UNIVERSITY OF NAIROBI
Institute of Nuclear Science and Technology

# DIRECT SCREENING OF MICRONUTRIENTS ON MAIZE PLANT LEAVES USING HANDHELD X-RAY FLUORESCENCE SPECTROMETER (HHXRF)

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**S56/70898/2014**

A thesis submitted in partial fulfillment for the Master of Science in Nuclear Science and Technology in the Department of Electrical and Information Engineering in the University of Nairobi.

# DECLARATION

This thesis is my original work and has not been presented for a degree in any other University.

Signature.................................... Date **15/08/2023**

Caroline J. Kemboi
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**Supervisors' approval**

This thesis has been submitted for examination with our knowledge as University supervisors.

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# DEDICATION

This work is wholeheartedly dedicated to my beloved Mum who has been my pillar and my daughter for being a source of inspiration. Also, my beloved husband, brothers and sister in-law for their words of advice, moral and financial support; not forgetting my nieces and nephews who always cheer me up to soar higher. Additionally, I appreciate my special friends, for their kind words and encouragement during this study.

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# ABSTRACT

Foliar nutrient analysis is an indication of soil's elemental compositions. However, its use has been limited by the short window available for plant sampling and analysis since different plant species utilize nutrients differently. With the emergence of quick, non-destructive, inexpensive, and portable-spectral techniques like handheld X-ray Fluorescence spectrometer (HHXRF), the merits of foliar analysis can be explored and utilized. Analysis can be carried out both in the laboratory or in-situ set up. In this study, maize leaves sampled at two growth stages were collected in Muguga Kenya. And were analyzed in three different sample matrices, i.e. green (fresh), oven dry, and milled (powder). Na, K, Ca, Cu Fe, Mg, Mn, Mo, Zn, S and P nutrients were studied using Handheld X-ray Fluorescence (HHXRF) spectrometer to assess its applicability. Milled samples gave higher concentrations for the elements: Na; 43.8mgkg, Mg; 3077.1mg/Kg, P; 1741.4mg/Kg, S; 1878.5mg/Kg, K; 37988.8mg/Kg and Ca; 5294.7mg/Kg; as compared to concentrations in oven-dried samples that gave Na; 10.54 mg/kg, Mg; 956.01 mg/Kg, P; 802.07 mg/Kg, S; 1055.53 mg/Kg, K; 20550.35mg/Kg and Ca; 3224.11mg/Kg; however, there was no significant difference between oven dry and milled samples ($P > 0.05$). Fresh samples recorded the lowest concentrations and milled samples presented the highest correlation ($r^2$> 0.95). A relation between nutrient concentrations with seasonal variations showed higher nutrient concentrations for P; 1038mgkg$^{-1}$ ±174mgkg$^{-1,}$ K; 22994mgKg$^{-1}$ and Calcium at early growth stage compared to tussling stage where the concentration were 791mg/kg$^{-1}$ and 20409.37mgKg$^{-1}$ for P and K respectively. Nutrient content showed inconsistency depending on specific element and plant part; K, S, P exhibited decreasing nutrient concentration from the leaf base; for example a concentration of 5630.16 mg kg$^{-1}$ and 2457.79 mg kg$^{-1}$ for Sulphur at leave base and apex respectively; on the other hand increase in concentration from leaf base to the apex were observed in Na,Fe,Mn and Zn; Iron had a concentration of 298.03 mg kg$^{-1}$, 315.14 mg kg$^{-1}$ and 423.59 mg kg$^{-1}$ at base ,middle part and apex respectively. Copper and Molybdenum was found to be uniformly distributed along leaf. However, it is necessary to carry out additional studies between elemental concentration in the soil and their respective content in plants. There is need to test applicability of the technique on different crops and sample matrix.

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# LIST OF ABBREVATIONS AND ACRONYMS

| | |
|---|---|
| AAS | Atomic Absorption Spectrometry |
| AFSIS | African Soils Information Site |
| ATP | Adenosine TriPhosphate |
| CIFOR | Centre for International Forestry Research |
| CRM | Certified Reference Material |
| FAAS | Flame Atomic Absorption Spectrometry |
| FAO | Food Agricultural Organization |
| FWHM | Full Width to Half-Maximum |
| HHXRF | Handheld X-ray Fluorescence |
| MDG's | Millennium Development Goals |
| ICP-MS | Inductively coupled-Mass Spectrometry |
| ICP-OES | Inductively coupled-Optical Emission Spectrometry |
| IFAD | International Fund for Agricultural Development |
| ICRAF | International Centre for Research and Agroforestry. |
| IR | Infra -Red |
| IRRI | International Rice Research Institute |
| MOH | Ministry Of Health |
| NCDA&CS | North Carolina Department of Agriculture and Consumer Services |
| NIST | National Institute of Standards and Technology. |
| NPK | Nitrogen, Phosphorous, Potassium |
| UNICEF | United Nations Children's Fund |
| USDA | United States Development Agency |
| QA | Quality Assurance |
| QC | Quality Control |

| | |
|---|---|
| RNA | RiboNucleic Acid |
| SDG | Sustainable Development Goal |
| TXRF | Total X-Ray Fluorescence |
| SSA | Sub Saharan Africa |
| WFP | World Food Programme. |
| WHO | World Health Organization |
| XRF | X-ray fluorescence |

# CHAPTER ONE

# INTRODUCTION

## 1.1 Background of the Study

Agriculture is the most important sector of Kenya's economy. Its performance influences the populations' quality of life and economic growth, of which approximately 85% live in remote areas and agriculture is their main source of income(Jerneck et al., 2013).

More than 10 million people (almost a quarter ) of Kenya's population of 46.7 million people are generally considered chronically food insecure (Lokuruka, 2020); and (FAO, IFAD, UNICEF, WFP, 2021). The country's nutrition and food insecurity are as a result of the performance of the agricultural sector and in most counties, agriculture is plagued by low productivity and inefficient plant nutrient utilization; based on blanket fertilizer recommendations (NAAIAP, 2014).

Plant nutrients are referred to as essential if they play at least one specific role in plant growth and are required in limited amounts for optimal plant growth. However, this does not imply they are not important in the life cycle of the crop since in their absence, plant growth is impaired.  According to Motsara *et al*., 2008; there are 16 nutrients that are essential for a plant to complete its life cycle. These are N, C, H, O, P, Ca, Mg, K, B, S, Zn, Fe, Mn, Cl, Cu and Mo. These nutrients are provided by soil organic matter, soil minerals, lime, amendments and fertilizers, while hydrogen, oxygen and carbon are either obtained from water or air, therefore generally not considered limiting (McGinnis *et a*l., 2012). The remaining 13 are usually applied as amendments e.g. fertilizer, manure, etc. if they are unavailable or inadequate in the soil (Johnston *et al*., 2004).

Crop production in Kenya and many other SSA countries over many decades rely mainly on fertilizers, particularly N, P and to some extend K and Ca. There is little focus on secondary nutrients and micronutrients on crop response, and those that exist; are limited and scattered research on response of these nutrients to crop productivity (Chianu *et al*., 2012). There has been growing evidence of crop response to application of the typically macronutrient-based fertilizers which are emphasized in smallholder farming. For instance studies by Kihara *et al*., 2017) indicate that there is positive response in crop productivity to applied nutrients and micronutrients for example application of nutrient Sulphur resulted in average yield 0.7 t ha$^{-1}$ (i.e., 20% more as opposed to before treatment. However, soil testing has been used sparingly as a tool to guide fertilizer decision. One key factor that has contributed to the lack of support of fertilizer recommendations by soil testing is due to the perception that the results obtained from tests for micronutrients are not satisfactory indices for predicting soil's ability to continuously supply nutrients to plants due to various complex distribution patterns of available nutrients among layers or chemical species in soils (Chen *et al.,* 2012);features of the soil governed by geochemical characteristics such as soil structure and texture, plant's capacity to accumulate nutrients and environmental factors (Tezotto et al., 2013).

Analysis of plant tissue is a preferred way for monitoring the soils nutrient status, the reason being, it provides information on the soils ability to transmit the element of interest until the day of sampling. The elemental quantification of the concentration of plant nutrients has been carried out using several methods such as inductively coupled plasma mass spectrometry (ICP-MS), colorimetry, flame atomic absorption spectrometry (FAAS), and inductively coupled plasma atomic emission spectrometry (ICP-OES) (M. B. Guerra et al., 2018). However, in applying these techniques; sample preparation requires destruction of sample matrix either partial or complete either by ashing or digestion with strong acids (Tavares et al., 2020).These sample preparation processes in analytical laboratories are often slow, tedious, costly, time consuming and requires the analyst to take caution as it involves use of hazardous reagents (acids).Furthermore, incomplete dissolution may affect the accuracy of some plant nutrients that are present in low concentrations. This was evident in a study carried out by (Reidinger et al., 2012),where the percentage of silicon in grass samples analyzed by the acid digest calorimetric method and HHXRF exhibited poor correlation between the two methods (Pearson correlation, **r** = 0.644, **n** =5, **P** =0.240).

There are more accurate, reliable, economical instruments with high sensitivity, accuracy, and applicability to real-world situations that include XRF systems. Portable X-ray fluorescence and in particular the HHXRF have opened a new window for accurate, fast, cost effective, non-destructive and non-consumptive survey of total elemental concentrations in plants, both insitu and laboratory system.

It has been successfully used in numerous studies to determine element concentration in environmental samples in multiple disciplines, such as archaeology, soil science and mining

(Potts and West, 2008 and Lemberget *et al*., 2000). The HHXRF technique offers a non-consumptive analytical technique for material characterization, determination of trace and major elemental composition and has several advantages compared to other multi-elemental techniques. These include: limited sample preparation, less hazardous and increased total speed, thus large number of samples can be analysed within a short period of time (Parsons et al., 2013).Furthermore, its portability, high quality measurements and capability of on-site analysis makes it ideal for field assessment (M. B. B. Guerra *et al*., 2014).

Various studies e.g. Guerra *et a*l., 2014 carried out a comparison analysis of pressed pellets using portable XRF and acid digestion of the same sample analyzed using benchtop EDXRF and achieved coefficient correlations of (r)= 0.9601-0.9918 for benchtop, and (r)=0.9094 - 0.9948 for portable XRF; similarly Towett *et al.*, 2016.carried out a comparison analysis of milled plant samples by direct surface analysis using HHXRF under vacuum conditions and analysis under atmospheric pressure and came to a conclusion that analysis under vacuum conditions improves sensitivity ($r^{2}$ )=0.97) of the analysis.

The studies above have lauded the ethics of utilizing HHXRF spectrometry for an extensive variety of plant applications. However, in most these research studies; samples have been presented to the instrument when milled or in powder form (Towett *et a*l., 2016).Therefore, there is little literature on the presentation of green/fresh and oven dried samples during analysis. There is also need to explore more on the distribution of nutrients along the leaf. As a result of this, a more extensive objective of plant tissue analysis can be expanded from the usual primary goal of diagnosing suspected nutrient toxicities or deficiencies to developing nutritional profile of plants at different growth stages and making recommendations on soil's nutrient status and fertilizer applications. In this study green, oven dried and milled maize leaves from Muguga farms in Central Kenya (Fig 2) were analyzed using HHXRF spectrometer.

### 1.2 Problem Statement

Soil testing has been down played as a guiding tool for fertilizer decision, due to perception that conventional tests for nutrient contents are not satisfactory indices for predicting soil's capacity to constantly supply nutrient to the plants (Kihara *et al*., 2016). In addition, quantification of plant nutrients has been carried out using digestion-based techniques which depends on the total destruction of sample matrices during analytical process. This is a major problem in tests where the amount of sample available is small and analysis for other aspects of plant nutrient composition is required, or situations where the samples need to be reanalysed.

Numerous studies; e.g. Campos, *et al.,* 2014; Lemberge *et al*., 2000;Munro *et al*., 2008; McLaren *et al*., 2011; Queralt *et al*., 2005; have praised the virtues of utilizing HHXRF spectrometry for a variety of applications and other disciplines e.g. archaeology, soil science and mining; however its applicability in the analysis of nutrients in maize leaves and other plant leaves has not been completely tried and a proper guidelines established for field applications so as to come up with a suitable protocol for such measurements in fresh or dried unhomogenised plant material (Potts and West, 2008).

Reidinger *et al.,* (2012) added that there are factors that vary in plant tissue analysis and that affect its precision and accuracy; these include mass and density of the matrix, which affects the energy of the characteristic X-ray for a particular element and its associated critical penetration depth as there is a difference between scanning one leaf tissue and stacking several leaves together as observed by Weindorf *et al*. (2014). Another factor is presence of moisture content, which is influenced by the plants' development stage and the sampled plant part (NCDA and CS, 2013). Mäkinen *et al*., (2005) added that in-situ (wet conditions) analyses of soils via HHXRF showed more variations than measurements made in the laboratory of dried and sieved samples. Furthermore, Kenya has the most fluctuated cereal production especially maize, as a result of among other factors nutrient deficiencies, rapid population growth, This means therefore farmers have to strive to produce enough food to cater for the population resulting in intense cropping, which leads to severe soil degradation and poor soil fertility (USDA, 2019; Bai and Lei,2020).

## 1.3 Objectives

### 1.3.1 General objective.

To assess the applicability of the Handheld X-ray Fluorescence spectrometer for direct tissue analysis for light and heavy elements in maize leaves from Muguga, Kiambu County.

### 1.3.2 Specific Objectives

The following are the specific objectives:

a. Evaluate the reliability of HHXRF results of maize leaf elemental composition under different sample presentation methods.

b. Determine the variations in elemental concentration in maize leaves at two growth stages.
c. Determine variations in major and trace elemental concentrations along various parts of maize leaves.

### 1.4 Justification and Significance

The Kenya Vision 2030 recognizes agriculture as a critical sector in the achievement of the second Sustainable Development Goal (SDG 2) of achieving food security, zero hunger and improved nutrition in Kenya thus attaining annual financial development rate (Vision 2030, 2007).It is also part of the government's big four agenda of achieving 100% food security and proper nutrition for all Kenyans (parliamentary service commission medium term plan 2018). However, dangers and vulnerabilities connected with agricultural production, such as, desert locusts and Fall armyworm (Evans and Inglesby, 2019); poor mineral nutrition and high production costs pose a major challenge in achieving high yield levels in tropical and sub-tropical regions (Ezeaku *et al*., 2013). Maize is Kenya's staple food ( Ojala *et al*., 2014; Khan *et al*., 2014), and one of the country's major income earner (occupies approximately 40% of arable land) to many rural households (FAO 2011-2013; Olwande, 2012;)**,**Therefore there is need to identify the weaknesses in this sector and find solutions that will help the industry grow (Ezeaku *et al*., 2002).To increase agricultural productivity requires the use of modern advanced equipment like HHXRF that goes in handy with SDG goal nine on innovation (Vision 2030, 2007).

Plant tissue is part of the plant that shows any nutritional disturbance and information on the nutrient status of the plant up until the day of sampling; therefore the most preferred way for monitoring the soils ability to transmit the element of interest (Borges *et al*., 2020).The HHXRF spectrometer was selected as alternative technique for maize tissue analysis as it is capable of simultaneous multi-elemental quantification of the essential plant nutrients within a short span of time (60seconds). Data can be used to develop HHXRF analytical guideline on suitable analytical parameters and sample presentation methods which will allow sample analysis and data acquisition on site .

### 1.5 Scope of the Study

Samples were collected from 16 sampling plots with maize plants; this was done in two plant growth stages with the collection of 32 Samples at each growth stage from Muguga farms in Kenya. The reason for choosing the site is due to its close proximity to the World Agroforestry Centre's (ICRAF-CIFOR) Soil-Plant Spectral Diagnostics Laboratory to enhance easy transportation of fresh samples for analysis.

The total elemental concentrations of the samples were determined using HHXRF spectrometer used in the lab setup as a bench top instrument. The study was focused on the analysis of fresh, oven dried and milled maize leaves for assessment of nutrients, which include light elements namely: Na, Mg, P, S, K, and Ca and heavy elements that is: Mo, Cu, Mn, Fe and Zn.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Foliar analyses

To optimize fertilization, it is important to determine the level of nutrients that are available to the plant. Normally, farmers use soil testing to assess nutrient availability. However, the interpretation of results obtained from soil analysis may not be able to reflect plant available micronutrients. The availability as shown by previous studies is regulated by factors such as plant types, as well as the chemical and physical properties of soils (Xue et al., 2017; Chen et al., 1996). Another limitation is that soil sampling is supposed to represent the soil portions explored by the root, which may be different for each crop, thus sometimes becomes a challenge.

Foliar analysis is regarded as one of the direct methods to evaluate the plant nutrient status compared to soil. The leaf is considered for micronutrient analysis since it is part of the plant where physiological activities occur, and if there is any nutritional disturbance, it can easily be identified (Malavolta, 2006; Mourão,2003).

## 2.2 Factors affecting plant nutrient uptake

Micronutrients are viewed as elements that are vital, and if the life cycle of a plant cannot be completed without them and cannot be supplemented by whatever other components, and they play out an immediate key role in the plant. Most micronutrients are accessible from the soil or if not, are connected as soil corrections such as fertilizers or lime and taken up from the roots to the leaves and different parts of the plant (Takahashi et al, 1990). The composition of micronutrients and other elements in plants reflect to some extent the chemical components of the growth media. The degree to which this relationship exists is in variable amounts and is controlled by various factors that impact on their availability to plants.

### 2.2.1 Environmental factors

Several processes are involved in the uptake of micronutrients from the growth media (soil) to the plant. The main pathway through which micronutrients get to the plant is the roots. The absorbed micronutrients are disintegrated in soil solution either as chelates, complexed or in ionic forms, but most importantly in solution forms (Towett et al., 2015). Those that are above the ground are absorbed by the plant from aerial deposition through the leaf stomata especially gases and aerosol particles. Absorption processes takes place at very low micronutrient concentration gradient in solutions, and the rate is determined by the presence of hydrogen ions ($H^{\dagger}$ ) and other ions (Bityutskii et al., 2017).In addition, the rate changes depending on the plant stage of development and species.

Temperature, aeration, moisture, and PH are some factors of the soil environment that influence mineral absorption processes. For instance, McGrath et al. (2007) found higher temperatures to greatly impact on the uptake of micronutrients by plants, while increase in pH levels influenced the availability and uptake of most micronutrients with the exception of Molybdenum. Excess moisture content enhances filtration of nutrients to lower horizons while dry conditions hinder root action at shallow levels and decrease the breakdown and flow nutrients to the plant (Xue et al., 2017;Ghosh et al., 2018).

As for soil texture, course sandy soils have less ability to hold nutrients compared to finely textured ones that tend to bind nutrients in forms not accessible to plants.

Root absorption of micronutrients can be described as either passive or active. Passive also referred to as non-metabolic takes place when the ions move from the outside environment to the root endodermis, while active (metabolic) needs energy since it takes place against the concentration gradient. The presence of ions in the soil solution is one of the key factors believed to influence the uptake of micronutrients by the plant, most importantly when the uptake is active (Morel et al., 1997). When the external cation concentration of soil solution is low, active absorption takes place, while at higher concentration passive process predominates.

Uptake mechanisms vary as per given element. For instance, Nickel and lead are absorbed passively while, Zinc, Molybdenum and copper are absorbed through active process. However, concentration of elements can pass over a physiological barrier when structural and biological properties of root cell are altered (Kabata-Pendias & Pendias, 2011).

### 2.1.2 Plant development stages

Several factors, which include plant part sampled, species, age (plant growth stage),genotype and various environmental conditions affect the sufficiency ranges of a particular nutrient (Stammer, 2015).For example, monocotyledonous species need less amount of Calcium concentration compared dicotyledons to obtain maximum growth rates(Nabi et al., 2006; Loneragan and Snowbell, 1996). Kovács et al., 2017 recommended that in sampling corn plants for nutrient assessment, a two-stage sampling is involved; that is Whole plant sampling at early vegetative stage (V6) and sampling of ear leaves at silking/flowering stage, which is the stage with the largest leaves on corn plants (Hotchmuth, 2012). Early-stage tissue sampling generally allows for a particular nutrient to be supplemented incase results obtained from the tests shows a deficiency; while on the other hand sampling at silking stage gives a perspective the nutrient condition of the maize plant before grain filling begins. Therefore, when sampling a plant for analysis, a well-defined plant part and stage of development must be considered (Hallmark and Beverly, 1991).

Plant foliar analysis differ from that soil analysis in that; it provides information on plant available nutrients up until the day of analysis thus soil nutrient availability can be predicted (Parks et al., 2012).Therefore, the plant part or age affects nutrient concentration to a certain degree (Römheld, 2012). As a plant matures the nutrient concentration and the sufficiency ranges on the whole plant decreases for most nutrients except phloem nutrients i.e. Ca, B and Mn (Römheld, 2012). A study done by Beatrix et al. (2014), shows fresh tissue had lower coefficient of variance ($r^2$) for majority of elements compared to dried and ground samples and the fresh concentration of had the covariance of zinc ($r^2$=0.76).

## 2.3 Maize in Kenya

Maize is the most important cereal crop and an important staple food for more than 1.2 billion People in Sub-Saharan Africa (SSA) and Latin America. It is also a major food crop in most Kenyan communities, and it accounts for between 30-50% of low income household expenditures in Eastern and Southern Africa. It is the major food crop in most Kenyan communities, and one of the most nutrient demanding crops

According to the United States Department of Agriculture, Kenya's maize production fell by 4.2 million bags in the western and parts of rift valley in the year 2016/2017 due to drought and a fall armyworm infestation as reported across 27 counties, this resulted in losses of up to $120 million ( USDA, 2019);Abate et al. (2015) also noted a declining trend in Kenya’s average yield production capacity that reduced by a significant 1kilogram per hectare per year (kg/ha/year), a rate which is much higher compared to the continent’s average in kg/ha/year. The decline in production is also as a result of increasing population density. Several low income and middle income countries (LMICs), particularly in Sub-

Saharan Africa (SSA), continue to experience rapid and consistent population growth (Bai and Lei, 2020; Espenshade and Serow, 2013).This means therefore farmers have to strive to produce enough food to cater for the population resulting in intense cropping, which leads to severe soil degradation and poor soil fertility with little or no supplement renewal. Therefore, plant tissue analyses can be a good tool to diagnose plant nutrient status throughout the growing season, and used as a complementary to the soil test results.

In addition, the analysis can be useful in determining if the soil fertility status as well as fertilizer applications translate to adequate crop nutrition (Stewart, 2016). In foliar analysis, the nutrient content in the analysed part is compared with the established critical or sufficient values that are based on development of response curves, surveys, and experience. Critical values refer to nutrient levels at which there is a 5 to 10 % reduction in crop yield, and is usually linked to visual signs of deficiency, while within the sufficiency range, there is no yield reduction due to either nutrient surplus or limitation.

Plant nutrient deficiency bear adverse effects on the health of human beings by altering normal metabolism, growth and physical wellbeing (FAO, 2007, Koning et al., 2008). In Kenya, micronutrient deficiencies are highly prevalent especially in vitamins and minerals which results to: impaired mental and physical development in children; high mortality rates in women and unborn children; reduced work productivity in adults and increased morbidity (Black et al., 2008).According to GOK(2011) children under the age period of five years are the most affected by Zinc (51%), Iron (73.4%) and vitamin A (84%) deficiencies. In addition, women especially pregnant women are at a higher risk of Vitamin A (39%) and Iron (60%) deficiency, and approximately, of 16% adult males suffer from Fe deficiency, causing anaemia.

Sufficient nutrient supply plays a vital role in human growth and development. According to the MOH (2012) approximately 1.5 to 2.1 million children are stunted therefore do not reach their full physical potential, which poses a serious national concern. On the other hand, iodine deficiency has been noted as the leading cause of brain damage and mental retardation in the world. It is estimated by the World Health Organization that 1.5 billion of the world's population live in Iodine deficient environments(Organization, 2002).

## 2.4 Nutrients to be studied.

When elements are deficient, plant metabolic processes and photosynthesis are disrupted and symptoms in terms of visible appearance, decreased growth rate and reduced crop yields become evident. There are other symptoms, which are not noticed visually and are quite specific to in terms of given essential elements, commonly known as hidden hunger signs (Bergmann, 1992). The mobility of an element influences the location where deficiency symptoms are likely to be noticed on the plant. An example is Calcium deficiency, which occurs at growing points or in storage organs like roots and fruits. Crops like other living beings have specific nutrient requirements, therefore there is need to understand their nutrient requirements, their translocation and sufficiency ranges in leaf so as to be assessed and diagnosed adequately (IRRI, 1999). Below, is a brief discussion of some of the nutrients considered in this study:-

### 2.4.1 Study of light elements

**Phosphorous**

Phosphorous is available as orthophosphate ($HPO^{2-}$, $H_2PO^{4-}$) ions. However, the orthophosphate combines with Calcium ($Ca^{2+)}$ ions or Magnesium ions to forms a soluble $Mg^{2+}$ or calcium orthophosphate $[Ca (H_2PO4)]_2$ which is readily adsorbed into the soil. Soil soluble P reacts with magnesium (Mg), aluminum (Al), calcium (Ca) and iron (Fe), forming complex compounds that are not readily available to the, process called “fixation.” Maintaining the soil pH between 6 and 7 increases availability of Phosphorous(Jones Jr, 2012)

Phosphorous plays a significant role in the storage of energy and transfer of ATP and ADP, TBN and DPN nucleotides. It is one of the elements that relay genetic information; since it is part of RNA and DNA. It is required in large quantities by growing parts like root tips, shoots, where cell division and metabolism is high, therefore initiates flowering and promote seed and fruit development. In addition, it helps plants survive harsh conditions such as winter, disease and pest incidence, hence improving the quality of the crops. It has low mobility and also very susceptible to reaction with soil solid and solution phases (Hodges 2010) .

Deficiency is shown by purple tints which may spread over the whole leaf blade and stems. The symptoms are visible on older leaves due to its mobility to younger growing sites. There is also a decreased in the number of leaves flowers.

Phosphorous deficiency can also lead to weak, slow and stunted growth, since it is heavily required for cell division during early stages, thus leading to delayed maturity and poor development of seed and fruit in addition there's development of spindly stalks that are either barren or with incomplete grain fill (Bittman et al.,2004).Study done by stammer et al.,2015 showed the Phosphorous tissue concentrations in maize leaves and plants, ranged between 2200 – 6900mg P kg-1 at V5-V6 early growth stage and 1000 - 4600 mg P kg-1 at R1 silking stage respectively.

### Potassium

Potassium is available to plants as $K^+$ and its uptake is optimum at between vegetative to silking stage and low at grain filling stage (Figure 2.1). It does not form part of any organic compound although it promotes metabolism through enzymatic activation, conversion of amino acids into proteins, conversion of sugars into energy storage compounds such as starch (Bittman et al., 2007).It also regulates water use in the plants as it controls the opening and closing of stomata, thus maintains electrical charges during photosynthesis. Through its role, it improves the size of grain and a seed hence improved quality of vegetable and fruits. Chlorosis/ scorching along leaf margins while the midrib remains green is a common deficiency symptom, which is first observed in older leaves due to high mobility of $K^+$ in the plant(Uchida, 2000). Due to its requirement in photosynthesis, inadequate / lack of K, leads to slow/ stunted growth, delay of silk emergence and in some plants, lodging due to breakdown of internal stalk tissue and weak stems, are common. Potassium tissue concentrations in maize leaves and plants ranged from 8900 – 60700mg K kg-1 at V5-V6 early growth stage and 3200 -25600 mg K kg-1, at R1 silking stage respectively (Stammer, A. J., 2015).

### Calcium

Calcium is available to plants as $Ca^{2+}$ ions. It aids in the formation of the cell wall membrane as well as contribute to cell division, therefore plays a role in maintaining cell wall membrane permeability and integrity. It also activates growth-regulating enzymes, improves translocation of nutrients, root absorption and acts as a detoxifying agent through neutralization of acids (organic and inorganic) in plants(Bittman et al., 2007). Furthermore, it is essential for protein synthesis in peanuts and improves crop yields by reducing acidity.

Since the element is stable and hardly translocated, Ca deficiency is observed in young leaves in which tips of roots and young leaves turn brown and die(Uchida, 2000). Finally, due to its role in maintaining rigidity, deficiency leads to leaves sticking together at the margins causing tearing as the leaves expand. The stem structure may be weakened, buds blossoms fall prematurely, slowed growth of new leaves and at times younger leaves are rankled and cupped with the deterioration of terminal buds.

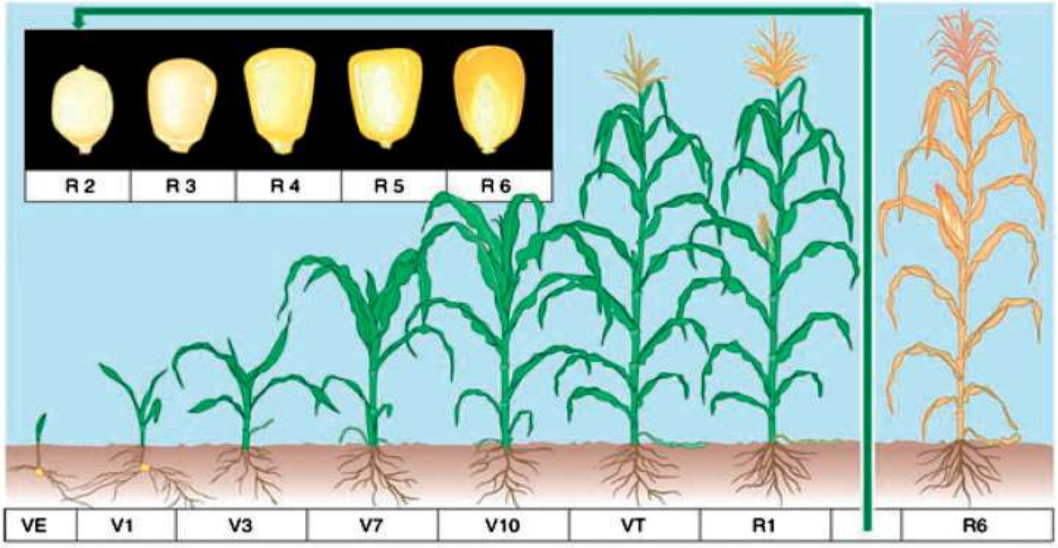


**Figure 2.1: Different growth stages of a maize plant, vegetative (V) and reproductive (R) stages (Lee, C. (2007).**

### Magnesium

It is available as the divalent cation $Mg^{2+}$; it is the main component of chlorophyll molecule and therefore plays a role in photosynthesis. It is a cofactor of many enzymatic reactions needed for the movement of phosphorus in the plant, as indicated by Calcino et al., 2000. It is involved in plant respiration, protein synthesis and assists in movement of sugar within the plant. Magnesium is a mobile element and interveinal chlorosis(Leaves appear striped, with yellowing and browning of leaf tips and edges) appearing on older leaves being the common deficiency symptom(Uchida, 2000). For maize, yellow stripes appear on leaf tissue with green veins. In extreme cases of deficiencies, younger leaves drop prematurely. Bittman et al., 2007 added that magnesium nutrient is mobile and easily translocated from older to younger tissues hence present at vegetative V stage (Figure 2.1)

**Sulfur**

In as much as it is considered a secondary nutrient; it is one of the nutrients that plays one of the major roles in the life circle of the plant. It absorbed through the root system into the plant as $SO_4^{2-}$ ions. It is part of the amino acid cysteine and thiamine, therefore involved in protein synthesis. It is also a component of s-glycosides (mustard oils) particularly in oil - producing crops, glucosides and contribute to the characteristic odour in some plants. In addition, is it is a component of vitamin biotine and thiamine and a major constituent of enzymes involved in the formation of the chlorophyll molecule and aids in nitrogen metabolism (Jones Jr, 2012, (Gunes et al., 2008).Sulphur deficiency causes the leaf chlorosis-for maize plants, interveinal chlorosis is observed while for other plants like wheat, a whole plant becomes pale white and spotted leaves are observed in potatoes. These symptoms generally lead to thin stemmed plants, stunted and consequently yield is reduced. It is immobile in plants therefore cannot be easily translocated to young parts of the leave. Sulfur deficiency symptoms are often similar to those of phosphorus and nitrogen therefore cannot be diagnosed by mere visual observation of symptoms((Gunes et al., 2008).

**Sodium**

The plant absorbs sodium as monovalent $Na^+$ ions, in most cases it's available as sodium chloride. It aids in metabolism and synthesis of chlorophyll. In some cases it performs the same role as potassium in the opening and closing of stomata thus improving water balance within the plant hence resulting cell expansion (Ed Bloodnick. 2018).When in the compound form sodium chloride (NaCl), it aids ionic balance within the cell and movement of water in and out of plant cells (osmosis) and maintains vegetative structures xylem tissues.Sodium deficiency is rare since in most cases it available in growing media that is water and soils (saline environments (Bloodnick, 1999).However the sodium deficiency symptoms exhibit appearance of Chlorotic blotches with necrotic spots on the margins or between the veins of the younger leaves and in some cases wilting of the plant may occur(Shone et al., 1969).At toxic levels necrosis or scorching appears on the leaf margins and tips. Deficiency occurs when Sodium concentration is below 2ppm while at a concentration above 70 ppm and concentration above 150 ppm, reverse osmosis occurs.

### 2.4.2 Study of heavy elements

#### Copper

Copper is available to plant as $Cu^{2+}$, and is essential for the synthesis and stabilization of chlorophyll, therefore involved in photosynthesis. It is a component of most enzymes thus plays key role in plants' physiological activities e.g. nitrate and carbohydrate metabolism, respiration, water permeability, disease resistance and reproduction (Regis, 1998 and Krämer, *et al*., 2006); and is also part of the chloroplast protein called plastocyanin, hence forms part of the electron transport chain in the plant. It is moderately immobile as it binds with organic matter and rarely leaches (Miotto et al., 2014). Cu deficiency leads to stunted growth, chlorosis in younger leaves, occurrence of multiple sprouts at growing points resulting in bushy like appearance, defoliation and die back of twigs and stems. In cereals like grain heads may not form in severe deficiencies and the plant become disease prone (McCauley et al., 2009).Copper tissue concentration ranges from 50-250mgKg$^{-1}$ while concentration below 2mgKg$^{-1}$ is considered critical (Aref et al., 2012).

#### Iron

Available to plants as $Fe^{2+}$ or $Fe^{3+}$ ions. However, $Fe^{2+}$ is readily available and stable ion. $Fe^{3+}$is readily oxidized therefore forming complex compounds with bicarbonates, resulting in limited uptake by plant since it cannot be easily absorbed by the plant .It is essential for the synthesis as well as maintenance of chlorophyll in plants; formation of the enzyme responsible for plant metabolic activities (photosynthesis and respiration) and it is also a requirement in sulphate and nitrate reductions, and takes part in protein metabolism. Deficiency leads to interveinal chlorosis in younger leaves, and due to its role in the production of chlorophyll; the entire leaf base may become bleached and sometimes may extend to the whole plant. Despite its abundance in the earth's crust, it's the most limiting nutrient; due to its low solubility at alkaline PH environments(Aref, 2012).Study by (Hodges, 2010) showed that iron ear leaf concentration at initial silk ranges 21-250mg kg-1 and in comparison within other studies ,it is within the sufficiency ranges.

#### Manganese

Manganese is available as $Mn^{+}$, $Mn^{2+}$and $Mn^{3+}$ and $Mn^{4+}$. However, plants only take up manganese as $Mn^{2+}$since its most stable and despite weak complexes; its dominant in tissues (Kabata-Pendias, 2011). Its concentrations however vary depending on the growth stage, soil conditions and plant species. Manganese is part of the redox reactions and electron transport systems, as it is a metalloprotein structural component (Regis, 1998; Haluschak et al., 1998).It also participates in photosystem II where in plays a role in photolysis. In addition, Manganese plays the role of amino acid synthesis by enzyme activation as it activates phenylalanine ammonia–Lyase (PAL) of tricarboxylic acid cycle (Aref, 2011).Deficiency symptoms manifested by appearance of pale mottled leaves followed by greenish –grey specks at the lower base of younger leaves in monocots and necrotic spots also known as marsh spots on the cotyledons of legumes. Manganese deficiency has a negative impact on these crops by reducing dry matter production and yield, weakening structural resistance to pathogens, and reducing tolerance to drought and heat stress (Hakala et al., 2006). Aref, 2012 added that manganese sufficiency ranges in maize ear leaf maize at initial silk between 20 -150mg $kg^{1}$ Furthermore, he added that concentration below 15 $mgKg^{-1}$ is considered critically deficient and concentration above 200 mg $kg^{-1}$ is considered excessive or toxic.

### Molybdenum

Available to plants as molybdate ions ($MoO^{4-}$) ions. It is necessary for nitrate reductase and nitrogenase enzymes required for assimilation and fixation of nitrogen. It also regulates the microorganisms needed for the uptake of anions.

Mo deficiency makes the plants leaves roll inwards and becomes necrotic. Other effects of Mo deficiency include spots appearing at leaf margins as a result of nitrogen accumulation, flowering may be restricted and conversion of nitrogen to proteins reduced(Uchida, 2000). In maize, molybdenum deficiency leads to decreases leaf areas, shortens internodes.

In maize, reproductive tissues, molybdenum deficiency can alter the phenotypes in developing plant parts which include poorly developed stamens, delayed emergence of tassels, and reduced pollen grain development as a result of small anthers and eventually poor grain filing(Kaiser et al., 2005). A study carried by Campbell, 2000 that Molybdenum concentration of 0.1ppm at tasseling is considered critical, and sufficient at a concentration between 0.1-2.0ppm. Molybdenum is moderately mobile in plants and thus readily absorbed when present in soluble forms (Kabata-Pendias & Pendias, 2011).

**Zinc**

Zinc is absorbed as divalent cations $Zn^{2+}$which is common and most soluble cation in the soil and it is in this form utilized by plants (Alina Kabata-Pendias, 2010,Haluschak et al.., 1998).

It plays a role as a metal component of enzymes (superoxide dimutase, carbonic anhydrase and RNA polymerase) for production of energy, protein synthesis and acts as growth regulator (Aref, 2012). In addition, it aids in moisture absorption along with potassium. It is effective in energy production in Krebs cycles therefore essential for crop production and optimal size of the fruit. Furthermore it plays a prominent role in internode elongation, nitrogen metabolism, chlorophyll synthesis, and aids in the plant resistance to biotic and abiotic stresses (Aref, 2011).

Deficiency symptoms include shortened internodes, interveinal chlorosis is observed especially midway between the margin and midrib, and small malformed leaves resulting in rosette symptoms in young growing cotyledons (Grundon, 1987).Zinc availability and uptake is affected by environmental and soil factors, and to some extend application of other nutrients. For example it decreases with increase in temperature and pH, and its uptake is inhibited by some metallic cations such as $Fe^{2+}$ and $Cu2^{+,}$ due to the same carriers for elements in plant roots. Aref, 2011 added that in addition to other researches done; analysis of maize ear leaf at silking stage zinc content were categorized as follows: less than 10 mg $kg^{-1}$ is considered deficient while a range of between 20-70 mg $kg^{-1}$ intermediate, a range of 71-100 high and concentration above100 mg $kg^{-1}$ is considered toxic. Zinc has intermediate mobility therefore it’s uniformly distributed along the leaf (McCauley et al., 2009).

## 2.4 X-ray Fluorescence Spectrometry

X-ray fluorescence spectrometry (XRF) has opened a new window for non-consumptive, safer, faster and relatively accurate method**.** It works on the principle that X-rays are emitted from the element in a sample when irradiated with high energy X-rays, from an external source such as X-ray tube. Incident X-rays eject an electron from the orbital that surrounds the nucleus within an atom in the sample; creating a vacancy. These photoelectrons leave with a kinetic energy (E-φ) which is normally the difference in energy between that of the incident particle (E) and the binding energy (φ) of the atomic electron. The vacancy left by the ejected electron in the atom's electronic structure is then filled with an electron from a higher energy shell. A characteristic X-ray photon is released, with the same energy as the difference in binding energies of the two electron shells. The characteristic x-rays are distinct for each element, thus acting as a fingerprint for that element (Towett et al., 2013). Detection of characteristic x-rays and measuring its energy acts as the principle for determination of the element and specific electronic transition from which it originated (Jenkins, 1988).

The emitted characteristic x-rays reflecting various atoms/elements are transmitted to the SiLi detector, producing an energy spectrum. The intensities of these x-rays serve as the foundation for elemental quantitative analysis. The preamplifier converts the characteristic X-rays into a low-voltage pulse. The pulse amplitude which is proportional to the energy of the received x-rays is amplified by the main amplifier then converted into a digital signal. This information is stored in a multichannel analyzer according to its amplitude and finally formatted to an XRF spectral line (A. Gürol, 2008).

## 2.5 Instrumentation

HHXRF spectrometer was used during this study. The instrument is equipped with vacuum technology, which provides ultimate light element sensitivity. It has powerful laptop based analytical software such as ArtaxS1PXRF that enable spectra analysis, a life time analytical display, and customized filters designed to optimize analysis of specific element to fit the application. Combination of software parameter control and X-ray operations control programs (X-ray Ops) allows the user to control voltage and current of the X-ray tube (Bruker, 2014 and Nicholas et al.,2014). The spectrometer provides elemental data in a variety of matrices, and the obtained results can be easily downloaded into Microsoft Excel (or other spreadsheets), allowing for quick and easy statistical evaluations of elemental concentrations and standard errors.

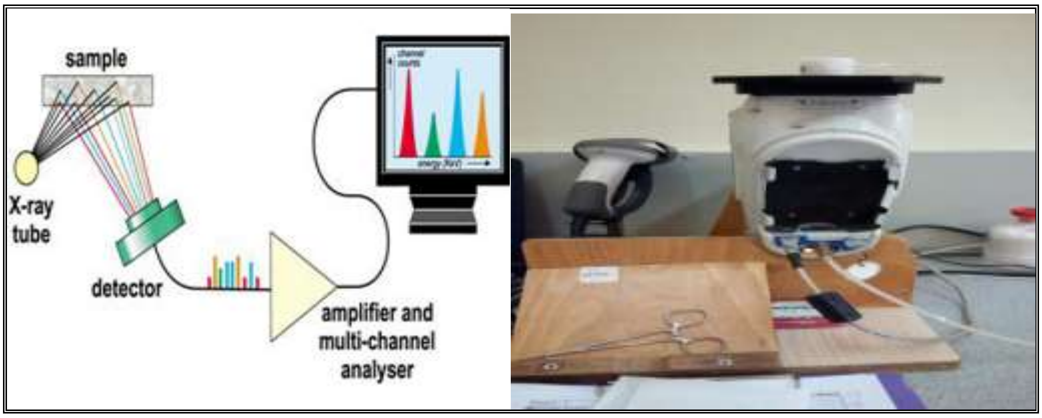


**Figure 2.2: Diagram of Handheld X-ray Fluorescence spectrometer operation principles and during analysis.**

The spectrometer has a silicon lithium drift detector -Si (Li), which has lower detection limits (David et al., 2014). When compared to digestion-based spectrometers, the use of monochromatic radiation and total reflection optics results in lower background noise, resulting in much higher sensitivities and a significant reduction of matrix effects (AfSIS, 2010). A technical specifications summary of HHXRF used in this study are as presented in the table 2.1.

***Table 2.1: Technical specifications of the Tracer SD III portable XRF spectrometer***

| | |
|---|---|
| X-ray tube | 40Kv, 15µA, Rh target |
| Element range | Mg to Pu |
| Optics | Multilayer monochromatic, 17.5 keV |
| Detector, area, resolution | x-flash Silicon drift, 10 mm2, 145 eV (FWHM) at 100,000 cps |
| Carrier | Sample cups with propylene film |
| Sample station | Portable XRF window |
| Control | PC, data transfer via serial interface |
| Size, weight | 30 x 10 x 28 cm, 2.04 kg |
| Power consumption | Maximum 150 W |

| | |
|---|---|
| Voltage, current | 15 to 40KeV ± 10%; 25 to 55µA |
| Vacuum pump | Operated at pressure < 10 Torr |
| Power | Si-Li batteries, Battery charger, Ac adaptor |
| Operating software | Bruker S1PXRF, Artax, X-ray Ops |
| Operating Temperatures | $+14^0$F to $122^0$F |
| Manufacturer | Bruker AXS Microanalysis GmbH |

The advantage using HHXRF spectrometer for analysis is that; fast, cost effective, easy to use and can analyze all forms of sample matrices which includes but not limited to solids, liquids and biological samples. In addition the analysis is non-destructive that is there is no use of chemical reagents, thus minimum sample preparation (Riaño et al., 2016).

Furthermore, a single spectrum gives comprehensive details of the sample elemental composition (Rossel et al., 2006; Nocita et al., 2015). The method is cheaper compared to conventional acid digest methods, and its development has enabled on-site analysis. The instrument is compact, hence it can easily be relocated and does not require a large laboratory space for storage hence allow in situ and laboratory measurement (Argyraki et al., 1997). It has widely been used in the mining, metal alloy testing, medicine (e.g. in the analysis of heavy metals in blood and glands), soil exploration, environmental testing and in the analysis of toy and consumer goods (Ports and West, 2008; Marco et al., 1997). Moreover, it is the latest advancement of convenient, accurate and precise method for assessing micronutrient concentration in plants.

HHXRF can be a cost-effective way for direct analysis of foliar and soil samples, both in situ and in prepared form. Consequently, it can be a useful tool for routine testing or screening for diagnosing soil micronutrient deficiencies for crop, livestock and human health. A study by Nyambura et al. (2013), sort to determine to reliability and accuracy of handheld XRF in determining the total elemental content in soil samples, in comparison to total X-ray fluorescence spectroscopy (TXRF). The study showed that for most elements, the total elemental concentrations obtained using the HHXRF spectrometer were comparable to those recorded using the TXRF technique. However, slight underestimation in the results was noted, hence the need for recalibration of the technique using a variety of soil materials. In addition, the study showed that the two techniques require minimal sample treatment, with better results being recorded for milled samples (< 50 microns). Therefore, proper calibration and sample preparation are necessary for optimal quantitative results.

In as much HHXRF has increased efficiency in terms of processing time compared to traditional methods, there are precautions to be taken when preparing samples for analysis. An example is the density of the sample in that, elements like Fe, their fluorescent energy have high penetration power therefore the density should be thicker.

Therefore, it is recommended that the thickness be approximately 4mm, and when scanning vegetation leaves are put together by clips to thicken the vegetation leaf surface perhaps 5 to 6 leaf layers (Weindorf et al. (2014).

Towett et al. (2015), carried out a study on elemental quantification of plant samples under different sample presentation modes such as analytical parameters, direct surface contact with the XRF window under vacuum conditions, sample loaded in a in a sample cup with a propylene film at the bottom, and analyzed without vacuum, as well as under sample analyzed with and without a filter. The highest accuracy and sensitivity for light elements i.e. Mg to P was reported under direct analysis on the surface of handheld XRF ($R^2$> 0.90). It was further noted that S, Ca and K could be reliably determined without vacuum ($R^2$> 0.99, 0.93 and 0.97 respectively. However, analysis without the aid of a vacuum was found to affect the lower limits of detection. Therefore, it can be concluded that the HHXRF technique is a cost-effective and faster way to provide plant data of sufficient accuracy for many applications.

McGladdery et al. (2018) used HHXRF to carry out an assessment on different vegetation samples (deciduous leaves, thatch, herbaceous plants, grasses and tree bark) collected from smelter-impacted area. Three scanning conditions of the samples were used i.e. field moist, oven dry, and powered. The optimal scanning conditions were developed relative to ICP atomic emission spectroscopy. Validation statistics indicated powdered samples as the optimal scanning condition, followed by field moist and oven dry in that order.

For instance, under field moist conditions, HHXRF could be used to effectively determine Cu and Zn, while under oven dry and pulverized condition, Pb, Fe, Cd, and Cu could be determined. Portable XRF thus proved to be a valuable for quick assessment of the elemental concentration in biological samples.

Handheld (Portable) XRF is clearly an effective light element analysis tool for nutritious crop management. A study by Russell (2015) tested the effectiveness of portable (handheld) XRF in analyzing light elements, Ca, S and K in soya beans.

Calcium measurement could not be determined directly using Kα peak due to overlaps with the potassium Kβ peak. Furthermore, three different presentation modes of the samples were analyzed, that is, direct measurements with vacuum, use of sample cups with vacuum and use of sample cups without vacuum. Sensitivity for light elements was best using vacuum with direct contact. For elements heavier than sulfur, there was no significant difference in sensitivity.

# CHAPTER THREE

# MATERIALS AND METHODS

## 3.1 Sampling location

This study was carried out in maize farms located in Muguga Kiambu County, in Kenya's Central region (1.18$^0$S, 36.65 0E**;** Fig 3.1). The region lies within an altitude range of between 1800 to 2400m and characterized by high rainfall of 1000 mm per annum. The area is a representative of the cool and wet medium altitude regions in Kenya like Uasin Gishu, Trans-Nzoia and Nandi hills where mixed farming is one of the economic activities and maize as the main crop grown. They also have dark red colored loamy soils which are much sought after because of their productivity.

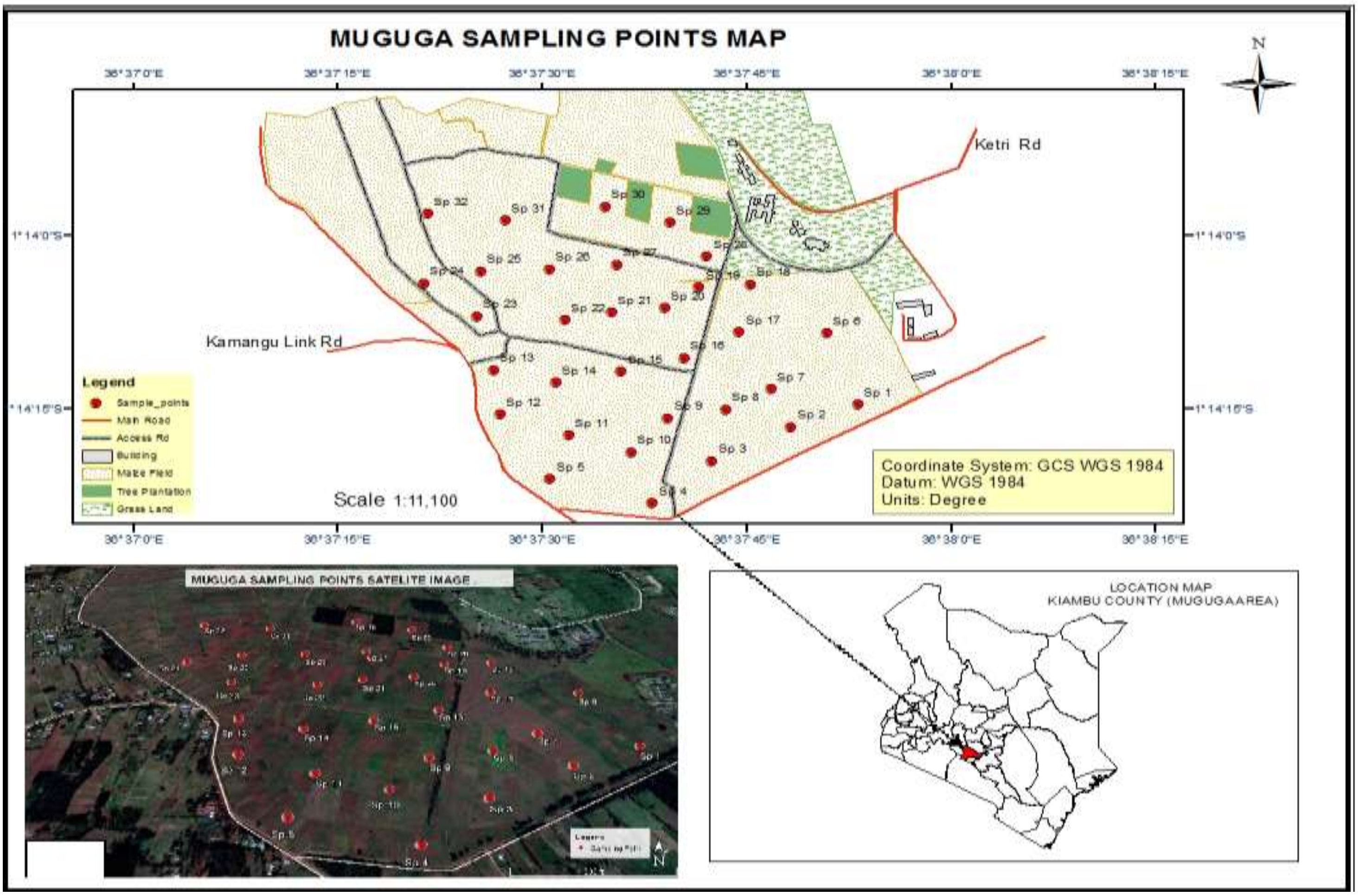


**Figure 3.1: Geographical location of Muguga Kenya and sampling points.**

## 3.2 Sampling design

A 50 m by 50 m grid was constructed over the site (250m by 250m) using off-set grid sampling pattern (Figure 3.3) giving a total of 25 plots. Sixteen sampling plots with maize plants within the sampling site were marked out, and two sampling points were identified within each plot giving a total of 32 sampling points.  At each sampling point, maize leaves were collected within a 3M radius.

The offset grid pattern was selected over the conventional grid pattern because it would provide more information by allowing random sampling of healthy maize plants within the radius, thus representing the entire area of interest

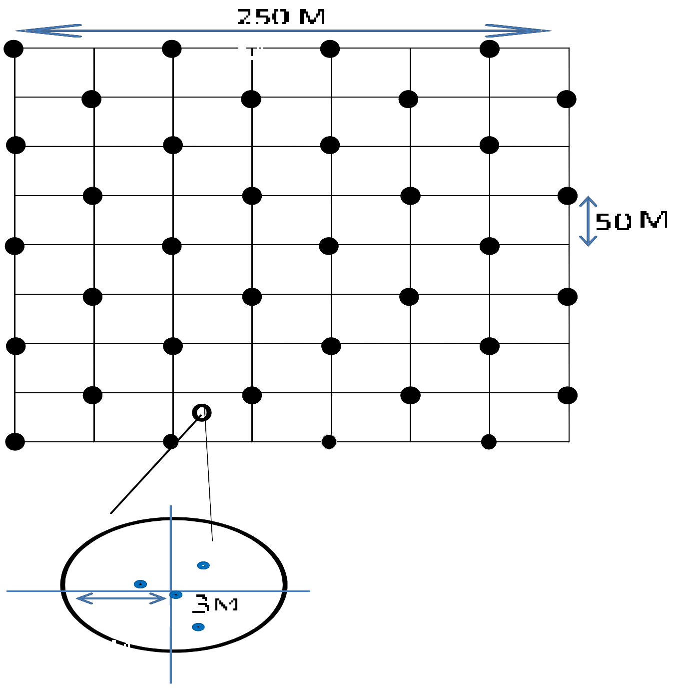


*Figure 3.2: Off-set grid sampling pattern (Richard and Gary, 2009).*

## 3.3 Sampling

This purpose of this study was to determine the applicability of HHXRF in scanning maize leaves. The Most Recent mature leaves were sampled, the reason being; it’s neither dull from age nor shinny green from immaturity hence best part of the leaf that  represent the nutritional status of the plant up until the day of sampling. At each point, sampling was done at two-plant growth stages i.e. early growth and tasseling as described below.

### 3.3.1 Sampling at Early Growth stage

At this stage, Plants were approximately above 12 inches tall. Health plants were identified and the Most Recent Mature leaf (whole leaf) of 12 to16 plants were picked randomly. The reason for sampling at this stage is that it allows for a particular nutrient to be corrected in case results obtained from the tests show either a deficiency/toxicity.

### 3.3.2 Sampling at Tasseling stage

At this stage, maize leaf samples were collected in the same sampling points identified in the early growth stage. The Maize plants had approached flowering and fruiting and the ear leaf (leaf adjacent to the uppermost developing ear) of between 8 to 10 plants were sampled randomly per each sampling site. Ear leaf at this growth stage is the best indicator of the nutritional status of the plant. Sampling at this stage gives a perspective the nutrient condition of the maize plant before grain filling begins.

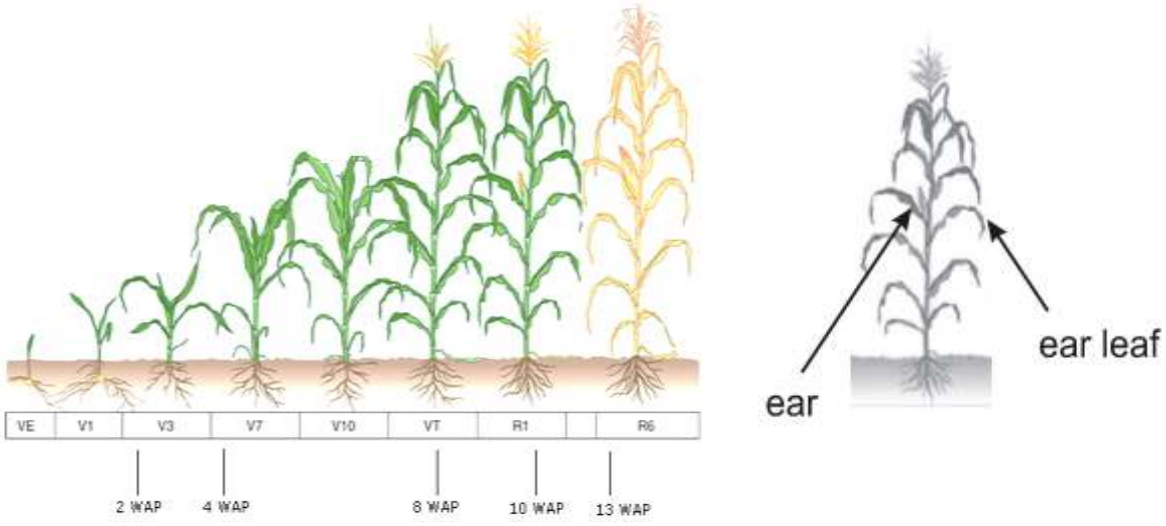


**Figure 3.3. Illustration indicating maize growth stages and the parts to be sampled.**

Careful sampling was done to ensure the effectiveness of plant analysis as a diagnostic tool. In this case, each leaf was removed by plucking downward (approximately an angle of < $30^0$) as this allowed the leaf to cut at the node without damaging the plant**.** At each sampling point, leaves from health plants were collected randomly at each site, placed in clean zip lock bags, sealed and transported to the laboratory. The labelled 32 samples were kept at temperatures of 4.4℃ to retain the freshness of the leaves. Sample preparation and analysis was done at World Agroforestry Centre's (ICRAF) laboratories.

## 3.4 Preparation and Cleaning of sample holders

Polyethylene sample cups (open-ended) with 20mm internal diameter and snap on the ring were soaked in warm soapy water for 30 minutes and washed thoroughly to remove any dust/solid particles. This was followed by rinsing with double distilled water and spread on a tray for one hour to dry.

After that the cups were carefully wiped with acetone-soaked tissue paper. The 4µm-(0.16 mil) thick X-ray polypropylene film (Mylar®) is laid on one of the open ends to about half the height and secured in position by a snap on ring.

**Figure 3.4: Preparation of XRF sample cups**

The cup was closed with a lid after sample was loaded.

## 3.5 Sample preparation

Samples were prepared in three different moisture conditions: Fresh, oven dried and powder (milled) forms.

### 3.5.1: Preparation of fresh samples

All the maize fresh leaf samples were cleaned with de-ionized water so as to be free from foreign substances such as dust particles, soil and residues as a result of foliar sprays, which may interfere with the results and air-dried.

The healthy leaf samples from each pack were selected randomly; divided equally into three parts Base (b), mid (m), apex (a) using a ruler and clipped in pairs. The mid rib (mr) was also removed from each of the leaf blades analyzed. The samples were then labelled ready for subsequent analysis.

**(a)** **(b)** **(c)**

**Figure 3.5.1: Fresh leaves (a), divided leaf into leaf base-b, mid-m, apex-a and midrib-mr(c).**

Fresh samples were stored in open ziplock bags and kept in a Refrigerator at $4^0$C to maintain the moisture content.

### 3.5.2: Preparation of oven dried samples

The fresh samples above were transferred to brown khaki bags to hold samples from different sub-plots; and dried in an oven at 60ºC(Fig 3.5.2) for 48 hours; they were then divided equally into three parts Base (b), mid (m), apex (a); these parts were clipped together ready for analysis. The mid-rib was also separated as above and prepared for analysis.

**(a)** **(b)**

**Figure 3.5.2: (a) Oven dried leaves and (b) leaf blades clipped together**

### 3.5.3: Preparation of milled samples

From the oven dried (60ºC) plant samples above; leaf blades were separated from the midrib and milled separately to pass 1mm sieve using Thomas-Wiley Laboratory Mill, a milling machine which consists of an all-steel interior with four rotating cutting blades, the samples were later passed through a McCrone micronizing mill, to give a fine (between 20-53μm), non-fibrous and homogenous powder (ICRAF, 2015).

a) Oven dried leaves b) milled leaves

**Figure 2Fig 3.5.3: (a) Leaves dried at 60°C and (b) milled leave samples.**

### 3.6: Sample Analysis.

Leaf samples of different leaf parts i.e. apex, mid, base and mid rib, as well as different moisture content fresh, oven dried and milled samples, were analyzed for elemental content using a Bruker III Tracer SD portable(HHXRF). The samples were analyzed under two categories: Light elements analysis(Na,Mg,K,S,P) and heavy element analysis(Fe,Mn,Zn,Mo and Cu).

### 3.6.1: Instrument verification

Instrument performance was verified by scanning of Certified Reference Materials (CRM's) from National Institute of Standards and Technology (NIST 1515-Apple leaves, 1547-Peach Leaves, and 1575a), also quality control and quality assurance (QC/QA) was carried out using laboratory's internal standards prepared from prunus leaves (*prunus africana*), white cow peas (*vigna unguiculata*) and mango leaves (*magnifera indica*) sourced from local (Kenyan) laboratories.

### 3.6.2: Light element Analysis.

These are elements that are considered to have low excitation energies and therefore need ambient conditions e.g. use of a vacuum to improve their detection limits. Two spatula full (approximate 250mg) of the sample was deposited directly on the XRF window (the window should be clean and free of any oils, oxidation and any contaminants) and bombarded with X-rays produced from a Rhodium tube operated at an anode current of 25µA and a voltage of 15 KeV, with the aid of a vacuum operated at <5 torr.

(a) (b) (c)

**Figure 3.6.2: a) Milled sample, b) fresh sample on the instrument window and c) HHXRF connected to a vacuum and IR sensor covered.**

This was done with fresh leaf samples, oven dried samples, powdered samples placed directly on the instrument table. The window was covered in order to protect the IR (Infrared) sensor and analysis done. Each scan was done in duplicates for a period of 180 seconds and results reported as a mean of both replicates.

### 3.6.3: Heavy element Analysis.

These are elements with high atomic numbers and therefore their excitation energies are not affected by factors such as moisture content. For milled samples; the cups prepared above (3.4) was filled with approximately 5g (2/3 sample cup height) and tapped lightly to enable even distribution of the sample at the base.

Before analysis; the instrument was fitted with 1mlTi/12 mil Al filter (for bruker series, its yellow in color). This filter allows all the X-rays with energy range between 12KeV to 40 KeV to reach the sample and exciting the above elements efficiently. There is small or no sensitivity to elements below Calcium within this energy range.

(a) (b) (c)

**Figure 3.6.3: Preparation and Analysis of heavy elements.**

The instrument was operated at a voltage of 40KeV, anode current of between 10-12µA, however, analysis was done in ambient air conditions (no vacuum) but with the use of a filter. A filter is designed to position x-ray energies above the absorption edges of particular elements of interest. Each scan was done in duplicates for a period of 60 seconds and results reported as a mean.

### 3.6.7 Data Analyses

Data collection and instrument control was carried out using S1PXRF software. In addition, Bruker spectra software ARTAX (7.4.6.1) Software was used to perform Bayesian deconvolution and qualitative analysis to correct for background counts, escape peaks, and simple elemental overlaps towards determining the net count rates per second and by extension the elemental concentrations.

Statistical analysis of data was conducted using MS Excel, to remove outliers, and present the acquired data in terms of means, standard deviation and concentration range. In addition statistical computing and graphic presentation of the data and Correlation in concentration levels between different leaf parts and growth stages was carried out using R(3.2.0) software with the MCMCpack package.

# CHAPTER FOUR

## RESULTS AND DISCUSSION

### 4.1 Overview

This study was aimed at assessing the applicability of HHXRF spectrometer for direct tissue analysis for light and heavy elements in maize leaves. The findings on the applicability of the method using different sample presentation methods, leaf parts and different growth stages will be presented in this chapter.

### 4.2 Quality Control Data.

Instrument performance was verified by scanning of Certified Reference Materials (CRM's) from National Institute of Standards and Technology (NIST 1515-Apple leaves, 1547-Peach leaves), the measured values against the certified values were as shown in the table below:-

**Table 4.1a: Measured elemental values and certified values for SRM NIST 1515 standard (mg/kg)**

| NIST 1515-Apple leaves | | | |
|---|---|---|---|
| Element | Measured values(Mg/Kg) | Certified Value s(Mg/Kg) | **% recovery** |
| **Ca** | 15333 ± 47 | 15260 ± 150 | 100.48% |
| **Mg** | 2803.72 ± 70 | 2710 ± 80 | 103.43 |
| **K** | 16200.25 ±101 | 16100 ± 200 | 100.62 |
| **Cu** | 56.7± 1.5 | 56.4± 2.4 | 100.53 |
| **Mn** | 53.9± 1.1 | 54.0± 3 | 99.81 |
| **Zn** | 12.52± 50 | 12.5± 3 | 100.16 |

**Table 4.1b: Experimental and certified values of the SRM NIST 1547 standards (mg/kg)**

| | NIST 1547Peach leaves | | |
|---|---|---|---|
| **Element** | Experimental values(Mg/Kg) | Certified Value s(Mg/Kg) | % recovery |
| **Ca** | 15035±500 | 15600±0.2 | 96.38 |
| **Mg** | 4075±100 | 4320±0.008 | 94.33 |
| **K** | 23935±75 | 24300±0.008 | 98.50 |
| **Cu** | 3.4±0.5 | 3.7±0.4 | 91.89 |
| **Mn** | 95±0.5 | 98±3 | 96.94 |
| Zinc | 18.2±1.0 | 17.9±0.4 | 101.67 |

From the results above (Table 4.1a and 4.1b), It is observed that the measured values are reproducible with the certified values of the NIST standards with percentage recovery ranging from 99.81% to 103.43% for NIST 1515 (Apple leaves) and a range of 91.89% to 101.67% for NIST 1515(Peach leaves).However, there was no significant difference in concentration between the two values ($P > 0.05$) in both standards. The reproducibility of the values therefore shows the validity of the method employed in this study.

In addition, quality assurance (QA) was also carried out by scanning laboratory's internal standards prepared from prunus leaves, white cow peas and mango leaves sourced from local (Kenyan) laboratories. This was done to demonstrate the capability and applicability of the HHXRF technique for the multi-elemental analysis of plant sample.

### 4.3 Results on different sample presentation methods.

In this study, the applicability of HHXRF under different sample presentation methods for plant samples was determined. Eleven elements consisting of light elements (Na, Mg, P, S, K, and Ca) and heavy elements (Zn, Cu, Fe, Mn and Mo) were analyzed in this assessment. Average elemental concentration obtained is shown in Table 2 and the same findings are presented in Figure 4.3.

**Table 4.2: Elemental concentration in mg/kg at different sample presentation methods**

| Sample matrix | Na | Mg | P | S | K | Ca | Mn | Fe | Cu | Zn | Mo |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Fresh | 8.77 | 383.85 | 100.66 | 146.79 | 6541.55 | 1008.19 | 62.17 | 241.01 | 11.80 | 33.73 | 5.51 |
| Oven dried | 10.54 | 956.01 | 802.07 | 1055.53 | 20550.35 | 3224.11 | 187.06 | 599.79 | 25.76 | 40.28 | 7.57 |
| Milled | 43.74 | 3077.06 | 1741.40 | 1878.53 | 37988.77 | 5294.68 | 98.76 | 253.29 | 6.13 | 26.80 | 4.07 |

From the results (Table 4.2), milled samples gave higher concentrations for the elements: Na, Mg, P, S, K and Ca; as compared to concentrations in oven-dried samples. Comparatively, lower concentrations were noted in the fresh samples for the elements: Na, Mg, P, S, K, Ca, Mn and Fe. Work carried out by McGladder et al. (2018), on elemental assessment of different vegetative samples using Handheld XRF showed that milled samples gave comparatively higher concentration for most elements. This observation can be attributed to sample homogeneity during the milling process(Angelova & Gjorgjeska, 2022), thereby uniform distribution of the elements contained therein(Towett et al., 2016).However, there was no significant difference between elemental concentrations for both sample presentation methods ($P > 0.05$) as shown in Appendix 3.1 and 3.2.

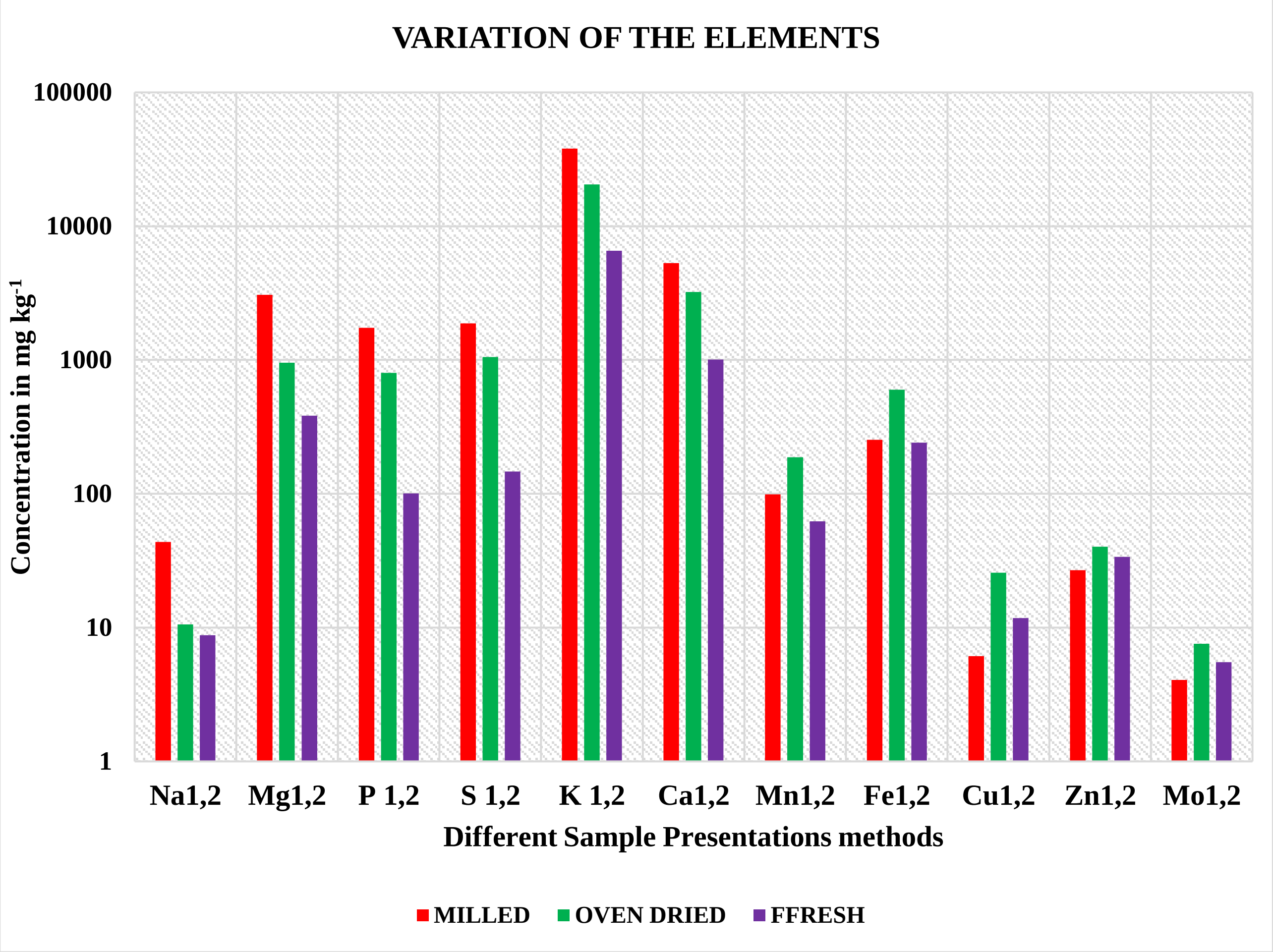


**Figure 4.3. Total elemental concentration for different sample presentations.**

From the results [Fig 4.3], it can be noted that milling of the samples leads to improved packing density in the samples holder and gives it a uniform geometry(Orlić et al., 2021). This in turn increases the probability of the X-ray beam interaction with the elements in the sample, hence intensity of the resulting characteristic X-rays increases. During the milling process, the samples are first oven dried; consequently, the moisture content in the samples, which was found to affect the accuracy of the XRF spectroscopy results (McGladdery et al., 2018; Boastos et al., 2012), is reduced hence improved efficiency.

For oven dried samples, higher mean elemental concentrations were recorded for Fe, Zn, Mo, Cu and Mn with a concentration of 599.8mg/Kg,40.3mg/Kg,7.6mg/Kg,25.8mg/Kg and 187.1mg/Kg respectively [Table 2]. Interestingly, these are heavy elements, while lighter elements were determined at higher concentrations in milled samples [Figure 4.3]. Additionally, the heavy elements did not exhibit significant variations for the different sample preparation methods compared to the lighter elements ($P > 0.05$) as shown in appendix 3.2.The greatest challenge in analyses of oven-dried samples was where the samples tend to crumble, especially for the young leaves, thereby the geometry of the sample varies for different samples, which could affect the obtained results.

Analysis of fresh samples recorded the lowest elemental concentrations in all the light elements Na, Mg, P, S, K, Ca with a concentration of 8.8mg/Kg, 383.9mg/Kg, 00.7mg//Kg, 146.8mg/Kg, 6541.6mg/Kg, 1008.2mg/Kg respectively; and Fe;241 mg/kg exhibited the same as the only heavy element [Table 2] in the study. Findings Similar to this, were reported by (Bastos et al., 2012), where the moisture content was found affect the accuracy of the obtained result by over 20 %, with greater impact being reported for the light elements ($Z < 30$). The increased moisture content was found to counteract with absorption of x-ray lines by replacing higher atomic number in the line, hence absorbing more energy thus diminished characteristic x-ray peak areas.

Similar studies have found high moisture content to greatly affect the accuracy of HHXRF since it contributes to attenuation of the photons, thus a key source of errors in field measurements (Parsons *et al.*, 2013: Weindorf *et al.*, 2012; Kalnicky et al,, 2001).

Generally, a concentration trend similar to one observed in this study where the concentration increased as follow: wet < oven dry < powder, was reported by Weindorf *et al.*, 2012 and Weindorf *et al.*, 2014. The magnitude of the increases was influenced by both the sample matrix and the element present.

### 4.4 Elemental concentration at different growth stages.

Variations in mean elemental concentration of essential nutrients at two growth stages was also considered in this study. Two stages were evaluated: early growth stage; when the maize plants were about 12 inches tall and during the tasseling stage i.e. the maize crop approached flowering and fruiting (Figure 3.3). The obtained results are presented in Figure 4.4, with Table 3 giving the overall mean.

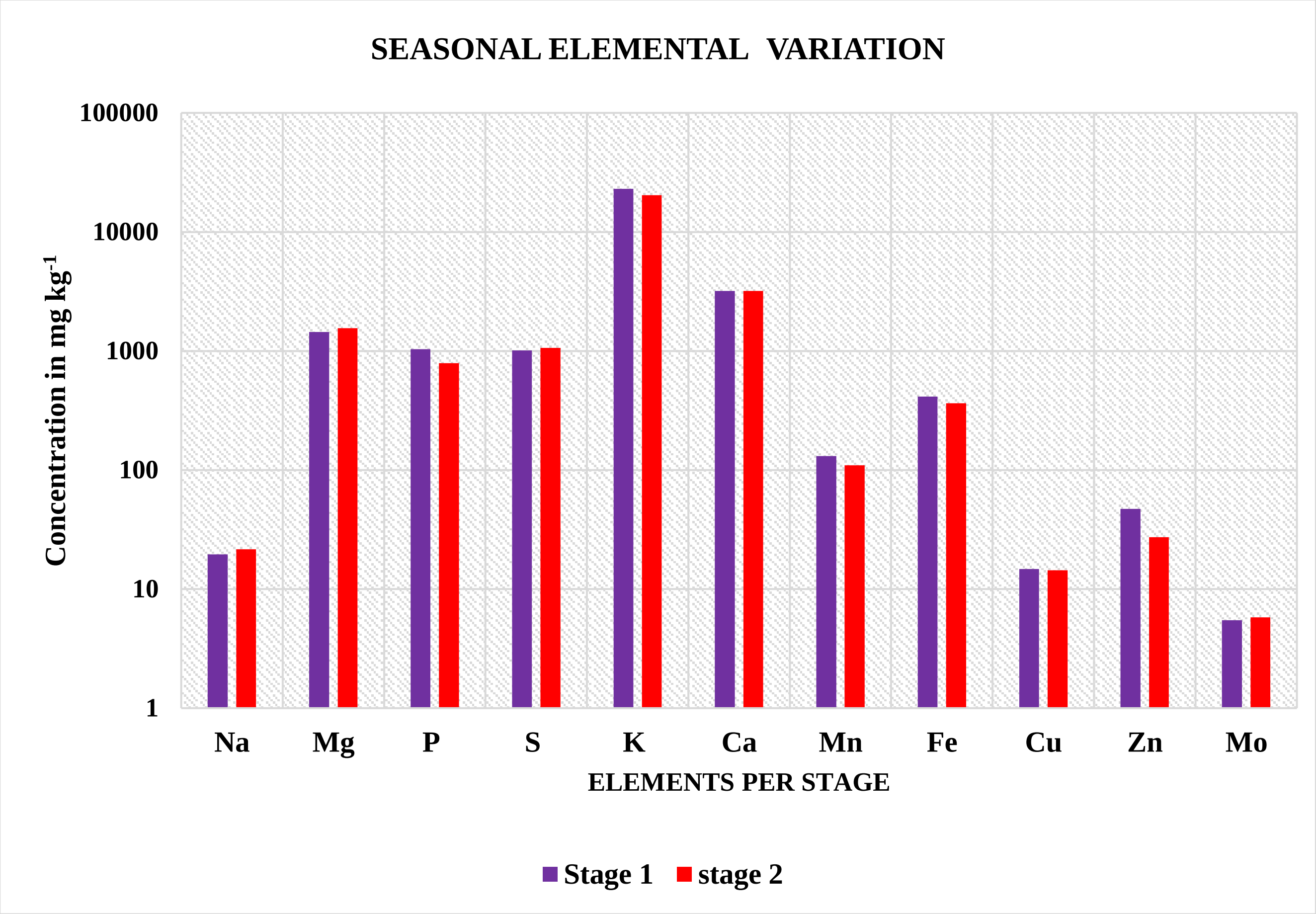


**Figure 4.4: Variation of the elemental concentration in two different growth stages**

From the results[Fig 4.4]; it can be observed that, for light elements; higher concentrations were obtained for P, K and Ca in the early growth stage, For example phosphorous recorded the highest concentration of 1038mgkg$^{-1}$ ±174mgkg$^{-1}$ compared to 791mg/kg$^{-1}$ at tussling stage, potassium recorded a concentration of 22994mg/Kg against 20409.37mgKg at tussling. While Na and Mg showed an increasing concentrations from early to tussling growth stages. For example Magnesium recorded the lower concentration 1440.878mgkg$^{-1}$ ±174mgkg$^{-1}$ of compared to 1551mg/kg$^{-1}$ at tussling stage. Similar studies was found by Borges et al.,2020, where mean adequate concentration for plant analysis was found to be high in in Calcium 81% and 90% for magnesium (Mg).

The high K and P concentration at early growth stage could be attributed to application of phosphatic fertilizers during planting and its requirements for root development and synthesis of ATP during early growth period (Hodges., 2010).

Regression analyses showed that there was no significant difference in micronutrient concentration between the two seasons ($P > 0.05$) as shown in Appendix 1. On the other hand sodium and magnesium were found to increase with age [Figure 4.4].

**Table 4.3: Heavy Elemental concentration at two growth stages.**

| Element | Stage 1(concentration mg//kg) | stage 2(concentration mg//kg) |
|---|---|---|
| Mn | 131.30 | 109.42 |
| Fe | 414.34 | 364.59 |
| Cu | 14.75 | 14.41 |
| Zn | 21.20 | 36.23 |
| Mo | 5.47 | 5.80 |

[Table 3] presents the mean heavy elemental content in maize leaf at different growth stages; early growth and during the tasseling stage. Mn and Fe exhibited lower mean concentrations in maize leaves at tasseling stage. For example, a mean Fe concentration of 414±35 mg $kg^{-1}$ was reported during early growth compared to 364-±35 mg $kg^{-1}$ at the tasseling stage, on the contrary zinc exhibited increasing concentration of 21.20mg/Kg and 36.23 mg/Kg was recorded at early and tussling stages respectively. Bake et al. (2016) noted a similar trend in Zn concentration, where the Zn content in the leaves was found to increase with age. This observation was attributed to increased adsorption capacity by the plant as it grows. The current findings are in agreement to those made by Grzebisz at al. (2008) and the study conducted by Subedi and Ma, (2005), where an intensive adsorption of most mineral nutrients, such as zinc, Copper and Manganese occurred during the tasseling phase.

Copper and Molybdenum were uniformly distributed across the two seasons .The current findings are in agreement(except Mn) to those made by Grzebisz at al. (2008) and the study conducted by Subedi and Ma, (2005), where an intensive adsorption of most mineral nutrients, such as zinc, Copper and Manganese occur during the tasseling phase.

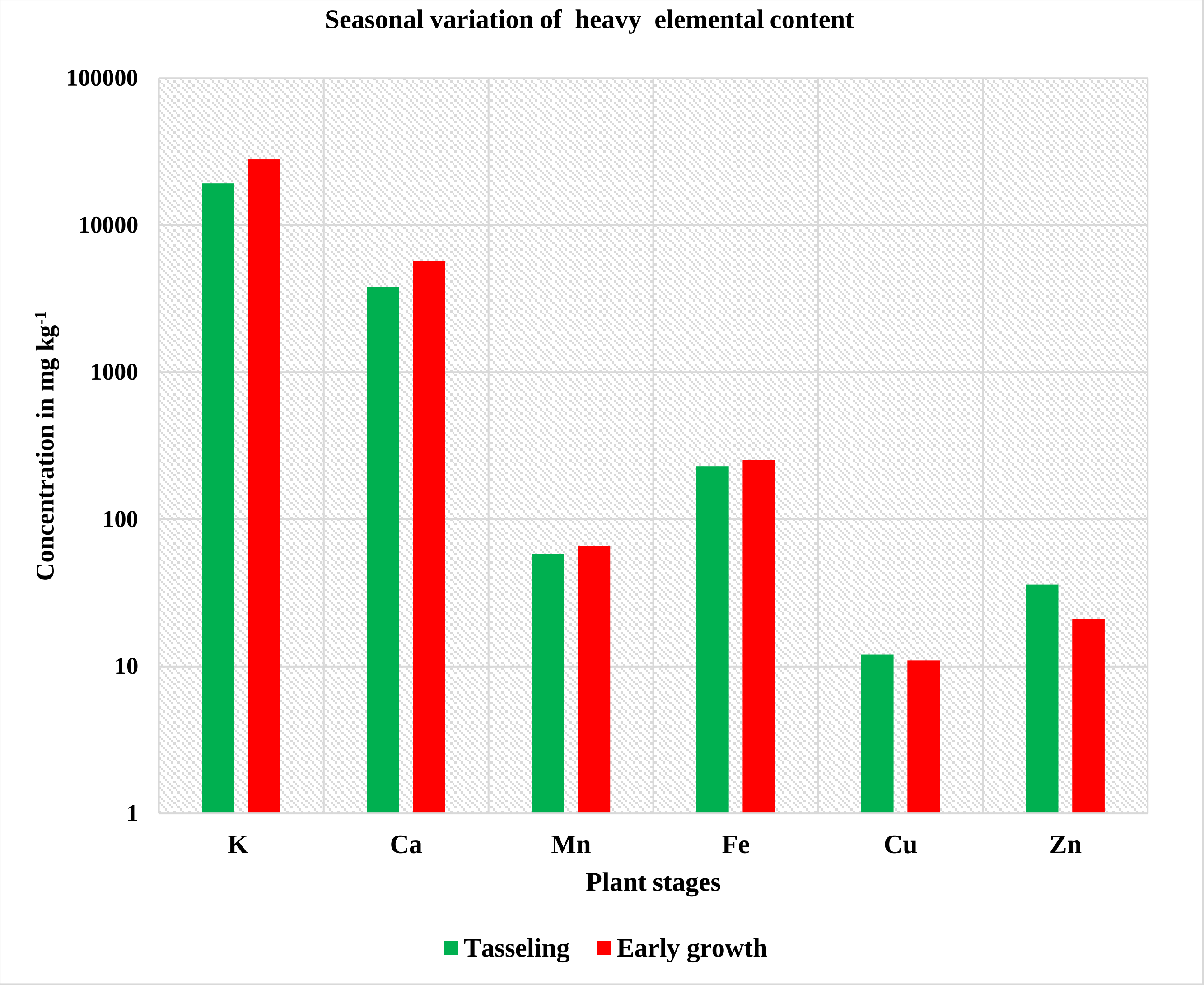


**Figure 4.5: Seasonal variation of heavy elemental contents in maize leaf samples**

## 4.5 Elemental Concentrations at different parts of maize leaf

Plant leaves have been used as an indicator of plants nutritional status and in assessment of plants response to nutrient supplementation (Balabanova et al., 2015; Prinzenberg et al., 2010). In this study, different parts of maize leaf sample were analysed to assess nutrient content concentration. This included leaf base (b), middle part of the leaf (m), leaf apex (a), midrib (mr), and a stack of 5 leaves together (th).

In addition, concentrations at either side of the leaf sample i.e. upper (1) and lower (2) were evaluated. Essential nutrients discussed above were considered and their variation between different leaf parts determined.

Figure 4.6 presents K concentrations at different parts of the leaf. The highest mean concentration was observed at the midrib part at 27334 ± 1060 mg kg$^{-1}$, with the apex recording the lowest mean at 14686 ± 422 mg kg$^{-1}$. A decreasing trend in K concentrations was realized towards the apex. For instance, while 19657 ± 6059 mg kg$^{-1}$ was recorded at the base of the leaf, 17327 ± 4438 mg kg$^{-1}$ and 14686 ± 4227 mg kg$^{-1}$, were recorded for the middle part and the leaf apex respectively. According to Kaiser et al. (2013), the expected K concentration range for corn ear leaves is 17000 to 25000 mg kg$^{-1}$. The mean values obtained in this study fall within this range an indication that the maize plant in the study area meet its K nutritional requirements. Potassium plays an important role in the photosynthesis process, activation of enzymes in biochemical reactions, water and nutrient transportation, starch and protein synthesis and stomatal activities (Rogiers et al., 2017; Gao et al., 2018; Wang et al., 2013).

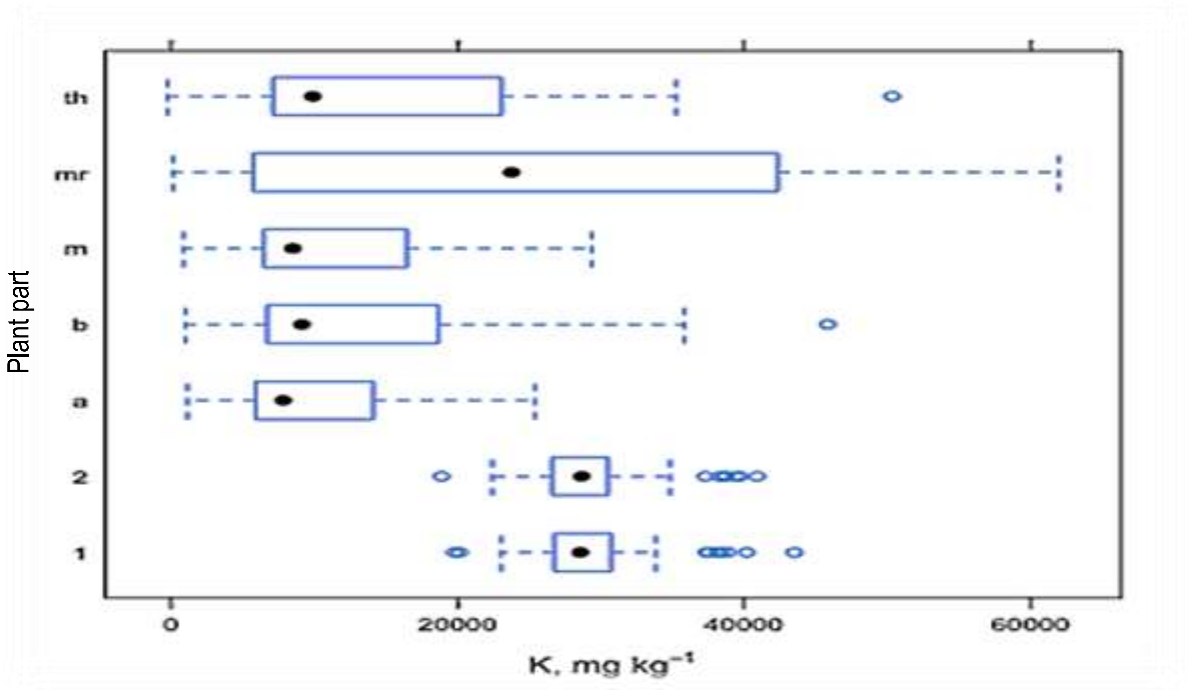


**Figure 4.6: Potassium content in different parts of maize leaf samples.**

Calcium is an essential micronutrient in plants that plays a structural role in cell wall and membranes, in addition to activation of enzymes (Chen et al., 2018; White & Broadley, 2003). According to Kaiser et al. (2013), the expected Ca concentration range for a healthy maize plant is 400 to 10000 mg kg$^{-1}$. In this study, Ca concentrations were determined in this range for all the leaf parts analyzed, ranging from a high of 3766 ± 198 mg kg$^{-1}$ at the midrib to a low of 2660 ± 970 mg kg$^{-1}$ at the leaf base (Figure 4.7). The Ca concentrations were found to increase towards the apex. Lower Ca concentrations were reported by

Kovacevic (1994), at a range of 210 to 590 mg kg$^{-1}$. The huge difference could be due to difference in soil medium on which the plant was grown and fertilizers applied.

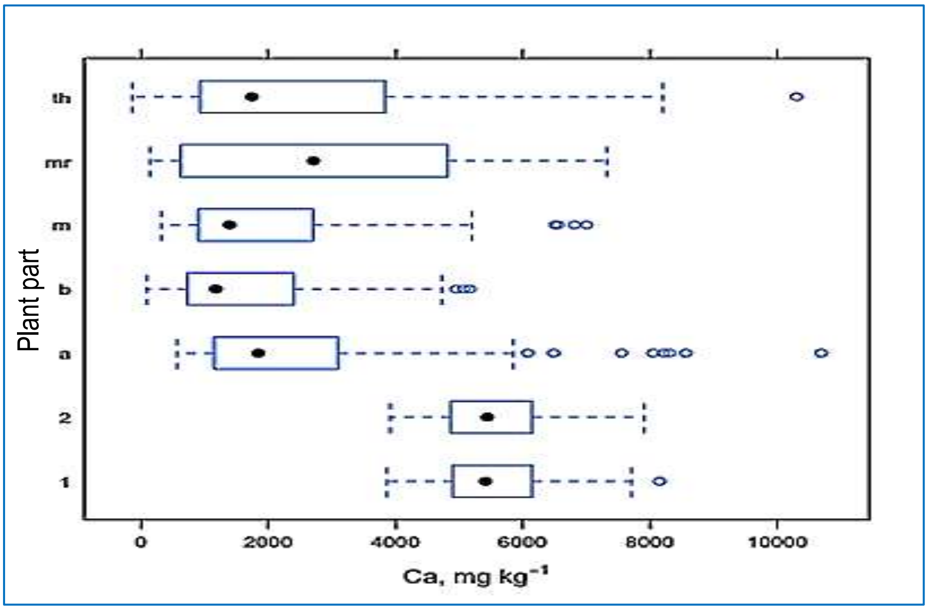


**Figure 4.7: Calcium content in different parts of maize leaf samples.**

Figure 4.8 presents the Cu concentrations obtained in this study. The lowest Cu concentrations were determined in the midrib (9 ± 3 mg kg$^{-1}$), contrary to the trend observed for Ca and K. In addition, Cu appeared to be uniformly distributed in the leaves, where no significant difference was noted between the base, (30±4 mg kg$^{-1}$), middle (31±3 mg kg$^{-1}$) and the apex (27±4 mg kg$^{-1}$) with ($P > 0.05$) as shown in appendix

2).

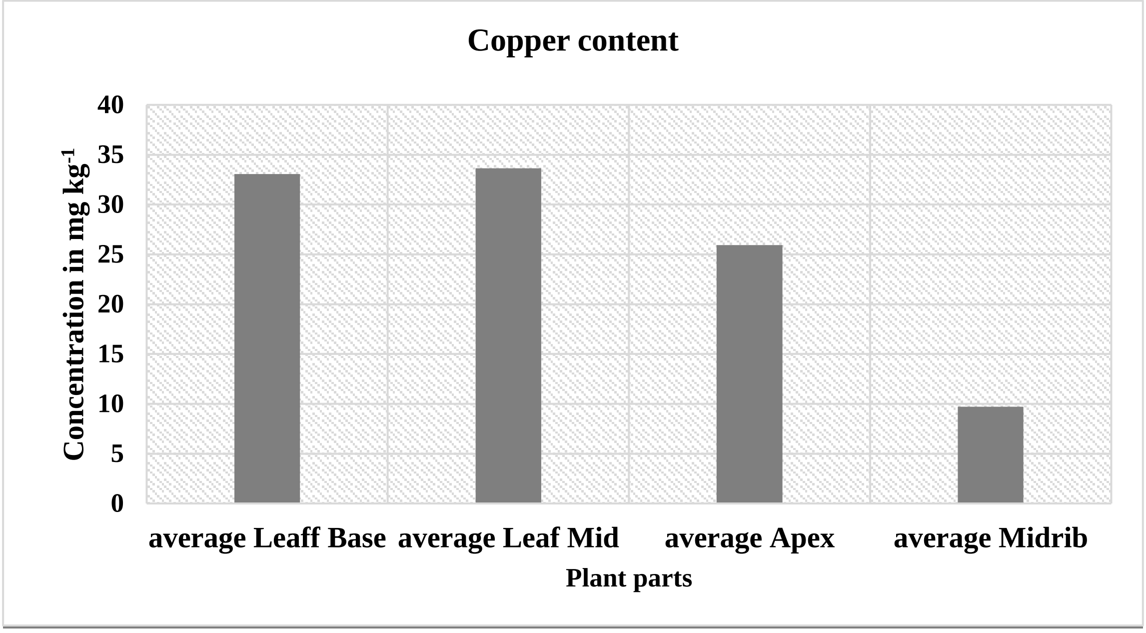


**Figure 4.8: Copper content in different parts of maize leaf samples.**

The Cu content in maize leaves in the study area is higher than the Cu concentration range reported by Kaiser et al. (2013) at 6 to 20 mg kg$^{-1}$. The leaf Cu concentration values were also above the normative values of 5 to 20 mg·kg$^{-1}$ in flowering maize as reported by Schulte and Kelling, 2000.

In maize plant, Fe has been found to be part of the chlorophyll molecule, which promote healthy green foliage and improve yield and grain quality. Its deficiency results in striping between the veins, running the entire length of the leaf and leaf chlorosis (Tako et al., 2015; Ancuceanu et al., 2015).

In this study, the highest mean Fe concentration was determined at the apex part of the leaf at 400± 23 mg kg$^{-1}$, while the lowest levels being determined at the midrib (200 ± 11 mg kg$^{-1}$) as shown in Figure 4.9. There was no significant difference ($P > 0.05$) in Fe concentrations among the apex, middle part and the leaf base (Appendix 2). A similar study by Kaiser et al. (2013), determined the Fe content in maize crop at a range of 50 to 350 mg kg$^{-1}$, values that are significantly lower than those observed in this study. A study carried by (Galgallo et al., 2014)) on elemental content in soils from the same study area(Muguga) showed a similar trend of high Iron content of 5.6% compared to worldwide study of 3.8%(Kabata-Pendias, 2010).This difference could arise from concentration difference in growth medium, whereby high Fe content has been reported in Kenyan soils (Muli et al., 2017; Akenga et al., 2014).

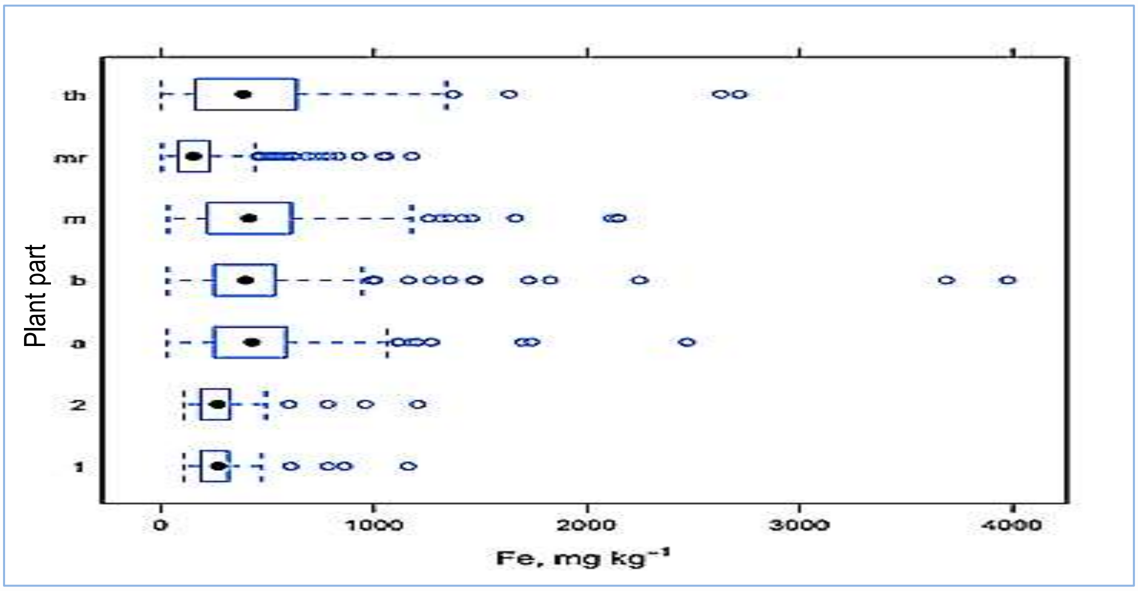


**Figure 4.9: Iron content in different parts of maize leaf samples.**

In this case, the characteristic soil type found in Kenyan central highlands is typically Nitisols which is well characterized by high Iron concentration (Akenga et al., 2014).

Figure 4.10 presents trends in Mn content at different parts of maize leaf. Generally, the apex contained higher Mn content at 105 ± 28 mg kg$^{-1}$, followed by the middle part at 92 ± 24 mg kg$^{-1}$, and 88 ± 27 mg kg$^{-1}$ at the base while the midrib recorded the lowest concentration. The Mn values in this study are within the sufficient range reported by Kaiser et al. (2013), at a range of 20 - 250 mg kg$^{-1}$.

Gaj et al. (2016) obtained comparable Mn concentrations in maize ear leaf, in a study to assess the impact of P and K fertilizers on Mn concentrations in maize. In addition, the Mn concentration was found to increase significantly in all maize parts after fertilizer application, with the highest concentrations being reported in the leaves.

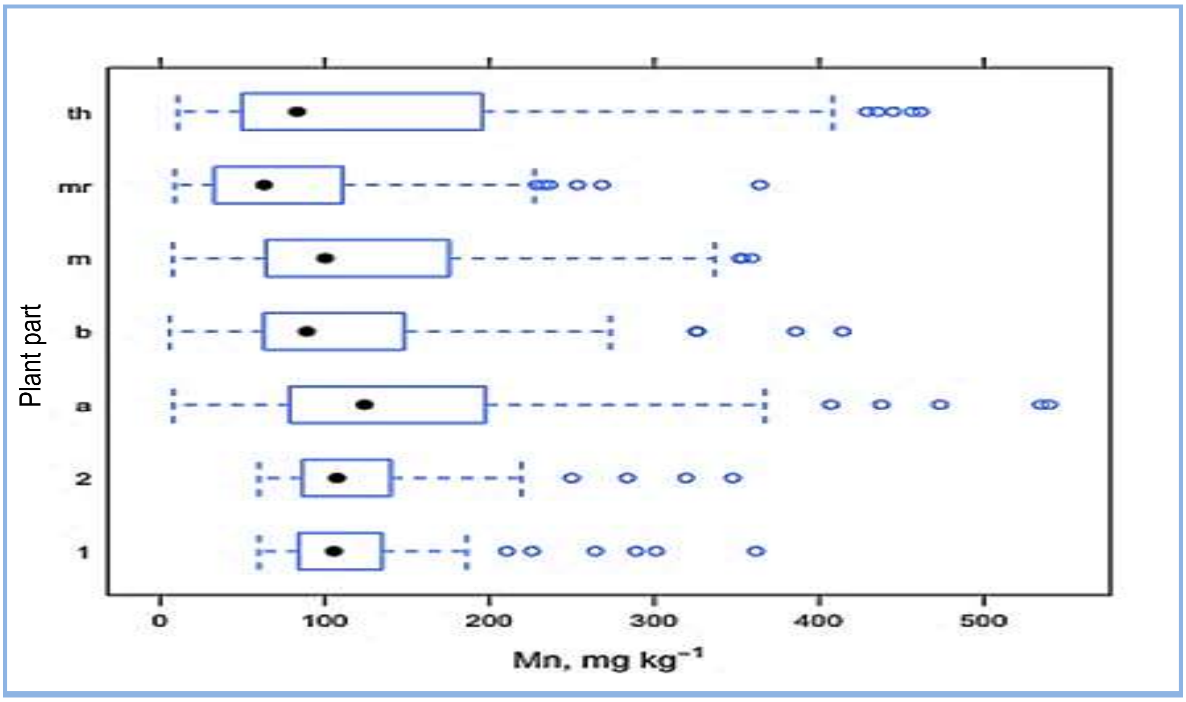


**Figure 4.10: Manganese content in different parts of maize leaf samples.**

Zinc is an essential micronutrient in plants. In this study, a mean concentration of between 28 to 44 mg kg$^{-1}$ was reported. The lowest mean Zn levels were determined at the midrib, while the highest at the apex (Figure 4.11). However, regression analyses showed that there was no significant difference between different parts of the maize leaf.

The Zn content in this study fall within the concentration range reported by Kaiser et al. (2013), for a healthy corn ear leaf at between 20 to 70 mg kg$^{-1}$. In addition, these levels can be considered sufficient based on a study by Zhang et al. (1991) that reported 20 mg kg$^{-1}$ in tissues as the threshold Zn concentrations in plants. Some of the main functions of Zn in plants include the activation of enzymes involved in protein synthesis, the formation of chlorophyll and carbohydrates, the conversion of starches to sugars, and the formation of auxins that promote stem elongation and growth regulation. Wronska et al. (2007), showed that good nutrition of maize with zinc could increase nitrogen and phosphorous absorption efficiency and consequently lower fertilization costs.

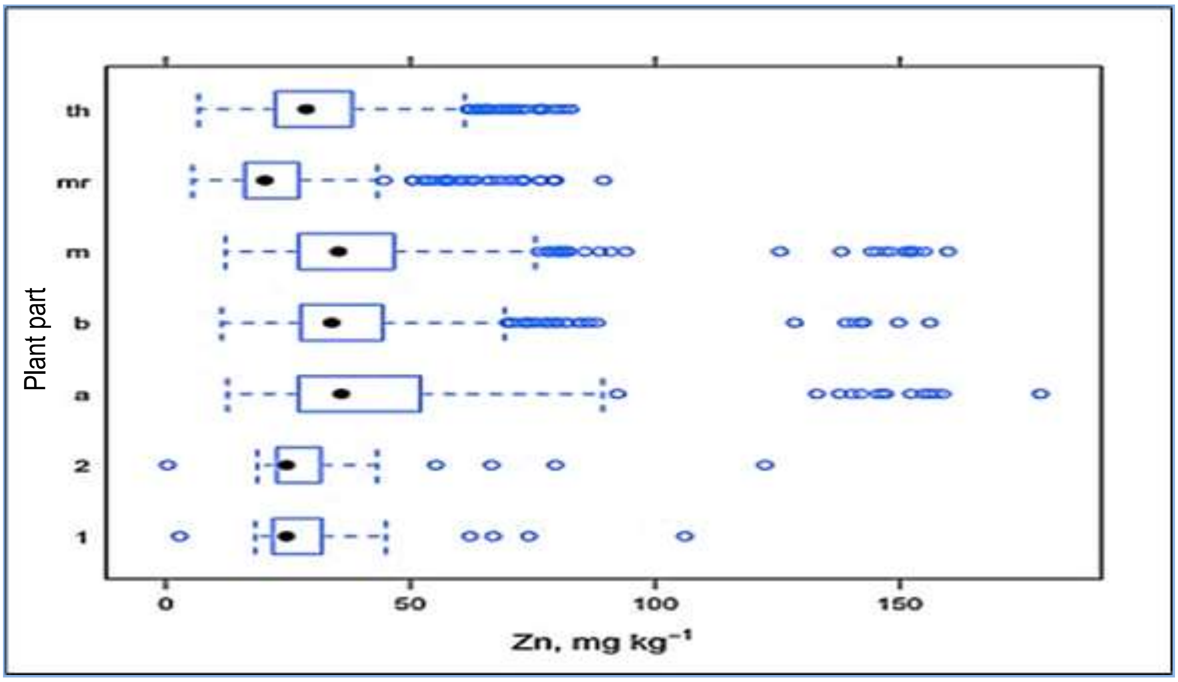


**Figure 4.11: Average Zn content in different parts of maize leaf samples**

Mo is a vital essential trace element in human diet. From the study, a concentration range of 5 to 7 mg kg$^{-1}$ was reported as displayed in Figure 4.12. The apex recorded a relatively higher amount as compared to the other parts of the maize leaf with a mean concentration of 7.2 mg kg $^{-1}$. The values reported in this study is slightly above the global range known to be 1 to 2 mg kg $^{-1}$ (Smith et al., 1997). This could to be attributed to the high levels in the soils (Kabata-Pendias and Pendias, 2011). There was no significant difference between the concentrations of Mo in different parts of the maize ($P > 0.05$) as shown in Fig 4.18 and Appendix 2. Alkaline soils, wet environmental conditions and high organic matter content has also been linked to the high levels of Mo in the plants as per Bodi et al. (2015), Muguga being a relatively wet highland region with a mean temperature of 17.6$^0$C; therefore climatic conditions could be the major contributor of high molybdenum content (Mwendia., et al.,2017).A similar study conducted by Brennan and Bolland, (2007) on spring wheat (*Triticum aestivum* L.) and reported total available Mo at 0.07 mg kg $^{-1}$.

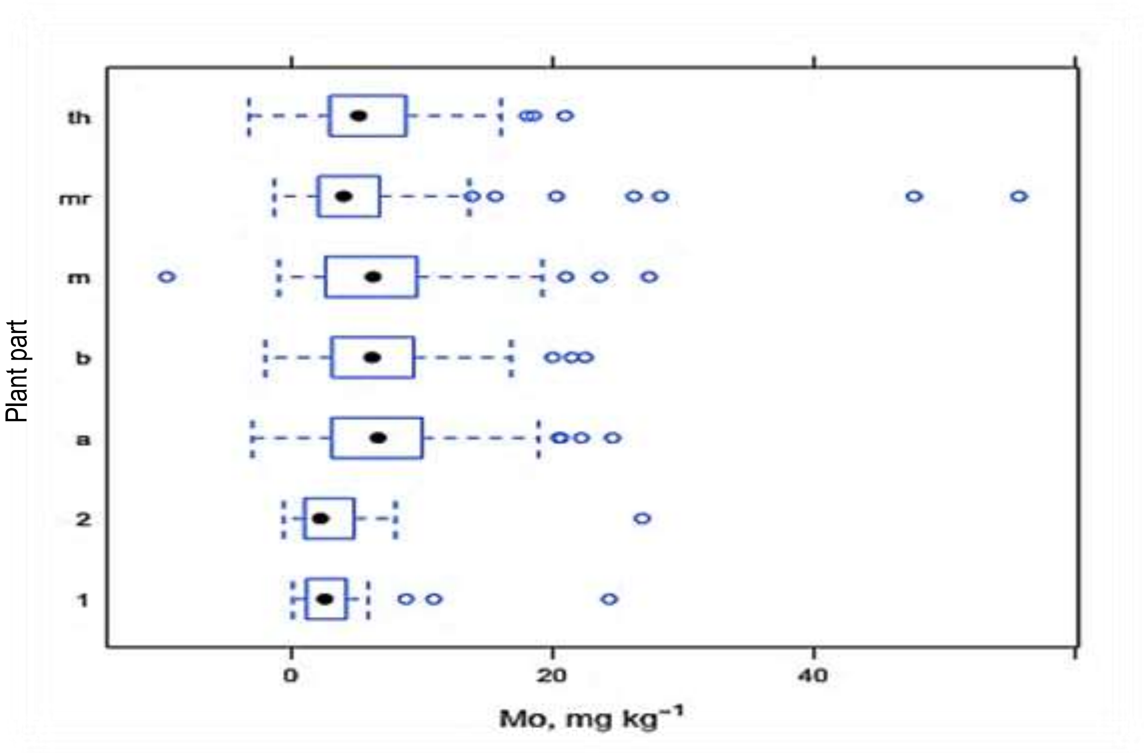


**Figure 4.12: Molybdenum content in different parts of maize leaf samples.**

P is known to play a very crucial role in maize plants. It assists the plant to withstand low temperature and low levels of water in its system. From the study, a concentration range of 493 to 647 mg kg$^{-1}$was reported as depicted by Figure 4.13. Apex part of the plant recorded high levels of Phosphorous as compared to the other parts of the plant. This shows that, the apex part of the plant bioaccumulate more P than other parts due to structural differences of the leaf. However, there was no notable difference in the concentration of the Phosphorous in different parts of the leaves as per the T-test ($P > 0.05$) as shown in Appendix 2. Different crops are known to bioaccumulate Phosphorous that varies from one part of the plant to another under a given climatic, land and soil management conditions (Kabata-Pendias and Pendias, 2011).

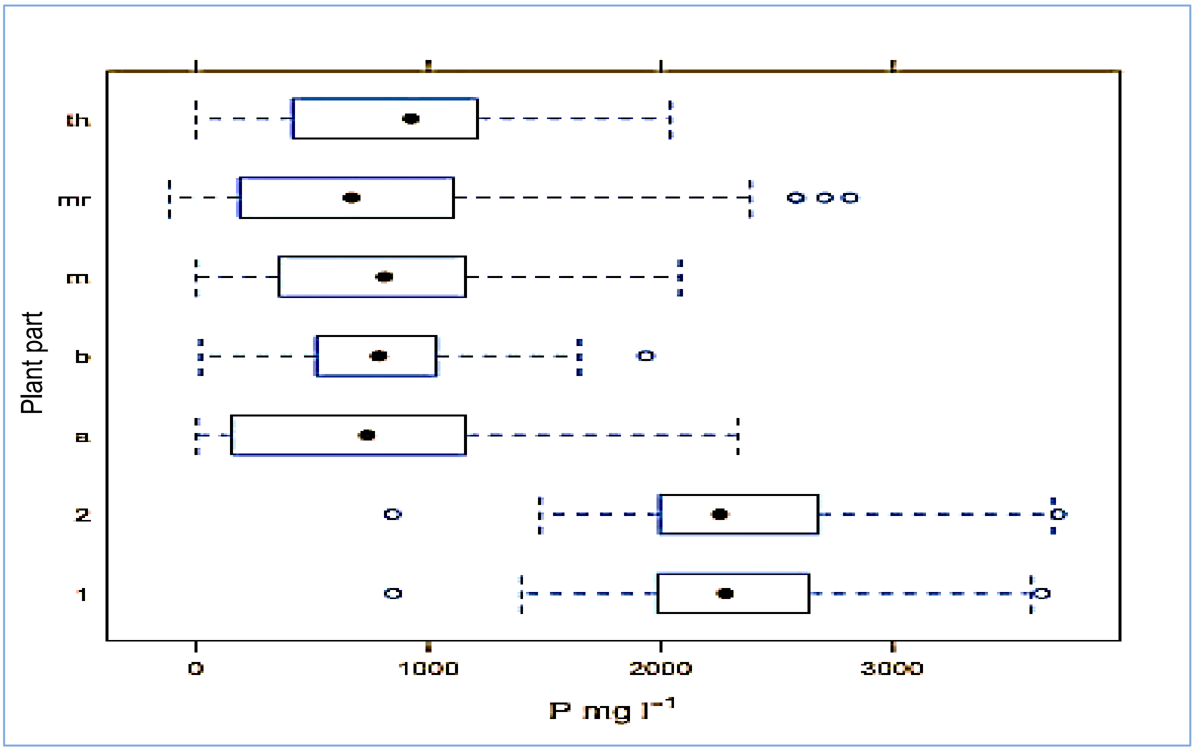


**Figure 4.13: Phosphorous content in different parts of maize leaf samples.**

Sulphur is a major nutrient that is required for plant growth and plays an important role in oil synthesis and chlorophyll formation. The recommended global range of Sulphur in plants is 1000 mg kg$^{-1}$ to 5000 mg kg$^{-1}$ (Sutar et al., 2017). From this study, an overall concentration range of 428 mg kg$^{-1}$ to 5630 mg kg$^{-1}$ was found. High concentrations of Sulphur were reported at the leaf base and lowest concentration being founded at the midrib. There was a significant difference in the amounts of Sulphur in the leaf base and the midrib ($P > 0.05$) with no notable difference being observed in other parts of the leaf ($P > 0.05$). The variations could be associated with the structural differences leading to distinct bioaccumulation capabilities of Sulphur. Bioaccumulation of the element by the plants relies on the concentration levels of the element in the soil, variety and parts of the plant (Kabata-Pendias and Pendias, 2011). Sutar et al. (2017), did a comparative study on the maize where a concentration of 60 kg ha$^{-1}$ of Sulphur was reported.

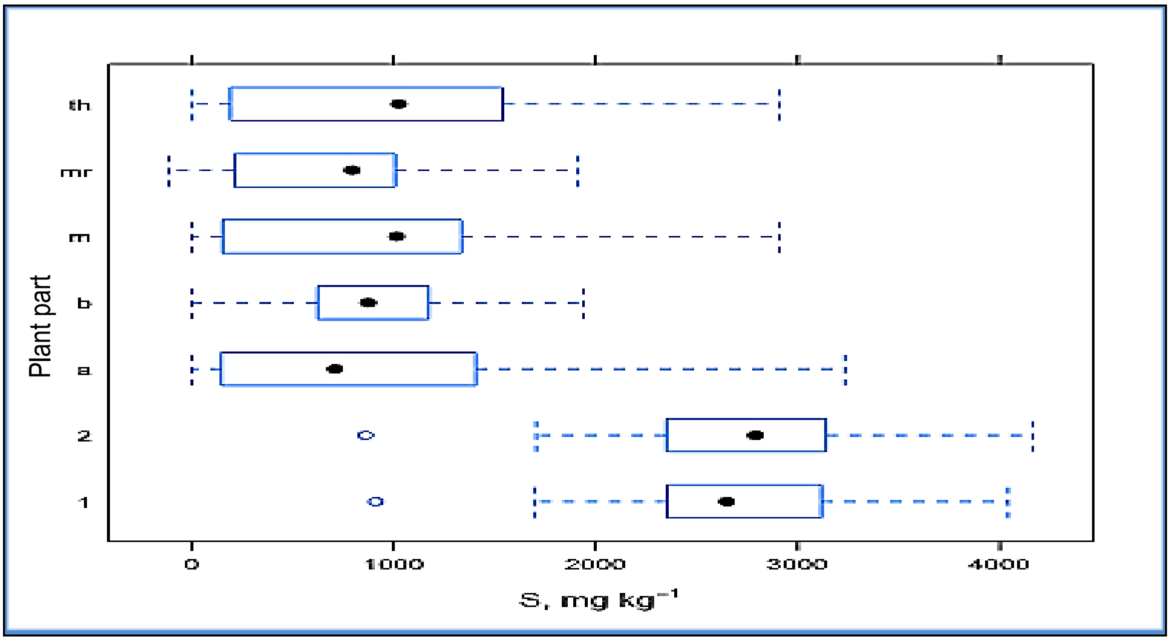


**Figure 4.14: Sulphur content in different parts of maize leaf samples.**

Na is a necessary element that is absorbed by the maize plant from the soils and water through the process of osmosis. From the study, a concentration range of 5.9 to 20.3 mg $kg^{-1}$ was observed. Highest concentrations of Na were recorded at the midrib part of the leaf with minimal values being observed in the leaf mid. However, there was no significant difference between the concentrations of Na in different parts of the leaves considered in the study ($P > 0.05$).

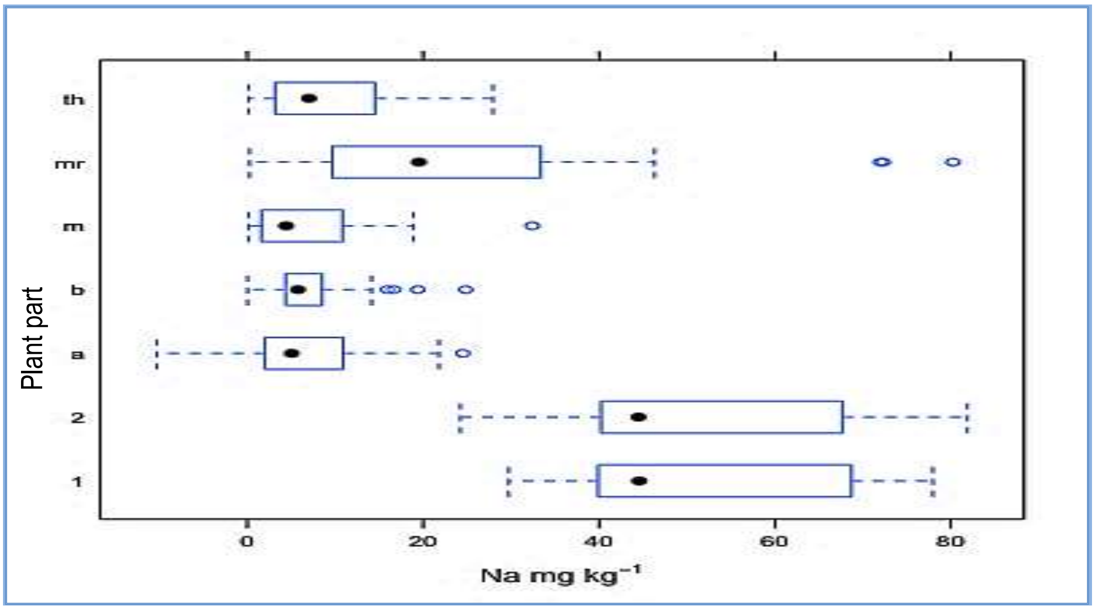


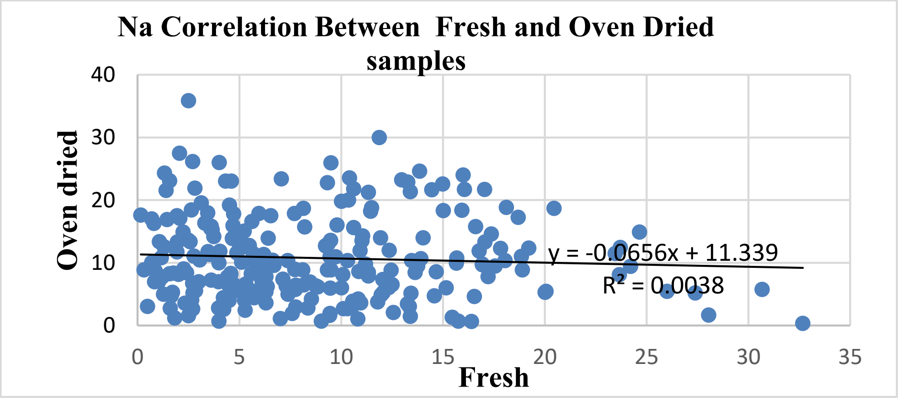
**Figure 4.15: Sodium content in different parts of maize leaf samples.**

From the analyses carried out the results obtained when a stack of five leaves put together, did not change any concentration values for all the elements.

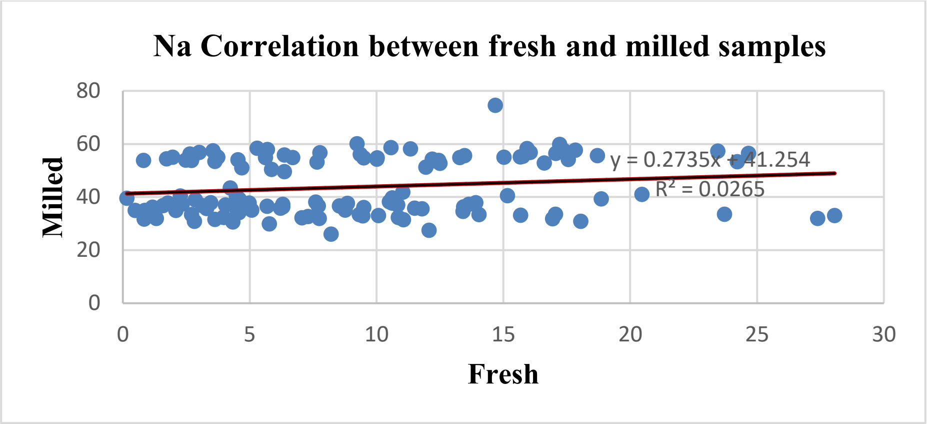
## 4.4: Correlation of the elemental concentration in different methods and parts of the leaf.

### 4.4.1 Correlation of the concentration of light elements in different sample presentation Methods.

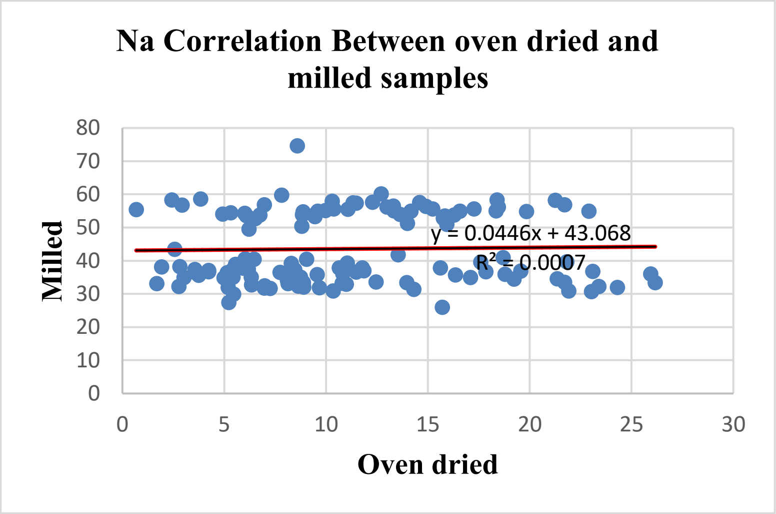
Correlation analysis was conducted on the light elements under distinct methods and results presented in fig 4.16. Sodium was picked to represent the light element category. From the results, Na in fresh and oven dried samples was found to be weak with a value of $R^2 = 0.004$ (Fig 4.16a) while the correlation between the Na in fresh against milled samples was found to be $R^2 = 0.03$(Fig 4.16b). There was no observed correlation between the Na in oven dried and milled samples with $R^2 = 0.00$(Fig 4.16c). Generally, a poor correlation was recorded for Na in the three methods considered in the study.



a)



b)

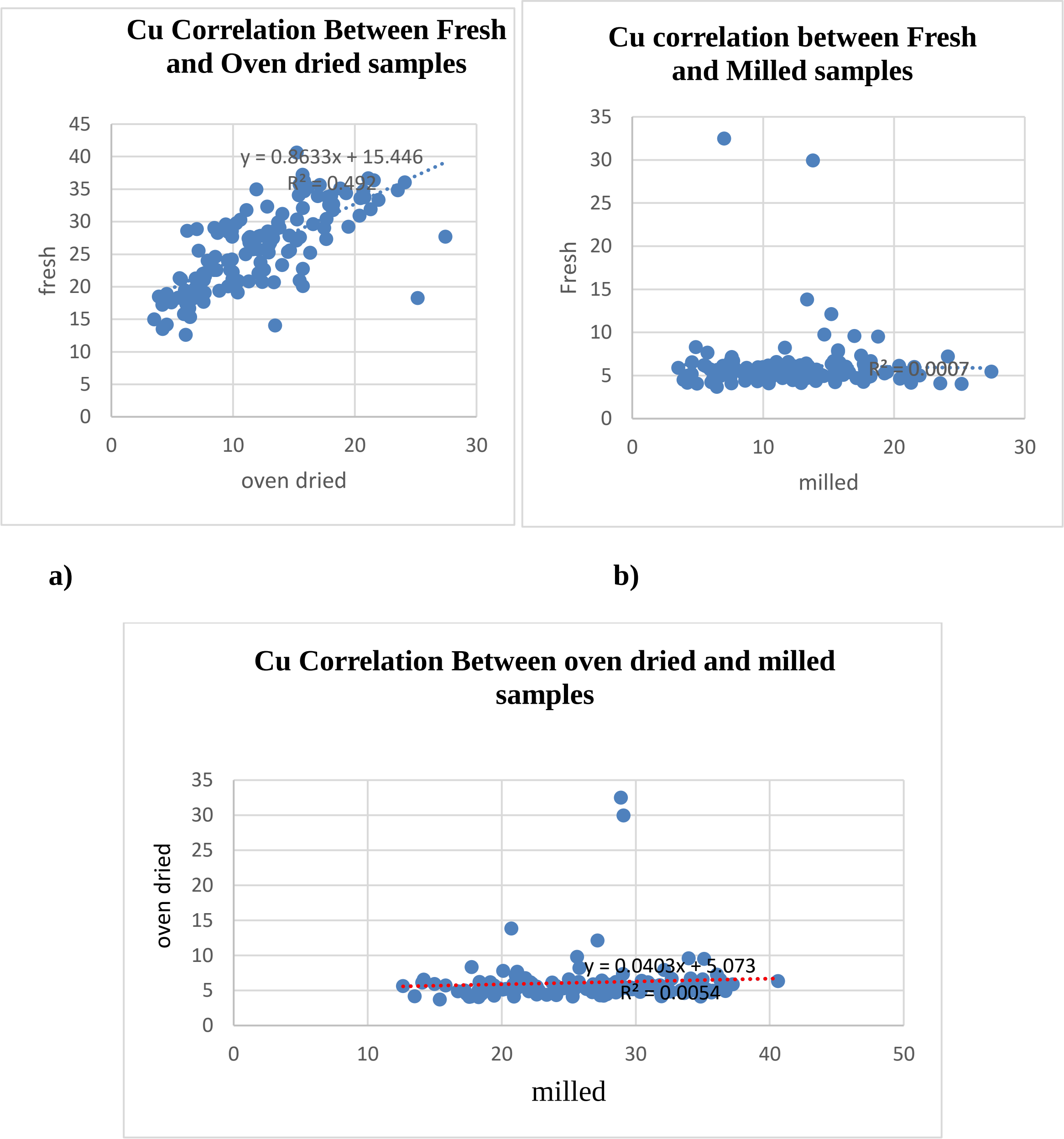


c)

**Figure 4.16. Correlation of Sodium in different sample presentation Methods.**

### 4.4.2 Correlation of the concentration of heavy elements in different sample presentation Methods.

Copper was picked to represent heavy elements. From the results; $R^2$ = 0.49 was reported for the correlation between the concentrations of Cu in the fresh against the oven dried samples. There was no correlation between the concentrations of Cu in fresh against the milled samples ($R^2$ = 0.00). For the milled against the oven dried samples a correlation of $R^2$ = 0.01. The poor correlation for the low and high Z elements could be attributed to the differences in the sample structure, which tends to affect the distribution of the elements in the maize plant (Fig 4.17)



**a)**

**b)**

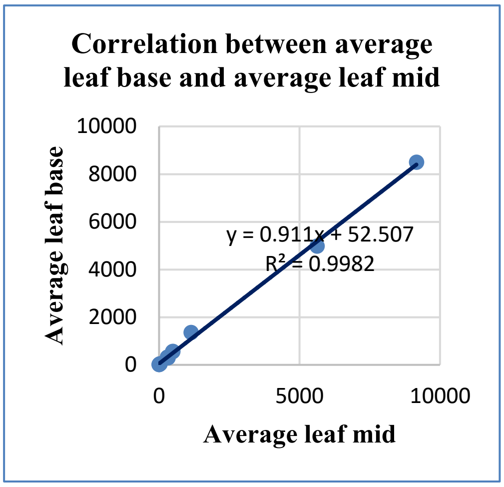
**c)**

**Figure 4.17. Correlation of Cu in different sample presentation Methods.**

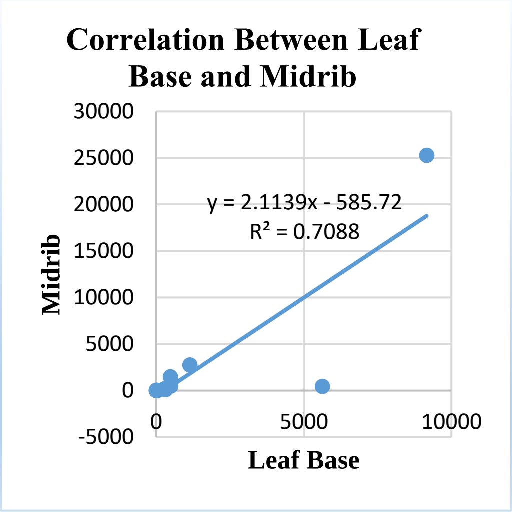
### 4.4.3 Correlation of the concentration of elements in different parts of the maize leaf.

Correlation analysis in different parts of the plant were conducted and the following results were recorded in Fig 4.18. The correlation in most of the elements between the leaf base and leaf mid; leaf base and midrib were found to be strongly correlated with $R^2 = 0.998$(Fig

4.18 a) and $R^2$ = 0.998(Fig 4.18e) while the correlation between elements in the leaf base and the apex; leaf base and midrib was found to be positively correlated with $R^2$ = 0.87 (Fig 4.18c) and $R^2$ = 0.7 (Fig 4.18b) for all the elements under study.



a)



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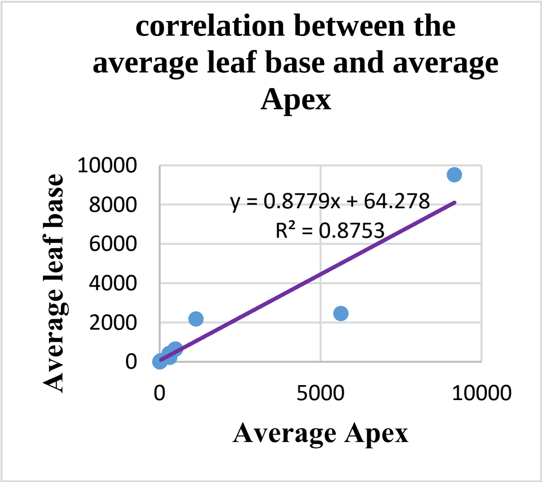

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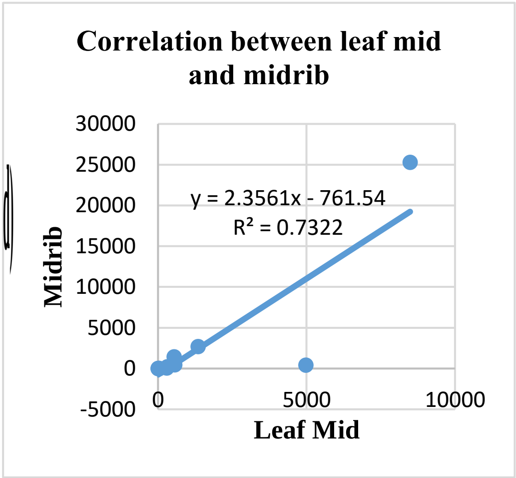

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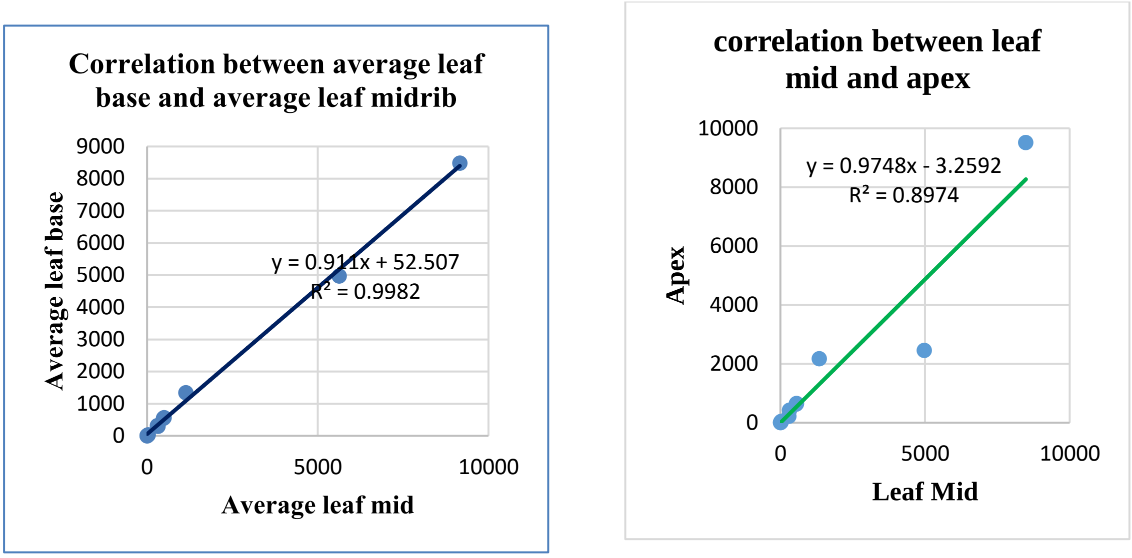

**e)** **f)**

**Figure 4.18. Correlation of the elements in different parts of the maize leaves.**

A strong correlation was also reported between the elements in leaf mid and the midrib with $R^2 = 0.73$ (Fig 4.18 d). For leaf mid vs the apex $R^2 = 0.89$ (Fig 4.18f) was observed rom the results presented, a strong positive correlation was reported in overall for the elements in different parts of the leaves. That could be attributed the similarities in formation factors of the leaf. The sampling technique used also could be linked to the observed relationship between the overall elements in distinct parts of the plant.

# CHAPTER FIVE

# CONCLUSION AND RECOMMENDATIONS

## 5.1 Conclusion

In this study, applicability of portable XRF under different sample presentation methods for maize plant samples was determined. For most elements (Na, Mg,P,S,K and Ca) recorded higher concentrations in milled samples, as compared to concentrations in fresh and oven-dried samples, although no significant difference ($P > 0.05$) was realized between the three methods. On the other hand, significantly lower concentrations were noted in fresh samples, which also recorded a poor correlation($R=0.03$) for the elements: Na, Mg, P, S, K, Ca, Mn and Fe considered in the study. The heavy elements (Fe, Zn, Mo, Cu and Mn) did not exhibit significant variations for the different sample preparation methods in comparison with the lighter elements with $P > 0.05$.

The mean elemental content in maize leaf at different growth stages that is; early growth stage when the maize plant was 12 inches tall and during the tasselling stage i.e. when the maize plant approached flowering and fruiting were determined. Generally, Potassium (K), Manganese (Mn), Iron(Fe), Calcium(Ca), and Phosphorous (P) recorded higher concentrations at the early growth stage; on the other hand, Zinc(Zn),Sodium(Na), and Magnesium(Mg) exhibited high concentrations at tasseling stage while Copper and molybdenum concentrations remained constant on both seasons. However, regression analyses showed that there was no significant difference in nutrient concentration between the two seasons. The high K and P concentration at early growth stage could be attributed to application of phosphate or NPK fertilizers during planting period.

In this study, different parts of maize leaf sample i.e. the leaf base (b), middle part of the leaf (m), leaf apex (a), midrib (mr), and a stack of 5 leaves together (th), were analysed for elemental content. Different concentration trends were obtained for different elements. There was decreasing trend from leaf base to the apex in potassium (K), Phosphorous (P) and Sulphur(S); these are nutrients required by the plant at the early stage of development in addition to nitrogen. A reverse trend was realized in Calcium, Iron, Manganese, Zinc and Sodium, while Copper and Molybdenum exhibited a uniform concentration along the maize leaf. In addition Potassium, Calcium and magnesium recorded the highest concentration at midrib (mr) compared to other parts of the leaf; it can be noted that these are elements that play structural roles in the plant e.g. K controls the opening and closing of the stomata, therefore found mostly in xylem tissues

Generally the study was able to identify suitable matrices for analysis of particular nutrients, in this case; all elements and in particular light elements can be analysed comfortably in milled form. Additionally, heavy elements can be analysed in oven dried form, while there is a challenge in elemental analysis of fresh samples. Furthermore the study was also able to demonstrate different nutrients and their stages of development that are absorbed, also their movement along the maize leaf. Therefore the main objective of assessing the applicability of HHXRF for maize plant tissue analysis was successful.

## 5.2 Recommendations

I. From the study, the precision between subsequent runs was poor probably due to sample inhomogeneity and differences in sample matrix, density and attenuation. More studies need to be carried out to come up with a standard method.

II. Plant nutrient mainly come from soil reserves. It is therefore necessary to carry out correlation studies between soil nutrient status and respective content in plants grown therein as well as in relation to crop productivity.

III. There is need to test applicability of the technique on different crops and sample matrices.

IV. This study was carried out in the laboratory set up, therefore there is need to carry out analysis in the farm and compare the results obtained in the lab from those in the field.

V. There also need to collect samples from a different farm, since Muguga is more of research farm

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# APPENDICES

## Appendix 1: T-test for the recorded results of elemental concentration in two growth stages

| | |
|---|---|
| t Stat | 1.071414 |
| P(T<=t) one-tail | 0.15458 |
| t Critical one-tail | 1.812461 |
| P(T<=t) two-tail | 0.30916 |
| t Critical two-tail | 2.228139 |

## Appendix 2: T-test for the recorded results of elemental concentration in different parts of maize leaf.

| **Apex vs midrib** | | **leaf base vs leaf mid** | | **leaf base vs apex** | |
|---|---|---|---|---|---|
| t Stat | -0.90917 | t Stat | 1.026965 | t Stat | 0.411789 |
| P(T<=t) one-tail | 0.192325 | P(T<=t) one-tail | 0.164319 | P(T<=t) one-tail | 0.344591 |
| t Critical one-tail | 1.812461 | t Critical one-tail | 1.812461 | t Critical one-tail | 1.812461 |
| P(T<=t) two-tail | 0.38465 | P(T<=t) two-tail | 0.328637 | P(T<=t) two-tail | 0.689182 |
| t Critical two-tail | 2.228139 | t Critical two-tail | 2.228139 | t Critical two-tail | 2.228139 |
| | | | | | |
| **leaf base vs midrib** | | **leaf mid vs midrib** | | | |
| t Stat | -0.75658 | t Stat | -0.79536 | | |
| P(T<=t) one-tail | 0.233375 | P(T<=t) one-tail | 0.222437 | | |
| t Critical one-tail | 1.812461 | t Critical one-tail | 1.812461 | | |
| P(T<=t) two-tail | 0.466751 | P(T<=t) two-tail | 0.444874 | | |
| t Critical two-tail | 2.228139 | t Critical two-tail | 2.228139 | | |

## Appendix 3: T-test for the elemental concentration at different sample presentation

### Appendix 3.1: T-test for elemental concentration for Light elements.

| **FRESH VS OD** | |
|---|---|
| t Stat | -3.14248 |
| P(T<=t) one-tail | 0.000885 |
| t Critical one-tail | 1.647795 |
| P(T<=t) two-tail | 0.001771 |
| t Critical two-tail | 1.964545 |

| **FRESH VS MILLED** | |
|---|---|
| t Stat | -34.4714 |
| P(T<=t) one-tail | 5.7E-80 |
| t Critical one-tail | 1.653658 |
| P(T<=t) two-tail | 1.14E-79 |
| t Critical two-tail | 1.973691 |
| **OD VS MILLED** | |
| t Stat | -32.6823 |
| P(T<=t) one-tail | 1.02E-76 |
| t Critical one-tail | 1.653607 |
| P(T<=t) two-tail | 2.03E-76 |
| t Critical two-tail | 1.973612 |

**Appendix 3.2: T-test for elemental concentration for heavy elements**

| **FFRESH VS OVEN DRIED** | |
|---|---|
| t Stat | -10.5191 |
| P(T<=t) one-tail | 4.82E-22 |
| t Critical one-tail | 1.650828 |
| P(T<=t) two-tail | 9.64E-22 |
| t Critical two-tail | 1.969274 |

| **FRESH VS MILLED** | |
|---|---|
| t Stat | 3.318181 |
| P(T<=t) one-tail | 0.000519 |
| t Critical one-tail | 1.650828 |
| P(T<=t) two-tail | 0.001038 |
| t Critical two-tail | 1.969274 |

| **OVEN DRIED VS MILLED** | |
|---|---|
| t Stat | 13.09998 |
| P(T<=t) one-tail | 1.18E-30 |
| t Critical one-tail | 1.650828 |
| P(T<=t) two-tail | 2.36E-30 |
| t Critical two-tail | 1.969274 |

## Appendix 4: Nutrient Concentration by leaf part (Fresh samples)

| | **Potassium (mgkg$^{-1}$)** | | | | | | | **Calcium(mgkg$^{1}$)** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SSN | B | M | A | MR | Thick | | SSN | B | M | A | MR | Thick |
| icr163783 | 9066 | 11207 | 8422 | 7910 | 11592 | | icr163783 | 1565 | 2074 | 1965 | 869 | 2335 |
| icr163784 | 7346 | 6374 | 6817 | 3295 | 7352 | | icr163784 | 922 | 1067 | 1309 | 328 | 1344 |
| icr163785 | 3506 | 4068 | 2235 | 701 | 4215 | | icr163785 | 831 | 937 | 1935 | 383 | 804 |
| icr163786 | 3924 | 3808 | 3913 | 1093 | 10370 | | icr163786 | 441 | 665 | 1048 | 215 | 1865 |
| icr163787 | 2099 | 5115 | 2872 | 2822 | 4075 | | icr163787 | 275 | 1365 | 1130 | 556 | 873 |
| icr163788 | 9077 | 8661 | 6948 | 11132 | 7763 | | icr163788 | 1635 | 2167 | 2673 | 1154 | 3044 |
| icr163789 | 8841 | 8893 | 7706 | 9258 | 9740 | | icr163789 | 1316 | 1419 | 2051 | 902 | 1501 |
| icr163790 | 8426 | 6779 | 6555 | 7114 | 7450 | | icr163790 | 1293 | 1590 | 2467 | 912 | 2215 |
| icr163791 | 6430 | 7172 | 6660 | 3690 | 7835 | | icr163791 | 592 | 762 | 1285 | 423 | 801 |
| icr163792 | 9609 | 7875 | 6716 | 9337 | 7424 | | icr163792 | 1173 | 1542 | 3621 | 1144 | 3354 |
| icr163793 | 13144 | 10654 | 9708 | 7765 | 15119 | | icr163793 | 1234 | 1348 | 1760 | 904 | 1695 |
| icr163794 | 8360 | 6968 | 6127 | 6279 | 8988 | | icr163794 | 1026 | 1122 | 1364 | 768 | 1228 |
| icr163795 | 8712 | 7918 | 7528 | 5362 | 9712 | | icr163795 | 820 | 927 | 1159 | 549 | 1025 |
| icr163796 | 7355 | 6792 | 6068 | 5490 | 8020 | | icr163796 | 714 | 873 | 1015 | 574 | 913 |

|  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| icr163797 | 7649 | 5766 | 5264 | 6571 | 7830 |  | icr163797 | 1119 | 1759 | 2406 | 684 | 1636 |
| icr163798 | 10372 | 9291 | 8190 | 9768 | 9506 |  | icr163798 | 942 | 1211 | 1488 | 1100 | 950 |
| icr163799 | 7840 | 7436 | 8321 | 5238 | 8528 |  | icr163799 | 799 | 931 | 1200 | 600 | 1041 |
| icr163800 | 14517 | 9786 | 11245 | 10239 | 11472 |  | icr163800 | 2175 | 2218 | 3432 | 1506 | 3456 |
| icr163801 | 8956 | 7810 | 8506 | 8799 | 10436 |  | icr163801 | 1054 | 1284 | 1408 | 872 | 1352 |
| icr163802 | 8374 | 8757 | 8917 | 6781 | 5040 |  | icr163802 | 758 | 1088 | 1551 | 685 | 591 |
| icr163803 | 7393 | 6193 | 5566 | 5611 | 7480 |  | icr163803 | 720 | 810 | 1006 | 608 | 848 |
| icr163804 | 6245 | 5724 | 5756 | 3917 | 6379 |  | icr163804 | 627 | 694 | 732 | 350 | 779 |
| icr163805 | 7633 | 8473 | 6833 | 2589 | 8605 |  | icr163805 | 770 | 1001 | 1343 | 267 | 1366 |
| icr163807 | 10555 | 6058 | 5580 | 4853 | 6597 |  | icr163807 | 1454 | 1268 | 2121 | 522 | 1872 |
| icr163807 | 7222 | 6413 | 6095 | 4114 | 7103 |  | icr163807 | 701 | 739 | 903 | 375 | 980 |
| icr163808 | 6699 | 4875 | 6229 | 3678 | 6310 |  | icr163808 | 577 | 500 | 788 | 383 | 622 |
| icr163809 | 8161 | 8377 | 8318 | 4974 | 9537 |  | icr163809 | 758 | 864 | 993 | 493 | 999 |
| icr163810 | 8175 | 7975 | 7287 | 3154 | 8609 |  | icr163810 | 812 | 895 | 959 | 289 | 928 |
| icr163811 | 5628 | 5674 | 4951 | 3549 | 6758 |  | icr163811 | 613 | 725 | 738 | 347 | 827 |
| icr163812 | 7102 | 7190 | 6893 | 4102 | 8093 |  | icr163812 | 902 | 1167 | 1146 | 440 | 1310 |
| icr163813 | 6133 | 6446 | 5739 | 3032 | 6752 |  | icr163813 | 680 | 1028 | 1528 | 310 | 979 |

|  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| icr163814 | 4016 | 5087 | 5173 | 3341 | 5300 |  | icr163814 | 1376 | 1336 | 1754 | 495 | 1586 |

**Manganese MgKg$^{-1}$** **Iron (mgkg$^{-1}$)**

| SSN | B | M | A | MR | Thick | | SSN | B | M | A | MR | Thick |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| icr163783 | 75 | 111 | 139 | 30 | 124 | | icr163783 | 370 | 455 | 564 | 73 | 572 |
| icr163784 | 53 | 81 | 97 | 16 | 38 | | icr163784 | 213 | 373 | 330 | 52 | 167 |
| icr163785 | 59 | 68 | 78 | 25 | 59 | | icr163785 | 237 | 256 | 239 | 53 | 185 |
| icr163786 | 86 | 115 | 93 | 26 | 96 | | icr163786 | 501 | 647 | 501 | 98 | 436 |
| icr163787 | 63 | 72 | 70 | 22 | 46 | | icr163787 | 396 | 296 | 330 | 76 | 193 |
| icr163788 | 89 | 105 | 95 | 23 | 84 | | icr163788 | 423 | 585 | 339 | 63 | 327 |
| icr163789 | 163 | 107 | 105 | 15 | 106 | | icr163789 | 1210 | 490 | 532 | 58 | 584 |
| icr163790 | 66 | 62 | 74 | 18 | 42 | | icr163790 | 299 | 366 | 325 | 51 | 196 |
| icr163791 | 82 | 68 | 92 | 41 | 64 | | icr163791 | 286 | 350 | 338 | 85 | 213 |
| icr163792 | 122 | 88 | 143 | 36 | 72 | | icr163792 | 443 | 323 | 308 | 62 | 254 |
| icr163793 | 103 | 101 | 108 | 54 | 116 | | icr163793 | 361 | 338 | 383 | 57 | 475 |
| icr163794 | 74 | 67 | 94 | 22 | 67 | | icr163794 | 272 | 331 | 694 | 31 | 527 |
| icr163795 | 109 | 136 | 104 | 43 | 94 | | icr163795 | 681 | 812 | 443 | 63 | 436 |
| icr163796 | 67 | 72 | 68 | 24 | 47 | | icr163796 | 170 | 237 | 166 | 16 | 131 |
| icr163797 | 66 | 82 | 150 | 32 | 93 | | icr163797 | 340 | 198 | 359 | 77 | 300 |
| icr163798 | 77 | 80 | 85 | 56 | 72 | | icr163798 | 198 | 213 | 233 | 24 | 179 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| icr163799 | 78 | 83 | 95 | 19 | 79 | | icr163799 | 334 | 412 | 470 | 58 | 341 |
| icr163800 | 79 | 66 | 69 | 29 | 58 | | icr163800 | 383 | 290 | 342 | 76 | 285 |
| icr163801 | 71 | 83 | 109 | 61 | 34 | | icr163801 | 285 | 236 | 279 | 205 | 55 |
| icr163802 | 52 | 67 | 95 | 30 | 50 | | icr163802 | 211 | 185 | 310 | 70 | 155 |
| icr163803 | 76 | 84 | 95 | 32 | 61 | | icr163803 | 340 | 426 | 244 | 56 | 239 |
| icr163804 | 82 | 72 | 65 | 57 | 70 | | icr163804 | 460 | 401 | 210 | 288 | 341 |
| icr163805 | 33 | 56 | 70 | 17 | 43 | | icr163805 | 145 | 185 | 245 | 17 | 145 |
| icr163807 | 40 | 53 | 94 | 17 | 35 | | icr163807 | 152 | 174 | 190 | 24 | 114 |
| icr163807 | 36 | 65 | 82 | 16 | 59 | | icr163807 | 121 | 180 | 289 | 35 | 169 |
| icr163808 | 67 | 69 | 79 | 29 | 51 | | icr163808 | 282 | 189 | 247 | 44 | 138 |
| icr163809 | 81 | 68 | 81 | 18 | 53 | | icr163809 | 285 | 282 | 313 | 21 | 219 |
| icr163810 | 54 | 71 | 72 | 20 | 37 | | icr163810 | 189 | 190 | 183 | 39 | 129 |
| icr163811 | 65 | 43 | 62 | 32 | 51 | | icr163811 | 171 | 137 | 178 | 26 | 131 |
| icr163812 | 53 | 65 | 65 | 14 | 50 | | icr163812 | 160 | 174 | 299 | 32 | 185 |
| icr163813 | 58 | 50 | 54 | 36 | 17 | | icr163813 | 199 | 179 | 205 | 129 | 18 |
| icr163814 | 58 | 59 | 83 | 15 | 45 | | icr163814 | 275 | 166 | 331 | 30 | 141 |

**Copper(mgkg$^{-1}$)**

| SSN | B | M | A | MR | Thick |
|---|---|---|---|---|---|
| icr163783 | 13 | 11 | 15 | 5 | 10 |
| icr163784 | 9 | 10 | 11 | 3 | 4 |
| icr163785 | 12 | 9 | 5 | 4 | 6 |
| icr163786 | 12 | 13 | 13 | 4 | 8 |
| icr163787 | 10 | 11 | 11 | 4 | 6 |
| icr163788 | 12 | 13 | 10 | 4 | 9 |
| icr163789 | 13 | 14 | 13 | 4 | 9 |
| icr163790 | 10 | 12 | 9 | 4 | 5 |
| icr163791 | 12 | 13 | 15 | 6 | 9 |
| icr163792 | 12 | 13 | 12 | 4 | 6 |
| icr163793 | 23 | 20 | 21 | 7 | 12 |
| icr163794 | 16 | 15 | 16 | 3 | 8 |
| icr163795 | 19 | 16 | 21 | 5 | 10 |
| icr163796 | 14 | 14 | 15 | 3 | 8 |
| icr163797 | 11 | 7 | 12 | 4 | 7 |

**Zinc(mgkg$^{-1}$)**

| SSN | B | M | A | MR | Thick |
|---|---|---|---|---|---|
| icr163783 | 46 | 41 | 38 | 18 | 30 |
| icr163784 | 32 | 37 | 33 | 14 | 27 |
| icr163785 | 31 | 32 | 45 | 12 | 22 |
| icr163786 | 32 | 37 | 37 | 14 | 23 |
| icr163787 | 29 | 33 | 37 | 16 | 21 |
| icr163788 | 34 | 38 | 69 | 12 | 23 |
| icr163789 | 37 | 38 | 43 | 12 | 27 |
| icr163790 | 29 | 28 | 36 | 13 | 20 |
| icr163791 | 39 | 46 | 47 | 21 | 31 |
| icr163792 | 34 | 38 | 42 | 14 | 33 |
| icr163793 | 29 | 18 | 22 | 8 | 28 |
| icr163794 | 16 | 18 | 17 | 8 | 13 |
| icr163795 | 16 | 18 | 19 | 13 | 12 |
| icr163796 | 19 | 15 | 16 | 8 | 13 |
| icr163797 | 35 | 26 | 44 | 18 | 27 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| icr163798 | 21 | 21 | 20 | 6 | 12 | | icr163798 | 22 | 19 | 25 | 11 | 17 |
| icr163799 | 16 | 14 | 14 | 4 | 9 | | icr163799 | 37 | 36 | 38 | 14 | 27 |
| icr163800 | 12 | 11 | 12 | 5 | 7 | | icr163800 | 35 | 37 | 37 | 19 | 23 |
| icr163801 | 15 | 16 | 19 | 10 | 3 | | icr163801 | 17 | 21 | 23 | 16 | 10 |
| icr163802 | 18 | 17 | 18 | 4 | 10 | | icr163802 | 19 | 26 | 20 | 11 | 16 |
| icr163803 | 18 | 17 | 17 | 5 | 9 | | icr163803 | 20 | 19 | 20 | 9 | 17 |
| icr163804 | 14 | 16 | 17 | 4 | 7 | | icr163804 | 14 | 13 | 15 | 10 | 13 |
| icr163805 | 13 | 16 | 17 | 5 | 10 | | icr163805 | 23 | 20 | 22 | 10 | 16 |
| icr163807 | 14 | 14 | 15 | 4 | 9 | | icr163807 | 14 | 17 | 18 | 7 | 14 |
| icr163807 | 7 | 15 | 17 | 4 | 9 | | icr163807 | 20 | 14 | 15 | 7 | 12 |
| icr163808 | 15 | 16 | 16 | 3 | 8 | | icr163808 | 16 | 14 | 16 | 7 | 12 |
| icr163809 | 15 | 16 | 16 | 5 | 8 | | icr163809 | 21 | 17 | 16 | 8 | 15 |
| icr163810 | 15 | 14 | 16 | 4 | 8 | | icr163810 | 19 | 19 | 20 | 10 | 15 |
| icr163811 | 14 | 15 | 15 | 4 | 9 | | icr163811 | 12 | 17 | 14 | 8 | 11 |
| icr163812 | 18 | 17 | 16 | 3 | 9 | | icr163812 | 14 | 15 | 16 | 7 | 15 |
| icr163813 | 14 | 16 | 17 | 8 | 4 | | icr163813 | 16 | 14 | 17 | 14 | 7 |
| icr163814 | 15 | 15 | 21 | 5 | 10 | | icr163814 | 14 | 16 | 16 | 7 | 13 |

## Appendix 5: Nutrient Concentration by sample presentation

| | Sodium MgKg-1 | | | | Magnesium MgKg-1 | | |
|---|---|---|---|---|---|---|---|
| SSN | Fresh | Oven Dried | Milled | | Fresh | Oven Dried | Milled |
| icr163783_a_1 | 13.1370 | 5.9461271 | 37.7795 | | 939.52 | 1007.75484 | 2825.49 |
| icr163783_a_2 | 0.46287 | 11.327858 | 57.4793 | | 412.902 | 1195.26687 | 3739.07 |
| icr163783_b_1 | 14.14592 | 5.41766439 | 37.22462 | | 759.3512 | 664.1969802 | 2799.349 |
| icr163783_b_2 | 7.326506 | 9.03770011 | 40.44619 | | 479.4433 | 978.3718234 | 2600.492 |
| icr163783_m_1 | 4.352425 | 2.9269475 | 56.75915 | | 361.6368 | 802.2051041 | 4124.188 |
| icr163783_m_2 | 4.028881 | 12.2770467 | 57.65169 | | 420.026 | 1271.794162 | 4345.543 |
| icr163783_mr_1 | 9.439422 | 18.6881873 | 40.97009 | | 707.821 | 1232.608715 | 2795.378 |
| icr163783_mr_2 | 14.71178 | 21.825464 | 39.65365 | | 1118.52 | 1721.921721 | 2659.689 |
| icr163783_th_1 | 8.288629 | 21.7138156 | 56.80756 | | 820.8656 | 1412.557761 | 3850.556 |
| icr163783_th_2 | 18.18574 | 18.4506918 | 56.16762 | | 1166.112 | 1435.443726 | 3947.218 |
| icr163784_a_1 | 0.719637 | 5.23047429 | 27.4308 | | 389.4174 | 1180.401053 | 2271.75 |
| icr163784_a_2 | 15.3203 | 15.70689 | 25.99276 | | 622.1726 | 1513.962923 | 2426.312 |
| icr163784_b_1 | 2.577096 | 5.31322723 | 54.44956 | | 191.3223 | 545.6646432 | 4364.771 |
| icr163784_b_2 | 7.542749 | 8.81081161 | 50.38897 | | 294.8909 | 1034.117453 | 4027.222 |
| icr163784_m_1 | 14.03679 | 1.69018182 | 33.08157 | | 363.1757 | 856.7588107 | 2224.46 |
| icr163784_m_2 | 5.935764 | 10.3402244 | 30.85672 | | 598.8943 | 1131.165217 | 1980.152 |
| icr163784_mr_1 | 8.446976 | 17.2596494 | 55.55961 | | 958.467 | 1126.778579 | 3952.067 |
| icr163784_mr_2 | 5.109091 | 21.2575008 | 58.16961 | | 871.0684 | 1501.540821 | 3735.886 |
| icr163784_th_1 | 2.853618 | 24.2980536 | 31.9889 | | 597.0971 | 1772.025758 | 2205.451 |
| icr163784_th_2 | 7.70785 | 21.9083893 | 30.8895 | | 373.1699 | 1747.032214 | 2155.49 |
| icr163785_a_1 | 8.453074 | 3.84797793 | 58.60966 | | 267.2965 | 829.0377766 | 4103.296 |
| icr163785_a_2 | 1.341765 | 9.49643039 | 54.17999 | | 414.0919 | 1074.562746 | 4243.792 |
| icr163785_b_1 | 5.785166 | 2.82656363 | 38.19836 | | 82.4064 | 698.4156172 | 2591.346 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| icr163785_b_2 | 1.62135 | 5.1378946 | 36.35863 |  | 224.385 | 817.2265186 | 2520.794 |
| icr163785_m_1 | 6.24691 | 8.87237396 | 54.73937 |  | 192.3126 | 886.25003 | 3994.928 |
| icr163785_m_2 | 1.976608 | 6.75177642 | 53.77467 |  | 306.9816 | 864.8098885 | 4167.516 |
| icr163785_mr_1 | 2.005995 | 8.28831174 | 39.19718 |  | 667.7248 | 903.842929 | 2371.716 |
| icr163785_mr_2 | 2.029148 | 23.0909525 | 36.73319 |  | 661.362 | 944.4043103 | 2455.713 |
| icr163785_th_1 | 3.05308 | 7.80984597 | 59.78009 |  | 226.3745 | 1078.313142 | 3976.916 |
| icr163785_th_2 | 1.372551 | 14.5842095 | 57.5386 |  | 204.8462 | 1576.684477 | 3899.863 |
| icr163786_a_1 | 1.257952 | 6.46784096 | 40.42736 |  | 132.0863 | 781.9885197 | 2409.288 |
| icr163786_a_2 | 4.756863 | 11.4758741 | 36.59842 |  | 528.0544 | 1116.531523 | 2620.042 |
| icr163786_b_1 | 9.886009 | 6.00523812 | 54.28409 |  | 60.78897 | 740.5809526 | 3617.171 |
| icr163786_b_2 | 3.648238 | 6.22129573 | 49.5542 |  | 145.1685 | 790.9575648 | 3696.194 |
| icr163786_m_1 | 10.15938 | 2.76723287 | 32.28834 |  | 89.91452 | 634.6983926 | 2147 |
| icr163786_m_2 | 5.632981 | 6.98711961 | 32.40035 |  | 244.7617 | 927.175551 | 2017.876 |
| icr163786_mr_1 | 3.339338 | 22.902698 | 54.89882 |  | 516.1636 | 1562.937675 | 3900.253 |
| icr163786_mr_2 | 3.770923 | 14.9017814 | 56.40121 |  | 248.2764 | 1275.646562 | 4314.45 |
| icr163786_th_1 | 0.543662 | 16.5675087 | 54.92121 |  | 449.1989 | 1347.122916 | 3598.919 |
| icr163786_th_2 | 7.944717 | 15.7561279 | 52.78777 |  | 475.5325 | 1287.946985 | 3500.909 |
| icr163787_a_1 | 2.522699 | 15.2404222 | 55.58673 |  | 136.0687 | 817.4107672 | 3832.429 |
| icr163787_a_2 | 0.734987 | 18.3512568 | 54.98643 |  | 323.8109 | 1571.450352 | 3741.045 |
| icr163787_b_1 | 7.405452 | 6.32651326 | 35.03908 |  | 115.4777 | 706.5301005 | 2303.685 |
| icr163787_b_2 | 16.53842 | 15.605703 | 37.80921 |  | 157.5909 | 1262.004091 | 2392.861 |
| icr163787_m_1 | 2.006057 | 8.38068746 | 37.70356 |  | 209.4791 | 950.0255731 | 2672.787 |
| icr163787_m_2 | 4.175254 | 10.3763694 | 55.56477 |  | 381.3514 | 1112.78676 | 4293.801 |
| icr163787_mr_1 | 10.91745 | 10.7902643 | 33.1801 |  | 668.136 | 1081.216877 | 2426.754 |
| icr163787_mr_2 | 14.814 | 18.7946803 | 35.8609 |  | 531.8141 | 1492.103691 | 2445.958 |
| icr163787_th_1 | 1.700142 | 13.3072643 | 56.50927 |  | 473.9193 | 1379.218729 | 3989.577 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| icr163787_th_2 | 4.881195 | 19.8347057 | 54.81682 | | 454.1594 | 1549.003667 | 4268.83 |
| icr163788_a_1 | 3.149684 | 3.02368143 | 34.9294 | | 299.2544 | 806.4603657 | 2361.321 |
| icr163788_a_2 | 0.169487 | 16.3539819 | 35.75797 | | 257.0412 | 1417.63566 | 2452.019 |
| icr163788_b_1 | 0.521505 | 6.97540366 | 56.81496 | | 103.9951 | 927.8300124 | 4061.268 |
| icr163788_b_2 | 6.90558 | 13.6387165 | 53.92578 | | 239.3614 | 1371.934956 | 3827.974 |
| icr163788_m_1 | 20.84421 | 17.0902077 | 34.93753 | | 195.5079 | 1339.150968 | 2361.076 |
| icr163788_m_2 | 4.218412 | 13.9662216 | 33.4445 | | 219.8919 | 1133.79149 | 2149.315 |
| icr163788_mr_1 | 0.645975 | 11.4868357 | 57.33979 | | 642.3766 | 1112.716902 | 3892.802 |
| icr163788_mr_2 | 4.490465 | 12.9919638 | 56.1542 | | 619.2463 | 923.6828405 | 3776.592 |
| icr163788_th_1 | 7.247062 | 26.1664384 | 33.36959 | | 621.6171 | 2049.873068 | 2385.189 |
| icr163788_th_2 | 3.585818 | 19.2231932 | 34.41489 | | 408.478 | 1402.239547 | 2311.725 |
| icr163789_a_1 | 15.16288 | 6.15338999 | 37.62884 | | 418.0103 | 984.5508466 | 2824.668 |
| icr163789_a_2 | 3.195417 | 9.56195887 | 35.80807 | | 421.9333 | 1053.077198 | 2434.618 |
| icr163789_b_1 | 3.852923 | 6.3444544 | 32.7284 | | 206.9494 | 861.500888 | 2242.192 |
| icr163789_b_2 | 1.318231 | 7.24946889 | 31.64797 | | 337.9928 | 985.1882745 | 2190.819 |
| icr163789_m_1 | 16.06653 | 6.5215142 | 52.74658 | | 214.8329 | 931.0590241 | 3543.852 |
| icr163789_m_2 | 5.192757 | 9.96552496 | 55.15397 | | 296.3768 | 1040.752154 | 3633.424 |
| icr163789_mr_1 | 0.505383 | 21.7139153 | 33.46669 | | 868.7065 | 1638.464823 | 2211.814 |
| icr163789_mr_2 | 0.215883 | 25.9414233 | 36.00944 | | 1132.06 | 1679.368337 | 2343.19 |
| icr163789_th_1 | 11.45176 | 13.9901663 | 51.23284 | | 445.1213 | 1445.97279 | 3992.76 |
| icr163789_th_2 | 11.19648 | 11.0668192 | 55.52772 | | 469.0806 | 1304.006273 | 4109.709 |
| icr163790_a_1 | 7.10341 | 5.42151982 | 35.04495 | | 345.7534 | 1029.127307 | 2271.279 |
| icr163790_a_2 | 9.534411 | 10.9892865 | 32.92017 | | 390.4571 | 1137.526358 | 2176.331 |
| icr163790_b_1 | 1.382606 | 4.92278158 | 54.07276 | | 134.4526 | 692.1845322 | 3676.771 |
| icr163790_b_2 | 4.564486 | 9.45070584 | 53.3313 | | 80.46649 | 1098.27041 | 3815.145 |
| icr163790_m_1 | 6.946216 | 2.56772631 | 43.47771 | | 121.2826 | 801.6627963 | 2718.925 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| icr163790_m_2 | 3.491398 | 13.5445843 | 41.79407 | | 253.9369 | 1349.812545 | 2745.798 |
| icr163790_mr_1 | 1.982721 | 14.1665522 | 54.96327 | | 947.8039 | 1103.024016 | 3748.048 |
| icr163790_mr_2 | 13.25913 | 15.8308558 | 53.46183 | | 689.5331 | 1153.072692 | 3817.829 |
| icr163790_th_1 | 1.800939 | 19.5524368 | 36.8349 | | 503.5554 | 1625.025034 | 2460.837 |
| icr163790_th_2 | 13.44644 | 21.3479304 | 34.58744 | | 483.3715 | 1555.632847 | 2376.324 |
| icr163791_a_1 | 0.114867 | 2.42844813 | 55.8665 | | 239.985 | 288.1554033 | 4013.121 |
| icr163791_a_2 | 7.097739 | 6.02102009 | 58.34727 | | 195.1734 | 937.9751069 | 4139.835 |
| icr163791_b_1 | 24.98852 | 0.68152733 | 53.20575 | | 52.92182 | 360.4497785 | 3484.821 |
| icr163791_b_2 | 2.36771 | 9.59122747 | 40.52917 | | 212.0638 | 824.1902 | 2692.591 |
| icr163791_m_1 | 17.74742 | 5.46296733 | 55.42576 | | 218.3528 | 450.3919402 | 3832.663 |
| icr163791_m_2 | 0.229344 | 23.0352361 | 54.90398 | | 214.8553 | 938.3716532 | 3975.404 |
| icr163791_mr_1 | 5.971245 | 4.23143114 | 29.90458 | | 716.099 | 818.940364 | 1959.362 |
| icr163791_mr_2 | 4.898815 | 11.0329907 | 30.68449 | | 1265.208 | 1527.300325 | 2121.979 |
| icr163791_th_1 | 7.319519 | 3.74447607 | 37.07654 | | 319.8096 | 590.9615751 | 3029.222 |
| icr163791_th_2 | 18.12092 | 8.09951954 | 39.30322 | | 320.73 | 1319.095241 | 2966.281 |
| icr163791_th_6.1 | 0.87601 | 3.55581489 | 35.58041 | | 205.4237 | 724.023596 | 2221.578 |
| icr163791_th_6.2 | 4.785392 | 12.7085281 | 34.08108 | | 215.4225 | 915.0185569 | 2367.238 |
| icr163792_a_1 | 12.19576 | 6.18947378 | 37.38142 | | 64.04402 | 1018.066765 | 2812.44 |
| icr163792_a_2 | 2.71943 | 8.73964609 | 60.11905 | | 339.5875 | 1229.526661 | 4439.092 |
| icr163792_b_1 | 8.302603 | 6.01645718 | 37.42278 | | 108.7282 | 709.3056553 | 2453.166 |
| icr163792_b_2 | 2.20138 | 6.08452387 | 35.01792 | | 256.1899 | 1059.431674 | 2286.141 |
| icr163792_m-1 | 3.56655 | 17.8496498 | 54.25794 | | 458.7757 | 603.1218434 | 3989.287 |
| icr163792_m_2 | 0.844505 | 23.388517 | 53.58401 | | 412.2901 | 909.1987395 | 3859.303 |
| icr163792_mr_1 | 12.82943 | 13.3385402 | 36.67466 | | 510.4851 | 1495.514179 | 2314.49 |
| icr163792_mr_2 | 10.77408 | 15.9293509 | 32.22042 | | 1215.441 | 1063.282944 | 2377.08 |
| icr163792_th_1 | 12.92541 | 6.9664062 | 55.04082 | | 249.592 | 1151.306641 | 4223.216 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| icr163792_th_2 | 5.662276 | 8.12962835 | 50.97648 | | 451.928 | 1276.576072 | 4081.718 |
| icr163793_a_1 | 3.539507 | 1.92579857 | 31.7117 | | 149.9832 | 714.6362709 | 2376.609 |
| icr163793_a_2 | 5.239352 | 8.83360105 | 33.08594 | | 161.6054 | 786.5860193 | 2342.766 |
| icr163793_b_1 | 6.150615 | 10.6482228 | 38.12434 | | 43.84343 | 634.0554841 | 2816.636 |
| icr163793_b_2 | 8.390048 | 11.8627717 | 53.81906 | | 292.462 | 924.5268145 | 4104.222 |
| icr163793_m_1 | 12.42748 | 18.3945962 | 37.84657 | | 266.3062 | 712.6702414 | 2356.366 |
| icr163793_m_2 | 2.142879 | 16.2880997 | 36.9986 | | 315.5809 | 1136.892296 | 2396.548 |
| icr163793_mr_1 | 8.143349 | 8.62949627 | 58.32448 | | 798.9356 | 1423.383589 | 4358.951 |
| icr163793_mr_2 | 11.32564 | 9.6747309 | 53.75454 | | 482.5628 | 1214.10171 | 4156.803 |
| icr163793_th_1 | 0.742094 | 8.59065494 | 32.35897 | | 474.9981 | 987.7330682 | 2132.094 |
| icr163793_th_2 | 1.995688 | 8.46362304 | 31.88232 | | 398.393 | 1238.628252 | 2063.105 |
| icr163794_a_1 | 2.135538 | 3.61321535 | 74.58843 | | 84.51678 | 708.9919892 | 5263.778 |
| icr163794_a_2 | 15.00223 | 8.90285735 | 37.28698 | | 121.8822 | 902.632499 | 2605.787 |
| icr163794_b_1 | 0.24723 | 17.5960334 | 36.29068 | | 171.2962 | 491.024357 | 2270.965 |
| icr163794_b_2 | 10.95067 | 10.8120328 | 32.00118 | | 262.0122 | 896.8043072 | 2229.137 |
| icr163794_m_1 | 0.132997 | 14.3149564 | 39.5838 | | 445.045 | 1039.697948 | 2698.134 |
| icr163794_m_2 | 8.858439 | 12.44692 | 36.1223 | | 402.1365 | 972.8160767 | 2472.462 |
| icr163794_mr_1 | 9.757901 | 4.23203525 | 31.41706 | | 668.6139 | 1218.021461 | 2278.796 |
| icr163794_mr_2 | 6.431951 | 10.2927531 | 33.5631 | | 798.0767 | 1170.47549 | 2201.829 |
| icr163794_th_1 | 10.94463 | 4.98250782 | 36.64839 | | 378.9024 | 883.812919 | 2978.842 |

|  | Phosphorous MgKg-1 |  |  |  | Potassium MgKg-1 |  |  |
|---|---|---|---|---|---|---|---|
| SSN | Fresh | Oven Dried | Milled |  | Fresh | Oven Dried | Milled |
| icr163783_a_1 | 214.5184 | 1119.406 | 1988.595 |  | 6468.052 | 12366.81 | 24917.07 |
| icr163783_a_2 | 165.2947 | 1526.463 | 2240.758 |  | 7707.258 | 19648.28 | 26560.28 |
| icr163783_b_1 | 86.63141 | 824.0637 | 1134.38 |  | 7632.559 | 15389.58 | 48765.41 |
| icr163783_b_2 | 242.9024 | 837.8643 | 1126.421 |  | 8895.814 | 25066.23 | 48555.32 |
| icr163783_m_1 | 210.0007 | 935.9499 | 2677.235 |  | 7645.475 | 16656.98 | 27737.23 |
| icr163783_m_2 | 364.1155 | 1341.656 | 2621.772 |  | 10110.39 | 22441.15 | 27728.87 |
| icr163783_mr_1 | 34.7114 | 133.9647 | 1311.408 |  | 7624.598 | 28141.62 | 49524.77 |
| icr163783_mr_2 | 11.57874 | 200.5515 | 1331.74 |  | 5616.354 | 24187.65 | 49418.68 |
| icr163783_th_1 | 278.6827 | 1035.648 | 2883.447 |  | 8500.706 | 26028.48 | 25087.49 |
| icr163783_th_2 | 414.2299 | 1591.167 | 2932.125 |  | 10271.15 | 23073.24 | 24654.39 |
| icr163784_a_1 | 162.0711 | 1063.479 | 1596.688 |  | 3820.248 | 13825.57 | 26651.98 |
| icr163784_a_2 | 64.44195 | 1614.045 | 1607.845 |  | 7308.705 | 19241.59 | 26826.77 |
| icr163784_b_1 | 19.95872 | 805.0856 | 2252.624 |  | 4168.58 | 17799.7 | 24102.64 |
| icr163784_b_2 | 91.42714 | 1280.236 | 2212.752 |  | 7950.217 | 20455.43 | 23528.98 |
| icr163784_m_1 | 27.90387 | 1087.67 | 994.9208 |  | 3282.849 | 13623.74 | 45416.41 |
| icr163784_m_2 | 108.4338 | 1469.598 | 1011.967 |  | 7781.042 | 18206.51 | 44102.27 |
| icr163784_mr_1 | 48.77617 | 192.8399 | 2519.616 |  | 5374.562 | 31132.89 | 28623.05 |
| icr163784_mr_2 | 59.84749 | 295.9244 | 2475.354 |  | 2989.728 | 27505.99 | 28867.36 |
| icr163784_th_1 | 240.9988 | 1416.674 | 981.9164 |  | 6722.545 | 24962.22 | 48878.57 |
| icr163784_th_2 | 1.666731 | 1630.949 | 952.2698 |  | 7801.336 | 24030.14 | 49365.89 |
| icr163785_a_1 | 69.37469 | 1471.327 | 2955.602 |  | 3647.908 | 8630.839 | 27674.29 |
| icr163785_a_2 | 68.61867 | 1758.972 | 2920.421 |  | 4040.389 | 12849.22 | 27924.34 |
| icr163785_b_1 | 125.8352 | 1500.307 | 1312.013 |  | 3870.106 | 10148 | 51048.47 |
| icr163785_b_2 | 30.49691 | 1495.836 | 1323.863 |  | 4571.25 | 13510.04 | 51174.06 |
| icr163785_m_1 | 8.067187 | 1637.654 | 2758.29 |  | 4750.338 | 11474.84 | 27304.43 |
| icr163785_m_2 | 106.2763 | 1505.147 | 2767.606 |  | 5296.694 | 13750.46 | 26759.7 |
| icr163785_mr_1 | 18.01655 | 301.7193 | 1223.542 |  | 1417.997 | 16041.79 | 52076.37 |
| icr163785_mr_2 | 147.4807 | 185.8632 | 1213.714 |  | 2382.372 | 9007.554 | 51549.76 |
| icr163785_th_1 | 23.56524 | 1433.433 | 2732.56 |  | 4644.236 | 14220.54 | 29847.6 |
| icr163785_th_2 | 72.44254 | 1870.694 | 2809.373 |  | 4051.428 | 15344.58 | 29870.46 |
| icr163786_a_1 | 20.09107 | 898.7552 | 1320.182 |  | 4054.226 | 11078.86 | 51342.49 |
| icr163786_a_2 | 34.64207 | 1061.211 | 1317.83 |  | 4960.339 | 16351.32 | 51363.19 |
| icr163786_b_1 | 56.56366 | 856.1638 | 2337.436 |  | 4213.609 | 19012.21 | 27893.48 |
| icr163786_b_2 | 141.7573 | 1033.819 | 2327.243 |  | 5367.044 | 21349.56 | 27542.86 |
| icr163786_m_1 | 57.56656 | 951.8026 | 1084.923 |  | 4176.714 | 13735.3 | 41681.38 |
| icr163786_m_2 | 138.817 | 1052.73 | 1103.896 |  | 5452.997 | 18830.63 | 41383.37 |

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|---|---|---|---|---|---|---|---|
| icr163786_mr_1 | 158.8958 | 306.741 | 2122.352 | | 3934.876 | 32815.92 | 31120.92 |
| icr163786_mr_2 | 33.64656 | 287.136 | 2198.356 | | 2935.232 | 22809.32 | 31763.27 |
| icr163786_th_1 | 133.1207 | 1356.267 | 1232.182 | | 6950.049 | 22441.57 | 52233.93 |
| icr163786_th_2 | 25.68496 | 1162.754 | 1210.891 | | 7392.426 | 22718.36 | 52329.35 |
| icr163787_a_1 | 22.99893 | 1133.183 | 2416.596 | | 3394.968 | 13496.49 | 29447.07 |
| icr163787_a_2 | 3.9046 | 1384.915 | 2426.415 | | 5290.688 | 19185.99 | 29430.56 |
| icr163787_b_1 | 100.6247 | 674.1199 | 1262.015 | | 5620.884 | 18003.37 | 49741.68 |
| icr163787_b_2 | 21.22451 | 1100.656 | 1267.991 | | 4540.32 | 27882.63 | 50194.05 |
| icr163787_m_1 | 105.129 | 1214.126 | 2037.391 | | 6016.648 | 15526.11 | 24706.9 |
| icr163787_m_2 | 107.7916 | 1191.069 | 2421.565 | | 6300.32 | 19861.5 | 26119.66 |
| icr163787_mr_1 | 91.56176 | 133.951 | 1157.044 | | 4014.546 | 19120.41 | 41443.96 |
| icr163787_mr_2 | 27.48365 | 183.8798 | 1108.102 | | 3344.857 | 18958.29 | 41645.06 |
| icr163787_th_1 | 39.6062 | 1179.484 | 1926.094 | | 4759.298 | 24803.96 | 30988.62 |
| icr163787_th_2 | 59.78433 | 1456.504 | 2026.441 | | 5144.976 | 22538.3 | 31782.84 |
| icr163788_a_1 | 4.957891 | 1089.973 | 932.1635 | | 5805.187 | 10706.01 | 51561.14 |
| icr163788_a_2 | 2.85486 | 1799.067 | 956.9261 | | 7962.449 | 20903.24 | 50996.63 |
| icr163788_b_1 | 181.6667 | 1156.065 | 1958.552 | | 8032.949 | 20427.31 | 29388.63 |
| icr163788_b_2 | 42.8626 | 1368.519 | 1930.746 | | 8662.025 | 25528.35 | 28991.95 |
| icr163788_m_1 | 81.4988 | 1162.993 | 921.2078 | | 7950.917 | 18193.16 | 48916.03 |
| icr163788_m_2 | 137.6439 | 1460.334 | 874.5432 | | 8258.809 | 20856.33 | 48482.02 |
| icr163788_mr_1 | 113.4293 | 343.8525 | 2368.039 | | 7091.938 | 31718.93 | 29304.54 |
| icr163788_mr_2 | 24.85075 | 364.8925 | 2316.875 | | 8249.587 | 22318.22 | 29132.34 |
| icr163788_th_1 | 74.11724 | 1634.8 | 1080.723 | | 7176.054 | 24078.67 | 49393.11 |
| icr163788_th_2 | 41.39353 | 1752.33 | 1060.578 | | 9690.695 | 27451.16 | 48673.68 |
| icr163789_a_1 | 25.96476 | 1397.85 | 1786.214 | | 6534.147 | 10438.27 | 27135.89 |
| icr163789_a_2 | 119.757 | 1421.694 | 1771.89 | | 7933.141 | 14024.14 | 26887.96 |
| icr163789_b_1 | 179.3978 | 1518.583 | 916.1151 | | 6630.237 | 13995.56 | 46339.18 |
| icr163789_b_2 | 12.53931 | 1520.329 | 885.8806 | | 7771.311 | 17604.17 | 46257.19 |
| icr163789_m_1 | 146.6648 | 1223.59 | 1988.62 | | 7766.98 | 13647.8 | 26594.56 |
| icr163789_m_2 | 36.28422 | 1706.496 | 1982.989 | | 7365.552 | 14584.92 | 27131.71 |
| icr163789_mr_1 | 48.62783 | 390.1473 | 999.9065 | | 5546.555 | 30457.4 | 45264.11 |
| icr163789_mr_2 | 47.47247 | 445.3749 | 1022.68 | | 7063.899 | 29235.57 | 45967.79 |
| icr163789_th_1 | 111.2825 | 1411.922 | 2036.19 | | 8610.078 | 17838.4 | 27220.6 |
| icr163789_th_2 | 214.4522 | 1689.835 | 2146.308 | | 8731.121 | 17863.37 | 26950.76 |
| icr163790_a_1 | 198.1978 | 1162.76 | 903.2627 | | 5401.83 | 13773.81 | 45888.14 |
| icr163790_a_2 | 283.4779 | 1228.311 | 952.0898 | | 6403.734 | 17071.76 | 45930.39 |
| icr163790_b_1 | 82.13187 | 773.5987 | 2841.596 | | 6442.784 | 19920 | 30529.12 |
| icr163790_b_2 | 47.09417 | 1268.84 | 2920.629 | | 6795.021 | 25013.06 | 30044.15 |
| icr163790_m_1 | 254.3822 | 1209.036 | 1838.075 | | 5798.48 | 13133.16 | 51566.73 |
| icr163790_m_2 | 177.3592 | 1500.984 | 1897.509 | | 6478.789 | 24132.2 | 51405.62 |

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|---|---|---|---|---|---|---|---|
| icr163790_mr_1 | 86.40111 | 305.1518 | 2175.063 | | 5238.91 | 28898.15 | 29924.54 |
| icr163790_mr_2 | 235.1918 | 417.9924 | 2155.273 | | 6258.982 | 26782.81 | 29457.78 |
| icr163790_th_1 | 276.5815 | 946.5797 | 1050.582 | | 6281.391 | 25384.83 | 49579.16 |
| icr163790_th_2 | 105.6639 | 1533.176 | 1044.889 | | 6652.235 | 28361.9 | 49562.87 |
| icr163791_a_1 | 83.17941 | 638.0229 | 2444.308 | | 5291.817 | 11306.87 | 27423.53 |
| icr163791_a_2 | 65.38159 | 1151.702 | 2508.511 | | 6902.638 | 17110.1 | 27650.25 |
| icr163791_b_1 | 63.41649 | 873.3101 | 1628.518 | | 6435.988 | 16080.96 | 50666.22 |
| icr163791_b_2 | 315.3778 | 1049.058 | 1324.885 | | 6992.41 | 25327.65 | 47755.16 |
| icr163791_m_1 | 11.50843 | 883.6021 | 2197.519 | | 6766.972 | 14164.82 | 26817.61 |
| icr163791_m_2 | 453.8354 | 1056.409 | 2221.713 | | 8638.35 | 21956.02 | 26775 |
| icr163791_mr_1 | 4.705196 | 242.6187 | 1113.092 | | 4418.811 | 18002.87 | 39138.48 |
| icr163791_mr_2 | 12.84101 | 283.0187 | 1158.154 | | 3951.896 | 24168.38 | 39288.2 |
| icr163791_th_1 | 46.69036 | 673.9222 | 2492.093 | | 7480.455 | 16111.26 | 27446.09 |
| icr163791_th_2 | 55.98772 | 1493.344 | 2524.318 | | 7546.88 | 26965.66 | 27252.32 |
| icr163791_th_6.1 | 119.8694 | 832.2432 | 1435.561 | | 5772.017 | 15313.56 | 43490.23 |
| icr163791_th_6.2 | 197.6853 | 914.2191 | 1443.73 | | 6404.677 | 17367.04 | 44324.5 |
| icr163792_a_1 | 39.3312 | 1168.728 | 2159.38 | | 6872.541 | 13076.12 | 25353 |
| icr163792_a_2 | 27.27541 | 1019.102 | 2464.816 | | 6238.207 | 21373.79 | 25464.1 |
| icr163792_b_1 | 79.73445 | 849.6991 | 1303.183 | | 7312.317 | 17881.19 | 45607.26 |
| icr163792_b_2 | 108.6095 | 1001.827 | 1294.553 | | 8296.814 | 24549.44 | 45600.76 |
| icr163792_m-1 | 102.4505 | 421.3422 | 2731.557 | | 5653.085 | 17101.51 | 34886.28 |
| icr163792_m_2 | 64.88867 | 640.3789 | 2701.094 | | 6152.245 | 13965.87 | 34718.95 |
| icr163792_mr_1 | 171.0102 | 509.0411 | 1214.52 | | 8551.908 | 39415.14 | 46870.3 |
| icr163792_mr_2 | 216.7317 | 509.1529 | 1205.742 | | 9296.56 | 23432.09 | 47052.9 |
| icr163792_th_1 | 0.245881 | 1296.948 | 2078.251 | | 7213.847 | 19217.59 | 34200.03 |
| icr163792_th_2 | 62.38792 | 1532.775 | 2036.444 | | 5915.54 | 24478.45 | 34061.88 |
| icr163793_a_1 | 3.791684 | 757.978 | 874.018 | | 7578.901 | 13251.2 | 41098.07 |
| icr163793_a_2 | 124.2397 | 1077.553 | 867.9882 | | 8157.529 | 20050.26 | 41148.15 |
| icr163793_b_1 | 18.44111 | 891.3898 | 2186.227 | | 9135.162 | 16016.5 | 32885.72 |
| icr163793_b_2 | 3.742626 | 1479.528 | 2475.871 | | 10172.77 | 21837.05 | 34421.34 |
| icr163793_m_1 | 23.41665 | 433.2906 | 827.7846 | | 6611.677 | 18171.94 | 48636.6 |
| icr163793_m_2 | | 695.3842 | 846.1065 | | 7456.999 | 26266.54 | 49651 |

| | **Calcium MgKg$^{-1}$** | | | | | **Manganese (MgKg$^{-1}$)** | |
|---|---|---|---|---|---|---|---|
| SSN | Fresh | Oven Dried | Milled | | Fresh | Oven Dried | Milled |
| icr163783_a_1 | 1721.61913 | 3414.128 | 6133.24634 | | 99.866901 | 224.9187 | 123.9156863 |
| icr163783_a_2 | 1803.334577 | 5010.166 | 6271.88373 | | 126.80824 | 240.6204 | 123.1895613 |
| icr163783_b_1 | 1291.464637 | 2264.043 | 6213.36055 | | 59.629215 | 87.88821 | 68.95591125 |
| icr163783_b_2 | 1243.408405 | 3206.14 | 6212.44154 | | 67.47342 | 139.8681 | 108.6240951 |
| icr163783_m_1 | 1545.357505 | 2936.45 | 5664.49713 | | 71.660077 | 183.2195 | 93.91418371 |
| icr163783_m_2 | 1548.718094 | 4576.237 | 5687.77372 | | 74.91583 | 276.9714 | 89.99373664 |
| icr163783_mr_1 | 868.9949338 | 3041.987 | 5593.79767 | | 24.269896 | 148.3339 | 73.80242323 |
| icr163783_mr_2 | 644.7380128 | 2758.315 | 5573.77261 | | 28.369922 | 190.1819 | 72.17747504 |
| icr163783_th_1 | 1792.720634 | 4674.934 | 5848.6724 | | 85.554797 | 235.4516 | 144.4588995 |
| icr163783_th_2 | 1619.414038 | 5303.453 | 5728.6618 | | 98.98294 | 119.5279 | 143.5345921 |
| icr163784_a_1 | 1631.776219 | 3637.665 | 5219.41199 | | 111.15808 | 209.009 | 129.0753755 |
| icr163784_a_2 | 1567.339902 | 5424.721 | 5273.24323 | | 61.402439 | 145.4193 | 102.4125505 |
| icr163784_b_1 | 867.9853963 | 2346.666 | 6536.96318 | | 90.739215 | 124.4113 | 113.92282 |
| icr163784_b_2 | 997.1920386 | 3230.251 | 6319.99721 | | 63.134031 | 136.2884 | 115.9119162 |
| icr163784_m_1 | 718.0949759 | 2661.707 | 4966.73987 | | 73.646727 | 179.7395 | 66.46735933 |
| icr163784_m_2 | 1254.01769 | 4372.757 | 4838.13643 | | 79.757716 | 209.8494 | 66.05953217 |
| icr163784_mr_1 | 557.027466 | 3074.708 | 5865.26779 | | 15.551958 | 123.9309 | 101.314106 |
| icr163784_mr_2 | 308.106364 | 2864.777 | 5925.43281 | | 14.977854 | 116.7147 | 103.8827991 |
| icr163784_th_1 | 1238.558067 | 5186.504 | 5277.37163 | | 57.912759 | 219.3773 | 57.8129723 |
| icr163784_th_2 | 1147.623861 | 6032.417 | 5355.21047 | | 54.452454 | 232.1562 | 59.97857033 |
| icr163785_a_1 | 1476.635655 | 2525.604 | 5917.58178 | | 116.3164 | 303.3752 | 108.253466 |
| icr163785_a_2 | 2021.009256 | 4564.836 | 5976.33636 | | 127.9081 | 393.8486 | 116.0098289 |
| icr163785_b_1 | 907.2460708 | 2168.693 | 5564.7399 | | 57.81041 | 216.1708 | 67.1463499 |
| icr163785_b_2 | 1144.86296 | 3097.593 | 5608.92056 | | 49.801824 | 256.5706 | 65.19626115 |

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|---|---|---|---|---|---|---|---|
| icr163785_m_1 | 1106.951531 | 3043.88 | 5764.38848 | | 76.981589 | 225.4695 | 118.0067239 |
| icr163785_m_2 | 1218.187439 | 3337.159 | 5647.38838 | | 101.99564 | 272.0347 | 123.724274 |
| icr163785_mr_1 | 296.7033135 | 2568.012 | 5478.66878 | | 26.102757 | 196.2821 | 63.33634623 |
| icr163785_mr_2 | 555.9942709 | 2018.449 | 5427.69757 | | 43.71442 | 202.2001 | 64.00685665 |
| icr163785_th_1 | 1123.836202 | 3572.483 | 5437.26583 | | 53.293213 | 300.4436 | 114.3688648 |
| icr163785_th_2 | 829.2575235 | 5251.93 | 5453.12224 | | 62.437176 | 308.3794 | 123.6923017 |
| icr163786_a_1 | 985.4402273 | 2359.478 | 5405.47604 | | 123.95615 | 208.2893 | 72.92021181 |
| icr163786_a_2 | 1574.629487 | 4143.781 | 5386.05427 | | 88.591476 | 308.2432 | 71.0858562 |
| icr163786_b_1 | 517.3423573 | 2428.445 | 4930.69996 | | 84.93205 | 162.6671 | 81.33179399 |
| icr163786_b_2 | 642.0237816 | 2762.877 | 4841.64619 | | 47.301397 | 173.5055 | 84.53428867 |
| icr163786_m_1 | 767.0175724 | 2413.544 | 4453.43505 | | 105.39068 | 196.5874 | 58.12733192 |
| icr163786_m_2 | 1014.947905 | 3212.214 | 4438.00847 | | 95.079572 | 255.1786 | 58.38108839 |
| icr163786_mr_1 | 374.7195751 | 3487.502 | 5645.89131 | | 29.863634 | 168.331 | 95.21978104 |
| icr163786_mr_2 | 514.514741 | 2838.756 | 5800.8709 | | 27.67305 | 140.4176 | 94.63548089 |
| icr163786_th_1 | 1437.904022 | 4622.472 | 4912.33802 | | 73.817571 | 265.5124 | 59.98206506 |
| icr163786_th_2 | 1406.576592 | 4049.911 | 4957.11918 | | 70.686925 | 290.9201 | 72.76033775 |
| icr163787_a_1 | 848.5074768 | 3383.776 | 5174.92516 | | 77.024636 | 196.6056 | 116.1566508 |
| icr163787_a_2 | 1545.719815 | 5487.182 | 5159.02846 | | 76.423205 | 226.6341 | 120.0526387 |
| icr163787_b_1 | 651.6735152 | 2480.345 | 5006.83214 | | 58.03813 | 113.3216 | 70.03044034 |
| icr163787_b_2 | 491.7217545 | 4899.684 | 5040.61485 | | 53.248624 | 167.0832 | 71.21243513 |
| icr163787_m_1 | 1056.764684 | 3520.372 | 5335.49944 | | 70.238358 | 203.4026 | 121.8219499 |
| icr163787_m_2 | 1297.077511 | 5354.704 | 5415.34919 | | 66.210967 | 240.1106 | 127.5068843 |
| icr163787_mr_1 | 414.3841806 | 2433.855 | 4994.47524 | | 47.913722 | 145.2012 | 71.82990706 |
| icr163787_mr_2 | 673.840016 | 2479.491 | 5028.97766 | | 21.399117 | 188.2389 | 75.11299893 |
| icr163787_th_1 | 1051.110578 | 5273.64 | 5009.06855 | | 37.348748 | 250.922 | 110.042919 |
| icr163787_th_2 | 770.100835 | 5915.651 | 5083.29157 | | 39.837839 | 251.0555 | 109.2545562 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| icr163788_a_1 | 1950.110754 | 3836.752 | 5164.38956 |  | 158.15703 | 324.2683 | 71.27881519 |
| icr163788_a_2 | 1698.901028 | 6251.025 | 5150.93304 |  | 46.074701 | 399.3161 | 72.10150082 |
| icr163788_b_1 | 974.4815013 | 3047.852 | 4827.78466 |  | 93.833367 | 201.9492 | 89.49443775 |
| icr163788_b_2 | 1391.535093 | 4470.179 | 4747.07232 |  | 87.047545 | 254.2392 | 91.00600259 |
| icr163788_m_1 | 1348.492765 | 3089.405 | 4954.47382 |  | 114.29677 | 296.8302 | 56.25884762 |
| icr163788_m_2 | 1654.260443 | 5134.051 | 4905.25045 |  | 56.552972 | 296.2546 | 59.03436523 |
| icr163788_mr_1 | 710.939297 | 3541.107 | 5218.42669 |  | 25.055125 | 123.3605 | 105.6409547 |
| icr163788_mr_2 | 841.0807568 | 2605.095 | 5251.31826 |  | 38.914752 | 128.6823 | 104.4072666 |
| icr163788_th_1 | 2249.738191 | 7269.103 | 5187.07414 |  | 63.624635 | 351.5332 | 69.61293711 |
| icr163788_th_2 | 1712.688741 | 6746.325 | 5163.31491 |  | 87.494033 | 384.1632 | 71.37398167 |
| icr163789_a_1 | 1681.245392 | 2965.712 | 5651.73547 |  | 100.87727 | 224.6746 | 92.29345389 |
| icr163789_a_2 | 1849.358054 | 4235.515 | 5543.04848 |  | 115.97255 | 266.491 | 90.56176703 |
| icr163789_b_1 | 941.6423468 | 2369.697 | 4917.99182 |  | 153.32302 | 163.5209 | 60.99982454 |
| icr163789_b_2 | 1235.759491 | 3546.981 | 4918.90455 |  | 92.464037 | 201.567 | 57.9666718 |
| icr163789_m_1 | 1256.482457 | 3028.909 | 5484.30157 |  | 162.36371 | 202.843 | 82.49987862 |
| icr163789_m_2 | 1237.083912 | 3650.136 | 5632.70104 |  | 112.11266 | 248.3264 | 87.5905911 |
| icr163789_mr_1 | 538.2743573 | 3564.793 | 5168.4858 |  | 26.306066 | 161.31 | 64.51533836 |
| icr163789_mr_2 | 788.3529007 | 3264.937 | 5248.93773 |  | 15.400353 | 139.3653 | 60.17788429 |
| icr163789_th_1 | 1154.86029 | 4415.426 | 6420.88607 |  | 98.1573 | 266.9606 | 93.20419302 |
| icr163789_th_2 | 1575.270188 | 3971.141 | 6320.35333 |  | 101.13004 | 239.3939 | 97.61114779 |
| icr163790_a_1 | 1673.863592 | 3834.174 | 5206.88823 |  | 117.57285 | 239.953 | 51.43527854 |
| icr163790_a_2 | 1941.838474 | 4944.384 | 5161.831 |  | 79.554425 | 348.2664 | 56.34397196 |
| icr163790_b_1 | 878.3506665 | 2547.094 | 6133.0301 |  | 70.541227 | 137.102 | 102.6942456 |
| icr163790_b_2 | 953.9751363 | 3549.906 | 6010.1739 |  | 60.782213 | 215.2683 | 110.6945315 |
| icr163790_m_1 | 1085.606315 | 3090.014 | 5829.23908 |  | 67.56449 | 196.0182 | 71.53900323 |
| icr163790_m_2 | 1302.918535 | 5230.726 | 5778.64963 |  | 68.109213 | 248.5858 | 72.0984884 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| icr163790_mr_1 | 622.4500363 | 2756.942 | 5402.58714 |  | 21.912366 | 129.2178 | 106.2747602 |
| icr163790_mr_2 | 766.9869281 | 2768.644 | 5296.42307 |  | 18.368143 | 115.8878 | 102.6439666 |
| icr163790_th_1 | 1326.294058 | 6095.302 | 5141.73966 |  | 56.74179 | 284.9583 | 67.84413357 |
| icr163790_th_2 | 1916.549477 | 5123.353 | 5152.83952 |  | 45.74759 | 268.2593 | 69.80493053 |
| icr163791_a_1 | 1024.168031 | 1490.229 | 5865.59132 |  | 108.99283 | 233.6371 | 134.4678408 |
| icr163791_a_2 | 1475.077473 | 2765.664 | 5877.9586 |  | 93.166955 | 146.0577 | 136.2694156 |
| icr163791_b_1 | 656.329043 | 1628.457 | 5175.20145 |  | 75.092913 | 137.4675 | 73.08981548 |
| icr163791_b_2 | 769.1923951 | 2557.263 | 5304.04625 |  | 58.25227 | 165.4977 | 72.24765129 |
| icr163791_m_1 | 814.5053531 | 1709.941 | 4457.14164 |  | 62.105022 | 145.3377 | 129.3931057 |
| icr163791_m_2 | 1102.065239 | 2778.343 | 4449.55478 |  | 61.074248 | 153.2484 | 129.0541841 |
| icr163791_mr_1 | 453.490006 | 1767.828 | 4144.1741 |  | 29.357596 | 208.0044 | 56.58490493 |
| icr163791_mr_2 | 443.7385648 | 2377.705 | 4163.12567 |  | 30.702913 | 163.7601 | 53.85920114 |
| icr163791_th_1 | 795.6194732 | 1914.18 | 5384.12463 |  | 51.072156 | 189.6643 | 276.5481862 |
| icr163791_th_2 | 754.6343947 | 3597.547 | 5340.11722 |  | 44.615307 | 227.5028 | 266.7094483 |
| icr163791_th_6.1 | 703.9353575 | 2683.548 | 4773.70882 |  | 73.513319 | 150.8551 | 123.0588637 |
| icr163791_th_6.2 | 888.1361548 | 3226.331 | 4866.14833 |  | 55.288675 | 155.4651 | 134.5113411 |
| icr163792_a_1 | 1037.29748 | 6511.598 | 5181.95676 |  | 67.021615 | 126.1713 | 143.0407872 |
| icr163792_a_2 | 3159.293059 | 5667.28 | 5248.49947 |  | 123.85183 | 181.8632 | 144.0511062 |
| icr163792_b_1 | 921.0513867 | 2778.087 | 4860.61248 |  | 97.23583 | 179.4103 | 70.51730176 |
| icr163792_b_2 | 1007.103131 | 4116.42 | 4839.59785 |  | 86.163453 | 191.1388 | 70.46831499 |
| icr163792_m-1 | 700.6815467 | 2172.178 | 5142.78007 |  | 52.332181 | 135.5381 | 175.6274753 |
| icr163792_m_2 | 1234.222095 | 3928.327 | 5131.15793 |  | 63.631555 | 191.8356 | 171.2817362 |
| icr163792_mr_1 | 950.1609678 | 4950.282 | 4817.79528 |  | 51.418093 | 215.2479 | 148.501244 |
| icr163792_mr_2 | 1286.029775 | 3144.646 | 4844.55882 |  | 34.94613 | 205.4181 | 147.202009 |
| icr163792_th_1 | 1191.444906 | 5019.211 | 5492.38394 |  | 92.213667 | 266.5818 | 136.9225067 |
| icr163792_th_2 | 3164.24451 | 5729.061 | 5503.25287 |  | 72.598943 | 238.3871 | 140.3438623 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| icr163793_a_1 | 1062.144102 | 2363.506 | 4198.05375 | | 90.887776 | 146.9537 | 66.90230282 |
| icr163793_a_2 | 1227.363714 | 3250.431 | 4182.21167 | | 80.446853 | 167.8456 | 65.17128037 |
| icr163793_b_1 | 884.3265548 | 2174.41 | 5215.38559 | | 90.56474 | 139.7295 | 225.6087758 |
| icr163793_b_2 | 1047.208442 | 2942.943 | 5180.71451 | | 80.606292 | 141.2239 | 226.1865325 |
| icr163793_m_1 | 776.2915125 | 1965.682 | 4734.22914 | | 82.226205 | 120.8879 | 80.08109242 |
| icr163793_m_2 | 880.0777646 | 3166.908 | 4819.8225 | | 58.926746 | 158.7378 | 78.3269383 |
| icr163793_mr_1 | 741.6250977 | 3913.814 | 5589.54002 | | 56.291822 | 254.7597 | 133.5072568 |
| icr163793_mr_2 | 1022.30703 | 3067.329 | 5668.58149 | | 47.619034 | 238.8027 | 130.0121259 |
| icr163793_th_1 | 1455.038465 | 2799.643 | 4510.10346 | | 131.16403 | 182.9612 | 65.29749816 |
| icr163793_th_2 | 1587.232072 | 3843.043 | 4543.22549 | | 144.46207 | 230.8873 | 67.07683314 |
| icr163794_a_1 | 1038.760482 | 2024.148 | 5278.97748 | | 71.793919 | 292.6268 | 101.0156621 |
| icr163794_a_2 | 1100.319161 | 3112.315 | 5322.37287 | | 108.34574 | 293.0571 | 102.7496482 |
| icr163794_b_1 | 967.5980584 | 1801.363 | 4589.49858 | | 115.06438 | 135.285 | 91.23333464 |
| icr163794_b_2 | 1076.415155 | 2786.073 | 4610.21201 | | 94.315841 | 210.9883 | 89.55709184 |
| icr163794_m_1 | 807.5693516 | 2421.861 | 5311.69515 | | 48.638081 | 153.0197 | 182.251118 |
| icr163794_m_2 | 852.0040505 | 3042.653 | 5235.77735 | | 54.84105 | 199.6352 | 192.7982818 |
| icr163794_mr_1 | 719.9319362 | 2648.047 | 4884.47508 | | 37.658037 | 192.2176 | 86.53766536 |
| icr163794_mr_2 | 734.402666 | 2104.318 | 4966.29173 | | 45.528802 | 223.2875 | 83.57755949 |
| icr163794_th_1 | 1039.286691 | 2870.652 | 6742.13932 | | 67.599172 | 229.8329 | 94.59832431 |

| | **Iron $MgKg^{-1}$** | | | | **Copper $MgKg^{-1}$** | | |
|---|---|---|---|---|---|---|---|
| SSN | Fresh | Oven Dried | Milled | | Fresh | Oven Dried | Milled |
| icr163783_a_1 | 476.8691 | 922.7485 | 347.6901 | | 18.79151 | 35.10623 | 9.523415 |
| icr163783_a_2 | 433.664 | 1248.776 | 411.3636 | | 15.1992 | 27.14748 | 12.13331 |
| icr163783_b_1 | 406.7366 | 409.9846 | 273.7329 | | 15.72335 | 20.10623 | 7.811576 |
| icr163783_b_2 | 325.1942 | 630.7845 | 431.8945 | | 13.36122 | 20.73318 | 13.83778 |
| icr163783_m_1 | 328.4152 | 836.6048 | 282.0622 | | 13.8116 | 29.10261 | 29.95884 |
| icr163783_m_2 | 305.5171 | 1052.64 | 271.9709 | | 7.013654 | 28.90507 | 32.4889 |
| icr163783_mr_1 | 63.9694 | 310.8554 | 246.5091 | | 5.733956 | 21.15729 | 7.681835 |
| icr163783_mr_2 | 76.71173 | 632.0781 | 259.5007 | | 4.850348 | 17.76773 | 8.319221 |
| icr163783_th_1 | 426.1916 | 729.5904 | 177.3569 | | 10.37809 | 19.14892 | 6.173026 |
| icr163783_th_2 | 479.1595 | 515.3095 | 177.0001 | | 13.44392 | 14.08284 | 6.122884 |
| icr163784_a_1 | 507.5276 | 779.45 | 241.5552 | | 16.96415 | 33.95075 | 9.603228 |
| icr163784_a_2 | 229.8452 | 502.6161 | 213.102 | | 7.700815 | 21.65253 | 6.721848 |
| icr163784_b_1 | 538.4251 | 697.406 | 312.3015 | | 15.7055 | 37.25591 | 5.886829 |
| icr163784_b_2 | 322.6448 | 509.7672 | 303.7351 | | 12.08301 | 22.11101 | 6.133757 |
| icr163784_m_1 | 413.3173 | 761.124 | 175.4216 | | 15.46176 | 35.74285 | 4.980275 |
| icr163784_m_2 | 379.9268 | 917.1879 | 166.9072 | | 12.91461 | 26.32252 | 5.194684 |
| icr163784_mr_1 | 59.25372 | 396.4873 | 176.7551 | | 4.537975 | 18.92117 | 5.190658 |
| icr163784_mr_2 | 45.3654 | 325.2023 | 178.0831 | | 4.193986 | 17.2412 | 4.98525 |
| icr163784_th_1 | 405.5505 | 983.6041 | 138.4181 | | 7.514234 | 22.03291 | 4.859973 |
| icr163784_th_2 | 314.114 | 1001.772 | 132.0941 | | 8.630559 | 22.6124 | 4.420512 |
| icr163785_a_1 | 229.1739 | 653.5914 | 267.9017 | | 12.80631 | 32.33814 | 5.493662 |
| icr163785_a_2 | 291.9629 | 675.4837 | 272.9609 | | 11.10883 | 31.80532 | 5.764468 |
| icr163785_b_1 | 272.084 | 558.3458 | 206.4896 | | 15.56278 | 35.46842 | 5.002833 |

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|---|---|---|---|---|---|---|---|
| icr163785_b_2 | 174.5633 | 548.091 | 181.7459 | | 10.27043 | 29.77854 | 5.152942 |
| icr163785_m_1 | 245.4644 | 515.9909 | 252.987 | | 15.39472 | 34.10698 | 6.696154 |
| icr163785_m_2 | 278.9386 | 605.8918 | 259.8774 | | 12.8407 | 28.52489 | 6.218549 |
| icr163785_mr_1 | 63.48689 | 483.2241 | 146.0475 | | 6.030917 | 19.44538 | 4.263723 |
| icr163785_mr_2 | 156.5164 | 270.629 | 146.4056 | | 4.929762 | 17.59153 | 4.091254 |
| icr163785_th_1 | 143.8934 | 646.5795 | 291.5822 | | 7.155027 | 25.55958 | 5.474932 |
| icr163785_th_2 | 178.9703 | 599.5682 | 290.0403 | | 7.899342 | 24.03119 | 5.660627 |
| icr163786_a_1 | 516.6516 | 569.3988 | 178.9085 | | 20.45384 | 33.63609 | 4.640755 |
| icr163786_a_2 | 355.4315 | 717.114 | 181.3832 | | 13.03482 | 26.7548 | 4.756911 |
| icr163786_b_1 | 482.1953 | 410.198 | 162.6738 | | 17.77091 | 33.82646 | 5.761508 |
| icr163786_b_2 | 234.9037 | 520.4935 | 165.0811 | | 8.728476 | 28.30671 | 5.901462 |
| icr163786_m_1 | 490.9494 | 645.8409 | 145.4427 | | 17.898 | 32.6009 | 4.854243 |
| icr163786_m_2 | 498.0474 | 742.8677 | 142.2766 | | 11.38267 | 27.68158 | 5.307693 |
| icr163786_mr_1 | 96.3589 | 437.0218 | 359.239 | | 5.482531 | 18.33933 | 6.202907 |
| icr163786_mr_2 | 138.4763 | 287.4551 | 354.3588 | | 4.556112 | 14.19292 | 6.535906 |
| icr163786_th_1 | 322.7051 | 692.1161 | 393.1514 | | 8.435695 | 22.59742 | 5.465384 |
| icr163786_th_2 | 299.5259 | 551.3526 | 556.5482 | | 12.38991 | 20.7534 | 5.498063 |
| icr163787_a_1 | 311.7975 | 583.4 | 254.465 | | 17.67957 | 30.43553 | 6.358285 |
| icr163787_a_2 | 217.0786 | 516.0406 | 248.6602 | | 11.01978 | 25.02498 | 6.569679 |
| icr163787_b_1 | 391.1152 | 418.8162 | 163.0965 | | 15.73892 | 22.76285 | 5.00213 |
| icr163787_b_2 | 233.1257 | 572.7689 | 181.4308 | | 9.96997 | 22.26594 | 5.980401 |
| icr163787_m_1 | 280.8993 | 693.8127 | 292.9343 | | 14.06141 | 31.20656 | 5.704348 |
| icr163787_m_2 | 203.8715 | 724.2852 | 300.6226 | | 9.888848 | 28.55305 | 5.74685 |
| icr163787_mr_1 | 307.9324 | 237.1796 | 175.6203 | | 25.17064 | 18.27538 | 4.058029 |
| icr163787_mr_2 | 60.8917 | 449.2101 | 180.5408 | | 4.212205 | 13.51146 | 4.170898 |
| icr163787_th_1 | 164.0599 | 744.4925 | 323.0227 | | 6.921536 | 21.28215 | 6.144443 |

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|---|---|---|---|---|---|---|---|
| icr163787_th_2 | 169.6044 | 590.4857 | 327.3536 | | 7.392 | 21.35354 | 6.306613 |
| icr163788_a_1 | 433.2318 | 1210.549 | 186.5412 | | 18.21153 | 31.81654 | 4.926779 |
| icr163788_a_2 | 182.1217 | 1686.259 | 187.7853 | | 6.236982 | 28.60165 | 4.974223 |
| icr163788_b_1 | 429.1417 | 1105.066 | 500.2657 | | 15.85715 | 34.70982 | 6.139881 |
| icr163788_b_2 | 539.8527 | 1361.976 | 499.675 | | 9.933463 | 27.70294 | 5.983404 |
| icr163788_m_1 | 579.9697 | 1320.312 | 175.2091 | | 20.78809 | 33.79082 | 5.363113 |
| icr163788_m_2 | 289.7999 | 1438.391 | 168.5604 | | 8.455842 | 29.05682 | 5.317547 |
| icr163788_mr_1 | 93.25377 | 360.0397 | 201.8671 | | 6.903228 | 19.82767 | 5.294508 |
| icr163788_mr_2 | 170.3468 | 352.7262 | 190.2579 | | 5.954905 | 15.82199 | 5.729164 |
| icr163788_th_1 | 299.9443 | 1642.752 | 148.2493 | | 10.42265 | 20.91218 | 4.112167 |
| icr163788_th_2 | 490.1223 | 1692.647 | 155.0244 | | 9.562297 | 24.0728 | 4.349614 |
| icr163789_a_1 | 464.8953 | 695.389 | 210.1318 | | 18.05983 | 34.01385 | 4.86623 |
| icr163789_a_2 | 536.0704 | 859.8742 | 199.1243 | | 13.34291 | 28.51961 | 4.712067 |
| icr163789_b_1 | 1083.204 | 707.6317 | 162.2504 | | 15.72167 | 32.12721 | 7.925879 |
| icr163789_b_2 | 595.9957 | 971.0002 | 161.7892 | | 11.65251 | 25.80052 | 8.230142 |
| icr163789_m_1 | 957.4312 | 853.8696 | 245.8283 | | 19.28082 | 34.40698 | 5.277286 |
| icr163789_m_2 | 519.7941 | 886.3268 | 240.6847 | | 14.4984 | 25.35998 | 5.054693 |
| icr163789_mr_1 | 98.27006 | 316.7288 | 189.9859 | | 6.156737 | 17.3939 | 4.514349 |
| icr163789_mr_2 | 52.25831 | 363.2525 | 188.5344 | | 3.904262 | 18.49742 | 4.509053 |
| icr163789_th_1 | 504.9175 | 888.6948 | 259.2091 | | 8.860253 | 19.4298 | 5.705599 |
| icr163789_th_2 | 700.2788 | 860.323 | 241.6708 | | 11.28957 | 20.86639 | 5.88137 |
| icr163790_a_1 | 287.4492 | 493.4662 | 150.819 | | 16.13032 | 35.30293 | 5.111189 |
| icr163790_a_2 | 297.2289 | 549.7089 | 158.0315 | | 9.606454 | 28.44281 | 5.974943 |
| icr163790_b_1 | 302.3982 | 549.7718 | 210.3076 | | 15.22666 | 40.628 | 6.333297 |
| icr163790_b_2 | 259.0295 | 795.7516 | 224.052 | | 9.397013 | 29.60041 | 5.166366 |
| icr163790_m_1 | 390.1997 | 651.5993 | 252.8001 | | 20.68705 | 34.74301 | 5.054985 |

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|---|---|---|---|---|---|---|---|
| icr163790_m_2 | 336.9634 | 754.1689 | 252.6314 | | 10.58496 | 30.34366 | 4.777751 |
| icr163790_mr_1 | 95.45744 | 500.9827 | 268.3377 | | 7.662765 | 19.0882 | 5.557624 |
| icr163790_mr_2 | 48.99363 | 348.3386 | 268.7969 | | 3.512671 | 14.99434 | 5.923919 |
| icr163790_th_1 | 184.4009 | 967.8812 | 215.603 | | 7.590265 | 21.06062 | 7.161632 |
| icr163790_th_2 | 171.8612 | 877.2993 | 214.3187 | | 7.534044 | 21.77282 | 6.744508 |
| icr163791_a_1 | 335.1223 | 495.182 | 325.9859 | | 21.954 | 33.37628 | 5.022287 |
| icr163791_a_2 | 282.1228 | 355.084 | 326.9211 | | 15.46484 | 20.98435 | 5.03782 |
| icr163791_b_1 | 258.062 | 422.4811 | 224.0227 | | 15.76422 | 34.75841 | 5.294811 |
| icr163791_b_2 | 221.9099 | 587.927 | 240.4611 | | 13.69464 | 29.90557 | 5.324966 |
| icr163791_m_1 | 313.0159 | 463.9099 | 668.5987 | | 18.22352 | 32.68418 | 6.673136 |
| icr163791_m_2 | 262.6839 | 539.3239 | 697.0124 | | 13.28802 | 27.48524 | 6.431368 |
| icr163791_mr_1 | 81.84994 | 260.363 | 137.7313 | | 6.393424 | 16.7339 | 4.88471 |
| icr163791_mr_2 | 62.90882 | 209.046 | 139.1133 | | 6.100331 | 12.63619 | 5.627691 |
| icr163791_th_1 | 182.8621 | 518.8276 | 325.5089 | | 9.994121 | 20.30206 | 5.219555 |
| icr163791_th_2 | 188.015 | 478.8008 | 335.4261 | | 9.93858 | 21.18924 | 5.371056 |
| icr163791_th_6.1 | 214.5393 | 459.8125 | 198.4264 | | 14.68406 | 25.62391 | 9.777018 |
| icr163791_th_6.2 | 174.2244 | 450.4655 | 225.5444 | | 11.3384 | 26.81767 | 5.896862 |
| icr163792_a_1 | 281.2144 | 442.0964 | 332.4141 | | 15.83764 | 36.3051 | 6.529122 |
| icr163792_a_2 | 244.2874 | 435.8557 | 338.3897 | | 11.9174 | 34.99754 | 6.596154 |
| icr163792_b_1 | 399.8526 | 572.7935 | 199.8532 | | 17.13019 | 35.65774 | 4.722194 |
| icr163792_b_2 | 259.3802 | 539.4078 | 193.5083 | | 12.26237 | 27.86212 | 4.476363 |
| icr163792_m-1 | 225.477 | 337.8426 | 580.2771 | | 11.27017 | 27.43932 | 5.451203 |
| icr163792_m_2 | 167.2301 | 370.9547 | 624.5276 | | 8.522962 | 24.6006 | 5.30495 |
| icr163792_mr_1 | 126.8537 | 358.6315 | 413.1997 | | 7.705226 | 22.14658 | 6.1688 |
| icr163792_mr_2 | 135.6741 | 360.7144 | 404.2868 | | 5.603687 | 21.35219 | 6.108069 |
| icr163792_th_1 | 236.0008 | 549.1766 | 307.4811 | | 15.25867 | 30.38834 | 4.950826 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| icr163792_th_2 | 275.6996 | 524.2975 | 281.0448 | | 11.48177 | 27.14517 | 4.721255 |
| icr163793_a_1 | 318.7093 | 594.0567 | 176.6433 | | 21.55944 | 36.40356 | 6.000715 |
| icr163793_a_2 | 276.4114 | 567.1283 | 180.7332 | | 16.57645 | 29.6527 | 5.40498 |
| icr163793_b_1 | 285.9009 | 508.5553 | 347.1221 | | 24.10846 | 36.07206 | 7.243818 |
| icr163793_b_2 | 290.4553 | 463.6819 | 345.5095 | | 17.49426 | 29.05478 | 7.335824 |
| icr163793_m_1 | 258.4343 | 461.7711 | 248.0777 | | 19.4682 | 29.23748 | 5.418117 |
| icr163793_m_2 | 220.177 | 488.5038 | 243.7081 | | 12.5324 | 22.62333 | 5.302651 |
| icr163793_mr_1 | 126.5207 | 455.4353 | 269.9175 | | 9.593133 | 20.09413 | 5.1085 |
| icr163793_mr_2 | 134.9461 | 403.5103 | 267.5825 | | 6.734108 | 18.25118 | 4.951115 |
| icr163793_th_1 | 455.3538 | 805.4613 | 192.1276 | | 17.65669 | 27.34217 | 4.275274 |
| icr163793_th_2 | 602.1814 | 831.9283 | 198.3051 | | 14.01911 | 23.36617 | 4.388638 |
| icr163794_a_1 | 353.7751 | 2395.848 | 273.1114 | | 20.38093 | 30.93075 | 6.156878 |
| icr163794_a_2 | 931.3754 | 2276.279 | 273.9504 | | 12.08776 | 25.75741 | 6.226632 |
| icr163794_b_1 | 526.5876 | 679.0117 | 161.1378 | | 21.30486 | 31.93456 | 4.17145 |
| icr163794_b_2 | 452.1405 | 970.5848 | 166.5853 | | 12.91733 | 25.30568 | 4.148657 |
| icr163794_m_1 | 216.8459 | 881.9811 | 195.8835 | | 12.09625 | 27.77658 | 4.746833 |
| icr163794_m_2 | 231.3671 | 792.6794 | 199.8407 | | 9.900594 | 24.21254 | 5.026254 |
| icr163794_mr_1 | 124.2858 | 574.8788 | 180.3073 | | 7.578703 | 17.69254 | 4.121247 |
| icr163794_mr_2 | 157.458 | 650.9229 | 180.1422 | | 6.463952 | 15.38067 | 3.6951 |
| icr163794_th_1 | 347.8712 | 758.1044 | 246.6031 | | 16.33071 | 25.24133 | 6.055815 |

| **SSN** | **Zinc MgKg$^{-1}$** | | | | **Molybdenum MgKg$^{-1}$** | | |
|---|---|---|---|---|---|---|---|
| icr163783_a_1 | Fresh | Oven Dried | Milled | | Fresh | Oven Dried | Milled |
| icr163783_a_2 | 47.50465911 | 52.3804102 | 48.17045 | | 19.16724 | 7.73077636 | 7.206903 |
| icr163783_b_1 | 36.49906733 | 51.7617531 | 52.71587 | | 9.75601 | 0.91354574 | 5.071699 |
| icr163783_b_2 | 45.00055107 | 39.9949298 | 34.50362 | | 13.19726 | 0.40776749 | 16.71497 |
| icr163783_m_1 | 38.61898575 | 49.2721513 | 34.87322 | | 4.333424 | 8.00507213 | 26.24123 |
| icr163783_m_2 | 43.03629142 | 41.8183036 | 17.63591 | | 5.873679 | 8.78901343 | 2.209291 |
| icr163783_mr_1 | 31.91255694 | 55.8810294 | 16.68617 | | 11.19182 | 11.3212262 | 2.151061 |
| icr163783_mr_2 | 17.36791876 | 54.0329455 | 36.22029 | | 4.190459 | 6.05279589 | 4.711067 |
| icr163783_th_1 | 14.53436905 | 54.1692199 | 34.22451 | | 10.46772 | 9.37829783 | 3.891842 |
| icr163783_th_2 | 30.15596067 | 53.0198075 | 41.30944 | | 7.243507 | 5.47086062 | 6.887791 |
| icr163784_a_1 | 30.88998417 | 33.9100104 | 39.38171 | | 7.122595 | 11.8419233 | 6.775774 |
| icr163784_a_2 | 45.15965866 | 54.1970536 | 27.27281 | | 2.950011 | 8.75213789 | 12.00344 |
| icr163784_b_1 | 26.61123564 | 41.697972 | 24.43014 | | 2.621616 | 6.73726399 | 8.156067 |
| icr163784_b_2 | 41.29479591 | 46.9374434 | 30.92578 | | 9.912922 | 3.68497066 | 2.089416 |
| icr163784_m_1 | 31.8386167 | 41.4971335 | 31.71737 | | 6.51131 | 11.0195159 | 4.003675 |
| icr163784_m_2 | 42.93712389 | 58.6762378 | 22.27605 | | 10.09245 | 14.231687 | 1.223301 |
| icr163784_mr_1 | 33.11488605 | 55.8618586 | 21.01287 | | 8.619254 | 5.96934171 | 3.283334 |
| icr163784_mr_2 | 15.80391858 | 41.4530611 | 24.09746 | | 6.703503 | 8.84776848 | 3.327825 |
| icr163784_th_1 | 14.46993978 | 40.2040388 | 24.24453 | | 3.250687 | 10.8521167 | 1.713184 |
| icr163784_th_2 | 30.88336471 | 48.4101158 | 20.66634 | | 6.635833 | 7.89268892 | 6.309525 |
| icr163785_a_1 | 26.58985809 | 47.0440357 | 20.70611 | | 5.94914 | 11.8059236 | 3.402671 |
| icr163785_a_2 | 53.20325245 | 58.1776326 | 21.6449 | | 7.855004 | 4.94879335 | 0.641161 |
| icr163785_b_1 | 37.29255272 | 44.3388511 | 21.83283 | | 7.881408 | 10.9731065 | 1.014671 |
| icr163785_b_2 | 36.24749928 | 55.3349769 | 17.48567 | | 7.243457 | 6.34392956 | 2.229323 |
| icr163785_m_1 | 31.48796302 | 53.4756863 | 18.10305 | | 16.10962 | 5.32455101 | 6.562657 |
| icr163785_m_2 | 40.72503642 | 57.5146871 | 22.57407 | | 2.91064 | 4.22429948 | 1.687752 |
| icr163785_mr_1 | 38.44608732 | 55.7074968 | 23.06335 | | 3.792385 | 1.16079195 | 1.444973 |
| icr163785_mr_2 | 14.97632261 | 41.1297647 | 18.53388 | | 8.485551 | 7.78154779 | 2.347157 |
| icr163785_th_1 | 14.60660794 | 41.5745442 | 17.59663 | | 7.994435 | 9.86587515 | 3.907954 |
| icr163785_th_2 | 23.81186757 | 51.6850169 | 28.06457 | | 6.329814 | 12.3979624 | 4.650291 |
| icr163786_a_1 | 24.67506223 | 51.3543469 | 27.39497 | | 6.269912 | 8.8888826 | 1.806029 |
| icr163786_a_2 | 46.59880362 | 59.9491922 | 33.50408 | | 4.320147 | 1.43412168 | 3.051448 |
| icr163786_b_1 | 31.35736859 | 63.0164799 | 33.87473 | | 15.09481 | 2.22559447 | 1.357221 |
| icr163786_b_2 | 41.60119712 | 54.9110828 | 26.68821 | | 8.743898 | 11.4891634 | 1.479023 |
| icr163786_m_1 | 29.59552018 | 55.5661759 | 27.66997 | | 12.08366 | 0.15660082 | 0.068694 |
| icr163786_m_2 | 44.589998 | 61.1563269 | 27.46218 | | 7.166371 | 10.6539676 | 4.47563 |
| icr163786_mr_1 | 34.33611453 | 57.8579153 | 26.66012 | | 3.75738 | 3.4174776 | 1.882847 |
| icr163786_mr_2 | 16.76499055 | 51.5757045 | 32.07201 | | 4.886222 | 3.45344483 | 1.819018 |
| icr163786_th_1 | 14.39874016 | 49.5085873 | 33.33638 | | 6.360274 | 5.66933626 | 2.596424 |
| icr163786_th_2 | 22.22594183 | 52.5979701 | 25.14599 | | 5.53812 | 5.08588812 | 1.222491 |
| icr163787_a_1 | 33.81930987 | 52.1302637 | 24.29446 | | 11.12602 | 12.291317 | 1.912429 |
| icr163787_a_2 | 43.95549334 | 60.4887871 | 25.3937 | | 6.024538 | 14.8926557 | 2.356619 |
| icr163787_b_1 | 31.76402678 | 46.6761673 | 25.85172 | | 5.821516 | 3.00657034 | 2.256411 |
| icr163787_b_2 | 38.61089211 | 39.9736184 | 17.90061 | | 7.130515 | 7.09116499 | 3.4455 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| icr163787_m_1 | 27.67428991 | 51.6549956 | 20.86675 | | 6.209244 | 12.3685925 | 5.776847 |
| icr163787_m_2 | 36.64360807 | 57.0979128 | 22.28804 | | 2.077714 | 6.98653993 | 2.506867 |
| icr163787_mr_1 | 29.42141453 | 55.298413 | 21.35818 | | 9.784693 | 12.4075065 | 2.718967 |
| icr163787_mr_2 | 48.59634114 | 39.9389802 | 17.80239 | | 6.34552 | 4.00428049 | 1.742096 |
| icr163787_th_1 | 16.03506471 | 40.9014889 | 19.21637 | | 4.651883 | 10.5233141 | 2.992323 |
| icr163787_th_2 | 22.28350403 | 50.1940931 | 31.59422 | | 2.361947 | 8.55654474 | 0.527505 |
| icr163788_a_1 | 21.92740392 | 50.2584438 | 31.94553 | | 8.062232 | 5.94812963 | 4.849071 |
| icr163788_a_2 | 51.15283489 | 63.4702638 | 27.92353 | | 12.31715 | 2.99717761 | 2.612142 |
| icr163788_b_1 | 57.47854618 | 57.1529487 | 27.08136 | | 9.368497 | 10.3936122 | 3.491263 |
| icr163788_b_2 | 40.8127821 | 55.5097978 | 44.25206 | | 9.444294 | 12.9465778 | 1.470946 |
| icr163788_m_1 | 31.00740636 | 55.5902264 | 41.61053 | | 10.12527 | 12.7018246 | 2.399344 |
| icr163788_m_2 | 54.00716251 | 54.7780646 | 26.0104 | | 7.706753 | 9.55229617 | 1.970131 |
| icr163788_mr_1 | 28.0568106 | 55.6626713 | 26.33121 | | 9.338796 | 11.7824062 | 3.275222 |
| icr163788_mr_2 | 16.6393371 | 36.1538099 | 22.65394 | | 8.905248 | 9.10633105 | 3.564228 |
| icr163788_th_1 | 16.15797614 | 35.1132555 | 24.39701 | | 3.46965 | 9.98631915 | 1.213993 |
| icr163788_th_2 | 26.05330277 | 52.1905804 | 21.90481 | | 6.378151 | 0.93898454 | 5.022989 |
| icr163789_a_1 | 25.31058849 | 57.7543178 | 21.34075 | | 4.664664 | 11.0487082 | 4.558947 |
| icr163789_a_2 | 45.49398549 | 49.19787 | 21.65071 | | 8.137315 | 7.49082959 | 0.684824 |
| icr163789_b_1 | 35.87753375 | 45.2087497 | 21.41809 | | 6.725845 | 6.83908133 | 1.219782 |
| icr163789_b_2 | 46.24393825 | 48.5075393 | 23.13571 | | 6.33902 | 9.17078159 | 26.43751 |
| icr163789_m_1 | 29.37258392 | 49.6329306 | 22.19435 | | 10.07447 | 7.93332529 | 29.56147 |
| icr163789_m_2 | 48.49162869 | 51.7475361 | 22.63294 | | 8.576206 | 5.02139548 | 2.368063 |
| icr163789_mr_1 | 35.5703364 | 47.4235607 | 21.63742 | | 3.700395 | 7.4420743 | 1.607988 |
| icr163789_mr_2 | 16.32948715 | 39.5376158 | 17.53586 | | 3.542727 | 5.90115094 | 5.537145 |
| icr163789_th_1 | 11.52050911 | 35.8715206 | 18.79774 | | 1.850429 | 6.28920277 | 2.773302 |
| icr163789_th_2 | 26.96207403 | 48.4638371 | 27.99519 | | 12.34051 | 2.81349744 | 1.217673 |
| icr163790_a_1 | 25.8831405 | 48.6844009 | 30.93791 | | 0.11803 | 4.9856473 | 1.946865 |
| icr163790_a_2 | 51.88714539 | 51.4801306 | 18.47577 | | 3.180902 | 8.42813047 | 1.550301 |
| icr163790_b_1 | 30.77708926 | 50.7900606 | 18.39063 | | 8.53021 | 7.89697197 | 0.534436 |
| icr163790_b_2 | 36.76262402 | 58.5385174 | 28.00587 | | 3.546567 | 1.61105425 | 4.295004 |
| icr163790_m_1 | 30.67579338 | 53.9459671 | 28.21302 | | 7.543117 | 9.19655402 | 1.217121 |
| icr163790_m_2 | 44.68096363 | 52.1967041 | 26.292 | | 1.966335 | 4.37003243 | 3.398858 |
| icr163790_mr_1 | 27.28736123 | 56.8814939 | 27.3582 | | 4.061133 | 2.17498321 | 4.303638 |
| icr163790_mr_2 | 22.66760208 | 44.9020286 | 65.07928 | | 3.919023 | 2.91696774 | 0.88431 |
| icr163790_th_1 | 13.29847405 | 44.4581397 | 73.49334 | | 9.196849 | 4.96205124 | 3.003675 |
| icr163790_th_2 | 24.17342792 | 47.936287 | 31.06821 | | 3.132816 | 14.6085789 | 5.278932 |
| icr163791_a_1 | 24.77378663 | 47.901036 | 30.32987 | | 7.484386 | 10.8127672 | 2.821594 |
| icr163791_a_2 | 51.78285182 | 60.7646509 | 22.70479 | | 4.840526 | 13.0938635 | 1.16793 |
| icr163791_b_1 | 42.31475618 | 48.6403197 | 21.67753 | | 3.12507 | 6.99488409 | 1.815946 |
| icr163791_b_2 | 40.5044649 | 52.7880412 | 20.5192 | | 7.159731 | 4.46513219 | 3.543441 |
| icr163791_m_1 | 35.768558 | 62.6992305 | 20.97453 | | 2.089029 | 7.87651579 | 2.808073 |
| icr163791_m_2 | 45.85740055 | 61.0163158 | 46.17652 | | 11.49431 | 4.46001853 | 3.144329 |

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|---|---|---|---|---|---|---|---|
| icr163791_mr_1 | 42.16511333 | 61.1766196 | 46.88019 | | 1.799191 | 9.72519451 | 4.188784 |
| icr163791_mr_2 | 20.73452885 | 60.7645696 | 17.78688 | | 7.740337 | 7.77263864 | 4.534421 |
| icr163791_th_1 | 17.81190183 | 60.6136379 | 18.23093 | | 9.58582 | 10.7098523 | 5.67023 |
| icr163791_th_2 | 32.01989058 | 64.8969052 | 25.12278 | | 7.513261 | 5.13026357 | 0.507675 |
| icr163791_th_6.1 | 28.65792814 | 67.398389 | 26.6212 | | 7.71045 | 0.84954942 | 6.015388 |
| icr163791_th_6.2 | 32.3121201 | 66.0537276 | 23.63573 | | 3.798297 | 14.3354745 | 2.723955 |
| icr163792_a_1 | 24.15664 | 63.2076223 | 22.82982 | | 3.723591 | 9.0910159 | 3.67481 |
| icr163792_a_2 | 41.50680395 | 57.7321801 | 23.11657 | | 1.951447 | 2.91864892 | 4.062836 |
| icr163792_b_1 | 38.51041668 | 55.2377943 | 22.4551 | | 6.199954 | 8.58545882 | 2.911147 |
| icr163792_b_2 | 38.44782513 | 60.8645818 | 23.28424 | | 5.693653 | 5.58986873 | 0.800499 |
| icr163792_m-1 | 35.66406129 | 58.326961 | 23.21785 | | 3.31962 | 8.9684366 | 3.019326 |
| icr163792_m_2 | 33.48295874 | 46.4194962 | 31.41959 | | 10.17943 | 6.82983108 | 5.744528 |
| icr163792_mr_1 | 28.22544102 | 57.4154452 | 32.47322 | | 3.22754 | 6.16822646 | 4.510979 |
| icr163792_mr_2 | 21.51437761 | 45.6862095 | 22.10311 | | 3.940518 | 8.24253142 | 5.691859 |
| icr163792_th_1 | 19.48928736 | 51.24119 | 22.22233 | | 8.025129 | 2.70935769 | 2.377242 |
| icr163792_th_2 | 46.6227031 | 64.02209 | 21.33353 | | 0.727058 | 20.0208157 | 1.21649 |
| icr163793_a_1 | 34.24162138 | 60.8182037 | 21.06941 | | 8.746659 | 15.0548351 | 2.375187 |
| icr163793_a_2 | 35.61021026 | 54.0280926 | 18.47547 | | 3.923478 | 8.41806435 | 3.07756 |
| icr163793_b_1 | 28.99573744 | 53.7889331 | 18.23723 | | 1.969748 | 0.23662617 | 3.643936 |
| icr163793_b_2 | 37.115652 | 54.4333373 | 30.06333 | | 5.187183 | 9.58801551 | 5.082927 |
| icr163793_m_1 | 30.31577238 | 51.2258025 | 30.98697 | | 5.573016 | 6.04559775 | 3.736326 |
| icr163793_m_2 | 27.77653555 | 47.3715055 | 21.739 | | 7.535773 | 5.09516974 | 4.570616 |
| icr163793_mr_1 | 18.52993745 | 40.6511669 | 22.04696 | | 1.509986 | 13.1102283 | 2.634443 |
| icr163793_mr_2 | 16.69732514 | 46.842631 | 22.77212 | | 2.014363 | 13.1028565 | 1.272563 |
| icr163793_th_1 | 17.18530916 | 44.2529378 | 23.55625 | | 6.787769 | 5.73434816 | 3.208947 |
| icr163793_th_2 | 42.47078814 | 51.7156107 | 18.09977 | | 3.094011 | 5.53759818 | 24.34902 |
| icr163794_a_1 | 32.72852684 | 49.8919737 | 17.87693 | | 2.846617 | 9.19949505 | 16.05573 |
| icr163794_a_2 | 38.98899505 | 50.8896438 | 21.44157 | | 2.673111 | 9.93098937 | 4.726985 |
| icr163794_b_1 | 24.7557289 | 50.2903119 | 22.71219 | | 4.852659 | 5.09452319 | 0.476771 |
| icr163794_b_2 | 35.54304966 | 53.3544947 | 19.27986 | | 6.558221 | 13.4272622 | 2.468182 |
| icr163794_m_1 | 28.06345487 | 47.1453804 | 20.03555 | | 5.209564 | 5.10017232 | 3.459557 |
| icr163794_m_2 | 21.02126931 | 38.7505354 | 32.40689 | | 3.26005 | 4.23014516 | 1.655331 |