings suggest that, the sufficient range of Mg concentration in the studied maize plant was achieved at applications of gypsites at 40, 80,100 for Pindiro deposit, and 20 and 40 kg ha^{-1} for Msagali deposit.

Results showed that S concentrations in maize shoots increased with increasing rates of gypsites applied, ranging from 0.14 - 0.22% with the highest value being 0.22% observed in 1.26 and 1.9 g applied gypsites from Pindiro and Msagali deposits, respectively (Table 12). The lowest S concentration of 0.14% was recorded in the control Pots where no gypsite was applied. The critical level of S in maize leaves is from 0.18 to 0.5% established for shoots of maize plants with age of 24 to 45 days after emergence (Lockman, 1984). The findings of this study indicated that S sufficient level was achieved with application of gypsites at 0.63, 1.26, 1.58, 1.9 g and 0.37, 0.73, 1.46, 1.83, 2.2g from Pindiro and Msagali deposits, respectively.

Increases in S concentration in maize shoots with gypsite application were also reported by Mahapatra *et al*. (2000), Toatia *et al*. (2000), Caires *et al*. (1999; 2003; 2004). Hitsuda *et al*. (2005) also found that S fertilization increased plant S concentrations. In addition, Farina and Channon (1988) reported enhanced S nutrition following gypsum application to maize and alfalfa. Similarly, Sanderson *et al*. (1996b) reported enhanced S nutrition in cabbage following gypsum application.

4.10.5 Micronutrients in maize shoots

Results on the effect of gypsites on some micronutrients concentrations in maize plant shoots are presented in Table 13.

The concentrations of Cu in maize shoots ranged from 5.34 to 9.59 mg kg^{-1} and 4.8 to 8.26 mg kg^{-1} (Table 13) for the application of gypsites from Msagali and Pindiro deposits, respectively. The sufficiency ranges of Cu in shoots of maize plants of 24 to 45 days after emergence are given as 6 to 20 mg kg^{-1} (Tisdale, 1993; Steinhilber and Salak, 2009). The sufficient range of Cu in the studied maize shoots was achieved when gypsites were applied at 20, 80,100,160 and 160 kg ha^{-1} from Msagali and Pindiro deposits, respectively. The highest level of Cu was recorded when gypsites were applied at 160 kg ha^{-1} with Cu concentration values of 9.59 and 8.26 mg kg^{-1} for Msagali and Pindiro deposits, respectively. This shows that application of high rates of gypsites could increase Cu concentrations in maize shoots but age of the maize plant should be specified. Ghosh *et al*. (2000) and Rahman *et al.* (2011) reported significant increase in Cu uptake by plants and attributed this with the acidification effect produced as a result of S addition from application of gypsum.

Table 13: Effect of gypsites on nutrients Zn, Cu, Fe and Mn concentrations in maize plant shoots

	Msagali deposit				Pindiro deposit			
Treatments	Zn	Cu	Fe	Mn	Zn	Cu	Fe	Mn
	mg kg^{-1}				mg kg^{-1}			
T1	40.57abc	5.34a	148.1c	22.95d	44.49b	5.60b	152c	24.0b
T2	45.88a	6.93a	163.6a	26.10b	39.50b	5.60b	192a	24.0b
T3	37.01c	5.87a	163.6a	24.0c	44.96b	4.80b	148c	23.65b
T4	43.89ab	8.26a	143.6ab	30.99a	40.21b	4.80b	146c	23.30b
T5	37.60ab	7.50a	143.6ab	24.35c	51.73a	5.60b	170ab	27.15a
T6	44.25ab	9.59b	207.9b	25.75b	43.65b	8.26a	190b	22.95b
Mean	41.53	7.24	161.7	26.7	44.1	5.78	167	24.18
LSD(0.05)	6.471	5.18	51.98	5.17	11.96	1.67	101	3.6
CV (%)	5.4	9.4	5.2	4.4	3.8	1.3	7.1	4.14

*Means in the same column followed by similar letter(s) are not statistically different at 5% level of significance according to Duncan Multiple Range Test

The concentrations of Fe in maize plant shoots increased with application of gypsites and ranged from 143.6 to 207.9 mg kg^{-1} and 146 to 190 mg kg^{-1} for Msagali and Pindiro deposits, respectively (Table 13). These levels of Fe are within the sufficiency range of 40 to 500 mg kg^{-1} given by Lockman (1984), Tisdale (1991) and Steinhilber and Salak (2009). This indicates that the growth of maize plants was not limited by shortage of Fe in the studied soil as also reported by Malewar and Ismail (1997).

Results also indicated that the concentrations of Zn in maize shoots ranged from 37.01 to 45.88 mg kg^{-1} and 39.5 to 51.73 mg kg^{-1} for the application of gypsites from Msagali and Pindiro deposits, respectively (Table 13). The sufficiency ranges of Zn for shoots of maize plants with age of 24 to 45 days after emergence are given as 20 to 60 mg kg^{-1} (Tisdale, 1993; Steinhilber and Salak, 2009). The highest levels of Zn in maize shoots were recorded in application of gypsites at 0.37 and 1.58g with values of 45.88 and 51.73 mg kg^{-1}, respectively. All treatments increased Zn concentration in maize shoots and all Zn concentrations fall within the sufficient range. This implies that maize plants could have taken up enough Zn released by the gypsites as one of its associate element or present in the natural soil being loosened by acidifying properties of S from gypsite (Ryant and Skládanka, 2009). The solubility of Zn increases with decrease in soil pH (Kisetu *et al.,* 2013; Yoo and James, 2003; Cui and Wang, 2005).

Results indicated that Mn concentrations in maize shoots ranged from 22.95 to 27.15 mg kg^{-1} and 22.95 to 30.99 mg kg^{-1} for the application of gypsites from Pindiro and Msagali deposits, respectively (Table 13). However, none of the treatments resulted into increased Mn concentration in maize shoots and all concentrations fall within the deficiency range. This implies that maize plants might not have taken up enough amounts of Mn present in the soil. The sufficiency ranges of Mn for shoots of maize plants with age of 24 to 45 days after emergence are given as 40 to 160 mg kg^{-1} (Tisdale, 1993; Steinhilber and Salak, 2009). Rahman *et al*. (2011) observed an increase in Mn uptake by maize plants with application of elemental S as a result of soil acidification although temporarily. Sanderson and Eaton (2004) reported increased leaf tissue Mn in low bush blueberry due to application of gypsum.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the results of this study the following conclusions were drawn

1. From the X-ray Fluorescence analysis, gypsites from different sources differ in terms of their quality as plant nutrient source and as soil amendment due to variations in their chemical composition. S contents of the gypsites followed the following trend Pindiro (15.32%) > Msagali (13.26) > Makanya (10.52%) > Itigi (6.65%).

2. All the studied gypsites samples contains potentially toxic elements, but the levels are not potentially toxic to plants and hence do not interfere with plant nutrient uptake.

3. Incubation study has revealed that the release of S from gypsite was slow, suggesting that gypsite takes long time to release nutrients. This leads to residual effect in soils that could benefit crop of next season and beyond.

4. Gypsite application has acidifying effect to the soils. In this study gypsite application reduced the pH by 0.4 units.

5. Application of gypsites did not increase N, P and K concentration in maize shoots. This could be due to low soil pH (<5) that affect some nutrients uptake by maize specifically phosphorus.

6. The tested gypsites increased Ca, Mg, S, Cu, Zn, Fe and Mn in soil suggesting that, they can be used to enhance availability of nutrients in soils with low levels of S and Ca.

5.2 Recommendations

1. Characterization of gypsites from other deposits in the country is required in order to generate information on their quantity and suitability for use on soil amendment for increased agricultural productivity of Tanzania soils. Also quantification of the good quality gypsite deposits is essential to ensure their long term availability.
2. The results from pot experiment should be extended to field level for verification under natural circumstances before concrete recommendations are made. Also the findings should be verified in other soils types.
3. Long term studies to assess the residual effect of gypsite on soil properties, maize yield and other crops are required.
4. Long term effects of PTEs in gypsite when applied in different soils should be studied.
5. Economic analysis on the benefits of using tested gypsites is important before attracting investors to process and sell to farmers.

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