CHAPTER ONE

GENERAL INTRODUCTION

1.1 Background of the Study

The term “potash” originally referred to impure form of potassium salt (mostly potassium carbonate) that were obtained from wood ashes. Potash mining became popular when it was discovered that the lager deposit exist beneath the earth’s crust and that burning entire wood for potash was unnecessarily wasteful (Hollerman *et al.,* 1985). Eventually potash became the common name for potassium carbonate and all other water – soluble potassium salt. These are almost exclusively retrieved through mining and it is now used as a collective grouping for the commercial product that can be derived from it (Hollerman *et al*., 1985).

Potash denotes a variety of mined and manufactured salts, which contain the element potassium in water soluble form (Jasinski, 2011). In some rare cases, potash can be formed with traces of organic materials such as plant remain, and this was the major historic sources for it before the industrial era. The name derives from “potash”, which refers to plant ashes soaked in water in a pot. (Dennis, 2006). Potassium derived its name from potash and was first derived by electrolysis of caustic potash, in 1808 by Cornishman Homphrey Davy (Hollerman *et al*., 1985). Potassium belongs to group one element in the periodic table. Potash became the term widely applied to naturally occurring potassium salt and the commercial product derived from them (Greenwood *et al*., 1997).

The chemical constituent of the water flowing into a potash bearing basin from precipitation run off , ground water, and hydrothermal springs have commonly been scavenged from the local country rocks. Source rocks of the constituent are most commonly acidic to the intermediate volcanic rocks, but also includes older saline rocks and continental sedimentary rocks (Alonso and Risacher, 1996; Risacher and Fritz, 2009). They have been explained as unusual marine evaporate , which are thought to be the result of , among things burial digenesis of normal marine evaporate or alteration of sea water composition within an evaporate basin (Borchert, 1997). Current global production and resources of potash are dominated by strata bond potash - bearing salt deposits. However, in some areas of the world, closed-basin potash bearing brines are the main source for production of potash. Closed-basin potash brines exist in many part of the world. Potash –bearing brine deposits have the potential ton contain significant economic contents of potash and other commodities; which includes salt (halide), boron, lithium and magnesium (Singer and Menzie, 2010). Most raw materials for industrial development are derived from natural resources (Maduka, 2001). The term is used by industries to refer to potassium chloride, as well as potassium sulphate, nitrate and oxide (Neuendorf *et al.*, 2005). Salts and potash deposits are natural mineral resources found in nature which are used in different industries. The industrial growth and development of a developing country depend largely on her available raw material resources as well as their exploitation and utilization (Maduka, 2001). Recent study conducted by the Raw Material Research and Development Council (RMRDC) has shown that the need to develop capacity for processing of these mineral into intermediate products is the most important requirement of the solid mineral in the country (Adetunji *et al.*, 2005). The Ministry of Solid Mineral Development coordinate these natural resources to enhance their utilization, sustainability, usability and to bring about accelerated national development (Aliyu, 1996). There are abundant deposits of natural potash in Yusufari Local Government Area of Yobe State, Nigeria that can be fully exploited for the production of potassium fertilizer. But people in the environ mine these potash locally for consumption and for animals feed supplement.

1.2 Statement of the Problem

Potash is generally used for food sweetening in local soup and it is also used as mineral supplement in animal feed. The composition of elements in potash deposit found in Yusufari Local Government Area of Yobe State, Nigeria have not been studied. This study would reveal the actual concentrations of major elements and that of some heavy metals. The result will be used as a guide to know the quality of potash and also the pollution level on potash deposit. There are abundance of Potash deposits in different areas in Yusufari Local Government Area which includes Madukuri, Kotufa, Kirba and the bordered villages between Yusufari and Niger Republic that need to be study.

1.3 Significance of the Study

Some of these salts are naturally occurring and are therefore liable to be contaminated with toxic elements which may affect the consumer. It is therefore very important to estimate the pollution load to ascertain whether it is safe for human consumption. Potash, whether naturally occurring or processed, has to be assessed for quality using most current instrumental techniques like atomic absorption and flame emission spectrophotometers. The results obtained would give a guide to consumers and will also create a base line study for future research work on potash deposits in the area.

1.4 Scope of Study

This research involves chemical analysis of potash deposits obtained from different locations in Yusufari Local Government Area of Yobe State, North eastern Nigeria using atomic absorption and flame emission spectrometers. The elements to be determined from the sample includes essential elements (Na, K, Mg, Ca) and the heavy metals (Zn, Fe, Cu, Pb, Cr and Cd). These instruments were chosen because they are very sensitive for these elements mentioned and can give desire result even at trace level.

1.5 Aim and Objectives

Aim:- The aim of this study is to estimate the quality of potash deposits found in Yusufari Local Government Area Yobe state, Nigeria.

The objectives of this study are-:

i. To determine the essential elements composition in potash

ii. To determine the heavy metal pollution load in potash

iii. To compare the concentration of non-essential components in potash with other standards

CHAPTER TWO

LITERATURE REVIEW

2.1 Sources of Potash

2.1.1 Natural Potash Deposits

Natural Potash deposits are formed as a result of evaporation of ancient lakes and seas over a long period of time. All the major solid potash deposits are of marine origin and were formed due to the evaporation of sea water in almost all geological systems in the Earth's history since the Cambrian period (Sonnenfield, 1984). In geological past, large inland seas existed for a time, which were separated from the ocean by straits and bars. These bars hindered or completely halted the influx of salt bearing sea water in the inland seas evaporate as if in a gigantic evaporation pan. As a result the salt concentration of the water increased and the dissolved salt crystallized, which were then deposited in the order of their solubility, first rock salt and later potassium and magnesium salt (Dennis, 2006). This process was repeated over millions of years and resulted in layers of rock salt with a thickness of several hundred meters and potash seams several meters in thickness being formed on top of each other. Later in the Earth's history, water-impervious clay strata settled on the salt deposits, thus preventing the salt from being dissolved again (*www.k-plus-s.com/en/wissen/vohstoff/)*. Large, deeply buried potash deposits are found in many marine evaporate and other formations through the world, and occur in every continent and most geological epochs from the Cambrian to the present (Sonnenfield, 1985).

A particular convincing case was the cretaceous potash evaporates of Brazil and Gabon as continental rift basin deposits derived from upwelling hydrothermal $CaCl_2$ brines Stefanson and Bjornson (1982).

During ancient geological ages, the potash bed were subjected to considerable folding and faulding (Singer, 1993;Menzie, 2010). Close-basin potash deposits contain the potential for extraction of multiple commodities including potash, lithium, boron, magnesium, and salt, and may include sodium sulphate, sodium carbonate, or sulphur (Erickson and Salas 1989; Casas *et al*. 1992. The geology within the drainage basin impacts chemistry of run off and spring waters and the resulting brine and thus controls not only which constituent and the ease with which a given potash can be extracted as reportal by these authors (Bryant *el al.,* 1994; Garrett, 1996; Carmona, 2000; Duan and Hu, 2001; Jones and Deocampo, 2003 and Jone *et al.*, 2009).

The sources of potassium in the rocks are weathered minerals such as arthoclose, microchine, biotite, leucite, and nepheline. Studies have found a positive correlation between potassium, lithium, and boron in brines (Zheng, 1984; Orris,1997; Carmona *et al.* 2000), which is probably indicative of their common origin in volcaniclastic terranes that typically are associated with convergent plate boundaries (Orris, 1997). Elevated levels of magnesium are also typical of many of the closed-basine brines (Orris, 1997). In addition to the potash- bearines, most of these basin have some surface or near- surface evaporates and salts. In some areas, such as the Qaidam Basin in China and the Chott el Djerid in Tunisia, extensive area of potash minerals may be found (Casas *el al.* 1992; Bryant *et al*. 1994). Duan and Hu (2001) reported that potash salt mineralization in the Qarhan playa in China ranges from disseminated potash mineral to stratoid lenses or layered bodies hosted by halide and other evaporates. The presence of an evaporated bearing salt lake may underlie much larger areas that are in part determined by the extend of a pre-existing lake and the porosity and permeability of the host sediments. Sub-basin may exist within larger basin and have distinctly different characteristic, such as chemistry or grade (Wang *et al*., 2005). Sizes of these deposits are highly variable, both in terms of area and the amount of potash contained within the brines (Jones *et al.,* 2009). However, on the basis of physicochemical consideration many potash salts were formed in a deeper setting because of the same mineralogical characteristic (Kovalevich *et al*., 1997).

2.1.2 Locally Manufactured Potash

Potash can also be produced locally apart from the natural occurring deposit on the earth crust. Local potash can be produced by burning broad leaf trees and wood in order to obtain ash. The ashes obtained from the burnt plant material are dissolved in water on a large pot. The dissolve ashes is leached in a large tron pots, hence the name "potash". After leaching, the solution of the potash then boiled using local fire wood in order to evaporate the water content. The solution is allowed to cool over night for crystallization to take place from the supersaturated solution of potash. Crystal of potash produced can now be used for local food sweetening or given to animal as feed supplement.

2.1.3 Common Names and Formular of Compounds that Contain Potassium

Table 2.1 Common Names and Formular of Compounds of Potassium

Common Name	Chemical Name	Formula
Potash Fertilizer	Potassium Oxide	K_2O
Caustic Potash or Potash lye	Potassium hydroxide	KOH
Carbonate of potash,	Potassium Carbonate	$K_2 CO_3$
Chlorate of Potash	Potassium Chlorade	$KClO_3$
Muriate of Potash	Potassium Chloride	KCl
Nitrate of potash or Salt peter	Potassium nitrate	KNO_3
Sulfate of Potash	Potassium Sulfate	$K_2 SO_4$
Permanganate of Potash	Potassium Permanganate	$K_2 MnO_4$

Source: Cameron (2008)

2.2 Potash Distribution and Trade

The importance of potash varies with local geology, with current and perceived future economic conditions, and with required need for that commodity (Casas et al., 1992) Potash was one of the most important industrials chemical in Canada. It was refined from the ashes of broad leaved trees and produced primarily in the forest area of Europe, Russia, and North America. The first U.S patent was issued in 1790 to Samuel Hopkins for an improvement "in making pot ash and pearl ash by a new apparatus and process" (Hoffman, 1988).

Potash production provided late 18 and early -19th century settlers in North America a way to obtain badly needed cash and credit as they cleared their wooded land for crops. Ashes from hard wood trees could be used to make lye (KOH), which could either be used to make soap or boiled down to produce valuable potash (Hoffman, 1988). In 1608 the first settlers in Virginia established a "glass house", and the first cargo to Britain included potash. Britain obtained most of its potash from Russia, but a potash crisis in about 1750 led parliament to remit the duty and led the society of Arts of London to offer premium for the production of potash in America (McCuster *et al*, 1985). Potash-making became a major industry in British North America. The American potash industry followed the woodman's ax across the country.

By 1850, potash had gained popularity as a fertilizer, but forest available for indiscriminate burning was becoming ever scarcer (Mcuster *et al*., 1985). The United States, having decimated its forests, joined most of the rest of the world in dependency on German potash. The dependency still existed when World War I cut off this source of supply. Frantic effort produced some domestic potash, notably from the complex brine of some western saline lakes (Mark, 2002).

The United States surmounted the wartime urgency, but the shortage directed attention to report of oil drilling that had brought up potash salts. These clues led to large deposit near Carlsbad, New Mexico. After 1931 a number of mines then supplied about 90 percent of the domestic requirement of potash, some 95 percent of this production became fertilizer (New Orleans, 2000). In 2005, Canada was the largest producer of potash with almost one-fourth of the world share followed by Russia and Belarus in soligorsk, according to the report of British geological survey. The most significant reserve of Canada’s potash is located in the province of Saskatchewan and controlled by the potash corporation of Saskatchewan (Canadian Encyclopedia, 2000). Unlike other producers, Israel’s Dead Sea work and Jordan’s Arab potash company use solar evaporation pans in the Dead Sea to produce carnallite from which potassium chloride is produced (Mark, 2002).

2.2.1 Locations of Potash Deposit

Some of the world's largest known potash deposits are spread all over the world from Saskatchewan Canada, to Brazil, Belarus, Germany, and more notably the Permian basin. The Permian basin deposit include the major mines outside of Carlsbad, New Mexico, to the world's purest potash deposit in Lea County, New Mexico, which is believed to be roughly 80% pure (Dennis, 2006). Canada is the largest producer, followed by Russia and Belarus. The most significant reserved of Canada's potash is located in the province of Saskatchewan and control by the potash corporation of Saskatchewan (Dennis, 2006). In the beginning of the 20th century potash deposit were found in the Dallol depression in Mustly and Crescent localities near the Ethiopian – Eritrean border. The estimated reserves are 173 and 12 million tones for Mustly and Crescent, respectively (New Orleans, 2000).

Table 2.2 Production and Resources of Potash in 2010.

Country	Production (Millions tonnes)	Reserves (millions tonnes)
Canada	9.5	4400
Russia	6.8	3300
Belarus	5.0	750
China	3.0	210
Germany	3.0	150
Israel	2.1	40
Jordan	1.2	40
United States	0.9	130
Chile	0.7	70
Brazil	0.4	300
United Kingdom	0.4	22
Spain	0.4	20
Other countries	-	50
World Total	33	7500

Sources: (Wikipedia Incyclopedia, 2012)

2.3 Potash as Fertilizer

Potash is the common name given to potassium carbonate and various mined and manufactured salts that contain the element potassium in water soluble form. Potash has been an important item of commerce for centuries; its principal uses are in the manufacture of fertilizer, soap, glass, and black gun powder (Hallbart, 1997). It became the principal product of the chemical industries in America before 1850 as a bye product of clearing the virgin forest land for agriculture. The total annual supply for these chemical uses, however never amounted to more than a few thousand tons for the entire world (Mcuster *et al.,* 1985).

Potassium is the third major plant and crop nutrient after nitrogen and phosphorus; it has been used as a soil fertilizer. Elemental potassium does not occur in nature because it reacts violently with water. Potash is important for agriculture because it improve water retention quality, yield, nutrient value, taste, colour, texture and disease resistance of food crops (New Orleans, 2000). Potassium fertilizers therefore make a decisive contribution to providing the growing world population with food, in term of both quantity and quality. Natural concentration of raw potash, consist of potassium salt rock, predominantly made up of the potassium mineral sylvite (KCl), Carnallite ($KMgCl_3 . 6H_2O$), kainite ($KMg[Cl|SO_4].2.75 H_2O$) and langbeinite ($K_2Mg_2(SO_4)_3$), or potassium – bearing salt solutions either underground or in salt lakes. (www.wikipedia.org/wiki/potash). Maximum crop production frequently requires the regular addition of soluble potash, even on relatively rich and virgin soils (Joseph, 2002). These deposits of sufficient concentration and suitable chemical composition formed in a deeper setting, depite having different stratigraphical position these potash deposits shows the same mineralogical characteristic (Kovalevich,1997).

2.4 Mining of Natural Potash Deposits

2.4.1 Conventional Underground Mining

Most potash occurrences are too deep underground for open – cast mining and thus this type of mining is therefore called underground mining. In deep mining, “room and pillars” method progresses along the potash seam, while pillars and timber are left standing to support the potash mine roof. Blasting methods utilize explosive to blast and break down ore and are more often applied in cases where potash seams are extremely variable or other limiting factors make continuous mining techniques impracticable. Blasting is most effective in managing mine sites with large variances in ore thickness, and requires less initial capital and maintenance than continuous mining, though generally result in higher cost over all (Joesten *et al.*, 1996). Continuous mining is used when the potash seam is sufficiently thick, stable and uniform. This allows miners to calibrate and apply continuous mining machines economically, despite their high initial cost and substantial maintenance, because they are incredibly efficient, are able to cut smoothly, provide low disturbance entry, and possess a high capacity (Mark, 2002).

In addition, continuous mining allows for the use of conveyor belt are haulage, allowing for the automation of the entire ore extraction process. In general, two type of continuous mining machine are used: Borer miners apply uniform cutting heads, and possess a higher capacity though they only cut a fixed seam thickness and with drum miners have rotating cutting heads that cut sideways against the face and despite their lower capacity, are better able to adapt to changing thicknesses (Joesten *et al.,* 1996).

2.4.2 Solution Mining

Solution mining is used when underground mines are very deep, have irregular deposit, or have become flooded and unworkable. The primary reason to utilize solution mining is based on the thickness of mineralization, the presence of faults, and the dip of potash beds, as an excessive dip can limit recovery (Mark, 2002). Resisting logging in boreholes may also of use in detecting saline brines because of the high conductivity and low resisting of saline brines, This techniques has been used by several of the recent exploration projects, where resistivity profile were constructed as part of the exploration effort (Houston, 2010). In solution mining, heat brine, a salt water solution is injected into the mine and circulated throughout to dissolve potash from the walls, once the compound have dissolved, submersible pump transport the solution to an evaporation pond, where the liquid cools and potash and salt crystals consequently settle to the bottom (Mark, 2002). This potash is eventually collected with floating dredges and then pumped to a mill for further processing.

(http://www.potash1.ca/,http://en.wikipedia.org/wiki/postash).

2.5 Importance of Potash to Humans and Animals

2.5.1 Potassium and Fitness

Potassium occurs abundantly in nature, being the 7th most common element in the earth's crust (Greenwood *et al*.1997). A diet that contains sufficient amount of potassium may reduce the risk of high blood pressure and stroke. A decrease in muscular strength is often due to a lack of this mineral in the diet (Barbara *et al.*, 2008). Sufficient potassium in your diet helps soothe feeling of anxiety, irritability and stress. Imagine being so fatigue you barely can get through the day. Your reflexes are slow, and your muscles are weak and often cramping. The depression that had you in its grip doesn’t seem to be lifting, and you frequently feel nauseated, the above signs are indication that your body is deficient in the mineral potassium. It is the third most abundant mineral in the body and is essential for your good health (Barbara *et al.*, 2008).

Foods rich in potassium are responsible for a number of health benefits. Sufficient amount in the diet helps keep your muscle strong (including that hard-working muscle, your heart) and help control blood pressure and the water balance in your cells. It also helps keep nerve impulses firing in top form, and releases energy from protein, fat and carbohydrates during metabolism. Sufficient amount in the diet helps protect the body against heart disease, hypoglycemia, diabetes, obesity and kidney disease. It helps keep muscles strong, bowels regular and work to eliminate irritability, confusion and stress. And it may help to lower high blood pressure, as well as protecting against the pressure, - boosting properties of sodium. The food and nutrition board of the National Academy of Science suggests the daily requirement for men and women is 2000-3500mg (U.S Food and Nutrition Board).

2.5.2 Uses of Potash

Potash has been used since antiquity in the manufacture of glass, soap and soil fertilizer (Godfrey, 1975). Potash is important for agriculture because it improve water retention, yield, nutrient value, taste, colour, texture and disease resistance of food crops (Joseph, 2002). It has wide application to fruit and vegetable, rice, wheat and other grains, sugar, corn, soybean, palm oil and cotton, all of which benefit from the nutrient quality enhancing properties (Joseph, 2002).

Potash has three main uses: fertilizer, livestock feed supplement and industrial processes. 95% of world's potash is use in fertilizer, while the rest is used for feed supplement and industrial production. In feed supplement, the key function of potash is to contribute to animal growth and milk production. Potassium fulfills numerous vital functions in various processes in plant, animal and human. Potash is used to make special type of glass; potassium silicate is used as a dehydrating agent, it is also used to produce pigment, printing ink and soft soap, for washing raw wool, and as lab reagent and general – purpose food additive (Cameron, 2008). Both sodium chloride and potassium chloride are essential to the electrolyte balance in the body fluid; good health depend on the proper ratio of potassium ions to sodium ions (Joesten *et al.,* 1996).

2.6 Effects of Sodium of Potash on Humans

2.6.1 Sodium and Cardiovascular Disease

For 4,000 years, It has been documented that sodium intake can affect blood pressure through signal to the muscles of blood vessels trying while to maintain blood pressure within a proper range (Barbara *et al*., 2008). It also known that a minority of the population can lower blood pressure by restricting dietary salt. And we know that elevated blood pressure “hypertension” is a well-documented marker or “risk factor” for cardiovascular event like heart attacks and strokes, a ”silent killer” reducing blood pressure can reduce the risk of a heart attack or stroke-depending on how it’s done. Some have suggested that since sodium intake is related to blood pressure and since cardiovascular risk is also related to blood pressure, that surely salt intake level is related to cardiovascular risk. This is the “salt hypothesis” or sodium hypothesis” data are needed to confirm or reject hypothesis (Cutler, 1995).

Blood pressure is a sign, when it goes up (or down) and it indicates an underlying health concern. Changes result from many variables, often still poorly – understood. High blood pressure is treated with life style interventions such as diet and exercise. Thus; until the 1990s, scientist had never tested the “salt hypothesis” by documenting whether reducing dietary salt actually reduces a person’s chances of having a heart attack or a stroke. The first seven “health outcomes” studies of sodium reducing, not a single study has found an association in the general population between low-sodium diet and reduced incidence of cardiovascular event like stroke or heart attacks (Cutler, 1995).

(i) An eight – year study of a New York city hypertensive population stratified for sodium intake level found those on low – salt diet had more than four times as many heart attacks as those on normal sodium diet – the exact opposite of what the "salt hypothesis" would have predicted (Cutler, 1995).

(ii) An analysis by NHLBI's Dr Jeffery R. Cutler of the first six year's data from the MRFIT data base documented no health out comes benefits of lower sodium diets. (Cutler, 1995)

(iii) An ten – year follow-up study to the huge Scottish Heart Health study found no improved health outcomes for those on low-salt diets (Cutler, 1995)

(iv) An analysis of the health outcomes over twenty years from those in the massive us National Health and Nutrition Examination survey (NHANES 1) documented a 20% greater incidence of heart attacks among those on low-salt diet compared to normal-salt diet (Cutler, 1995).

(v) A health outcomes study in Finland, reported to the African Heart Association that no health benefits could be identified and concluded "our result do not support the recommendations for entire population to reduce dietary sodium intake to present coronary heart disease". (Cutler, 1995).

(vi) A further analysis of the MRFIT data base, this time using fourteen years' data, confirmed no improved health benefit from low-sodium diets.

Its author conceded that there is “no relationship observed between dietary sodium and mortality.” (Cutler, 1995).

(vii) A study of Americans found that sodium–dense diets did reduce cardiovascular mortality of one population sub-set, over weight men – the article reporting the finding did not explain why this obese group actually consumed less sodium than normal – weight individuals in the study (Cutler, 1995).

2.6.2. Effects of Pollution Load on Potash Deposit

Salt and potash are usually found as a deposit on the earth crust, formed as a result of deposition of rocks that contains high amount of K and Na. Heavy metals can be deposited as well which can cause pollution load on the deposit, this heavy metal can cause adverse effect on humans and animals that consumed it. Human activities contribute to the pollution load on the soil which are release and easily taken up by the plant or leached into the soil which caused environmental pollution (Ogbonnal *et al*. 2007). Under certain environmental conditions, heavy metal may accumulate to toxic concentration and cause ecology damage (Wang and Mullingan, 2009). The effect on organism includes biological and pathological reactions, reproductive problems and mortality (Janssens *et al*., 2003). Accumulation in soils is of concern in agricultural production due to the adverse effect on food quality, crop growth and environmental health (Mal *et al.,* 1994; Msaky and Calvert, 1990; Fergusson, 1990). The mobilization of heavy metal into the biosphere by human activity has become an important process in the geochemical cycling of these metals (Bilos *et al.,* 2001). Heavy metals may enter the human through inhalation of dust, direct ingestion of soil or potash and consumption of food plants grown in metal – contaminated soil (Combra *et al.,* 1999; Dudka and Miller, 1999).

Lead

Inorganic lead can replace calcium in bones thus resulting to bone malfunction and osteoporosis in sheep, rabbit and children (Churchill and Donald, 1982 ; Pillai, 1991; and Dara, 2008). According to Tardon *et al.*, (2002). Physician hard established the following clinical symptoms to be associated with Pb poisoning; these are abdominal collie, blue gum, wrist drop, muscular westing, tremor and anaemia. Lead toxicity also cause kidney dysfunction and brain damage in children and induce aggressive behaviour in animals and possibly humans (Mengel *et al.*, 2006). The introduction of Pb into food chain may affect human health, and thus, studies concerning Pb accumulation in vegetables have increasing important (Coutate, 1992). Maximum Pb limit for human health has been established for edible parts of crops (0.2mg/kg) (Chinese Department of preventive Medicine, 1994).

Cadmium

Cadmium competes with more ambivalent Zn for bonding sites and thus interfered with some essential function of Zn as an enzyme co-factor. Cadmium can cause high-blood pressure and kidney damage and sterility in male (Haggin *et al.*, 1975). Base on the regression equation the established limit of cadmium concentration in vegetable products is 0.05nig/kg fresh weight (GBN 238-84 in China).

Iron

Iron toxicity cause diarrhea; reduce growth and efficiency of feed utilization coupled with sign of phosphorus deficiency. In acute cases, vascular congestion in tissues and organs, metabolic acidosis and some time death has been reported in pigs and rabbit (Churchill *et al.*, 1982).

Copper

Copper toxicity causes jaundices haemoglobinuria and tissue necrosis in sheep and calves (Churchill *et al.*, 1982). Farm workers involved in the use of copper (II) containing algaecide and fungicide often develop respiratory diseases called “vine yard sprayer lung’s” which can lead to cancer (Dara, 2008). The critical food Cu threshold for human health has been established to be 10mg/kg (Chinese Department of Preventive Medicine, 1995).

Zinc

Depression of appetite is one of the clinical symptoms associated with energy zinc content in sheep (Churchill *et al.*, 1982). Knowledge of Zn toxicity in human is minimal. The most important reported is its interference with Cu metabolism (Baron *et* al., 1998; Goyorffy and chan, 1992). The symptoms that an acute oral Zn dose may provoke include: tachycardia, vascular shock, dyspeptic nausea, vomiting, diarrhea, pancreatic and damage of hepatic parenchyma (Salgueiro *et al.,* 2000). The critical dietary Zn threshold for human health has been established to be 20mg/kg (Chinese Department of preventive Medicine, 1995).

Chromium

Effect of chromium as soil pollutant has not been observed in human. Although lung cancer, kidney and liver damage as well as contamination effect through drinking water has been observed in experimented animals and humans (Dara, 2008).

2.7 Analytical Instrumentation Techniques

2.7.1 Flame Emission Spectroscopy

The principle of flame photometry was discussed by different authors like, Christian (2007), Ogugbuaja (1995), Goltenman (1996) and Harvey (2006) The main principle in flame photometry is emission of radiation when atoms are excited to a higher energy level. The emitted radiation corresponds to the concentration of element in the sample. According to Mark plank atoms have discrete energies and that they could absorb or emit energy in discrete unit. This leads to the formulation of planks equation

$$E = hv = \frac{hc}{\lambda} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

where h is the Plank's constant, E is the energy, v is the frequency, c is the speed of light (Skoog *et al*, 2004). The intensity of emission is directly proportional to the concentration of the analyte in the solution been aspirated. So a calibration curve of emission intensity as a function of concentration is prepared. Side reaction in the flame may decrease the population of free atoms and hence the emission signal. Flame photometry has been found particularly convenient for the determination of alkali and alkaline earth metals. Flame is difficult when the wet method is the only available option because of the emission from other ions (Goltenman *et al.*, 1978).

The flame must be hotter in atomic emission than for the same element in atomic absorption because as large a fraction as possible of the vaporized atom must be energetically excited rather than simple dissociation (Havey, 2006). The burner used in Flame photometry is usually of the type known as total consumption burner. The sample is aspirated into the flame by either the fuel or oxidant but the gases are not premixed (Galen, 1975). The power of the radiation from the flame of a wavelength characteristic of particular elements is found to be very closely proportional to the concentration of the metal, if a background correction is first made (Harris, 2007).

The background luminosity is caused largely by the presence of other metals, since in general each excitable cation will give some radiation over a wide spectral region, even at a considerable distance from its describe lines. Any scattering in the monochromator or photometer will also contribute. In filter flame photometer correction are usually made on an empirical basis (Galen, 1975). Atomic emission from sample is separated into its constituent wavelength by the wave length isolation device. This separation can take place in a monochromator or polychromator (Skoog *et al.*, 2004). Flame photometer uses monochromator which isolate one wavelength at a time at a single exit slit. The isolated radiation is converted into electrical signals by a single tranducer or an array detector. The electrical signal are then processed and provided as imput to the computer system. (Skoog *et al.*, 2004).

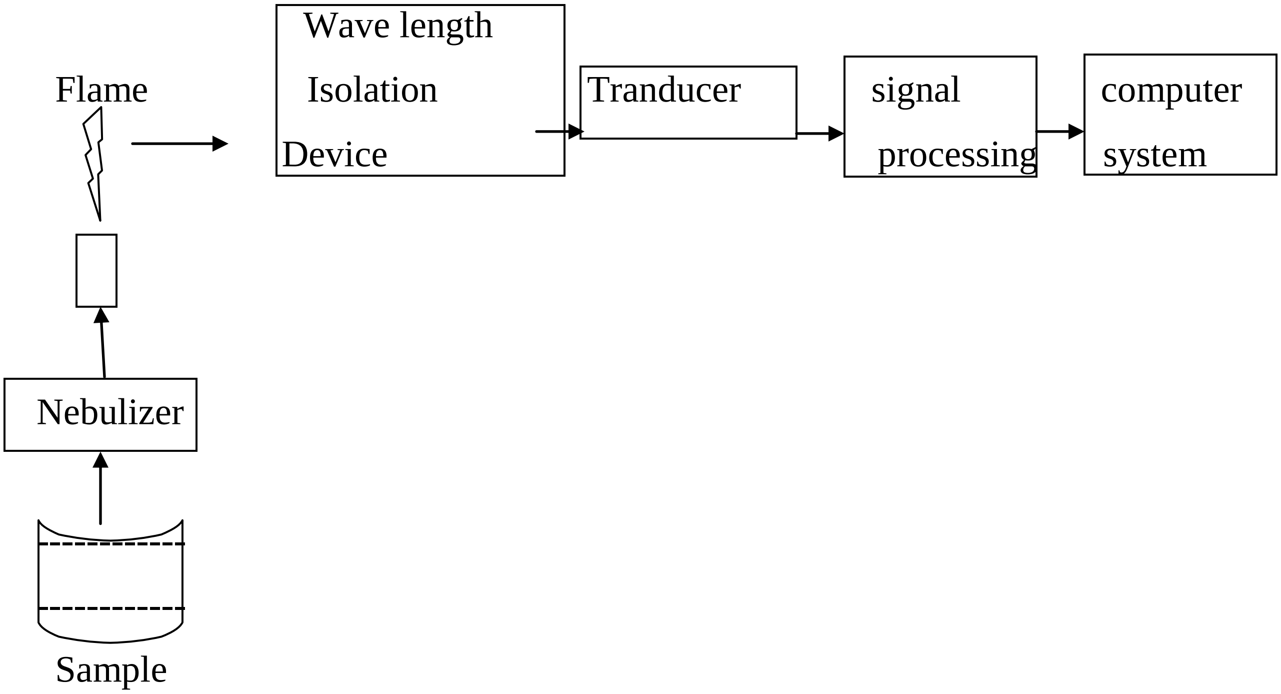

Figure 2.1 Block Diagram of Flame Photometer

Table 2.3 Flame Analysis Working Conditions

Elements Analysed	wavelength	working range
Potassium	766.5nm	0-10mmol/l
Sodium	589.0	120-160mmol/l

Source: (Menham *et al*, 2006)

2.7.2 Atomic Absorption Spectroscopy

The principles of AAS have been described by many authors (Skoog and West,1980; Harvey, 2006; Menham *et al.*, 2006; Christian, 2007; and Ogugbuaja, 1995). The main principle in atomic absorption spectroscopy is absorption of radiation when atoms are excited to higher energy level. The absorption of radiation by the atoms corresponds to the concentration of element in the sample. Only atoms of particular elements will absorb photons at its characteristics wave length (Lawrence, 2000). According to Beer's law, absorbance is directly proportioned to the concentration of the absorbing medium A = abC where, a is a proportionality constant called the absorptivity of the substance, b is the path length and C is the concentration.

A= Log P_o / P = Log abC (Skoog *et al.*, 2004).----------------(ii)

The most useful radiation source for atomic absorption spectroscopy is the hallow cathode lamp it consist of a tungsten anode and a cylindrical cathode sealed in a glass tube containing an inert gas such as argon at a pressure of 1 - 5 torr (Harris, 2007). The cathode is either fabricated from the analyte or serves as a support for a coating of that metal. The application of about 300v across the electrodes causes ionization of the argon and generation of current of 5 to 10ma as the argon cation and electron migrate to the two electrodes. The argon cations strike the cathode with sufficient energy to dislodge some of the metal atoms and there by produce an atomic cloud by a process called sputtering (Harris, 2007). Some of the sputtered metal atoms are in an excited state and emit there characteristic wavelength as they return to the ground state (Skoog *et al.*, 2004). Atoms producing emission line in the lamp are at a significantly lower temperature and pressure than the analyte atoms in flame. Thus, the emission lines from the lamp are broadened less than the absorption peak in the flame. The sputtered metal atoms eventually diffuse back to the cathode surface or to the walls of the lamp and are deposited (Skoog *et al.*, 2004).

Electrodeless – discharge lamps are also useful source of atomic line spectra. These lamps are often one to two orders of magnitude more intense than their hollow – cathode counterparts. It is constructed from a sealed quart tube containing an inert gas such as argon, at a pressure of a few torr and a small quantity of the analyte metal or it salt (Havey, 2006) The lamp contains no electrode but instead is energized by an intense field of radio frequency or microwave radiation (Oliver, 1992). The argon lonizes in the field, and the Ions are accelerated by the high frequency component of the field until they gain sufficient energy to excite (by collision) the atom of the metal whose spectrum is sought (Skoog *et al.*, 2004).

In atomic absorption measurement the radiation from the actomizer is eliminated by the monochromater which is always located between the atomizer and the detector. The effect of analyte emission is reduced by modulating the out put from the hollow cathode lamp so that its intensity fluctuates at a constant frequency (Harris, 2007). The detector thus receives an alternating signal from the hallow cathode lamp and a continuous signal from the flame and convert these signal into the corresponding type of electric current. The electronic system eliminate the unmodulated dc signal produced by the flame and passes the ac signal from the source to an amplifier and finally to the readout device (Skoog *et al.*, 2004).

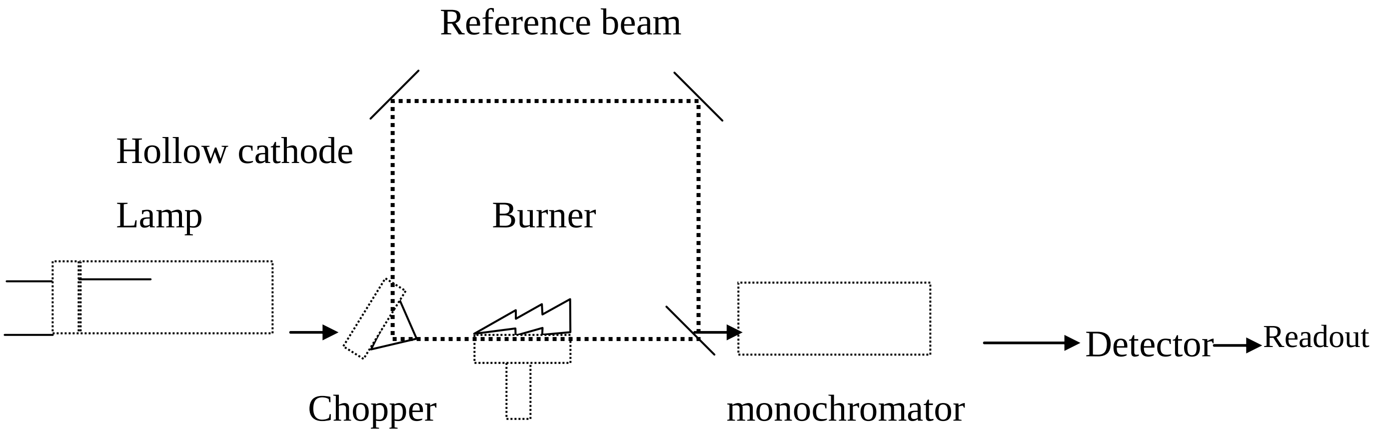

Figure 2.2 Schematic Diagram of Atomic Absorption Spectrophotometer

Table 2.4 Elements analyzed using atomic absorption spectrophotometer and Operating Conditions

Elements	Wavelength	Working range
Calcium	422.7nm	0.05-6.0ppm
Chromium	357.9nm	0.04-10.0ppm
Copper	324.8nm	0.005-5.0ppm
Iron	248.3nm	0.05-5.0ppm
Magnesium	285.2nm	0.005-1.50ppm
Lead	283.3nm	0.08-20.0ppm
Zinc	213.9nm	0.08-2.50ppm
Cadmium	228.8nm	0.75-2.0ppm

Source: (Mendham *et al.*, 2006)

CHAPTER THREE

MATERIALS AND METHOD

3.1Materials Required

3.1.1 Instruments/Apparatus

Analytical weighing balance, Buck Scientific 210VGP atomic absorption spectrophotometer and PFP7 flame photometer.

Materials that were used for the analysis included the following: laboratory glass ware, Whatman No. 42 filter paper spatula, mortar, pistle and biomega H4000-HS hot plate.

3.1.2 Chemicals/Reagents

60% $HClO_4$, H_2SO_4 SG:1.84, HNO_3 SG:1.42, NaCl, KCl, $MgCl_2.6H_2O$, $CaCl_2$, $FeCl_3$, $Pb(NO_3)_2$, $Zn(NO_3)_{2,}$ $CuSO_4$, $Cr(SO_4)_3.6H_2O$, $3CdSO_{4.}8H_2O$, and distilled water.

3.2 Area of Study

Yobe state lies between latitude 12º00′N and longitude 11º30′E. In the western part, it is bordered by Jigawa and Bauchi States, it is also bordered by Gombe State in the Southern part, and bordered in the eastern part by Borno State (Figure 3.1). Yusufari lies between latitude 13º04′06″ N and longitude 11º10′33″ E with altitude of 305 m and area of 3,928 km^2. Local Government Area where the potash samples were obtained is in Yusufari (Figure 3.2).

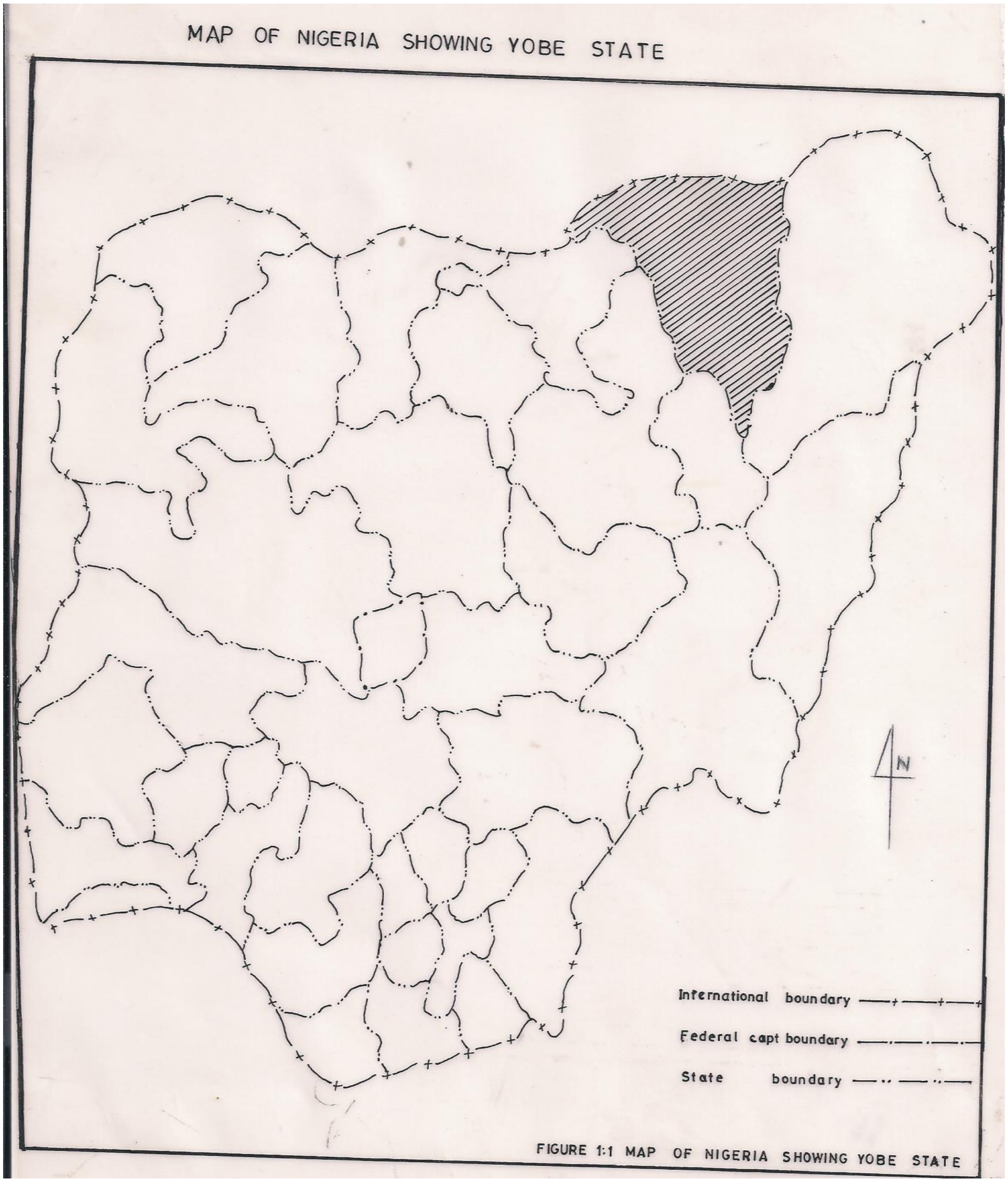

Fig 3.1 Map of Nigeria showing Yobe State.

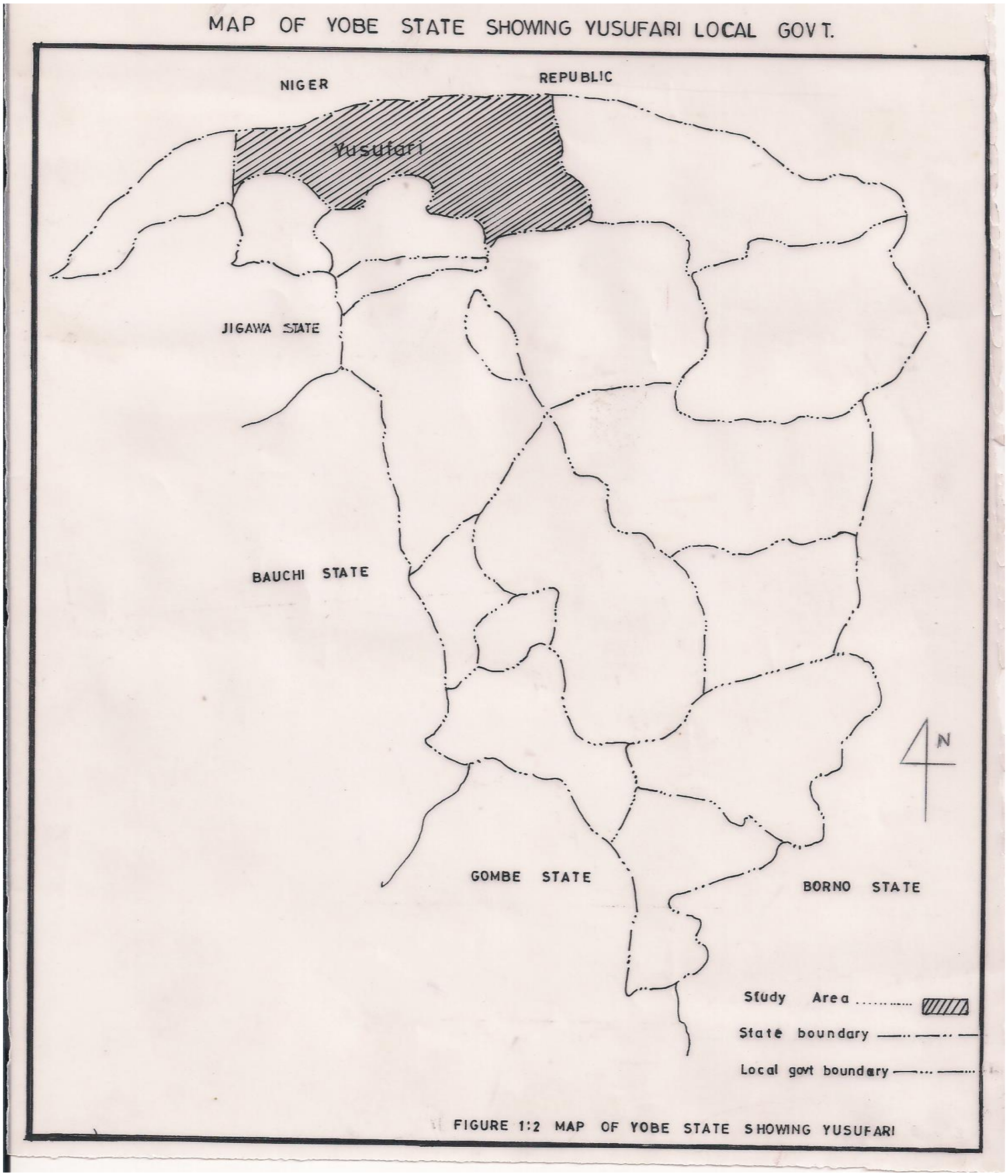

Fig 3.2 Map of Yobe State showing Yusufari.

3.3 Sampling and Samples Preparation

3.3.1 Sampling

Figure 3.3 shows the map of Yusufari Local Government Area in Yobe State where samples were collected. There were nine sampling locations where the samples were collected. Areas where the samples were collected include Madukuri, Kotufa and Kirba.The potash was sampled using the method described by Crosby and Patel (1995). Samples were all exposed on the surface at the sampling site. The top of the sample was chiseled to expose a fresh sample point. At each sampling point, three locations were chosen at random. These locations were chiseled to obtain samples which were mixed to obtain a gross sample weighing about 1 kg

MAP OF YUSUFARI LOCAL GOVT. AREA.

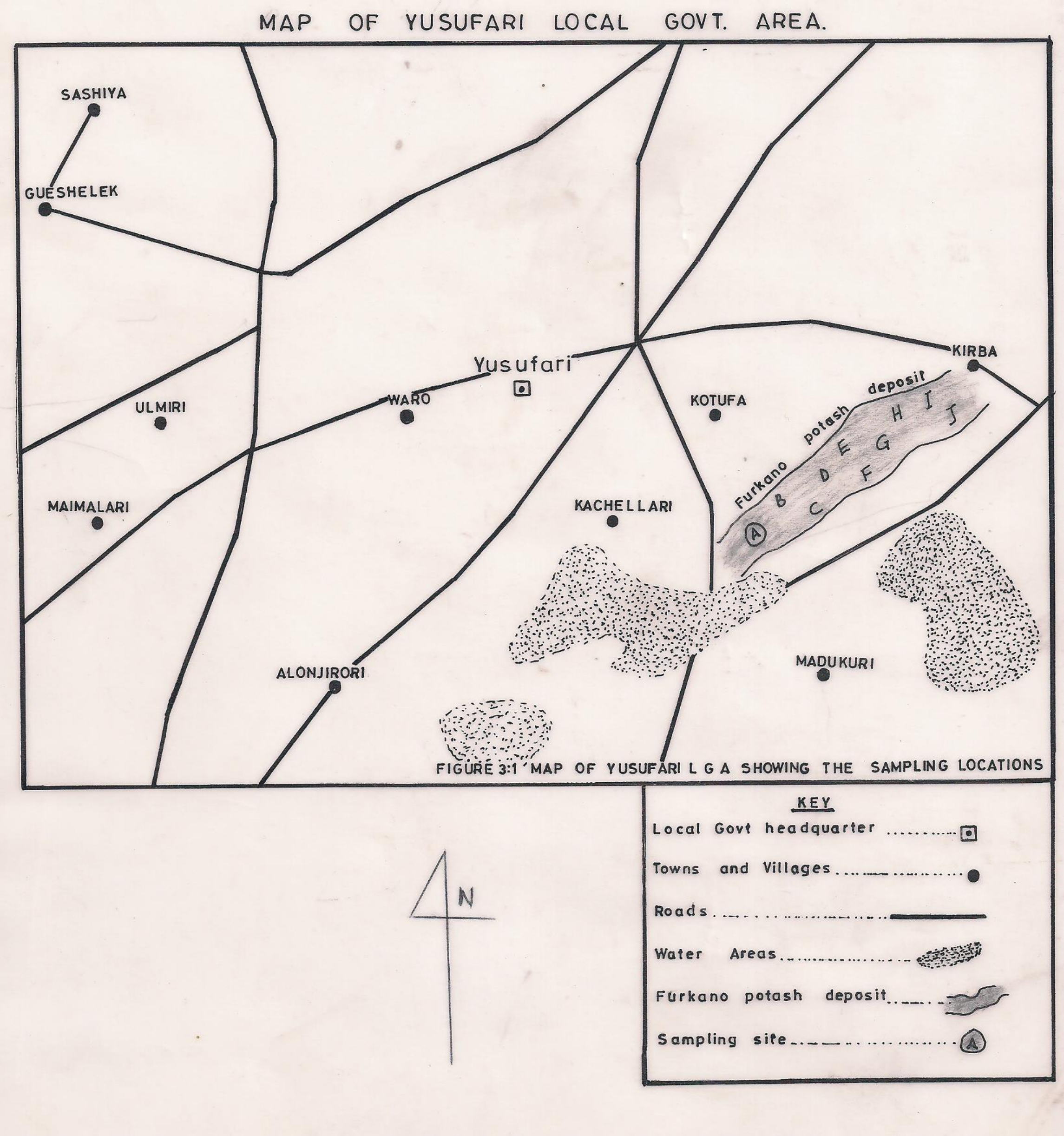

FIGURE 3:1 MAP OF YUSUFARI L G A SHOWING THE SAMPLING LOCATIONS

3.3.2 Samples Preparation

The sample preparations were done according to the method described by Posypaiko and Vasina (1984). The samples were air dried in the laboratory and crushed to smaller particle using hammer. The gross sample weighing about 1 kg was mixed, ground and quartered to obtain a representative sample weighing about 100 g. This was stored in polypropylene bottles for subsequent analytical determinations.

3. 4 Sample Digestion

Sample digestion was done according to the requirement for determination of elements using atomic absorption spectrometry and flame emission spectrometry (FES).The digestion method has been described by Ibitoye (2005). 5 g of powdered sample was weighed into a 12 mL Erlenmayer flask. 4 mL of perchloric acid, 25 mL nitric acid and 2 mL sulphuric acid were added under a fume hood. The content was mixed and heated gently on a hot plate under fume cupboard. Heating continued until dense white fumes appeared, it was allowed to cool, and 50 mL distilled water was added. The solution was cooled and filtered into a 100 mL Pyrex volumetric flask and made up to mark with distilled water shaken to obtain a solution. The solutions were then kept for the determination of elements using flame photometer and atomic absorption spectrophotometer.

3.5 Preparation of Standard Solutions for Calibration

Standard solutions of Na, K, Mg, Ca, Zn, Fe, Cu, Pb Cd, and Cr were prepared, for calibration of the instruments. Na and K salts were used for calibration of the flame photometer, whereas, the salts for the other elements were used for calibration of the atomic absorption spectrophotometer.

(a) 1000 ppm of Sodium

The standard solution of sodium was prepared using sodium chloride. 2.52 g of NaCl was weighed using analytical weighing balance and dissolved in 1000 cm^3 volumetric flask, and made up to mark with distilled water (A.O.A.C,1970).

(b) 1000 ppm of potassium

The standard solution of potassium was prepared using potassium chloride 1.89 g of KCl was weighed using analytical weighing balance and dissolved in 1000 cm^3 volumetric flask, and made up to mark with distilled water (A.O.A.C,1970).

(c) 1000 ppm of Zinc

The standard solution of zinc was prepared using zinc nitrate.

4.37 g of $Zn(NO_3)_2$ was weighed using analytical weighing balance and dissolved in 1000 cm^3 volumetric flask, and made up to mark with distilled water.

(d) 1000 ppm of Copper

The standard solution of copper was prepared using copper (II) sulphate. 2.49 g of $CuSO_4$ was weighed using analytical weighing balance and dissolved in 1000 cm^3 volumetric flask, and made up to mark with distilled water.

(e) 1000 ppm of Magnesium

The standard solution of magnesium was prepared using hydrated magnesium chloride.8.20 g of $MgCl_2.6H_2O$ was measured using analytical weighing balance and dissolved in 1000 cm^3 volumetric flask, and made up to mark with distilled water.

(f) 1000 ppm of Calcium

The standard solution of calcium was prepared using calcium chloride. 2.49 g of $CaCl_2$ was weighed using analytical weighing balance and dissolved in 1000 cm^3 volumetric flask, and made up to mark with distilled water

(g) 1000 ppm of Iron

The standard solution of iron was prepared using iron (III) chloride.

2.81 g of $FeCl_3$ was weighed using analytical weighing balance and dissolved in 1000 cm^3 volumetric flask, and made up to mark with distilled water

(h) 1000 ppm of Lead

The standard solution of lead was prepared using lead (II) nitrate 1.58 g of $Pb(NO_3)_2$ was weighed using analytical weighing balance and dissolved in 1000 cm^3 volumetric flask, and made up to mark with distilled water

(i) 1000 ppm of Chromium

The standard solution of chromium was prepared using hydrated chromium (III) sulphate.6.90 g of $Cr(SO_4)_3.6H_2O$ was weighed using analytical weighing balance and dissolved in 1000 cm^3 volumetric flask, and made up to mark with distilled water

(j) 1000 ppm of Cadmium

The standard solution of cadmium was prepared using hydrated cadmium sulphate. 6.71 g of $3CdSO_4.8H_2O$ was weighed using analytical weighing balance and dissolved in $1000cm^3$ volumetric flask, and made up to mark with distilled water (.A.O.A.C, 2002)

3.5.1 Serial Dilution

From the standard stock solutions prepared various working solutions for each salt was prepared by serial dilution in accordance with the expression below:

$C_1V_1 = C_2V_2$ where

C_1 = concentration of stock solution (1000ppm)

V_1 = volume of the stock solution to be taken

C_2 = final concentration

V_2 = final volume

3.6 Determination of Na and K using Flame Photometer

The procedure adopted was that of Goltenman *et al.* (1996).

The flame photometer was set according to the instruction manual.

The instrument readout was calibrated using the standard solutions. The meter reading was set at 100% emission while aspiring the top concentration of the standard. The % emission reading of all the intermediate standard solutions was recorded, then a calibration curve was plotted. The samples solutions were aspired and the reading was obtained. The sample concentration was obtained through the standard using the calculation by the least square method appendix II. Concentration obtained in ppm was converted into mg/kg for each element using the formula.

$$\mathbf{mg/kg} = \frac{\mathbf{ppm \times V}}{\mathbf{W}}$$

Where V = volume of digested sample in cm^3

W = weight of sample in grams.

3.7 Determination of elements using Atomic Absorption Spectrophotometer

The procedure adopted was that of Mendham *et al.* (2007).

The Buck Scientific 210 VGP atomic absorption spectrophotometer was ascertained for its good working condition. Hallow cathode lamp for each metal was selected and fixed. The instrument was switched on and allowed to warm up for 10 minutes in order to stabilize. Air and acetylene were used as oxidant and fuel, respectively. The current and resonance line wavelength for each metal were selected and gas control system adjusted to give a fuel rich flame. Distilled water was used as blank and the instrument was set to zero reading. The prepared standard solutions were aspirated in order of decreasing concentration and each followed by aspiration of distilled water. The standard absorbances were used for the construction of calibration curves. The unknown sample solutions were read for absorbance on the AAS screen after instrument adjustment for calibration solutions. Then the sample concentration was obtained in ppm by calculation using the least square method appendix II. Concentrations obtained in ppm were then converted into mg/kg for each element using the formula.

$$\mathbf{mg/kg} = \frac{\mathbf{ppm \times V}}{\mathbf{W}}$$

where

V = volume of digested sample in cm^3

W = weight of sample in grams.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Essential Elements Composition of Potash at Different Locations

Presented in Tables 4.1 – 4.3 are the mean results for the essential elements K, Na, Ca and Mg in potash at different areas

Table 4.1; Mean Concentrations (mg/kg) of Essential Elements in Potash at Madukuri.

		Essential Elements (mg/kg)			
Area	Sample Locations	K	Na	Ca	Mg
Madukuri					
	A	18035±2.2 (0.012)	5368±1.3 (0.024)	544±0.9 (0.17)	53.4±0.8 (1.50)
	B	10869±2.9 (0.027)	3800±1.8 (0.047)	885±1.1 (0.12)	57.5±0.7 (0.012)
	C	9625±2.5 (0.026)	3751±1.6 (0.043)	660±1.2 (0.18)	58.5±0.5 (0.85)

Each value is the mean values of three determinations ± S.D

Each value in the parentheses is the coefficient of variation CV%

S.D is the standard deviation

A- Northern Madukuri

B- Central Madukuri

C- Southern Madukuri

Table 4.2; Mean Concentrations (mg/kg) of Essential Elements in Potash at Kotufa.

		Essential Elements (mg/kg)			
Area	Sample Locations	K	Na	Ca	Mg
Kotufa					
	D	10827±2.8 (0.029)	3912±1.8 (0.046)	933±1.5 (0.16)	58.4±0.3 (0.51)
	E	8855±1.5 (0.017)	3625±1.9 (0.052)	838±1.8 (0.21)	58.8±0.2 (0.34)
	F	12493±3.1 (0.025)	3822±2.1 (0.055)	448±1.7 (0.38)	57.4±0.05 (0.09)

Each value is the mean values of three determinations ± S.D

Each value in the parentheses is the coefficient of variation CV%

S.D is the standard deviation

D- Northern Kotufa

E- Central Kotufa

F- Southern Kotufa

Table 4.3 Mean Concentrations (mg/kg) of Essential Elements in Potash at Kirba.

Area	Sample Locations	Essential Elements (mg/kg)			
		K	Na	Ca	Mg
Kirba					
	G	25436±3.2 (0.013)	5535±3.2 (0.058)	828±1.4 (0.17)	54.4±0.6 (1.10)
	H	11604±3.4 (0.029)	3659±1.9 (0.052)	603±1.4 (0.23)	58.3±0.9 (1.54)
	I	11472±2.9 (0.025)	3535±2.1 (0.059)	765±1.7 (0.22)	57.6±0.2 (0.35)

Each value is the mean values of three determinations ± S.D

Each value in the parentheses is the coefficient of variation CV%

S.D is the standard deviation

G- Northern Kirba

H- Central Kirba

I- Southern Kirba

The results of the analysis were treated using different statistical tools such as the mean, standard deviation and coefficient of variation to analysed the data. Potassium and sodium were highly concentrated in all the areas (Madukuri, Kotufa and Kirba) compared with Ca and Mg. K however is much higher than Na in all the areas and at all locations this is in accordance with the work reported in (Canadian Encyclopedia,2000). K levels showed these ranged; Madukuri (9625 to 18035 mg/kg), Kotufa showed (10827 to 12493 mg/kg) and Kirba showed (11472 to 25436 mg/kg) with the CV% ranged as follows; Madukuri (0.012 to 0.027%), Kotufa (0.017 to 0.029%) and Kirba (0.013 to 0.029%) for Tables 4.1, 4.2, and 4.3 respectively. These showed that there is no much variations in the mean concentration of K at each location because the deposit shows the same mineralogical characteristic as report by (Kovalevich *el al.*, 1997). Na levels at the different areas are; Madukuri (3751 to 5368 mg/kg), Kotufa (3625 to 3912 mg/kg) and Kirba (3535 to 5535 mg/kg) with the CV% ranged; Madukari (0.024 to 0.047%), Kotufa (0.046 to 0.055%) and Kirba (0.052 to 0.059%) for Tables 4.1, 4.2, and 4.3 respectively. This showed that there is no much variation between the mean concentrations of Na at all the locations. The essential element Na showed significant concentration in all the locations because, potash –bearing brine deposits contain components like sodium carbonate and sodium sulfate which may contributes to the higher level of Na in potash as reported by (Erickson and Salas, 1989; Casas *et al*., 1992).

Calcium and magnesium being the next essential components are much lower in concentrations compared to the essential elements K and Na in all the areas and all the locations. Ca however is much higher in concentration than Mg in all the areas and locations studied. Ca levels at different areas showed the concentration ranged as follows; Madukuri (554 to 885 mg/kg), Kotufa (448 to 933 mg/kg) and Kirba (603 to 828 mg/kg) with the CV% which ranged; Madukuri (0.12to 0.18%), Kotufa (0.16 to 0.38%) and Kirba (0.17 to 0.23%) for Tables 4.1, 4.2, and 4.3 respectively. These shows that there no much variation s between the mean concentration of Ca in all the location. There is a connection between $MgSO_{4,}$ potash and $CaCl_2$ brine in magnetically active rift basins that caused the accumulation of these component as reported by Stefansson and Bjornsson (1982). For Mg the levels are ; Madukuri (53.4 to 58.5 mg/kg), Kotufa (57.4 to 58.8 mg/kg) and Kirba (54.4 to 58.3 mg/kg) with the CV% which ranged as follows; Madukuri (0.012 to 1.5%)Kotufa (0.09 to 0.51%) and Kirba (0.35 to 1.54%) for Tables 4.1, 4.2, and 4.3 respectively. Elemental level of Mg are also typical of many closed –basin brine s as reported by(Orris, 1997). The essential elements content showed the dominance of K in all the locations and areas studied while Mg had the lowest values. The main component in potash was K which may be attributed to the most abundant components in potash like potassium chloride and potassium oxide in Yusufari L.G.A were similar to the deposit of western Canada and Qaidam basin as reported by (Wang *et al*, 2005). The potash deposit in Yusufari L.G.A contain high amount of K the principal element for the production of potash fertilizer as reported by (Dennis, 2006). From the results one can conclude that the levels of the essential components are in the order of decreasing order as K >> Na >> Ca > Mg.

4.2 Comparison of Essential Elements at Different Areas

Figure 4.1 summarizes the comparison of essential elements K and Na at the different areas. This figure confirms that K levels were very significantly much higher in all the areas (Madukuri, Kotufa and Kirba) as compared with Na. (Figure 4.2) summarizes the comparison of essential elements Ca and Mg at different areas (Madukuri, Kotufa and Kirba). This figure also confirms that Ca levels were significantly much higher compared with Mg in all the areas (Madukuri , Kotufa and Kirba) and in all the locations studied.

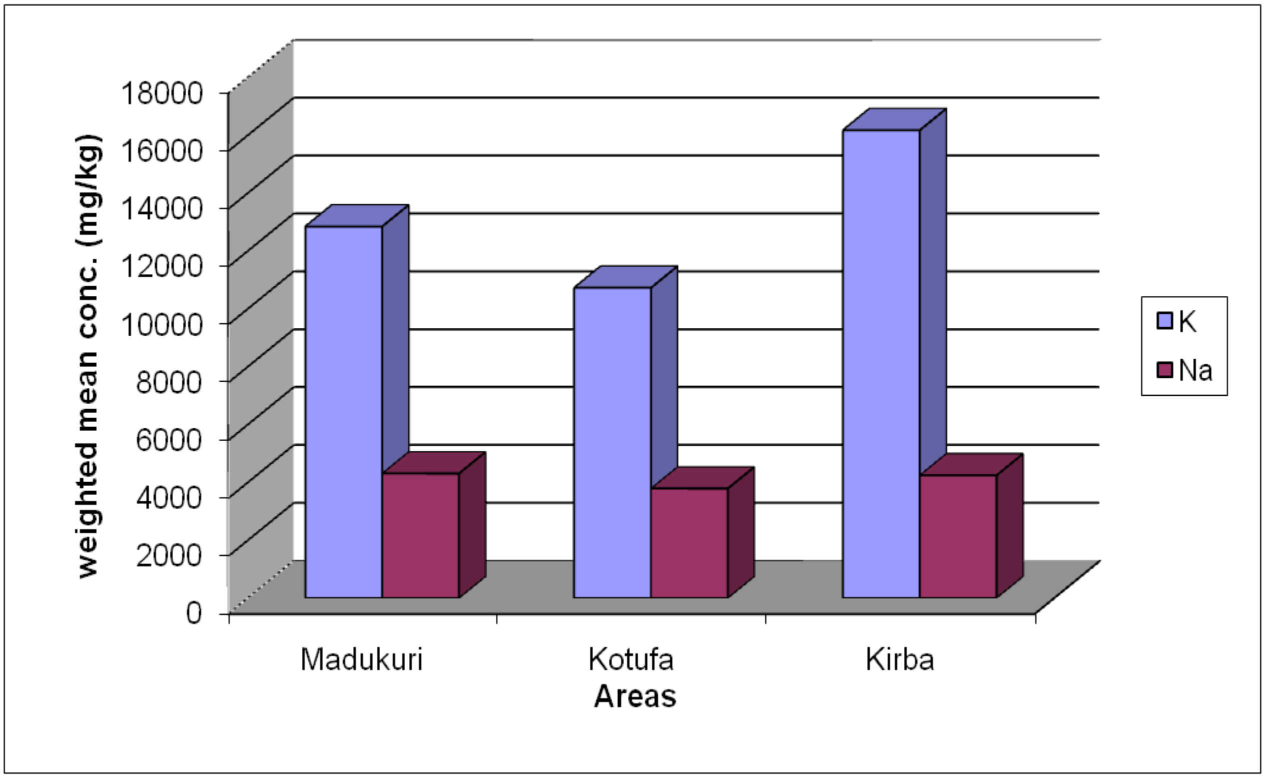

Figure 4.1; Comparison of K and Na at Different Areas

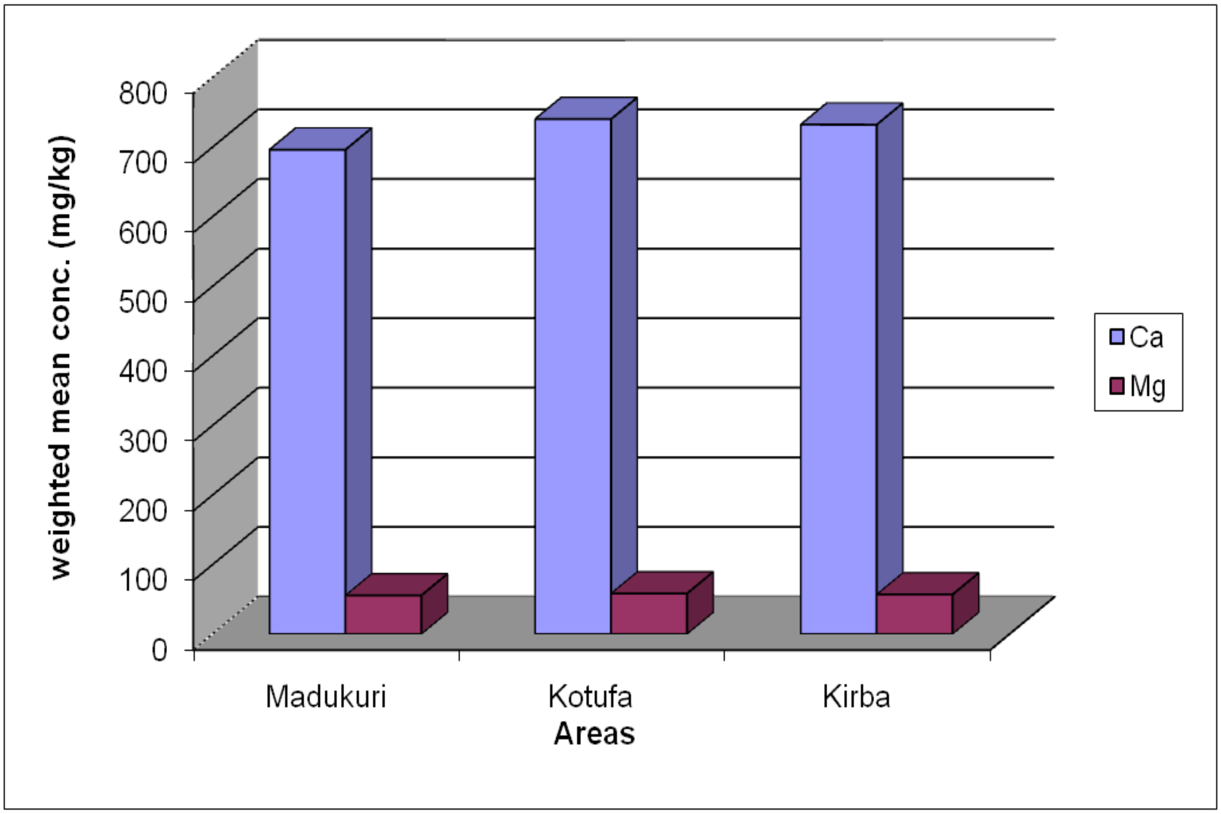

Figure 4.2; Comparison of Ca and Mg at Different Areas

4.3 Heavy Metals Composition in Potash at Different Locations

Presented in Tables 4.4 – 4.6 are the mean results for the heavy metals in potash at different areas.

Table 4.4 Mean Concentrations (mg/kg) of Heavy Metals Level in Potash at Madukuri

		Heavy Metals (mg/kg)					
Area	Sample Locations	Cd	Cr	Cu	Fe	Pb	Zn
Madukuri							
	A	22.0±0.05 (0.23)	<0.04	17.2±0.08 (0.47)	300±2.2 (0.73)	66.9±0.3 (0.45)	2.3±0.06 (2.61)
	B	22.4±0.03 (0.13)	<0.04	19.6±0.02 (0.10)	448±2.5 (0.56)	67.4±0.5 (0.74)	5.3±0.07 (1.32)
	C	20.7±0.09 (0.43)	<0.04	20.3±0.1 (0.49)	449±1.9 (0.42)	71.5±0.8 (1.12)	8.4±0.05 (0.59)

Each value is the mean values of three determinations ± S.D

Each value in the parentheses is the coefficient of variation CV%

S.D is the standard deviation

A- Northern Madukuri

B- Central Madukuri

C- Southern Madukuri

Table 4.5 Mean Concentrations (mg/kg) of Heavy Metals Level in Potash at Kotufa

		Heavy Metals (mg/kg)					
Area	Sample Locations	Cd	Cr	Cu	Fe	Pb	Zn
Kotufa	D	22.4±0.08 (0.36)	<0.04	18.0±0.4 (0.22)	428±1.8 (0.42)	69.5±0.3 (0.43)	5.1±0.01 (0.20)
	E	24.6±0.09 (0.37)	<0.04	17.9±0.02 (0.11)	446±2.1 (0.47)	62.2±0.2 (0.32)	5.4±0.02 (0.37)
	F	22.1±0.01 (0.05)	<0.04	19.1±0.08 (0.42)	457±1.9 (0.42)	72.4±0.9 (1.24)	7.6±0.03 (0.39)

Each value is the mean values of three determinations ± S.D

Each value in the parentheses is the coefficient of variation CV%

S.D is the standard deviation

D- Northern Kotufa

E- Central Kotufa

F- Southern Kotufa

Table 4.6 Mean Concentrations (mg/kg) of Heavy Metals Level in Potash at Kirba

		Heavy Metals (mg/kg)					
Area	Sample Locations	Cd	Cr	Cu	Fe	Pb	Zn
Kirba							
	G	22.4±0.01 (0.04)	<0.04	16.2±0.03 (0.19)	245±1.8 (0.73)	66.4±0.08 (0.12)	1.8±0.002 (0.11)
	H	22.5±0.06 (0.27)	<0.04	16.3±0.02 (0.12)	439±1.5 (0.34)	66.7±0.06 (0.09)	5.3±0.01 (0.19)
	I	22.2±0.02 (0.09)	<0.04	18.3±0.05 (0.27)	425±1.6 (0.38)	65.6±0.02 (0.03)	7.1±0.07 (0.99)

Each value is the mean values of three determinations ± S.D

Each value in the parentheses is the coefficient of variation CV%

S.D is the standard deviation

G-Northern Kirba

H- Central Kirba

I- Southern Kirba

The heavy metal Fe had significantly much higher concentration in all the locations and all the areas (Madukuri , Kotufa and Kirba). Fe does not poise much health risk to human and animal because it is important in the formation of haemoglobine the pigment in red blood cells.The Fe levels showed the following ranged as follows; Madukuri (300 to 449 mg/kg), Kotufa (428 to 457 mg/kg) and Kirba (245 to 439 mg/kg) with this CV % which ranged as follows: (0.42 to 0.73%) , Kotufa (0.42 to 0.47%) and Kirba (0.19 to 0.12%) for Tables 4.4, 4.5, and 4.6 respectively. This shows that there is little variation in the mean concentration of Fe at various locations with the highest value of CV% of 0.73% . Heavy metals Pb and Cd showed significant levels in all the locations and all the areas, however the concentration of Pb is higher compared to Cd. The levels of Pb is found to be below the recommended National Environmental Board (2004) for soil standard limit of 400 mg/kg , but the level of Pb were above the recommended European Union Standard (2001) for the maximum level of heavy metals in foodstuff which ranged from (0.1 to 0.5 mg/kg) appendix 1. Pb levels at different areas showed the ranged as follows; Madukuri (66.9 to 71.5 mg/kg), Kotufa (62.2 to 72.4 mg/kg) and Kirba (65.6 to 66.7 mg/kg) with the following CV% ranged ; Madukuri (0.45 to 1.12%) , Kotufa (0.32 to

1.24%) and Kirba (0.34 to 0.73%) for Tables 4.4, 4.5, and 4.6 respectively. This means that the mean concentration of Pb does not varied much because the highest value was 1.24 % variation . The level of Cd were found to be lower than the recommended National Environmental Board (2004) for soil standard limit of 37 mg/kg appendix I, but the level are found to be above the recommended European Union Standard (2001) for the maximum level of heavy metals in foodstuff which ranged from (0.1 to 1.0 mg/kg) appendix I. Cd level at different areas showed the ranged as follows; Madukuri (20.7 to 22.4 mg/kg), Kotufa (22.1 to 24.6 mg/kg) and Kirba (22.2 to 22.5 mg/kg) with the CV % ranged as follows; Madukuri (0.13 to 0.43%), Kotufa (0.05 to 0.37%) and kirba (0.04 to 0.27%) for Tables 4.4, 4.5, and 4.6 respectively. There was no much variation in the mean concentration of Cd level in all the areas and the highest value recorded was 0.43 %. The higher values of Cd and Pb may be attributed to the mobilization of heavy metals into the biosphere by human activities which cause the geochemical cycling of these metals(Bilos *et al*., 2001).

The level of Cu at different areas showed the ranged as follows; Madukuri (17.2 to 19.6 mg/kg), Kotufa (17.9 to 19.1 mg/kg) and Kirba (16.2 to 18.3 mg/kg) with the CV% ranged as follow; Maduguri (0.1 to 0.49%) Kotufa (0.11 to 0.42%) and Kirba (0.12 to 0.27%) for Tables 4.4, 4.5, and 4.6 respectively. The mean concentration of Cu also showed less variations because the highest CV% was 0.49 %. The level of Cu were higher in the sample compared to the Chinese Department of Preventive Medicine Standard (1995) of Cu (10mg/kg) critical food threshold. The concentration of Zn was the least among the heavy metals, Zn level at different areas showed the ranged as follows; Madukuri (2.3 to 8.4 mg/kg), Kotufa (5.1 to 7.6 mg/kg) and Kirba (1.8 to 7.1 mg/kg)) with the CV% ranged as follow; Maduguri (0.59 to 2.61%) Kotufa (0.02 to 0.39%) and Kirba (0.11 to 0.997%) for Tables 4.4, 4.5, and 4.6 respectively. The mean concentration of Zn showed some variation because the highest CV% was 2.69% in Maduguri. The level of Zn in the sample were lower compared to the Chinese Department of Preventive Medicine Standard (1995) for Zn (20mg/kg) critical dietary threshold for human health. Cr was below the detectable limit of atomic absorption spectrophotometer in all the locations and at all the different areas studied. The heavy metals content showed the dominance of Fe in all the location and at all the areas while Zn had the lowest value. The heavy metals Fe, Pb and Cd showed higher values which may indicate some possible human activities around the potash deposits site as reported by (Ogbonnal et al., 2007). Human activities contribute to the pollution load on the soil which are released and easily taken up by the plant or leached into the soil, which have high probability of soil, potash deposit, plant, water and environmental pollution as reported by (Ogbonnal *et al*. 2007). From the results one can conclude that the levels of heavy metals are in decreasing order as Fe >> Pb > Cd > Cu > Zn.

4.4 Comparison of Heavy Metals at Different Areas

Figure 4.3 summarizes the comparison of heavy metals Fe, Pb, Cd, Cu, and Zn at different areas. This figure confirms that the Fe levels were significantly much higher compared to the other heavy metals at all the areas (Madukuri, Kotufa and Kirba).The figure also confirms that the level of Pb were higher compared to Cd at all the areas (Madukuri, Kotufa and Kirba). The figure further confirms that the levels of Cu were higher compared to Zn which was the least among all the heavy metals in all the areas (Madukuri, Kotufa and Kirba). this showed that Fe is the most abundant heavy metal in all the areas (Madukuri, Kotufa, and Kirba), while Zn is the heavy metal with the least concentration in all areas studied.

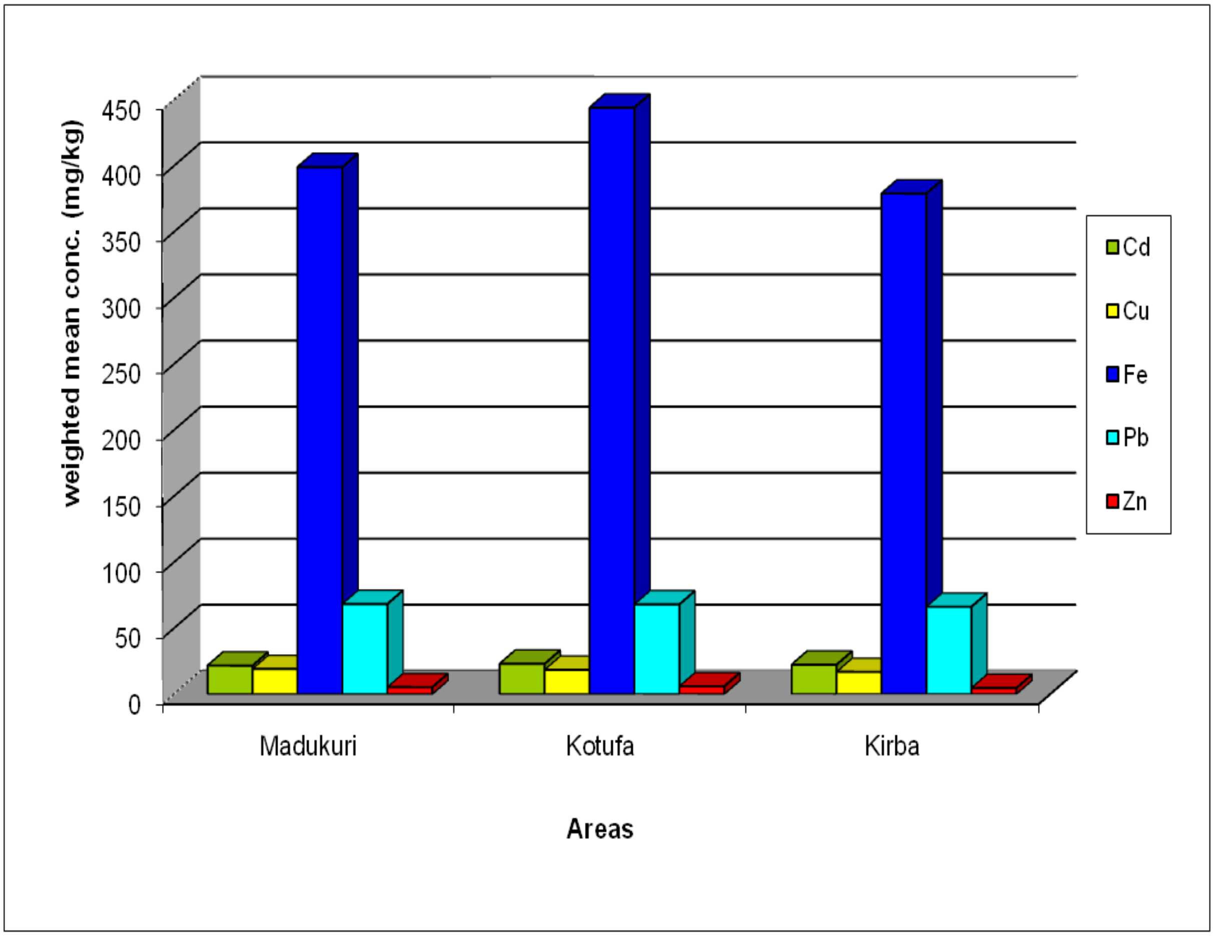

Figure 4.3; Comparison of Heavy Metals at Different Areas

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The elements determined in potash were essential elements K, Na, Ca and Mg and the heavy metals Fe, Pb, Cd, Cu and Zn. The following conclusions were made;

(i) The essential elements K and Na were found at elevated levels in all the areas and locations. The K levels were much higher compared to Na in all the areas and locations.

(ii) The Ca and Mg levels were much lower than K and Na, however the Ca level were much higher compared to Mg at all the areas and locations.

(iii) The order of concentrations of the essential elements are in the order

K >> Na >> Ca > Mg.

(iv) The heavy metals levels showed that Fe is significantly much higher than all the other heavy metals at all the areas and locations.

(v) Heavy metals (Pb and Cd) have being found to be of significance with levels below the recommended National Environmental Board (2004) soil standard, but the levels were found to be above the recommended values for European Union (2001) Standard for foodstuff

(vi) The levels of Cu and Zn were lower than the other heavy metals, in all the areas and locations; however the level of Cu is higher compared to Zn which is the least among all the heavy metals.

(vii) The order of concentration of the heavy metals were Fe >> Pb > Cd > Cu > Zn.

5.2 Recommendations

After carrying out these studies on the elemental composition of potash deposit found in Yusufari Local Government Area of Yobe State in North eastern Nigeria, the result showed that the potash contained essential mineral supplement (Na K, Mg, and Ca,) and heavy metals (Cd, Cu, Zn, Fe and Pb). I Therefore recommend that if processed to reduce the level of heavy metals potash can be used as a source of mineral supplement to human and animals. More so, the potash if unprocessed should be used with caution in human being because some heavy metals like Cd and Pb were found to be above the recommended standard for foodstuff, it means that there may be health risk associated with it when too much quantity of potash is consumed.

This study also showed that potash deposit in Yusufari Local Government Area contained high amount of potassium, therefore it can be used as a source of potassium in manufacturing potassium fertilizer which can boost agricultural production. Moreover, potash deposit in Yusufari Local Government Area of Yobe State, North eastern Nigeria can be exploited for industrial purpose for the production of glass and soap. Potassium silicate which is obtained from potash is used as dehydrating agent, it is also used to produce pigment, printing ink, soft soap and as laboratory reagent, therefore I recommend that the abundant potash in North eastern Nigeria can be utilized for various industrial purposes.

I also recommend that Raw Material Research and Development Council (RMRDC) and Ministry of Solid Mineral Development should make effort to exploit the potash in Yusufari Local Government Area of Yobe State, Nigeria. Finally, I recommend that more research should be carry out to determine other components like $KSiO_2$, K_2O, KCl, K_2CO_3, K_2SO_4,Na_2O, NaCl,Na_2CO_3, $MgCl_2$, $MgCO_3$, MgO, $CaCl_2$, $CaCO_3$ and CaO which could further reveals the quality of potash deposits.

Contribution to Knowledge

Potash is mined locally for human consumption and animal feed supplement by many people around Yusufari Local Government Area of Yobe State, Nigeria without the knowledge of what this potash contains. This studied had revealed the concentrations of essential element and some heavy metals present in potash that will guide people and give them more knowledge about some elemental composition in potash deposits around the areas. Furthermore, this studied will give more information about the danger of consuming too much quantity of potash because of the risk associated with some toxic heavy metals presence in potash deposits. This studied also gives more knowledge about the important uses of analytical instruments like flame photometer and atomic absorption spectrophotometer in determination of the elemental composition of potash deposits elsewhere.

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APPENDIX I

National Environmental Board Standard (2004) and European Union Standard 2001

Maximum Limit of Pb and Cd in Soil

	Heavy Metals (mg/kg)	
	Cd	Pb
Limit	37	400

Source; National Environmental Board (2004).

Permissible Limit Range of Cd and Pb in Foodstuff

	Heavy Metals (mg/kg)	
	Cd	Pb
Limit range	0.1 – 1.0	0.1 – 0.5

Source: European Union Standard (2001).

APPENDIX II

Evaluation for the Concentration of Elements in the Sample by the Least Square Method.

Calculation for the Concentration of K

Conc.of std. in ppm (X_i)	Absorbance (Y_i)	X_i^2	$X_i\ Y_i$
0.0	0.0	0.0	0.0
10.0	4.0	100	40.0
20.0	8.0	400	160
30.0	12.0	900	360
40.0	17.0	1600	680
50.0	20.0	2500	1000
$\sum x_i = 150.0$	$\sum x_i = 61.0$	$\sum x_i^2 = 5500$	$\sum x_i \sum y_i = 2240$

$$\bar{x} = \frac{150.0}{6} = 25 \qquad y = \frac{61.0}{6} = 10.2 \qquad (\sum x_i)^2 = (150)^2 = 22500$$

$$b = \frac{\cap \sum x_i y_i - \sum x_i \sum y_i}{\cap \sum x_i^2 - (\sum x_i)^2} = \frac{4290}{10500} = 0.41$$

$$a = \bar{y} - \bar{b}x = 10.2 - 0.41 \times 0.25 = -0.05$$

$$y = bx + a = 0.41x + (-0.05)$$

$$x = \frac{y + 0.05}{0.41} =$$

For the values of y = 370, 212, 195, 210, 181, 232, 531, 238, 203, and 226

$y = 370$

Therefore

$$x = \frac{370 + 0.25}{0.41} = 902.6$$

$$x = \frac{212 + 0.05}{0.41} = 517.2$$

$$x = \frac{195 + 0.05}{0.41} = 475.7$$

$$x = \frac{210 + 0.05}{0.41} = 512.3$$

$$x = \frac{181 + 0.05}{0.41} = 441.6$$

$$x = \frac{232 + 0.05}{0.41} = 566.0$$

$$x = \frac{531 + 0.05}{0.41} = 1295.2$$

$$x = \frac{238 + 0.05}{0.41} = 580.6$$

$$x = \frac{203 + 0.05}{0.41} = 495.2$$

$$x = \underline{226 + 0.05} = 551.3$$

Calculation for the Concentration of Pb

Conc.of std.in ppm X_i	Absorbance Y_i	X_i^2	$X_i\ Y_i$
0.00	0.000	0.00	0.000
5.00	0.019	25.00	0.095
10.00	0.071	100.00	0.710
15.00	0.167	225.00	2.505
20.00	0.249	400.00	4.980
25.00	0.288	625.00	7.200
$\sum x_i$ =75.00	$\sum y_i$ = 0.794	$\sum x_i^2$ = 1375	$\sum x_i\ y_i$ = 15.490

$\bar{X} = \frac{75.00}{6} = 12.50 \qquad \bar{y} = \frac{0.794}{6} = 0.132 \qquad (\sum x_i)^2 = (75.00)^2 = 225$

$$b = \frac{\cap \sum x_i y_i - \sum x_i \sum y_i}{\cap \sum x_i^2 - (\sum x_i)^2} =$$

$$\frac{6 \times 15.49 - 75 \times 0.749}{6 \times 1375 - 5625}$$

$$b = \frac{2.94 - 59.55}{8250 - 5625} = \frac{33.39}{2625} = 0.0127$$

$a = \bar{y} - b\bar{x} = 0.132 - 0.0127 \times 12.50 = 0.132 - 0.15875$

$a = 0.027$

$y = bx + a$

$y = 0.0127x + (-0.027)$

$X = \frac{y + 0.027}{0.0127} =$

For the values of y = 0.015, 0.016, 0.018, 0.017, 0.013, 0.019, 0.015, 0.015, 0.016, and 0.018

We have

$x = \frac{0.015 + 0.027}{0.0127} = 3.31$ ppm

$x = \frac{0.016 + 0.027}{0.0127} = 3.39$ ppm

$x = \frac{0.018 + 0.027}{0.0127} = 3.54$ ppm

$x = \frac{0.017 + 0.027}{0.0127} = 3.46$ ppm

$x = \frac{0.013 + 0.027}{0.0127} = 3.15$ ppm

$x = \frac{0.019 + 0.027}{0.0127} = 3.62$ ppm

$x = \frac{0.015 + 0.027}{0.0127} = 3.3$ ppm 1

$$x = \frac{0.016 + 0.027}{0.0127} = 3.39 \text{ ppm}$$

$$x = \frac{0.018 + 0.027}{0.0127} = 3.54 \text{ ppm}$$

STUDIES OF SOME ELEMENTAL COMPOSITION OF POTASH DEPOSITS FOUND IN YUSUFARI LOCAL GOVERNMENT AREA OF YOBE STATE, NIGERIA

BY

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M. TECH/CH/07/0083

A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF DEGREE OF MASTER'S OF TECHNOLOGY IN ANALYTICAL CHEMISTRY, CHEMISTRY DEPARTMENT SCHOOL OF PURE AND APPLIED SCIENCES MODIBBO ADAMA UNIVERSITY OF TECHNOLOGY, YOLA

JANUARY, 2014.

DECLARATION

I hereby declare that this thesis was written by me and is the record of my own research work. It has not been presented before in any previous application for higher degree. All references cited have been duly acknowledged.

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Signature of student **Date**

DEDICATION

This work is dedicated to my wife Mrs. Lucy Patrick Daniel, and also to my parents Mr. and Mrs. Daniel Sudi for their Patience and encouragement during this research work.

APPROVAL PAGE

This is to certify that the research work ‘Studies of some Elemental Composition of Potash Deposit found in Yusufari Local Government Area of Yobe State, Nigeria’ has been presented by Mr. Patrick Daniel Sudi (M. Tech/CH/07/0083) of Department of Chemistry, Modibbo Adama University of Technology Yola, and has been read and approved as meeting part of the requirements for the award of Masters of Technology (M. Tech) Degree in analytical chemistry.

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Patrick Daniel Sudi

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ABSTRACT

The elemental composition of natural potash deposits obtained in Yusufari Local Government Area of Yobe state has been determined. The samples were obtained in three areas namely; Madukuri, Kotufa and Kirba. The highly concentrated essential elements were potassium followed by sodium. K distribuhtion showed; Madukuri (9625 to 18035 mg/kg), Kotufa (8855 to 12493 mg/kg) and Kirba (11472 to 25436 mg/kg) . Na distribution showed; Madukuri (3751 to 5368 mg/kg), Kotufa (3625 to 3912 mg/kg) and Kirba (3535 to 5535 mg/kg).The next essential components were Ca followed by Mg. Ca distribution showed; Madukuri (554 to 885mg/kg), Kotufa (448 to 933 mg/kg) and Kirba (603 to 828 mg/kg). Mg distribution showed; Madukuri (53.4 to 58.5 mg/kg), Kotufa (57.4 to 58.8 mg/kg) and Kirba (55.4 to 58.3 mg/kg). Heavy metals determined were: Fe, Pb, Cd, Cu, and Zn. Fe has the most significant levels ranging from; Madukuri (300 to 449 mg/kg), Kotufa (446 to 468 mg/kg) and Kirba (254 to 439 mg/kg). The other elements found in significant levels were Pb and Cd with levels ranged as follows; Pb (66.2 to 72.4 mg/kg) and Cd (20.7 to 24.6 mg/kg). The elements with low concentrations were Cu (16.2 to 20.3 mg/kg) and Zn (1.8 to 8.4 mg/kg), While Cr was below detectable limit of AAS in all the sample. It generally showed that the levels of heavy metals present decrease in the order Fe>>Pb>Cd>Cu>Zn. The result for Pb and Cd levels are above the standard requirements for food intake.

Keywords: studies, elemental, composition, potash, Yusufari.