DIAGNOSIS OF SOIL AND PLANT NUTRIENT CONSTRAINTS IN SMALL-SCALE GROUNDNUT (*Arachis hyopaea*) PRODUCTION SYSTEMS OF WESTERN KENYA USING INFRARED SPECTROSCOPY

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DECLARATION

I present this masters thesis as my original work for in partial fulfillment of a **Master of Science degree in Soil Science** at the University of Nairobi. I confess that similar work has never been presented in any other academic institution for similar academic reason.

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Dedication.

To my family particularly, two special ladies in my life; my beloved wife Bella Tonatula and my mum Elizabeth Khayela

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LIST OF ACRONYMS AND ABBREVIATIONS

IR... Infrared spectroscopy
NIR .... Near infrared spectroscopy
MIR.. Mid infrared spectroscopy
SSA... Sub-Saharan Africa
SFIs.. Soil Fertility Indicators
UN.. United Nations
UNDP...................................... United Nations Development Program
USDA.....................................United States Department for Agriculture
MDG... Millennium Development Goals
FAO-STAT..........................Food and Agricultural Organization statistics
PLSR.............. .... Partial Least Square Regression
PCA... Principle Component Analysis
AGRA.......................... Alliance for the Green Revolution for Africa
AEZ... Agro-Ecological Zones
AAS ....Atomic Absorption Spectrometer
BNI ....Biomass Nutrient Indicator
SOM.. Soil Organic Matter
FTIR ....Fourier Transform Infrared
LM... Lower Midland
UM .... Upper Midland

Abstract

Soil fertility degradation is a major problem in Africa leading to food insecurity, ecosystem degradation and poverty. Nutrient depletion and disease epidemics have contributed to a decline in groundnut yields of 25% in the past decade in Sub-Saharan Africa. Studies have demonstrated that infrared spectroscopy (IR) may permit rapid and cost effective analysis of tropical soil nutrients. Trial and error and field observations methods used by farmers are inefficient and have led to inappropriate soil nutrient management strategies and options in small-scale crop production systems.

This study sought to survey the prevalence of soil nutrient constraints in the small-scale groundnut production systems of western Kenya and to explore the potential of IR as a diagnostic tool for soil nutrient constraints. The soil properties examined were soil pH_w, total carbon (TC), total nitrogen (TN), extractable phosphorus (Ext. P), exchangeable potassium (K), exchangeable calcium (Ca), exchangeable magnesium (Mg) and particle size distribution (PSA) while for plant macronutrients, nitrogen (N), phosphorus (P) potassium (K) were examined and micronutrients, copper (Cu), zinc (Zn) iron (Fe) and manganese (Mn). Reference data that were used for developing calibration models were analyzed using standard laboratory methods widely used for tropical soils and plants. Soil pH was determined using an electrode pH meter for saturated soil paste. Exchangeable Ca and Mg were determined by the use of the atomic absorption spectrometry (AAS). The Olsen method was used to colorimetrically determine Ext.P. Total carbon (TC) and (TN) were determined using the C: N analyzer and particle size analysis (PSA) was determined using the hydrometer method. The plant macronutrients N, P, K, were determined by Kjeldahl distillation method, while the micronutrients Cu, Zn, Mn and Fe were analyzed by ashing

prior to determination by AAS. The reference data were then calibrated to soil and plant reflectance. Stable calibration models were developed for several key soil nutrients using the near-infrared (NIR) and mid-infrared (MIR) diffuse reflectance spectroscopy and partial least square regression (PLSR) statistical analysis. Robust calibration model were obtained; soil pH_w (r^2=0.85), TC (r^2=0.98), TN (r^2=0.97), Ca (r^2=0.95) and Mg (r^2=0.94), sand r^2=0.85) silt r^2=0.82 and clay r^2 =0.81 for the MIR spectral region. Extractable P and Exch. K had weak calibration models with r^2 values of 0.66 and 0.50 for MIR respectively, 0.50 and 0.32 for NIR respectively. Similar results were obtained for above-ground groundnut biomass although P and K yielded good calibration models. Attenuated total reflectance (ATR) yielded robust calibration for TN from saturated soil pastes with r^2 values of 0.94.

The study demonstrated the utility and potential of IR spectroscopy as a diagnostic screening tool for soil and plant nutrition in small-scale production systems. Principal component analysis (PCA) was used to summarize the variability in soil properties. Soil fertility indicators (SFIs) that were developed from the principal components were then used to evaluate soil nutrient levels based on critical nutrient levels. The SFIs were successfully calibrated to soil reflectance measured in the laboratory with cross validated r^2 values of 0.97 and 0.87 for MIR and NIR, respectively. Groundnut farms were critically deficient in principal nutrients; TN (75%), Ext.P (65%), and Exch. Ca (100%) which fell below the critical nutrient levels based on soil and plant MIR spectral predictions. Replenishment of these principle nutrients is crucial for sustainable groundnut productivity in western Kenya.

CHAPTER 1

INTRODUCTION

1.0 General Introduction.

1.1 Background Information

Land degradation and nutrient depletion threaten soil productivity and are a major reason for food insecurity and abject poverty in sub-Saharan Africa (SSA) (Sanchez et al., 2003; Bekunda et al., 1997). Human-induced soil fertility degradation (including nutrient depletion) has affected 15% of global land area (UNDP, 2000) and 65% of arable soils in Africa (Bationo et al., 1998). Soil nutrient depletion has become an increasingly urgent problem in tropical agriculture, an observation confirmed by small-scale farmers, soil scientists and policy makers. In Kenya, nutrient depletion as a form of soil fertility degradation is the main biophysical constraint that causes decline in crop productivity in small-scale agricultural production systems (Sanchez, 2003).

Asia and Africa accounts for more than 94% of world groundnut *(Arachis hyopaea .L* production, with most of the crop being produced in the small-holder sector, with low input use (http://www.icrisat.org/GroundNut/GroundNut.htm). In Kenya, western Kenya is the main national zone producing groundnut (*Arachis hypogaea* L.). Twenty five percent of groundnuts yield loss has been realized between 1975-2000 (FAO-STAT, 2004) and has been attributed to soil nutrient depletion among other concomitant, and often related problems of disease epidemics. Groundnut *rosette* is a disease epidemic that has been reported to cause decline in groundnut yield in SSA (Wangai et al., 2001). *Rosette* attack can cause 100% loss in pod yield when symptoms occur before flowering of groundnuts (Naidu et al., 1999). Problems of groundnut *rosette* combined with soil nutrient depletion have not been addressed sufficiently for small-scale farmers.

For more than three decades, farmers in western Kenya have engaged in small-scale groundnut production, as a food and cash crop. As a source of protein, groundnut is important to the diet of rural poor small-holder farmers. The crop plays a significant role in attainment of food security and nutrition to the rural poor. In most of the sub-Saharan African (SSA) countries, women predominantly grow and manage groundnuts. Therefore, groundnut cultivation has a direct bearing on the overall economic and financial well-being and nutritional status of women and children. Despite this significant role soil nutrient status has been on a decline trend on small-scale farms thus affecting groundnut production.

Soil nutrient depletion and especially nitrogen (N), potassium (K) and phosphorus (P) are limiting with other multiple soil nutrient constraints occurring together that include soil acidity (Sanchez, 2003). Continuous cropping without replenishing lost nutrients is common among smallholder farmers and has led to soil nutrient mining (Sanchez and Jama, 2002). Although small-scale groundnut farmers are aware of nutrients depletion, diagnosis of soil/plant nutrient constraints has been a key challenge.

There is little systematic information on integrated management approaches that link soil nutrient deficiency and disease epidemics in groundnut production on small-scale farm fields in Kenya. High costs incurred in conventional analytical methods prohibit large area soil fertility and crop disease surveys. Small-scale farmers have resorted to trial and error methods and use of indigenous knowledge as fertility diagnostic tools for potential nutrient problem areas (Mairura et al., 2004). Consequently, small-scale farmers have little information on soil nutrient constraints and are limited to using field observations and experience in designing soil fertility replenishment and disease management strategies (Mairura et al., 2004). A significant challenge is to achieve an integrated approach that links soil nutrient management and groundnut disease prevalence for optimum productivity. In this view, practicable options for diagnosis of soil/plant nutrient status and nutrient amelioration strategies are a prerequisite.

Knowledge of principal soil nutrient constraints and causes of crop stress is an important prerequisite for designing integrated approaches for effective and sustainable resource management in small-scale groundnut production systems (Pannell and Glenn, 2000). Designing integrated approaches and pragmatic local solutions for nutrient management integrated with groundnut disease prevalence is therefore needed in small-scale groundnut production systems. This goal can be achieved through acquisition of sufficient data on soil nutrient and groundnut disease prevalence.

Over the past decade infrared (IR) spectroscopy has emerged as a promising analytical method for rapid characterization of soil properties (Shepherd and Walsh, 2007). The potential of IR for use in analytical work was noted as early as the mid-1950s (Ben-Gera and Norris, 1968). The technique has been used in food industry to rapidly analyze protein, oil and moisture in wheat grain (Ben-Gera and Norris, 1968). Infrared spectroscopy has also been used to determine indicators of soil fertility in undiluted soils such as elemental mineralogical analysis, organic carbon, nitrogen and cation exchange capacity (Janik and Skjemstad, 1995; Janik et al., 1998).

Infrared (IR) spectroscopy is based on the interaction of IR light with matter. The characteristic of IR light gives distinctive properties that correlate uniquely with property of matter (Suits, 1983). The shape of IR spectra responds to organic matter, mineralogy, and particle size distribution, which also principally determine soil productivity. It has also been used extensively to determine the composition of forages (Williams and Norris, 2001; Ciurczak and Drennen, 2002), foods (Osborne and Fearn, 1993), pharmaceutical products (Workman, 2001), characterization of moulds (Jonas, 2006) and to characterize soil properties (Shepherd and Walsh, 2002). Infrared spectroscopy has demonstrated effectiveness as a management tool for assessing, determining and monitoring soil nutrients status (Janik et al., 1998; Shepherd and Walsh, 2007).

The main advantages of infrared spectroscopy are that it is rapid, simple, non-destructive, reproducible, and inexpensive and thus enables processing of large numbers of soil samples, such as in large area soil fertility surveys (Janik et al., 1998; Shepherd and Walsh, 2002). However, poor predictions have been reported by researchers while using near infrared (NIR) in characterizing extractable phosphorus (Ext. P) and exchangeable potassium (Exch.K) in the soil. Limited investigations have explored the potential of mid-infrared (MIR) attenuated total reflectance (ATR) to predict Ext. P and Exch. K from soil pastes. Linker et al. (2006) explored the possibility of determining nitrate concentrations in soil using ATR from soil pastes. Therefore, exploring the potential of ATR to characterize Ext.P in agricultural soils from soil pastes using spectroscopic techniques is a prerequisite and could be a breakthrough for adoption of IR as a rapid soil nutrient diagnostic tool.

1.2. Problem Statement

Soil scientists have argued that degradation of soil resources has played a significant role in food insecurity, rural poverty and ecosystem degradation in the world (Sanchez, 1997). Sanchez (2003) observed that most tropical countries are faced with the problem of soil nutrient depletion resulting in declining trend in crop yields including groundnut. Incidences of groundnut *rosette* have led to decline in groundnut yields by 25% for the last two decades in Kenya (Wangai et al., 2001). Mitigation of nutrient depletion by diagnosis, identification and mapping of soil nutrient status, groundnut disease prevalence and problem areas is paramount if optimum yields are to be realized in small-scale groundnut production systems.

Small-scale farmers have adopted trial and error methods, and field observation for identification, assessing and monitoring of soil nutrient depletion (Mairura et al., 2004). This is due to limitations associated with conventional analytical methods of soil tests. High cost for analysis using conventional analytical methods has been a setback in identification of soil/plant nutrient constraints. Few farmers who manage to deliver soil samples for soil tests using conventional methods wait for a long time for soil fertility recommendations due labour intensity and time spent on conventional analytical methods. Most Small-scale farmers resolve to work without the soil fertility recommendation from the soil tests in an attempt to maximize on availability of rains by timely planting in rain-fed groundnut production systems. Furthermore, conventional methods are expensive worldwide and much more so for poor small-scale groundnut producers in SSA. Conventional methods are complex and difficult in data interpretation even for agricultural extension officers.

The 2003 World Food Prize Winner, Professor Pedro Sanchez, described IR as the method of the future that may play a pivotal role if adopted in management of tropical soils, and more importantly in addressing land degradation and food insecurity problems. Infrared spectroscopy technique has potential in assessing large areas and huge numbers of soil and plant samples to identify constraints. Several researchers attribute low adoption of infrared spectroscopy for soil fertility testing to its poor performance while measuring Ext P and Exch.K (Malley, 1999; Viscarra et al., 2005).

1.3 Justification for study

Of the one billion poor people in the world today, 75% make their living in typical rural areas, dependent on subsistence agriculture for their livelihood. Agricultural productivity is key to rural development in poverty-stricken regions (World Bank, 2008). Strategies for economic growth in SSA pay most attention to improvements in agricultural productivity to achieve poverty reduction goals like Millennium Development Goals (MDGs).Unlocking the potential of small-scale farming systems in rural areas of SSA which are subject to frequent nutrient depletion should therefore be given high-priority if the MDGs are to be realized by 2015 (Sanchez, 2003). Alliance for the Green Revolution in Africa (AGRA) was formed to help in addressing soil fertility problems in small-scale farms of Africa. This requires innovative and viable soil management options and strategies at both farm-scale and large scale without compromising sustainable land productivity for optimum crop productivity. Acquisition of high quality information relating to soil nutrient status and dynamics over large areas could play a pivotal role towards attaining a sustainable soil resource. Infrared spectroscopy has demonstrated such potential as a cheap and rapid method for acquiring such data over large areas. Often, multiple soil constraints occur together (e.g. low soil pH and phosphorus deficiency): IR, by providing an integrated measure of soil properties, may be helpful in diagnosing these syndromes.

Groundnut is a self- pollinated, herbaceous legume, grown in western Kenya, and has demonstrated potential in assisting rural farmers to improve their livelihood (Smartt, 1994. Groundnut production could play a significant role in increasing income for the small-scale farmers as a cash crop. All the parts of groundnut plant are useable. In the Rift Valley province yields of 465 kg/ ha of shelled groundnut of Red Valencia variety and 810 kg /ha of Manipinta variety can be realized (Kipkoech, 2007) The nuts are used for human consumption in many developing and is the principal source of digestible protein (25 to 34%), cooking oil (44 to 56%), and vitamins like thiamine, riboflavin, and niacin (Savage and Keenan 1994). In many sub-Saharan African (SSA) countries, women predominantly grow and manage the crop. Therefore, groundnut cultivation has a direct bearing on the overall economic and financial well-being and nutritional status of women and children. The seeds are processed to make groundnut oil, peanut butter or candy. Groundnut seeds are important in processing of non-food stuffs such as soaps, medicines, cosmetics and lubricants (Smartt, 1994). The leaves and vines can produce high quality hay rich in proteins which can be utilized as livestock feed (Page et al., 2002). Incorporation of crop residues into the soil through tillage generates high residual nitrogen and potassium which is used by the subsequent crop hence reducing nitrogen fertilizer requirements (Lemon, 1999; Page et al., 2002). Groundnuts form an important component in crop rotation system for control of pests and disease-pathogens build-up by avoidance of host crops (Putman et al., 1991).

1.4 Research questions

The following research questions guided this study;

- Can infrared spectroscopy (IR) predict complexes of soil nutrient deficiencies from air-dried soil samples?
- What are the major soil constraints to plant production in the main groundnut growing areas of western Kenya?

- Can simple infrared spectroscopy procedures/techniques for predicting content of soluble nutrients using soil pastes and soil solutions be developed?

1.5 Objective

The broad objective of the study was to investigate the applicability of infrared spectroscopy in the characterization of soil fertility status in small-scale groundnut production systems in western Kenya.

To be able to attain this broad objective the following specific objectives will be pursued

- To evaluate infrared approaches for predicting soil test values.
- To diagnose nutrient deficiencies in soil and plant tissues using IR in small-scale groundnut growing region.
- To establish syndromes and prevalence of important soil and plant nutritional constraints facing groundnut growers

1.6 Hypothesis

The following hypotheses guided this study;

- Infrared spectroscopy can provide rapid and accurate diagnosis of soil and plant nutrient constraints for groundnut production in western Kenya relative to conventional reference methods.
- Soil P-deficiency, potassium, Ca and micronutrient deficiencies in that order are the most prevalent constraint to groundnut producers in western Kenya.
- Prevalence of the groundnut *rosette* is high where major and multiple soil constraints occur.

CHAPTER TWO

LITERATURE REVIEW

2.1 Nutrient depletion small-scale groundnut production systems in western Kenya

Agriculture is a major economic sector in western Kenya that has engaged more than 70% of the inhabitants especially rural poor. Western Kenya supports one of the densest rural agricultural populations in the world as a result of large initial settlements attracted by the originally fertile soils in the area (Vanlauwe et al., 2002). Nutrient depletion along with concomitant problems of crop diseases cause low per capita food production (Sanchez and Jama, 2002). Over the past 30 years, average annual depletion of macro-nutrients N, P and K has been estimated to be 22, 2.5 and 15 kg ha^{-1}, respectively for 37 African countries in SSA (Sanchez, 2003). This has affected soil quality, a holistic concept that recognizes soil as part of a dynamic and diverse production system with biological, chemical and physical attributes that relate to the demand of human society (Stocking, 2003). Annual nutrient depletion has detrimental effects on soil productivity that cause decline in crop yield. Several policies, technologies and innovations of enhancing soil fertility and quality, particularly replenishing soil nutrients, have been introduced in western Kenya (Place et al., 2005).

Despite the introduction of soil fertility replenishment technologies and innovations, methods of assessing, diagnosing and identifying soil nutrient status and problem areas has had little consequence for soil nutrient management on small-scale farms. Designing and improving simple and robust nutrient diagnostic methods could be remedial for attainment of sustainable soil management. Sanchez (2003) suggested implementation of such soil fertility projects to scale-up nutrient replenishment in SSA. A rapid and cost effective diagnostic method of soil nutrient constraints and monitoring changes in soil nutrient stocks is fundamental. However, this is a key challenge that has not been sufficiently addressed. Such diagnostic methods may set benchmarks for identification of areas with nutrient constraints. Over the past decade infrared spectroscopy has demonstrated potential as a rapid and inexpensive analytical tool that can be an instrumental tool in diagnosis of soil nutritional constraints over large-scale assessments (Janik et al., 1998, Shepherd and Walsh, 2007).

2.2 Origin, distribution and global production of groundnut crop.

Groundnut (*Arachis hyopaea L*) is an ancient crop that originated from South America (southern Bolivia/north west Argentina) where it was cultivated as early as 1000 B.C.. Introduction of groundnuts to Africa occurred in the 16th and 17th centuries with the discovery voyages of the Portuguese, British and Dutch (Krapovickas, 1973; Hammons, 1982; Isleid et al., 1994). Today, groundnut is cultivated in 108 countries on about 22.2 million hectares of which 7.39 million hectares are in SSA and 13.9 million ha in Asia. Global production is 29 million tonnes of pods and India, China and the United States of America are the leading producers growing about 70% of the world's groundnuts (Consultative Group International Agricultural Research, 2000)

2.3 Significance of groundnut in Kenya

Groundnut (*Arachis hyopaea L*) is a valuable crop for small-scale farmers in Kenya and is widely grown in SSA (Wangai et al., 2001; Kipkoech, 2007). Groundnuts represent about 10% of the world total oilseed production of 333 metric tonnes according to a forecast done by the United States Department of Agriculture (USDA) in the years 2003/2004 (FAS,2003). Developing countries contribute to 90% of the oilseed total production. The crop gives relatively high returns from a limited land area and is well adapted to hot semi-arid tropical conditions (Wangai et al., 2001).

Groundnuts play a significant role to the lives of small-scale farmers. It contributes to generation of household income and is used as an ingredient in snacks or main dishes (Kipkoech, 2007). The kernel is rich in edible oil, containing 36-54% oil and 25-32% protein (Knauft and Ozias-Akins, 1995). About two thirds of the world production is threshed for oil, which makes it an important oilseed crop (Woodroof, 1981). The oil is used primarily for cooking, manufacture of margarine and soaps. Seeds are consumed directly either raw or roasted, chopped in confectioneries, or ground into peanut butter.

In folk medicine, groundnut is a medicinal plant and is used for aphrodisiac purposes, treatment of inflammation, cholecytosis, nephritis and as a decoagulant. In China, the oil is taken with milk for treating gonorrhea, and externally for rheumatism (Duke and Wain, 1981). In Zimbabwe, groundnuts are used in folk remedies for plantar warts (Duke and Ayensu, 1985)

2.4 Ecology and fertility requirements for groundnuts

Groundnuts require abundant sunshine and warmth for normal development (Page et al., 2002). It is a self- pollinated, herbaceous legume, with climatic requirements of dry areas and altitudes above 1500 meters above sea level. Optimum temperatures range from 27-30 °C for vegetative growth and 24 -27 °C for reproductive grow that have been reported as ideal for optimum yields (Putman et al., 1991). Unlike other crops that take up soil nutrients, the plant helps in reviving the productivity of soil because of its ability to symbiotically fix atmospheric nitrogen in the soil (Lemon, 1999). Groundnut is an important tropical grain legume-crop which contributes to food security and soil fertility maintenance through biological nitrogen fixation. For example, Okito et al., (2004) reported the contribution of groundnuts to nutrient replenishment through biological nitrogen fixation and calculated amount of nitrogen fixed using nitrogen isotope (N^{15}) data as about 40 kg N ha^{-1}. Adequate rainfall amount range is from 300-600 mm and even distribution is essential for proper groundnut growth and optimum yields (Gascho 1992).

Soils suitable for groundnuts should be of low organic matter content, deep, well drained, sandy, sandy loam or loamy sand which facilitate development of fruits into the soil (Putman et al., 1991; Tisdall and Oades, 1982). The crop grows well in slightly acidic to near neutral soils with soil pH_w range of 5.3-7.3 (Gascho and Davis, 1995). Phosphorus, potassium, magnesium and calcium are essential nutrients for high yield and good quality seed.

Phosphorus (P) deficiency in crops affects root growth that impairs nutrient and water absorption and affects their overall productivity (Gascho and Davis, 1995). Calcium plays an important role in lengthening the roots and shoots and thereby improving the growth and development the crop in groundnuts (Sumner et al., 1988). Calcium requirement of groundnut plant is quite high and the requirement is high during the pod-filling stage (Sumner et al., 1988). For good yields of quality groundnut pods, adequate amount of calcium should be present in the soil from early flowering of the crop to maturity (Csino and Gaines, 1986). Calcium is absorbed directly from the soil by the developing pod and low calcium levels lead to empty shells or "pops (Csino and Gaines, 1986). Supplemental calcium sources like lime or gypsum are used to raise soil calcium levels (spread over the row after planting). Lime should be applied and incorporated into the soil well before planting.

2.5 Disease prevalence and soil nutrient

Groundnut *rosette* has contributed to low groundnut yields in Kenya (Wangai et al., 2001). Soil nutrients play a major role in crop disease management and adequate nutrients can either make the crop tolerant or resistant to diseases (Ingham, 1991). Research evidence has shown that nutrients such as calcium can reduce incidences of club root in cabbages (Sullivan 2004). Managing soil pH and calcium levels has been an efficient tool in reducing incidences of potato scab (Ingham, 1991). These examples clearly indicated the significant role played by soil nutritional status in crop disease prevalence. The same principles can be applied in groundnuts production. However, there is very little information on groundnut disease prevalence in relation to soil nutrition.

The high prevalence of crop diseases related to soil have led to use of the categories of *suppressive soils* and *non- suppressive*. Suppressive soils are described by Baker and Cook (1974) as those in which disease severity or incidences remain low in spite of the presence of a disease pathogen, a susceptible host plant, and climatic conditions favorable for disease development. Suppressive ability of soil is linked to nutrient levels in the soil, microbial biodiversity and soil physical properties (Baker and Cook, 1974; Sturz, 2000). In this context, soil suppressiveness to crop disease is a characteristic of any given soil and depends on both soil biotic and soil nutrient levels (Cook and Baker, 1983; Hoitink et al., 1997, Peters et al., 2003). A key challenge is an approach that could integrate management of nutrient level in soil by enhancing the soil suppressiveness ability on small-scale farm. Infrared spectroscopy could be instrumental as a management tool for rapid diagnostic tests for plant and soil nutrient status and perhaps even diagnose soil suppressive ability.

2.6 Definition of Infrared spectroscopy

Infrared spectroscopy (IR) is defined as the study of the absorption of infrared radiation by substances (Smith, 1999). Infrared is part of the electromagnetic spectrum and it is divided into three main regions according to wave numbers; near infrared (NIR) 12500-4000 cm^{-1}, mid-infrared (MIR) 4000-400 cm^{-1} and far infrared that is less than 400 cm^{-1} (Figure 1). Measurements obtained in IR spectroscopy are spectral signatures, collected using specialized machines known as spectrometers. Spectrometers have been used in for more than the past 10 years to study location and spacing emission and absorption in specific wavelengths to detect functional groups in characterization of materials (Smith, 1999).

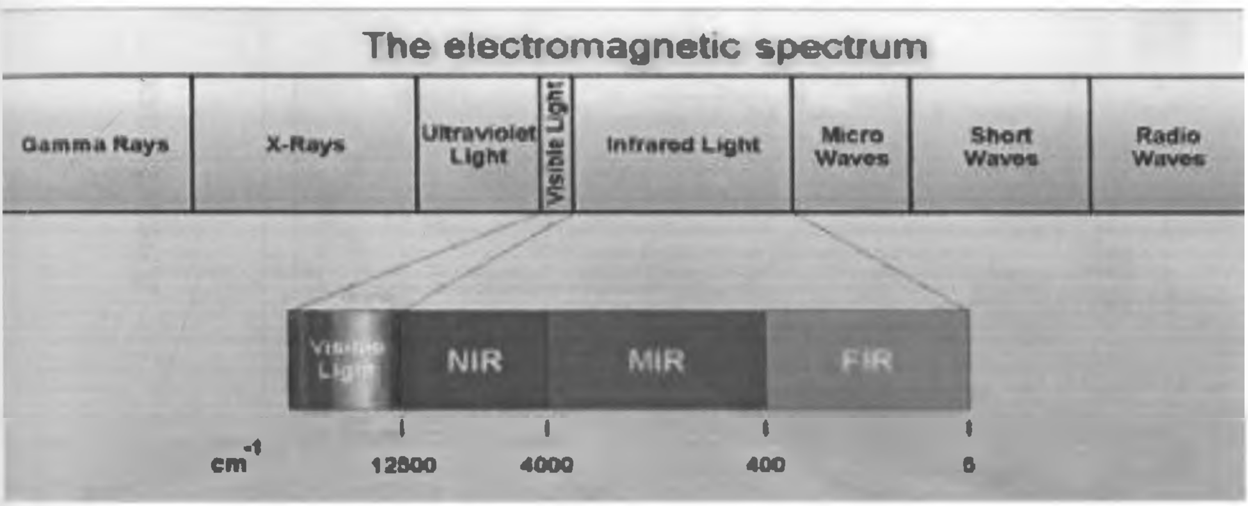


Figure 1: Electromagnetic Spectrum (Source: Bruker tutorial, 2004)

Spectral signatures (Figure 2) are measurements of percent reflectance or absorbance or transmittance (relative to a standard) as a function of wavelength (cm^{-1}) along the electromagnetic spectrum (Shepherd and Walsh, 2002). Infrared spectroscopy is a fast and non-destructive technique that provides multi-constituent analysis of virtually any matrix (gas, liquid and solids) (Stuart, 2004). The target material is illuminated with infrared light and IR energy absorbed by functional groups made up of atoms and molecule causing bending, stretching, and twisting of bonds which leads to the characteristic absorbance and reflectance patterns (Chalmers and Griffiths, 2002). Spectra are characterized quantitatively by observing positive and negative peaks, which occur at specific wavelengths and quantified statistically to determine constituents of target materials such as soil and plant (Viscarra et al., 2005).

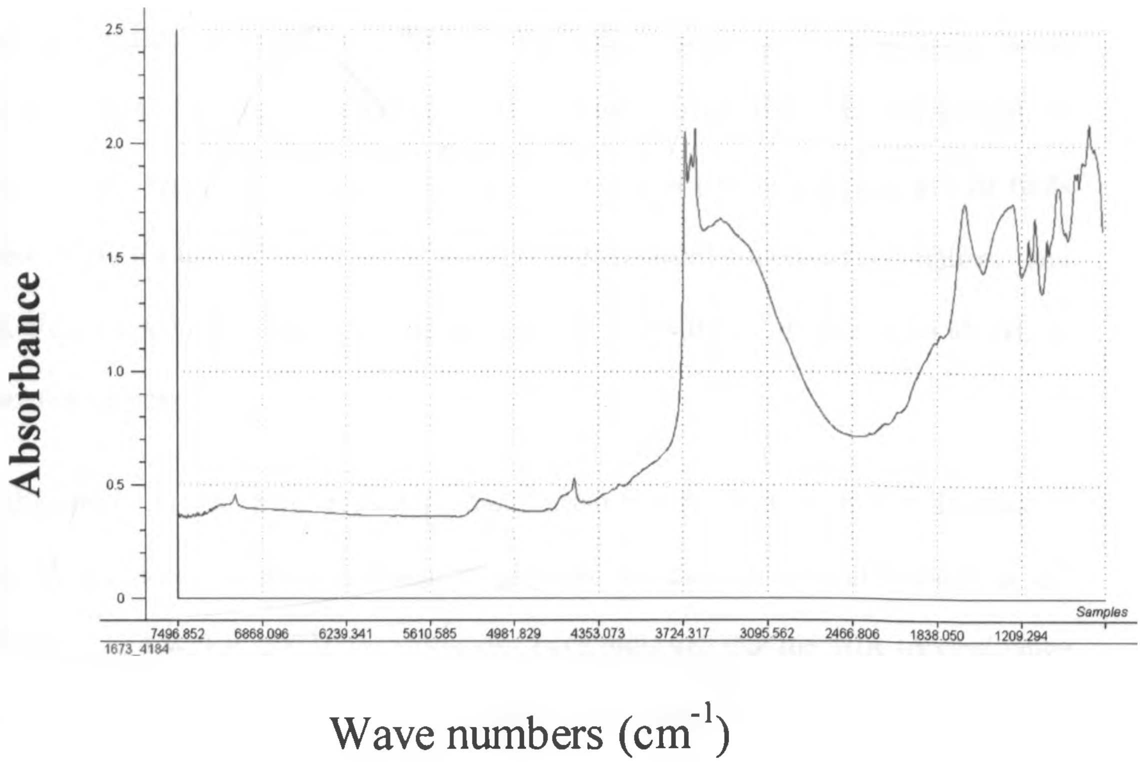


Figure 2: Spectral signature of soil from the MIR spectral region

Fundamental vibrations due to stretching and bending of various functional groups (molecular) dominate the MIR region and provide valuable information about the structure of a substance (Janik et al., 1998; Stuart, 2004). The NIR region encompasses weak transitions that correspond to combinations and overtones of vibrational modes observed in MIR region. NIR absorptions are generally broad and therefore strongly overlapping, it is difficult or impossible to arrive at specific assignments for individual absorptions in the NIR region (Ciurczak and Drennen, 2002; Burns and Ciurczak, 2001).

Mid-infrared is energetic enough to excite molecular vibrations to higher energy levels (Chalmers and Griffiths, 2002). Therefore the MIR region has more fundamental structural information compared to NIR that has major weakness of absorption bands accruing as overtones of the fundamental bands residing in the MIR. The wavelength of infrared absorption bands is characteristic of specific types of chemical bonds, and IR finds its greatest utility for identification of organic and organometallic molecules (Chalmers and Griffiths, 2002). The high selectivity of the IR method makes the estimation of an analyte in a complex matrix possible.

Absorption in the MIR region includes contributions from complex interacting vibrations giving rise to generally unique fingerprints for each compound (Lindon et al., 2000; Shepherd and Walsh, 2002). Investigations have indicated that the MIR spectral range when used in soil characterization, for instance soil organic carbon, the accuracies achieved is greater than NIR spectral range (Reeves, 1999).

2.7 Principle of infrared spectroscopy

Infrared (IR) spectroscopy based analyses are founded upon the spectrum of IR, which utilizes the interaction of IR light with matter to reveal certain properties of matter, displayed in reflected IR light radiation (Suits, 1983). The characteristic of IR light gives distinctive properties which correlate uniquely with property of matter (Suits, 1983). Infrared spectroscopy works because chemical bonds have specific frequencies at which they vibrate corresponding to energy levels (Chalmers and Griffiths, 2002). The vibrational frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and, eventually, by the associated vibronic coupling (Chalmers and Griffiths, 2002).

For a molecule to be IR active, it needs to have a changing dipole (Smith, 1999). In particular, in the Born-Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a quantum harmonic oscillator in the neighborhood of the equilibrium molecular geometry, the resonant frequencies are determined by the normal modes corresponding to the molecular electronic ground state potential energy surface (Smith, 1999). The resonant frequencies can be in a first approach related to the length of the bond, and the mass of the atoms at either end of it (Smith, 1999). Thus, the frequency of the vibrations can be associated with a particular bond type. Bonds vibrate in six different ways, symmetrical and asymmetrical stretching, scissoring, rocking, wagging and twisting (Chalmers and Griffiths, 2002). Vibrations of molecules and atoms of functional groups produce characteristic troughs and peaks along the spectral signature depending on percentage reflectance/ absorbance /transmittance (Shepherd and Walsh, 2002).

All compounds within a soil sample collectively form a specific finger print of the sample (Lindon et al., 2000). Molecules containing nitrates commonly exhibit asymmetric stretching vibration of the nitrate group at 1660-1500 and 1390 cm^{-1}. Linker et al. (2006) explored the potential of using soil pastes to determine nitrates concentration in the MIR spectral region using attenuated total reflectance. With this technique, the sample is illuminated via a diamond crystal in direct contact with the sample and the reflected light passing back through the crystal is detected. Principal soil nutrients like phosphorus are dominated by compounds containing phosphorus and oxygen (P-O) linkages, which are termed as phosphates, a functional (structural) group (Corbridge, 1990). Spectra are used to study molecular specification by analyzing absorption bands that originate from P-O stretching vibrations, which appear in the regions of 900-1300 cm^{-1} and 1260 cm^{-1} (Gielser et al., 2005), (Figure 3)

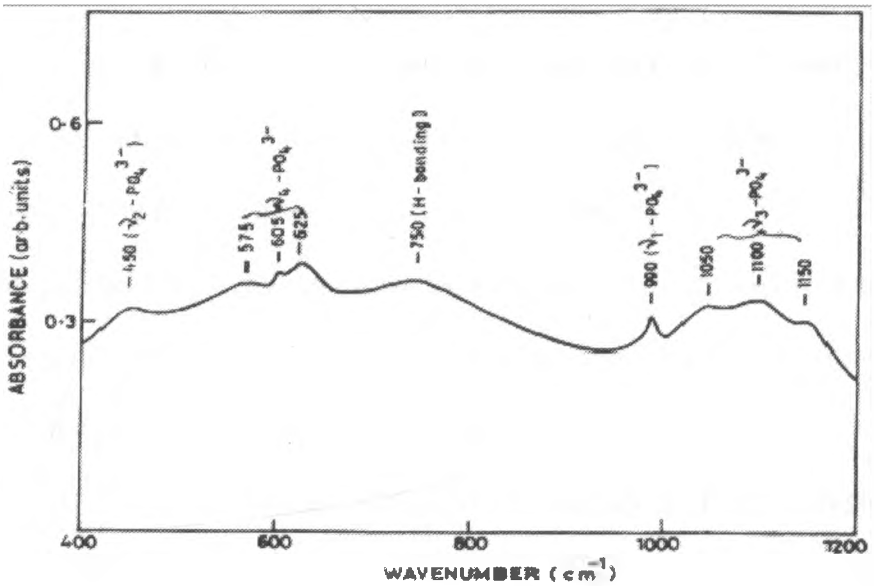


Figure 3: Finger print regions for phosphate ions (Corbridge, 1990)

Infrared spectroscopy has several advantages which include;

- Infrared spectroscopy is universal technique (Smith, 1999). Spectrometers used for scanning and collection of spectral signatures are universally standard, at least with certain types of spectrometers e.g. the Fourier Transform infrared (FTIR) spectrometers.

Hence there is very minimal variation in between spectral measurements of same analyte taken from different laboratories.

- Rapid, straightforward and accurate compared with conventional methods (Reeves et al., 2001; Shepherd and Walsh, 2002; Viscarra et al., 2005). It is less labour intensive and inexpensiveness makes it possible to analyze large numbers of soil samples in a short period of time (Janik et al., 1998). For instance, in a day more than 300 samples can be scanned and analyzed for a wide range of soil parameters. Recent development of new and more robust spectrometers has enhanced the capability of capturing information from soil about the constituents and high quality spectra.
- Virtually any state (solutions, pastes, powder, pastes and fibers) of sample may be studied using the spectroscopic techniques (Stuart, 2004).
- The IR method is environmental friendly and does not require use of chemicals (Viscarra et al., 2005; Shepherd, Personal communication, 2006). Chemical disposal is hazardous to human health when handled recklessly.
- The IR method produces analytical results which have a higher degree of repeatability and reproducibility compared with those obtained from conventional laboratory methods (Shepherd and Walsh, 2007).
- A single spectrum of IR allows for simultaneous characterization of various soil constituents (Shepherd and Walsh, 2002; Viscarra et al., 2005).

The main disadvantages of IR technique is that it is quite sensitive to the presence of functional groups in a sample hence sample must contain chemical bonds that are diagnostic of the problem under study in order to make useful measurements. Single atomic entities contain no chemical bonds hence its difficult to make spectral measurements. Also if compounds of interest are present at very low concentrations they may have small influence on the spectral signature.

2.8 Applications of infrared spectroscopy

The potential for use in analytical work was noted as early as the mid-1950s. The technique had caught the attention of the agricultural community and was first developed and applied in the food industry more than three decades ago for rapid analysis of protein, oil, and moisture in wheat grain (Ben-Gera and Norris, 1968). It has also been used extensively to determine the composition of forages (Williams and Norris 2001), foods (Osborne and Fearn, 1993) pharmaceutical products (Workman 2001, Robert et al 2004,) and as a possible tool for characterizing soil properties, (Shepherd and Walsh, 2002, two workers who established spectral libraries for tropical soils). Spectroscopic techniques are highly sensitive to organic and inorganic phases of the soil making its application to soil characterization possible (Viscarra et al., 2005).

Over the past years diffuse light spectroscopy has developed into a robust analytical methodology in agricultural production systems for acquiring soil information about soil quality (Shepherd and Walsh, 2007). Key soil properties in tropical soils have been determined using infrared spectroscopy. Some success has been reported in sensing soil organic matter in the field (Sudduth and Hummel, 1996) as well as in discriminating soil types from satellite multi-spectral data (Coleman et al., 1993). Dalal and Henry (1986) were also able to predict total organic C, total N, and moisture content. Linker et al. (2006) was able to determine nitrates from soil pastes using attenuated total reflectance (ATR) spectroscopy in the MIR spectral region and by employing quantitative statistical techniques.

Quantitative information is obtained from spectra data using various multivariate techniques which relate spectra information to the analyte (Chang et al., 2001). The calibration techniques employed include partial least squares regression (PLSR), and principal component analysis (PCA) (Chang et al., 2001). However, there is no universally adopted calibration technique for spectral analysis and there is need for judicious choice of calibration techniques in order to obtain robust predictions.

The ability to rapidly and non-destructively characterize soils using infrared spectroscopy permits thorough sampling and acquisition of information about nutrient status and variation within a target population of soils (Stenberg et al., 1995). Successful strategies of managing soil nutrients can be realized by acquisition of high quality data using robust rapid techniques like infrared spectroscopy.

2.9 Conventional methods of soil analysis

The basic technique used in conventional analytical methods for soil characterization is mineralogy and granulation. Modern conventional methods were developed in the early 1940s (Jones 1999) and have been modified to suit individual needs. An example is the Olsen P method for determining extractable phosphorus, which can only determine extractable P within certain soil pH ranges, and hence modifications have been developed to overcome this limitation. Conventional methods have generated an extensive debate as analyses for some soil parameters still have controversies (Noveas and Smith., 1999) that have not been sufficiently addressed, like those concerning sulfur (Landon 1980).

Conventional methods are associated with several limitations which include the following;

- The costs involved in the soil analysis are quite expensive (Dematte et al 2001) for small-scales farmers who opt to diverting their resources to more pressing needs such as paying for children education and reconstruction of shelter.
- The methods are time consuming. For instance, in the determination of soil organic carbon using the wet oxidation method, soil samples are kept for 12 hours at room temperature (24°C) before colorimetric determination. Furthermore, the conventional methods are complicated in terms of mastering procedures and preparation of various chemical reagents to be utilized for analysis.
- The chemicals used in laboratory analysis are hazardous in terms of disposal; pose a threat to the environment in terms of pollution with the pressing issue of climate change, and human health in term of inhalation of toxic fumes.

Hence, there is need for better practical methods that can rapidly estimate soil properties which are needed to improve qualitative assessment of soil resource in terms of land degradation (Shepherd and Walsh, 2002) including soil fertility degradation

CHAPTER THREE

METHODOLOGY

3.0 Research Methodology

3.1 Study Site

The study was conducted in Busia, Teso, Siaya, Homabay/Suba districts located in the western Kenya. The highlands of western Kenya cover 85,000 km^2 and represent 15% of Kenya's total land area (Amadalo et al., 2003). The area has high population densities ranging from 500 to 1200 persons per km^2 with a population growth rate of 3.4% per year (Ministry of Planning, 1997). The study area is characterized by rampant poverty and low crop productivity, shortened or non-existent fallow period and low fertilizer inputs (Place et al., 2005). The annual rainfall ranges from 1200 – 1800 mm and is bi-modally distributed. The long rains season starts from March to July and short rains from October to December. Short rainy season is traditionally less reliable hence crops with early maturity are given priority during planting.

Selection of these sites was based on (i) these districts comprise of a wide range and distinct characteristics with agro-ecological zone AEZ ranging from LM_1 to LM_4/UM_4 that captures climatic variation, presented on Figure 4. According to Jaetzold and Schmidt (1982), an AEZ is a geographical area which can be defined on the basis of its moisture supply, differences in the soil patterns as well as the associated crops and livestock it can support. (ii) The districts comprise of poor tropical small-scale production systems with diverse soil types and problem of nutrient deficiencies (Sanchez, 2003).

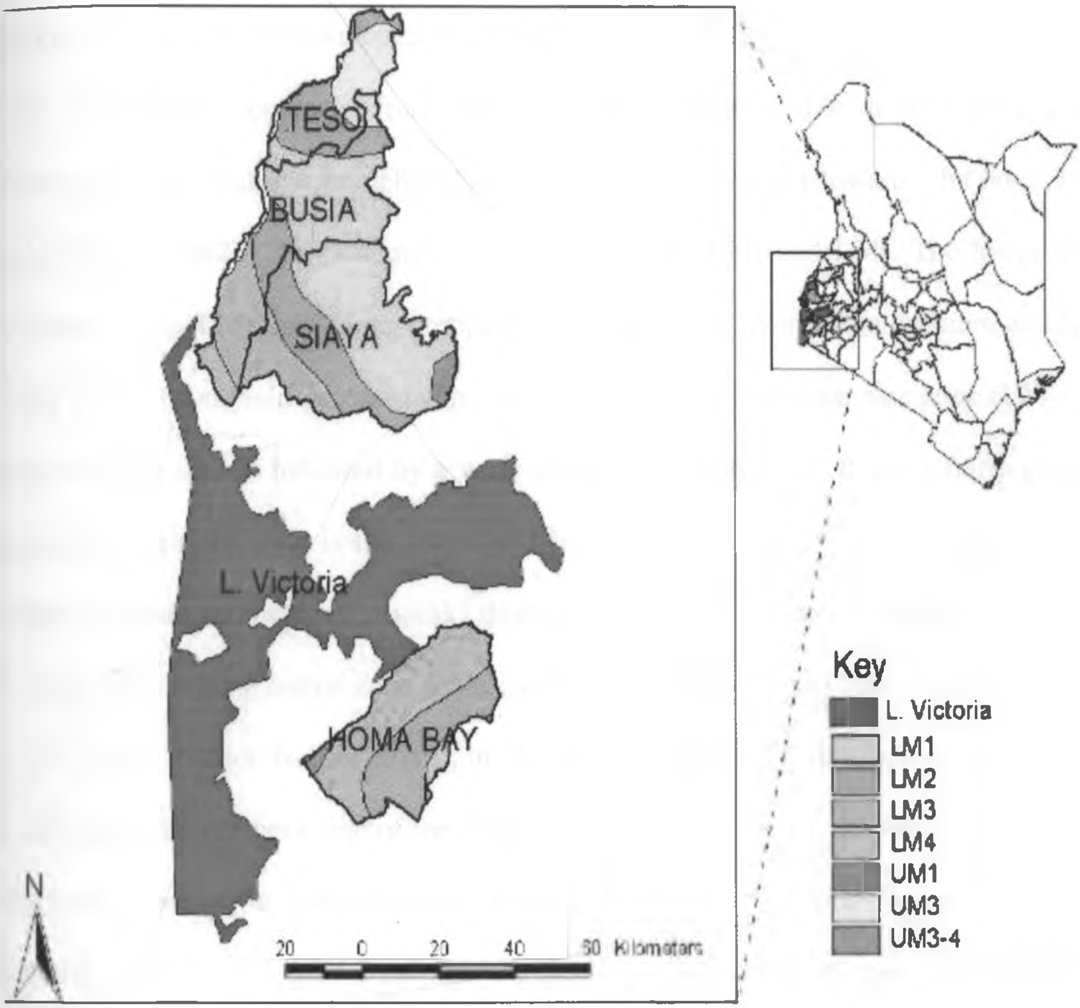


Figure 4: Map of agro-ecological zones for the study area (Source; World Maps)

Busia and Teso districts are located 30°N and 34°E bordering Uganda on the western side. Majority of the inhabitants are Luhya and Teso communities whose main economic activities are small-scale farming and trading. The soils are underlain by plinthite at a shallow depth of approximately 50 cm, resulting in low moisture retention and limiting land productivity. However, plinthite has been utilized effectively as a cheap source of building material generating income for small-scale farmers (Farmer, personal communication, 2006).

Regosols, cambisols, vertisols and solonetz (Somborek et al., 1982) are the dominant soils in the area and are developed from basic igneous rocks. Average annual temperature is 27°C and precipitation range from 900-2000 mm per annum. The districts have six agro-ecological zones that can be delineated across from north-south towards the lake (Jaetzold and Schmidt, 1982). The dominant AEZ include LM_1, LM_2 and LM_3. The lower midland sugarcane zone (LM_1) has a long cropping season followed by medium or intermediate rains. It has a very good yield potential. The second is the marginal sugarcane zone (LM_2) with a long cropping season followed by a weak medium to short rains. It has a fairly good yield potential. The third zone is the lower midland cotton zone (LM_3) with a medium to long cropping season followed by a (weak) short or very short one. The fourth AEZ extends up to the lake, the marginal cotton zone (LM_4), with a (weak) medium to short cropping season.

Siaya district is the largest in Nyanza Province and lies within the lake basin extending to the northern side of the Lake Victoria and bordering Busia district on the west. The land is mainly a peneplain and slopes very gently from east to west (Jaetzold and Schmidt, 1982). The annual rainfall ranges from 800 to 1900 mm the annual mean temperature is 28°C. The rainfall pattern is bimodal with long rains occurring from March to June and short rains from September to December. Lower regions have dominant soils that include humic gleysols, while ferralo-orthic ferralsols, orthic acrisols and chromic luvisols are the most common soils on the higher areas (Jaetzold and Schmidt, 1982; FAO 1995). The lower midland sugarcane zone (LM_1) with a long cropping season followed by medium or intermediate rains. The zone has a very good yield potential. The second is the marginal sugarcane zone (LM_2) with a long cropping season followed by a weak medium to short rains. It has a fairy good yield potential. The third zone is lower midland cotton zone (LM_3)

with a medium to long cropping season followed by a (weak) short or very short one. The fourth AEZ ecological zone extends up to the lake, the marginal cotton zone (LM_4) with a medium to short cropping season (weak) and intermediate rains.

Homabay/ Suba districts are located to the southern part of Lake Victoria and the main inhabitants are the Luo community. The main economic activity is fishing and small-scale-farming and the districts are also characterized by high levels of poverty. Dominant soils are vertisols which are mainly common in the lowlands of the districts and have been attributed to sporadic floods during rainy seasons due to their characteristic poor drainage and flat topography. Gleysols, solonetz, cambisols and regosols are also common soils in the area (Somborek et al., 1982). In addition, to the above mentioned AEZs is upper midland 4 (UM_4). This is a zone in which both maize and coffee can do very well and it has subsequently been defined as a coffee and maize zone (Jaetzold and Schmidt, 1982). The altitude ranges from 1500-1800 m above sea-level with an annual mean temperature of 20° C and rainfall of between 1200-1600 mm annually.

3.2 Sample collection

Soil sampling is a prerequisite for determining soil nutrient status. Soil samples represent the "population" of a plot, field or an AEZ, from which the nutrient status of the soil sample is determined (Okalebo et al., 2002). A survey was carried out based on a total of 150 small-scale groundnut farms with 394 soils sampled from 5 districts. Stratification was done along AEZs LM_1, LM_2, LM_3 and LM_4/UM_4 for the purposes of sampling across the 5 districts.

(a) Soil sample collection

The number of farmers growing groundnuts varied between agro-ecological zones (AEZs) in the five districts. From each of the selected AEZs groundnut farms were randomly selected using the systematic random sampling procedure from approximately 900 groundnut farms registered under Lucrative Legume Project of (ICRISAT).Out of the available list of groundnut farms396 soils samples were sampled from 150 farms randomly selected farms. Prior to this study quality groundnut seed had been distributed to small-scale farms in the study area under the Lucrative Legume Project (ICRISAT) to enhance and ameliorate the declining yield trends and improve farmer's income. The groundnut farmers were distributed randomly within the districts and across the AEZs (LM_1 LM_2 LM_3 LM_4/UM_4). Soil sampling was carried out to determine average nutrient status on small-scale groundnuts farms. Soil sampling was conducted using a zigzag scheme on the groundnut field (Figure 5). Five points along the scheme for every acre were considered appropriate. From each sampling point, a soil sample was extracted using an Edelman-Dutchman soil auger with a diameter of 6 cm, at depths of 0-20 cm and 20-50 cm. A composite sample of extracted soil samples was taken for each depth separately, mixed thoroughly in a bucket and 1 kg sub-sample and packed in a plastic bag. The samples were labeled according to depth, a unique field research identity, farmer's name, AEZ and the location. The sub-sampled samples were taken to the laboratory for spectral and chemical measurements.

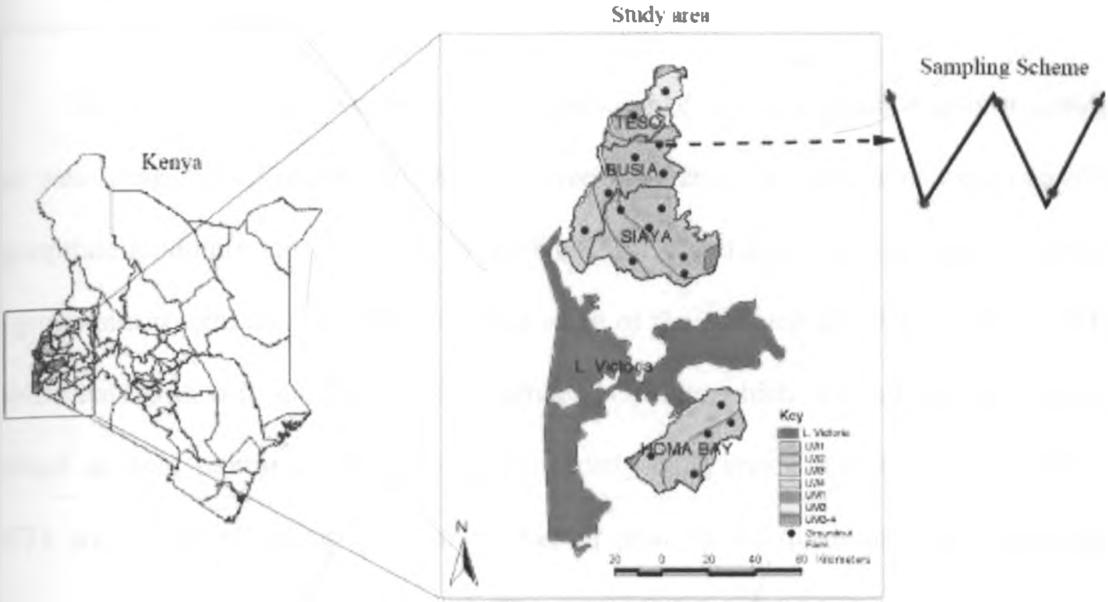


Figure 5: The soil sampling scheme

(b) *Plant sampling*

Within the vicinity of the five soil sampling points selected in the zigzag scheme (Figure 5), a groundnut plant was collected at random which was used to make a composite groundnut plant sample for above-ground biomass nutrient analysis. The whole above-ground portion of plant was harvested and the plant material composited. The plant samples were packed in a paper bag to prevent respiration. Labeling of the plant was done, to allow correlation of soil samples with the groundnut farm and correlating soil data obtained by individual farmers.

3.3 Disease surveillance

An assessment of severity involved counting of diseased plants within a sampling unit measuring 5 by 5 meters (Figure 6). Three quadrants for every acre were considered appropriate randomly located on the groundnut farm. Careful record was made of presence of groundnut rosette and crop phenological stage of the sampled plants to facilitate linking disease data with soil nutrient status. Number of plants which showed rosette symptoms, defined as mild mottling and flecking, but mostly dark green, severe stunting (Gibbons, 1977), were counted out of the total number of plant in the quadrant. The percentage of diseased plants over total population in the quadrant (prevalence) was computed. Seventy groundnut farms were assessed for groundnut rosette prevalence and selection of groundnut farms were random using the systematic random sampling procedure.

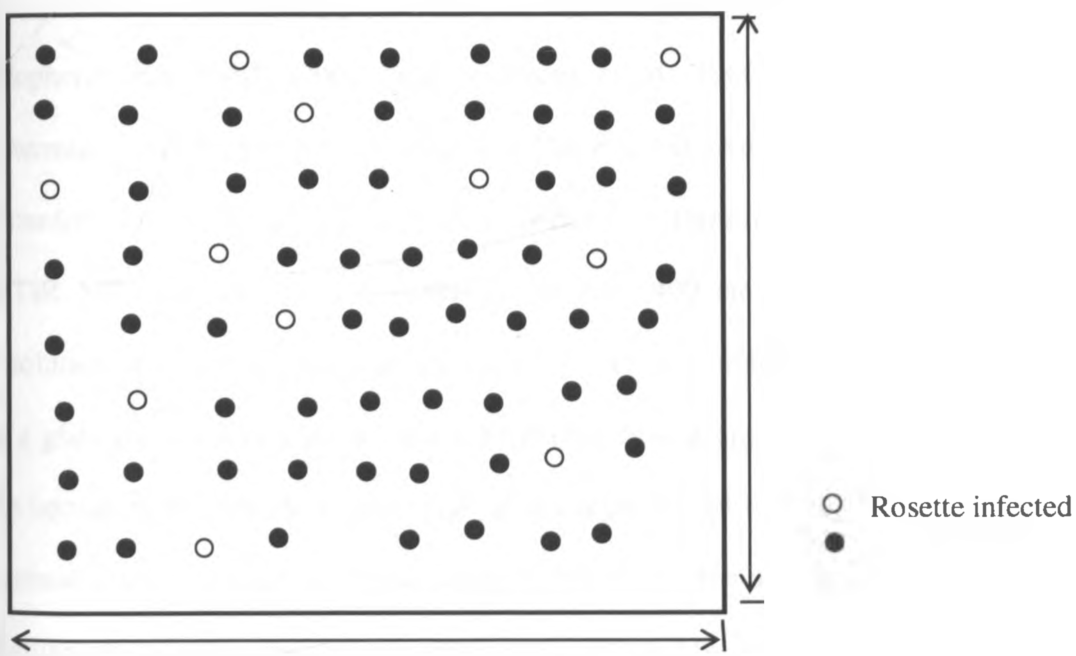


Figure 6: Illustration of an example of a quadrant

3.4 Laboratory Methods

(a) Preliminary sample preparation

Soils were pretreated by air-drying and sieving to 2 mm fractions and put in paper bags for convenience of handling, storage and to minimize variation due to soil moisture (Ben-Dor et al., 1999). Special laboratory identification which correlated to the unique field research identity was assigned on each soil sample. Plant samples were dried in an oven at 60^0C (Anderson and Ingram, 1993) then ground to pass a 1-mm sieve.

3.5 Spectral measurements

(a) Scanning of soil and plant samples

Infrared spectroscopy was used for rapid assessment of soil quality as outlined by Shepherd and Walsh (2002) and Shepherd et al., (2003). Reflectance spectra were determined on all plant and soil samples. The near infrared (NIR) reflectance spectra was recorded for soil samples using a Bruker Fourier Transform Infrared Multi-purpose Analyzer (FTIR MPA) (Figure 7) at wavelengths of 4000-400 cm^{-1} spectral range at a spectral resolution of 8 cm^{-1}. During scanning 20 grams of soil sample from each sample was placed in a glass petri-dish or glass sample vial (plants). Soil /plant samples were scanned through the bottom of the petri-dish / glass vial on an integrating sphere window. The machine has an internal; computer controlled gold reference which permits automatic spectra acquisition at regular intervals. The spectral signatures were collected by averaging 32 scans (automated in the FTIR) and saved for quantitative determination.

Figure 7: Bruker Transform Infrared multi-purpose Analyzer (Source; ICRAF Spectral Laboratory)

Finely ground soil samples were also analyzed in the mid-infrared (MIR) (4000 – 600 cm^{-1}) diffuse reflectance using a Bruker High-Throughput-Screening (HTS-XT) accessory attached to a Bruker Tensor 27 FT-IR spectrometer. Five grams of soil were loaded into aluminum micro-plates (Figure 8) that enabled spectral measurement in the MIR spectral region. An empty cell was used as background reference.

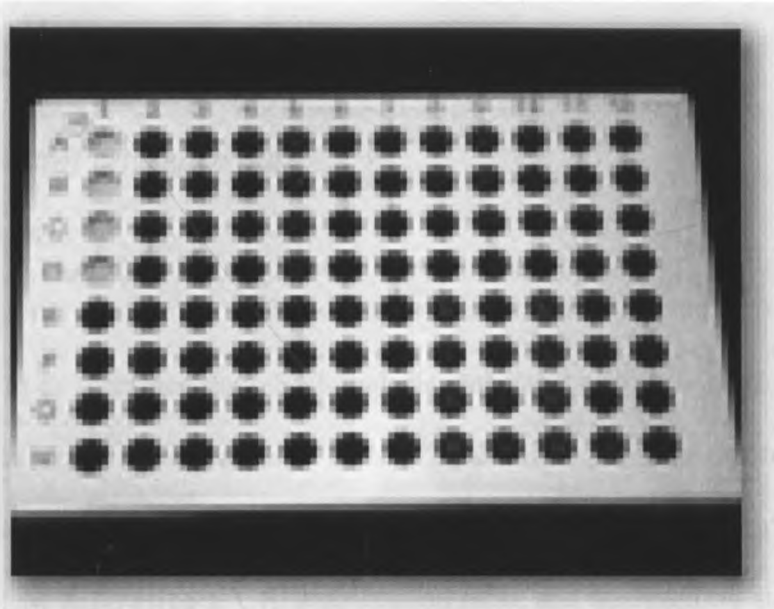


Figure 8: Aluminum micro plate used to scan ground soil samples

(b) Selection of soil and plant samples for reference data

Representative samples were selected for developing calibration models and validation using standard laboratory soil chemical analysis techniques. Selection of samples to be used as reference data was based on recorded spectral diversity using Euclidean distances calculated from principal component scores. Euclidean distances were then ranked in an ascending order. From the first quartile of distances, the soil sample with the smallest Euclidean distance was selected, while from the last quartile the sample with the highest quartile was selected. These two samples give the extremes of the spectral diversity. From each quartile and additional 24 soil samples were selected randomly. This gave a total selection of 100 samples out of the 395 samples scanned for conventional laboratory analysis.

3.5Development of reference data

(a) Soil reference data

Conventional laboratory analysis was conducted only for the 100 sample subset, herein referred to as reference data. Soil analysis was done using standard methods widely used for tropical soils (Shepherd and Walsh, 2002). Soil pH was determined using an electrode pH meter for saturated soil paste using a 1:2.5 soil/solution ratio. Samples were extracted with 1 M KCL using a 1:10 soil/solution ratio, and analyzed by atomic absorption spectrometry (AAS) for exchangeable calcium and magnesium (ISFEIP, 1972; Yurimaguas Experiment Station Staff, 1989). The Olsen method (pH 8.5, modified Olsen) was used to determine extractable phosphorous (Ext. P) using molybdate reaction for colorimetric detection with a flame emission spectrometer (ISFEIP, 1972; Yurimaguas Experiment Station Staff, 1989). Total organic carbon (TC) and total nitrogen (TN) were determined on finely ground soil samples using the C: N analyzer by dry combustion technique (Wright and Bailey, 2001). The samples were weighed and packaged into tin capsules for analysis. Particle-size analysis was determined using the hydrometer method after pretreatment with hydrogen peroxide to remove organic matter (Gee and Bauder, 1986). The hydrometer method of silt and clay measurement relies on the effects of particle size on the differential particle velocities of the particles through a water column-Stoke's law. This is dependant upon temperature, viscosity, diameter of particle and specific gravity of the falling soil particle.

(b) Plant reference data

Sixty groundnut plant samples were selected for reference analyses based on the spectral diversity. The analyses conducted were total nitrogen, determined by sulphuric digestion following micro-Kjeldahl distillation and titration. Phosphorus was analyzed by sulphuric digestion prior to vanadium molybdate colorimetry. Potassium was analyzed by sulphuric digestion prior to determination by flame emission spectroscopy (Cornforth, 1984; Pinkerton et al., 1997; Mills and Jones, 1996). Copper (Cu), zinc (Zn) and manganese (Mn) were analyzed by ashing (500°C for 6 hours) prior to determination by atomic absorption spectrometer (AAS). (Cornforth 1984; Pinkerton et al., 1997; Mills and Jones, 1996).

3.6 Saturated soil pastes and water extract experiment

(a) Preparation of soil water extracts

Soil sample extracts were prepared from the soil sample using deionized water. Ten grams of soil sample was weighed in a centrifuge tube for each of soil samples selected. Twenty millimeters of deionized water was added to weighed soil sample to obtain a 2:1(water/soil) ratio followed by bunging the tube. The tube were shaken vigorously for 30 minutes on a machine shaker and immediately the saturated mixture put in a centrifuge machine for separation of liquid and solid phases. The supernant was poured in filter bottles. Filtrate (water extract) was taken for spectral measurements using optical glass curvets and scanned using the transmission mode in the NIR spectral region.

For MIR spectral measurements, 20 μm of the soil water extract was loaded on a single well (duplicates for each sample) of the silica micro-plate. The silica plate was dried for 30 minutes at a temperature of 40°C. Upon drying, the dry skins on the silica micro-plates (Figure 9) were taken for MIR spectral measurements using the HTS-XT accessory.

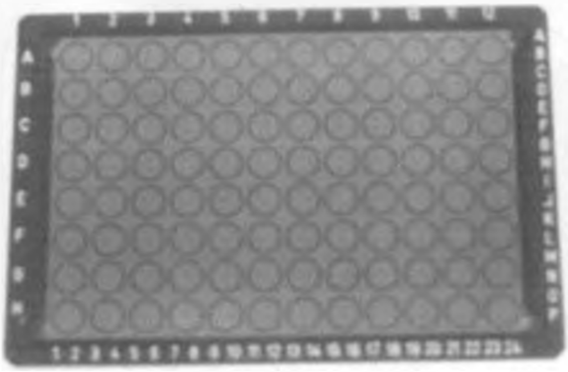


Figure 9: Silica micro-plates for dry skins

(b) Preparation of soil paste

Soil paste were prepared by mixing air-dried soil sample and deionized water (ratio variable depending on soil type) vigorously with a vortex shaker for 1 minute to obtain a saturated paste. The sample was placed onto the diamond crystal of a pike miracle attenuated total reflectance (ATR) accessory, inserted into the sample compartment of a Bruker Tensor 27 FT-IR spectrometer (Figure 10). For each soil sample, an average of 32 scans over the MIR region was collected for each soil sample. Spectra of deionized water was regularly recorded in- between soil paste spectral signatures for baseline purposes as adopted by Linker et al., (2006)

Figure 10: A crystal of a pike miracle attenuated total reflectance (ATR) accessory, inserted into the sample compartment of a Bruker Tensor 27 FT-IR spectrometer

3.7 Statistical methods

(i) Spectral data analysis

(a) Calibration and validation

Data organization was the first step i.e. spectral and reference data that facilitated establishment of calibration models. It was done by identifying the respective soil samples with soil spectral reflectance.

Calibration is establishment of a robust empirical relationship between two variables. The objective of calibration was to establish a model, which was be used for prediction of soil properties of the whole data set. The soil spectra were pretreated by selection of the optimum wavelengths for inclusion in calibration models, done using the Opus Lab procedure of (OPUS version 6.5 Bruker).The optimization of spectral data with soil parameter was done to remove noise signals from spectral signatures.

Calibration models were developed using partial least square regression (PLSR) to extract spectral information from spectral data and relate it to principle soil chemical properties (soil pH, TC, TN, Ext.P and Exch.K, Ca, Mg and particle size distribution (Shepherd and Walsh, 1998; Chang et al 2001). Data transformation was carried on soil and plant data to achieve normally distribution. Natural log transformation of soil pH, TC, TN, Ext.P and exchangeable cations; (K, Ca, and Mg) was necessary to meet homogeneity criteria for PLSR and PCA analysis for the soil variable. Back transformation by looking for the exponential of the transformed values was carried out to obtain the original form of the soil and plant data.

Partial least-squares is a bilinear regression method that extracts a small number of factors, which are combination of independent variables (spectral reflectance) and uses these factors as regression generator for the dependent variables or chemically measured values (reference data). The first derivative of spectra, with 17 smoothing points was obtained and used to regress against the soil property using OPUS Lab software Version 6.5 (Bruker)

Calibration models developed using cross-validation could give over-optimistic actual performance of calibration models (Tormod et al., 2002). Shepherd and Walsh (1998) adopted the use of independent soil data sets to validate calibration models when developing spectral libraries. The goodness and robustness of the calibration model was evaluated using cross validated statistics; coefficient of determination (r^2) *(i)* and the root mean square error of cross validation (RMSECV) *(ii)* and bias *(iii)* for the soil pastes and water extract experiment (Tormod et al., 2002; William and Norris 2001)

$$r^2 = \frac{SSR}{TSS} \qquad (i)$$

$$RMSECV = \sqrt{\sum_{i=1}^{N_p} \frac{(\hat{y}_{CV,i} - y_i)^2}{N_p}} \qquad (ii)$$

$$Bias = \sqrt{\sum_{i=1}^{N_p} \frac{(\hat{y}_i - y_i)^2}{N_p - 1}} \qquad (iii)$$

Where SSR is the sum square of regression, and TSS is the total sum of squares, $\hat{y}_i$ and y_i are the predicted and measured reference values and N_p is the number of samples to be tested. The goodness and robustness of calibration model depend on the property of interest which depends on the degree to which the soil property can be modeled from spectral information (McCarty et al., 2002).

The calibration set for this study consisted of 100 soil samples and 60 plant samples for calibration model development. The resulting calibration models were used to estimate (predict) the modeled soil/plant properties for 393 soil samples and 135 groundnut plant samples respectively for samples that had spectral properties falling within the domain of the calibration set.

(b) Analysis of soil nutrient variation using Principal Component Analysis

Principal component analysis (PCA) was used to statistically analyze data to assess variation of all soil properties (all combined) and take advantage of the strength of the relation among soil properties to arrive at soil fertility indicators. For example, extractable P may calibrate poorly to IR individually but useful information on it may be predicted from IR due to its association with other properties. PCA is a multivariate analysis in which a data reduction technique is applied to develop new composite variables (principle components) as a result of a linear combination of original variables (Manly, 1986). PCA recombines the original variables into components, or factors, which are independent (not correlated), with one another. The principal components were used to determine important soil nutrient variables and how they influence each other. The first few components explain most of the variation in the entire original data set and show the influence of main variables for each principal component. Success has been reported in several literatures where PCA as a statistical technique has been employed for analyzing soil data (Dwivendi, 2001; Ray et al., 2002).

The principle components were renamed as soil fertility indicators (SFIs) upon which soil classes were developed depending on a soil fertility score. A simple regression was conducted between the soil nutrients and the soil fertility indicators to determine the strength of the relationship by comparing the coefficient of determination. The assessment of the potential soil nutrient constraints for different soil variables was based on critical concentrations levels (Okalebo et al., 2002).

CHAPTER 4

RESULTS AND DISCUSSION

Summary statistics of the soil nutrient variables for the reference data are provided in Table 1. Soil pH_w values for the reference data from the groundnut farms did not exceeded 8.5 while the highest concentration of TC was 3.2 %. The high values were predominant in the agro ecological zones LM_4/UM_4. There was a normal distribution in the particle size distribution (sand, clay and silt) data. Generally sand levels were higher in majority of the groundnut farms compared to other soil particle fractions, silt and clay. The ranges in the soil reference data set demonstrated that the selection of calibration set was suitable for the calibration.

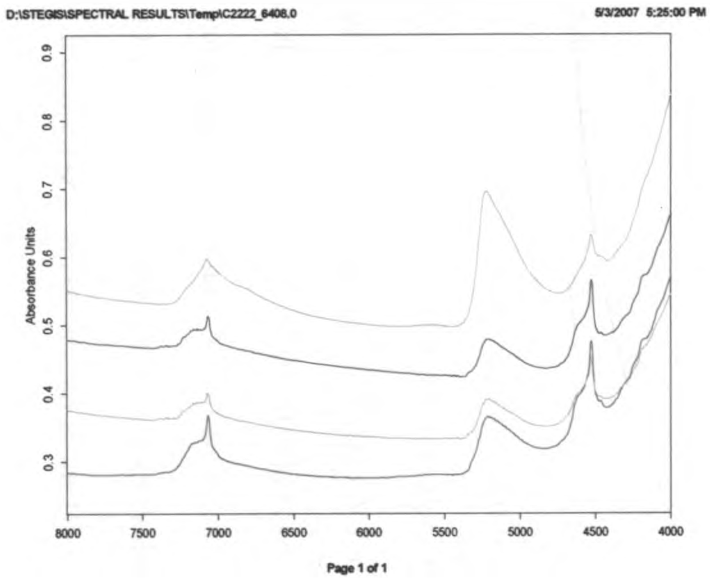
Table 1: Descriptive statistics for soil reference data

Soil Variable	*n*	*Mean*	*Minimum*	*Lower Quartile*	*Median*	*Upper Quartile*	*Maximum*
Soil pHw	100	5.88	4.76	5.35	5.78	6.22	8.35
Total carbon (%)	100	1.27	0.42	0.78	1.09	1.72	3.21
Total nitrogen (%)	100	0.11	0.03	0.07	0.1	0.14	0.23
Extractable phosphorus ($cmol_c\ kg^{-1}$)	100	6.77	0.45	1.46	2.73	6.58	70.45
Exchangeable potassium ($cmol_c\ kg^{-1}$)	100	0.49	0.06	0.2	0.34	0.66	1.91
Exchangeable calcium ($cmol_c\ kg^{-1}$)	100	6.75	0.8	2.4	4.4	7.05	41.4
Exchangeable magnesium ($cmol_c\ kg^{-1}$)	100	1.77	0.2	0.65	1.1	1.95	7.4
Sand (%)	100	47.65	17	36.5	45	59	78
Silt (%)	100	20.46	5	11	21	29	47
Clay (%)	100	30.88	13	24	32	38	49

4.1 Spectral signatures

Soil samples exhibited distinct spectral reflectance signatures for NIR and MIR spectral regions as shown in Figure 11 (a) and (b) respectively for selected soil samples from sampled sites.

(a)



(b)

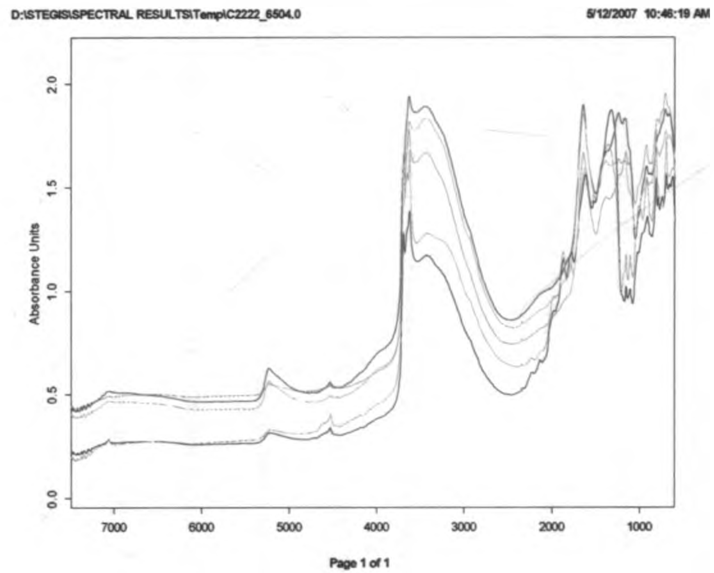


Figure 11: Spectral Signature for air-dried soils (a) NIR (b) MIR

Prominent absorption features for air-dried soil samples were found in the wavelength region of between (4400- 4600, 4800-5400 and 7000- 7400) cm^{-1} in the NIR spectral region. The predominant features could have been as a result of C-H and O-H stretching vibrations as observed by Workman (2001) and various functional groups present in a soil sample.

The MIR spectral signatures (Figure 11 b); absorption features were dominant in the ranges of 1200-2000, 3200-3500, 4500-4500 and 5200-5500 cm^{-1}. Specific molecular vibrations along wavebands in MIR spectral range were sensed and could be associated with functional groups; methoxy C-H stretching, carbonyl associated C-H stretching; and N-H from primary amides, secondary amides (Workman 2001). Triple bonds such as nitrile group (C≡N) and double bonds such as C=C stretching are characteristic of the MIR region due to high constant force of bonds (Stuart 2004). Spectral absorption signatures of soil are affected by clay type, amount of organic matter, particle size and presence of iron and aluminum oxides (Janik et al., 1998, Chang et al., 2003).

4.2 Calibration models for soil variables

Cross validated statistics for soil chemical and textural properties for MIR and NIR spectral region are shown in Table 2 and 3 respectively. The best calibration models were deemed to have the highest r^2 and the lowest RMSECV for both calibration and validation models (Chang et al, 2003; Islam et al., 2003). Maleki et al., (2006) reported that calibration models for soil samples with r^2 values > 0.90 are classified as excellent, moderate for r^2 values of 0.80-0.90 and fair for r^2 values of 0.50- 0.79. Values of r^2 close to 1 indicated that calibration model developed was almost as good as the laboratory technique against which it was calibrated. However, in reality there are errors in the laboratory methods themselves and these are also reflected in the calibration error (Shepherd et al., 2005).

The cross validated statistics for the calibration model in the data set of soil parameters reveal a high degree of correlation between spectral information and reference soil chemical data. The r^2 values (predictions) for MIR spectral region were better (higher) than for NIR and TC had the highest value of 0.98. Robustness of MIR prediction models was further illustrated by RMSECV values which were lower than for NIR. McCarty et al., (2002) indicated similar results where MIR spectral region performed better than the NIR spectral region while predicting soil organic carbon. The reason for good prediction for MIR could be attributed to the fact that the region is energetic enough to excite molecular vibrations to higher energy levels (Chalmers and Griffiths, 2002). Therefore the MIR region has more fundamental structural information compared to NIR that has major weakness of absorption bands accruing as overtones of the fundamental bands residing in the MIR.

Table 2: Calibration statistics for soil variable in the NIR spectral region

	Calibration set				Validation set		
Soil Variable	*n*	*Outliers*	r^2	*RMSECV*	*n*	r^2	*RMSECV*
Soil pHw	95	5	52.3	0.072	95	30.1	0.0813
Total C	98	2	87.9	0.184	98	81.3	0.216
Total N	99	1	72.9	0.258	97	64.9	0.281
Ext. P	97	3	35.1	0.765	96	31.0	0.862
Exch. K	100	0	32.0	0.643	100	29.0	0.649
Exch.Ca	98	2	83.6	0.350	98	80.8	0.378
Exch. Mg	99	1	76.8	0.433	99	70.0	0.471
Sand	92	8	85.7	6.37	92	79.1	7.26
Clay	97	3	59.4	5.70	97	56.9	5.77
Silt	95	5	76.9	5.04	95	65.9	5.29

Key; n = sample size r^2= coefficient of determination, RMSECV=Root Mean Square Error of Cross validation.

Table 3: Calibration statistics for soil variable in the MIR spectral region

	Calibration set				Validation set		
Soil Variable	*n*	*Outliers*	r^2	*RMSECV*	*n*	r^2	*RMSECV*
Soil pHw	93	7	91.0	0.040	93	84.6	0.033
Total C	96	4	98.1	0.071	96	97.3	0.082
Total N	98	2	93.6	0.093	98	94.8	0.108
Ext. P	94	6	51.4	0.668	94	57.6	0.738
Exch. K	96	4	50.2	0.525	96	34.8	0.585
Exch.Ca	97	3	96.7	0.180	97	94.5	0.199
Exch. Mg	89	11	94.1	0.203	89	91.9	0.227
Sand	93	7	85.9	6.04	93	83.4	6.34
Clay	93	7	81.9	4.15	93	76.6	4.71
Silt	96	4	82.6	3.77	96	75.5	4.71

Key; n = sample size r^2= coefficient of determination, RMSECV=Root Mean Square Error Cross validation.

Figure 12 shows a plot of actual soil pH_w values against predicted values for MIR and NIR spectral regions. Prediction accuracy was better when soil pH_w was predicted with MIR spectral region (r^2 =0.92, RMSECV= 0.033). Cross validated statistics; r^2 =0.50 and RMSECV=0.717 for the NIR spectral region were obtained for soil pH_w with the r^2 value lower compared to those of MIR spectral region. However, higher r^2 values for soil pH_w were reported by Janik and Skjemstad (1995) r^2 = 0.72, Reeves et al., (1999) r^2 0.74 and Shepherd and Walsh (2002) r^2 ̄0.70 Islam et al., (2003) r^2 = 0.71 with NIR form air dried soils. The difference in the results could be attributed to difference in the laboratory methods and technician used to develop the reference data that result to difference in errors and precision.

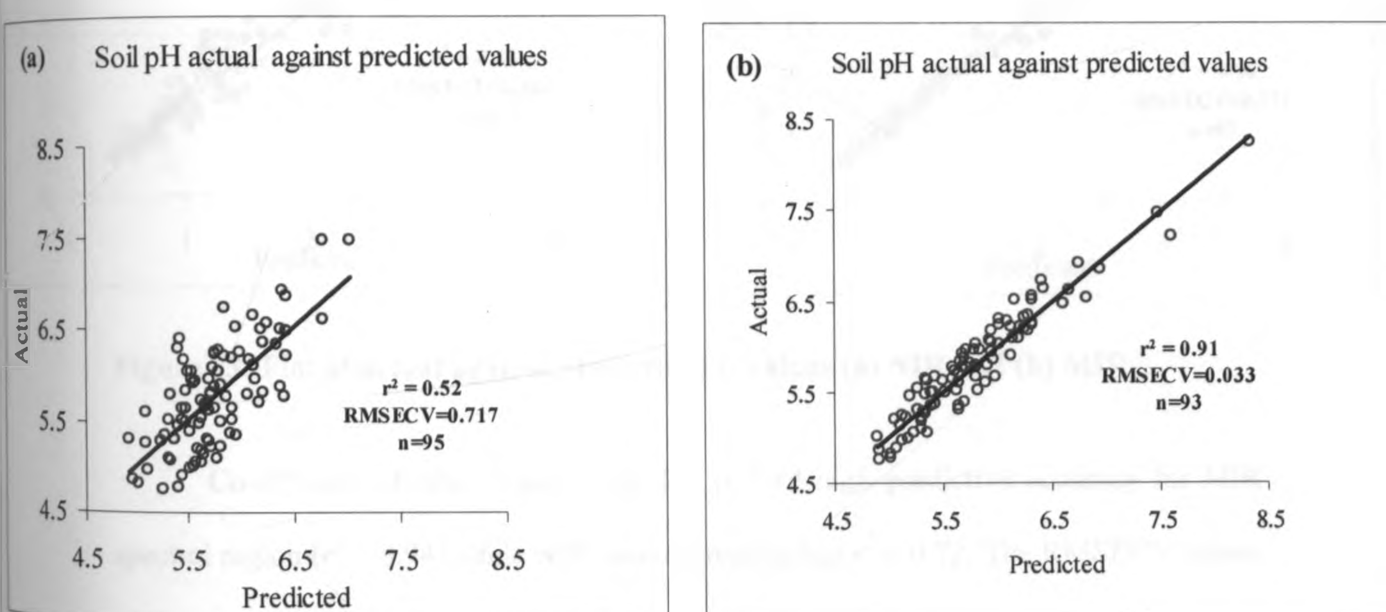


Figure 12: Plot of actual against predicted soil pH (a) NIR and (b) MIR

The calibration model developed from TC was excellent for MIR and moderate for the NIR (Figure 13). Prediction accuracy was excellent for both NIR (r^2= 0.88, RMSECV=0.184) and MIR (r^2=0.98 and RMSEP=0.071) spectral regions (Figure 13). Better prediction for calibration model developed for TC can be associated with the high presence of various functional groups (-CH, OH –NH) in soil organic matter (William and Norris 1987). The predictive results model was similar to predictive model reported by other researchers (McCarty et al., 2002, Dunn et al., 2002, Shepherd and Walsh 2002).

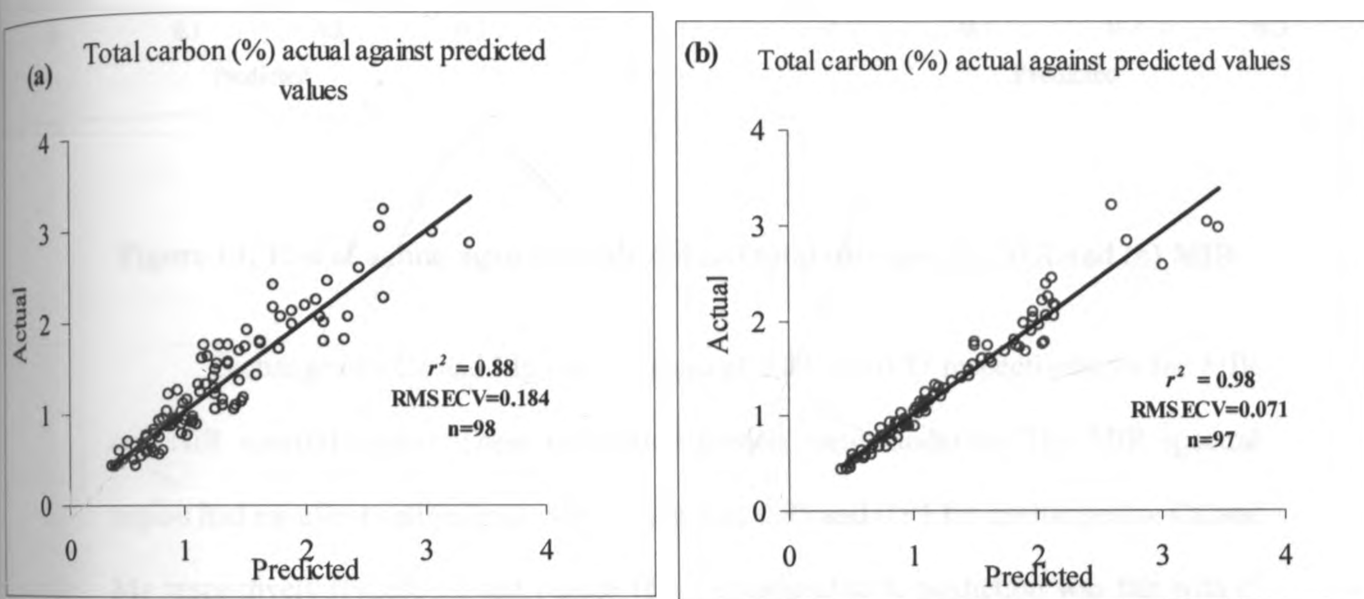


Figure 13: Plot of actual against predicted TC values (a) NIR and (b) MIR

Co-efficient of determination for TN yielded high predictive accuracy for MIR spectral region (r^2 = 0.94) while NIR spectral region had r^2 = 0.72. The RMSECV values of 0.093 and 0.258 for MIR and NIR respectively illustrates (Figure 14) robust calibrations for TN. These results were almost similar and more accurate to those reported by other researchers (r^2 = 0.96, Reeves et al., 1999 and r^2=0.85; Chang et al.,

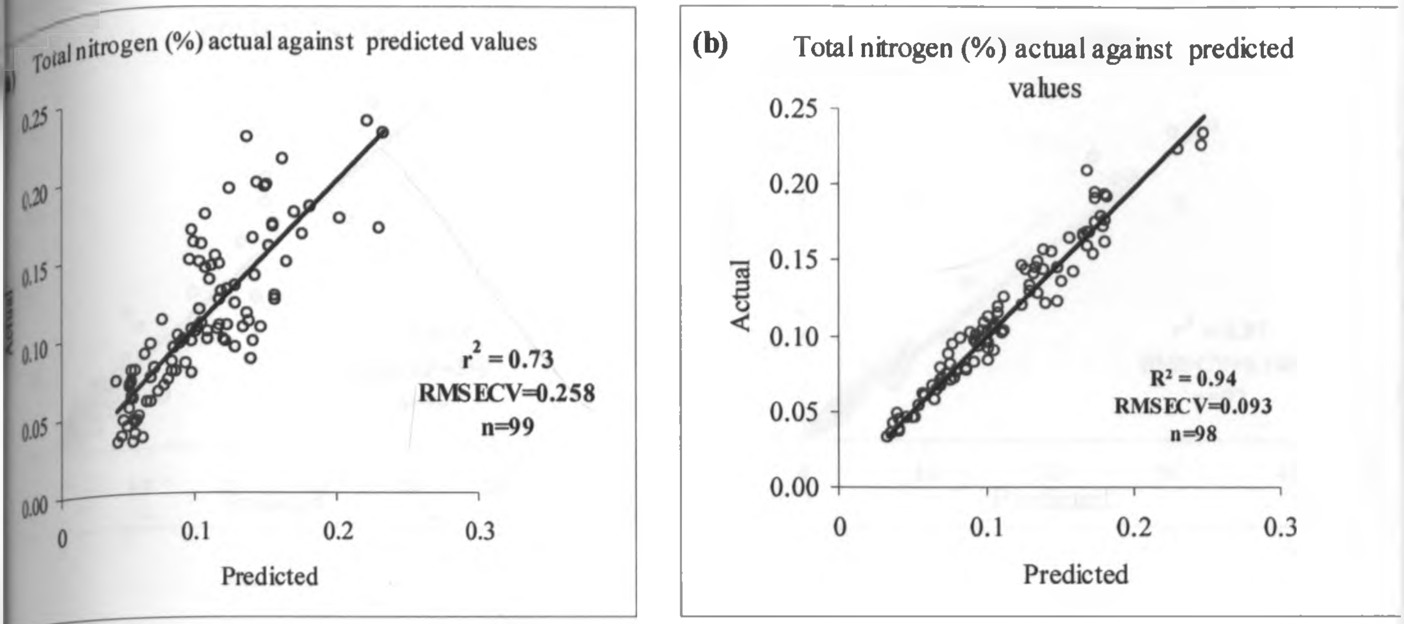


Figure 14: Plot of actual against predicted soil total nitrogen (a) NIR and (b) MIR

Exchangeable Ca and Mg had r^2 values of 0.84 and 0.77 respectively for the MIR and NIR spectral region. These calibration models were moderate. The MIR spectral region had excellent calibrations with r^2 values of 0.95 and 0.94 for exchangeable Ca and Mg respectively (Figure 15 and Figure 16). Exchangeable K prediction was fair with r^2 value of 0.58 for MIR spectral region. Most literatures have sighted reason to poor prediction of exchangeable K as narrow range in data set (Islam et al., 2003) but it could also be due to the laboratory analytical technique itself not relating well to the fundamental soil properties detected by IR, in which case the efficacy of the soil test may be in question. This can only be validated through crop response trials.

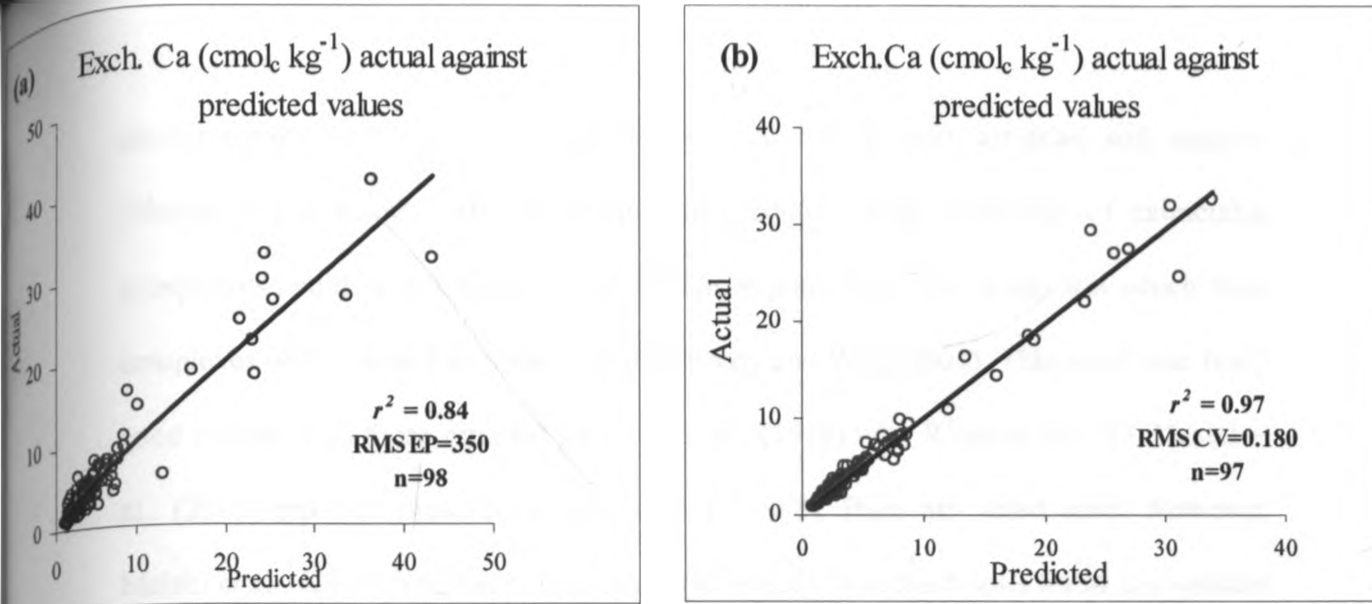


Figure 15: Plot of actual against predicted exchangeable calcium (a) NIR (b) MIR

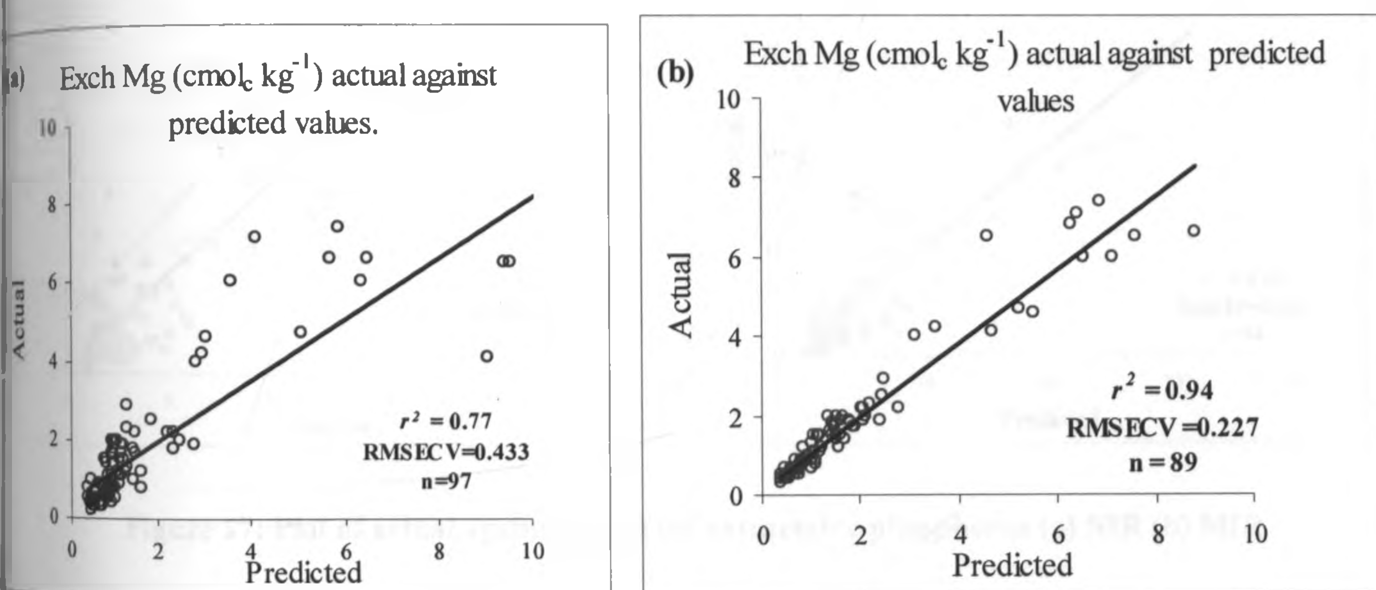


Figure 16 : Plot of actual against predicted exchangeable magnesium (a) NIR (b) MIR

Fair calibration were found for Ext. P (r^2=0.51) for MIR spectral region and poor (r^2=0.35) for NIR spectral region (Figure 17). Previous research findings have indicated similar results with poor R^2 values for NIR for Ext. P from air-dried soil samples (Shepherd and Walsh 2002; Yong and Song 2006). Poor prediction of extractable phosphorus could be attributed to the fixation of phosphate ions in the soil which form complexes with iron and aluminum oxides (Brady and Weil, 2001). This result was fairly good compared to those reported by Janik et al., (1998) with R^2 value of 0.07. Daniel et al., (2003) reported moderate results with R^2 =0.81 from air- dried soils. However, Maleki et al., (2006) reported better results (R^2 =0.88) from fresh soils for *in situ* spectral measurement of P from wet soils.

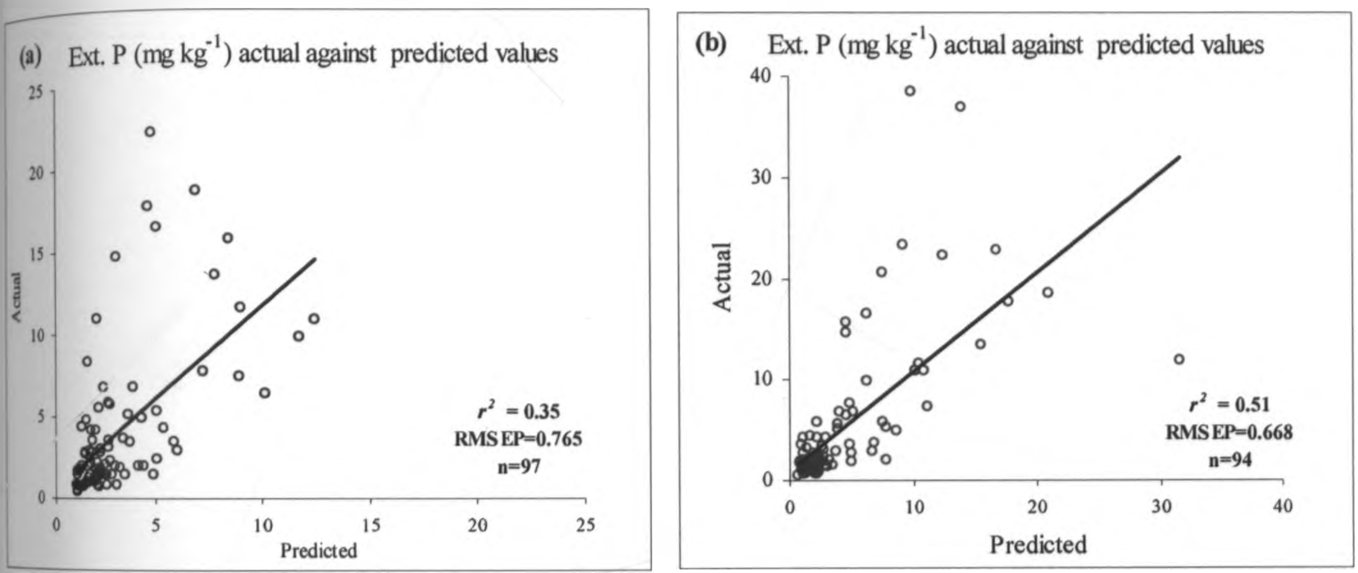


Figure 17: Plot of actual against predicted extractable phosphorus (a) NIR (b) MIR

4.3 Saturated soil water paste and water extracts experiment

Figure 18 shows the spectral signatures derived from saturated soil water pastes. Saturated soil water pastes had characteristic toughs and peaks in the regions 1800- 1400 cm^{-1}, 1200-800 cm^{-1} for MIR. Noise signals were dominantly present below 550 cm^{-1} and above 4000 cm^{-1}. There were characteristic finger print regions and absorption feature present in within 3900 and 600 cm^{-1} spectral range. Spectral signatures for soil water pastes were regular .i.e. followed a similar pattern and had absorption feature at specific ranges.

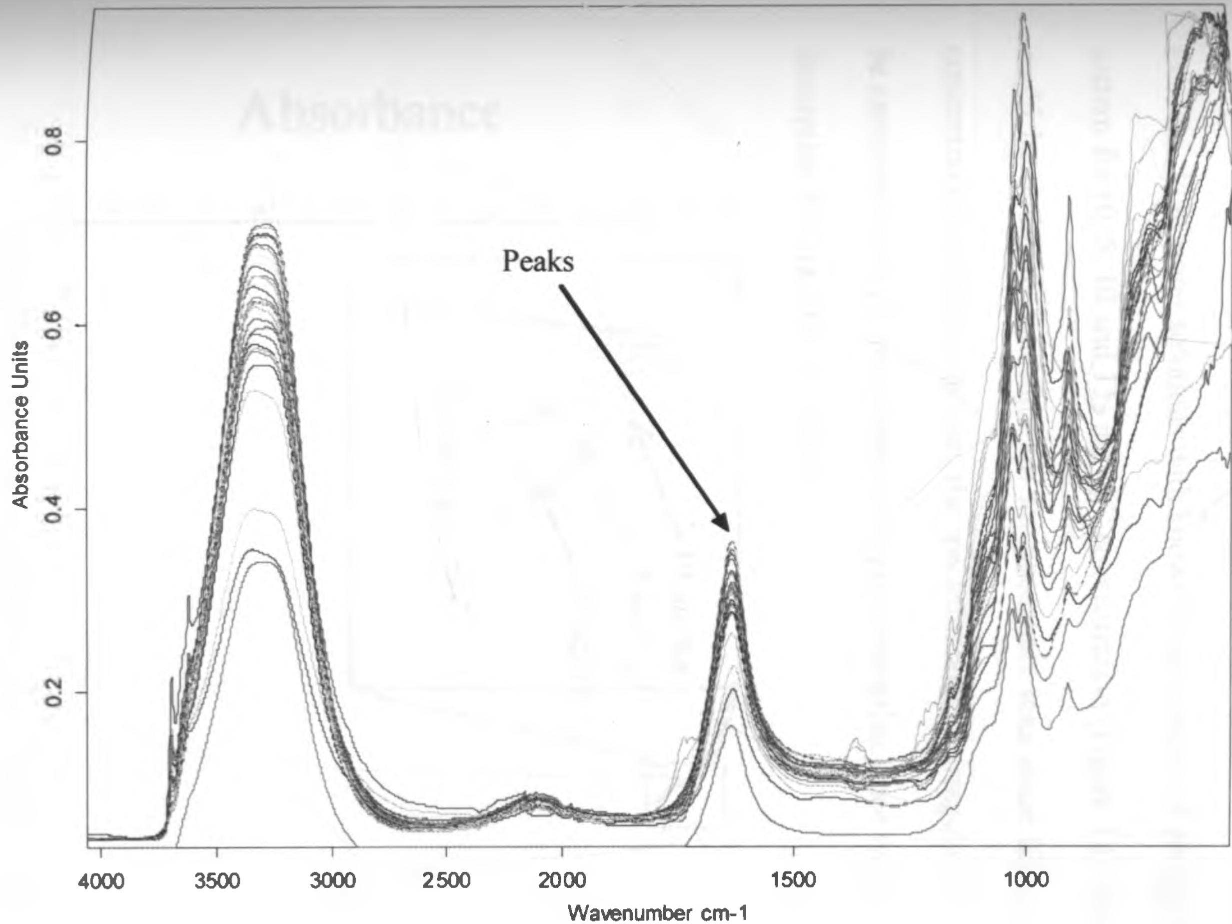


Figure 18: Spectral signature for soil saturated paste in MIR spectral region.

For the soil water extract spectra, there were minimal absorption features. Characteristic peaks and toughs were not present in the spectral signatures. And symmetrical absorption which is the ratio of the left side to the right side of feature at full width at half maximum was not present. Hence, common trends for the spectral signatures where prominent absorption features could not be identified for the water extracts. Pure water solutions with known concentration of phosphate ions had a regular pattern for (0, 5, 10 and 15) mg kg^{-1} concentration (Figure 18). Presumably, 15 mg kg^{-1} could be optimum concentration for phosphate ions since higher (above 15 mg kg^{-1}) concentrations in pure solutions, the spectrum became irregular. This phenomenon could be associated with the interference of water absorption since water is known to have high absorption features (Stuart, 2004).

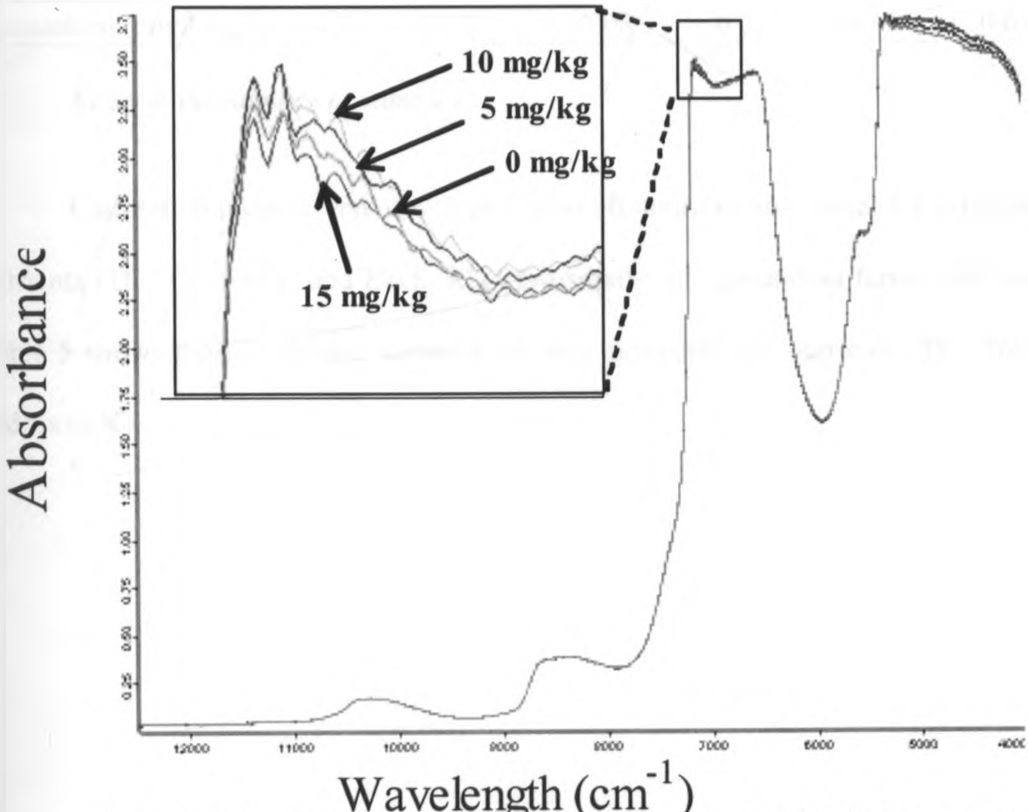


Figure 19: Spectral signature for soil water extracts in NIR spectral region

Table 14 below are descriptive statistics for the principle soil nutritional properties (TN, TC, Ext.P and Exch. K) for groundnut farms soil samples used for saturated pastes experiment.

Table 4 : Descriptive statistics for saturated soil pastes reference data

Soil nutrient variable	*n*	*Mean*	*Minimum*	*Lower Quartile*	*Median*	*Upper Quartile*	*Maximum*
Total carbon (%)	30	1.2	0.46	0.79	1.05	1.46	3.03
Total nitrogen (%)	30	0.11	0.04	0.08	0.1	0.14	0.23
Extractable phosphorus (mg kg^{-1})	30	6.26	0.50	1.44	2.77	6.5	38.55
Exchangeable potassium ($cmol_c$ kg^{-1})	30	0.47	0.08	0.21	0.37	0.67	1.61

Key n = the number of samples

Calibration models were developed from 30 saturated soil pastes for principle soil nutrients (TC, TN, Ext P. and Exch. K.) from small-scale groundnut farms soil samples. Table 5 shows cross validated statistics for four principle soil nutrients (TC, TN Ext.P and Exch.K).

Table 5: Calibration statistics for saturated soil pastes in the MIR spectral region using ATR

	Calibration				Validation			
Soil Nutrient	*n*	*Outliers*	r^2	*RMSECV*	*N*	*Outliers*	r^2	*RMSECV*
SOC	27	3	0.93	0.331	27	3	0.46	0.343
TN	30	0	0.94	0.012	30	0	0.72	0.024
Ext.P	28	2	0.38	4.32	28	2	0.25	-5.32
Exch.K	27	3	0.53	0.11	27	3	0.44	0.25

Key: n = sample size r^2*= coefficient of determination, RMSECV=Root Mean Square Error of cross validation*

The cross validation statistics were averages of three replicates of the 30 saturated soil pastes. Excellent calibrations models were obtained for TN with r^2 values 0.94. Linker et al., (2006) had similar r^2 values while predicting nitrates from soil saturates pastes, although TN and nitrate N are not necessarily related. Extractable P yielded poor predictions from the entire spectral range (4000-500cm^{-1}) with r^2 values of 0.38. This could be due to the fact that P not relating well with spectral due to high absorption by water (interference) in the saturated soil paste. However, the prediction yielded better results when the spectral range that is characteristic of phosphate ions (900-1200cm^{-1}) was considered. It gave better results calibration r^2 value of 0.66 and validation r^2 value of 0.53. Exchangeable potassium had fair predictions with r^2 values of 0.54. Exchangeable TN had a good prediction but the calibration model was unstable as indicated by the big difference between r^2 for validation (0.46) and 0.93 for calibration. Figures 18 (a) - (d) shows graph plots of actual values against predicted of saturated soil pastes for TC, TN, Ext.P and Exch.K respectively.

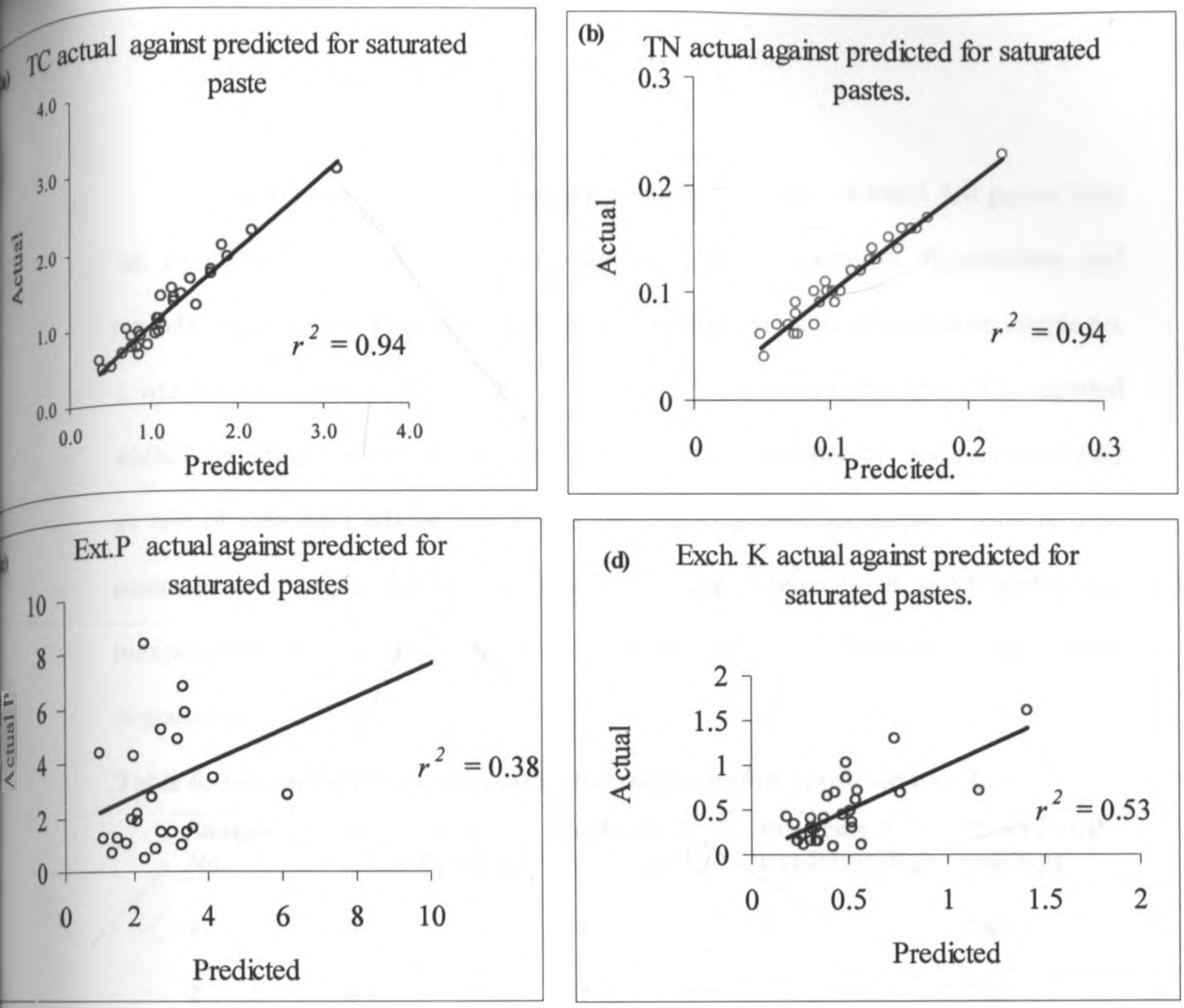


Figure 20: Calibration plots of actual against predicted soil saturated pastes in MIR region using ATR (a) Total carbon (b) total Nitrogen (c) Extractable phosphorus (d) Exchangeable potassium.

Although the prediction yielded by Ext.P were poor using saturated soil pastes, the estimated Ext. P levels from soil pastes were more reproducible and repeatable (Table 6). Thus it may be important to note that even though poor prediction was yielded for Ext.P, the protocol for soil extract preparation and spectral technique were okay. Hence poor prediction could be probably being attributed to laboratory analytical errors.

Table 6 presents results of predicted values for some saturated soil pastes from the experiment for Ext. P. The results indicated a degree of repeatability and reproducibility for the three replicated. An example is the saturated soil paste sample no. 1 which had a value of 0.4 mg kg $^{-1}$. Workers, Shepherd and Walsh (2002) reported while developing spectral libraries also noted accuracy, repeatability and reproducibility as one of important advantages of this modern diagnostic technique. This is quite essential with the increasing global need for larger amounts of good quality and inexpensive spatial soil data to be used in management and rehabilitation of soil fertility degradation.

Table 6: Selected samples from saturated soil pastes for predicted Ext. P.

Sample No.	**Replicate 1 Ext.P (mg/Kg)**	**Replicate 2 Ext.P (mg/Kg)**	**Replicate 3 Ext.P (mg/Kg)**	**Mean Ext.P (mg/Kg)**
1	0.4	0.4	0.4	0.40
2	8.0	6.5	-	7.25
3	0.7	1.1	0.7	0.83
4	0.1	0.1	0.1	0.10
5	5.6	5.1	6.4	5.70
6	0.5	0.5	0.8	0.60
7	4.3	3.8	3.7	3.93
8	0.3	0.4	-	0.35
9	0.7	0.5	0.5	0.57
10	0.1	0.1	0.1	0.10

4.3 Summary statistics of plant reference data

The means, median, minimum, maximum and quartiles for each of the above-ground groundnut biomass for reference data sets (60 samples) are listed in Table 7. Nitrogen concentration ranged from 3.04 to 4.27 (%). There were higher values of iron recorded by the laboratory methods. This can be attributed to laboratory procedures for micronutrients determination such as iron, which have several analytical stages thus increasing the probabilities for error.

Table 7: Descriptive statistics for reference data of above-ground groundnut biomass

Plant nutrient Variable	*n*	*Mean*	*Minimum*	*Lower Quartile*	*Median*	*Upper Quartile*	*Maximum*
Nitrogen (%)	60	3.04	2.06	2.70	3.02	3.39	4.27
Phosphorus (%)	60	0.43	0.20	0.34	0.47	0.51	0.61
Potassium (%)	60	0.22	0.12	0.18	0.21	0.26	0.36
Copper (mg kg^{-1})	60	30.53	9.02	15.01	19.61	30.19	154.0
Iron (mg kg^{-1})	60	2595.61	707.50	1681.59	2234.89	3420.70	6104.0
Zinc (mg kg^{-1})	60	49.63	25.24	40.76	46.00	56.70	106.20
Manganese (mg kg^{-1})	60	200.34	71.83	148.31	187.19	249.04	504.00

4.4 Calibration models of above- ground biomass nutrient variables

Table 8 and 9 presents cross validation statistic for MIR and NIR spectral regions respectively. The cross validation results indicated that MIR spectral range had a high prediction accuracy compared to NIR spectral range for the characterized nutrients although nitrogen yielded fair predictions with r^2 value of 0.58. However, previous nitrogen predictions have been reported to be higher r^2 values 0.96 (Moron and Cozzolino 2002). The r^2 values were higher and RMSECV values were lower compared to those of NIR spectral region.

Table 8: Calibration statistics of groundnut biomass for MIR spectral region

	Calibration set				Validation set			
Nutrients	*n*	*Outlier*	r^2	*RMSEP*	*n*	*Outlier*	r^2	*RMSCV*
Nitrogen	59	1	58.09	0.284	59	1	45.06	0.311
Phosphorus	60	0	70.75	0.061	60	0	56.44	0.0711
Potassium	58	2	72.52	0.028	58	2	51.92	0.035
Copper	58	2	83.50	0.245	58	2	70.89	0.309
Zinc	60	0	46.56	0.221	60	0	30.50	0.240
Manganese	60	0	30.53	0.366	60	0	12.43	0.423

Key; n = sample size r^2= coefficient of determination, RMSECV=Root Mean Square Error of Cross validation.

Table 9: Calibration statistics for groundnut biomass from the NIR spectral region.

	Calibration set				Validation set			
Nutrients	*N*	*outlier*	R^2	*RMSEP*	*n*	*Outlier*	R^2	*RMSCV*
Nitrogen	55	5	75.37	0.203	55	5	68.21	0.220
Phosphorus	59	1	70.14	0.0626	59	1	57.79	0.070
Potassium	59	1	50.7	0.373	59	1	36.72	0.041
Copper	58	2	74.73	0.308	58	2	59.19	0.367
Zinc	60	0	9.48	0.278	60	0	1.60	0.285
Manganese	60	0	32.51	0.357	60	0	17.30	0.389

Key; n = sample size r^2= coefficient of determination, RMSECV=Root Mean Square Error of Cross validation.

Total potassium (K) percent had r^2 value of 0.76 for MIR and 0.51 for NIR spectral regions. Good predictions for K were better compared to calibrations from soil data, r^2= 0.50 and 0.33 for MIR and NIR respectively. This could be due to the fact that soil is heterogonous; made up of complex clay minerals and organic matter (Brady and Weil, 2001) while above-ground plant biomass for groundnuts is more or less homogenous in comparison to soil. Phosphorus had moderately good predictions in both spectral ranges when high accuracy is not needed, while zinc had very poor prediction for both spectral; ranges. The results in this current study for K and P agreed with those reported elsewhere (Shenk et al., 1981: Clark et al., 1987).

The MIR calibration statistics for groundnut nutrients were in a decreasing order similar to that of NIR calibrations, with Cu having the highest r^2 value of 0.83 and Mn having the lowest of 0.31. Nitrogen and Mn were better predicted in the NIR region than MIR spectral region contrary to expected results. This can be attributed to the fact that groundnut being a legume had a high concentration of –NH functional groups. Similar results were obtained by Vazquez de Aldana et al. (1995) for forages. Figure 21- 27 (a) and (b) - show the relationship between spectral data obtained in both MIR and NIR spectral region and the reference data for groundnut macro (nitrogen, phosphorus and potassium) and micro (iron, copper zinc and manganese) nutrients. Zinc and Mn were among poorly predicted micronutrients in both MIR and NIR spectral ranges. Lower numbers of outliers were observed while developing the calibration models (less than 10%). Nitrogen had the highest number of outliers. Less contamination and sample size could be the reason for lower numbers of outliers.

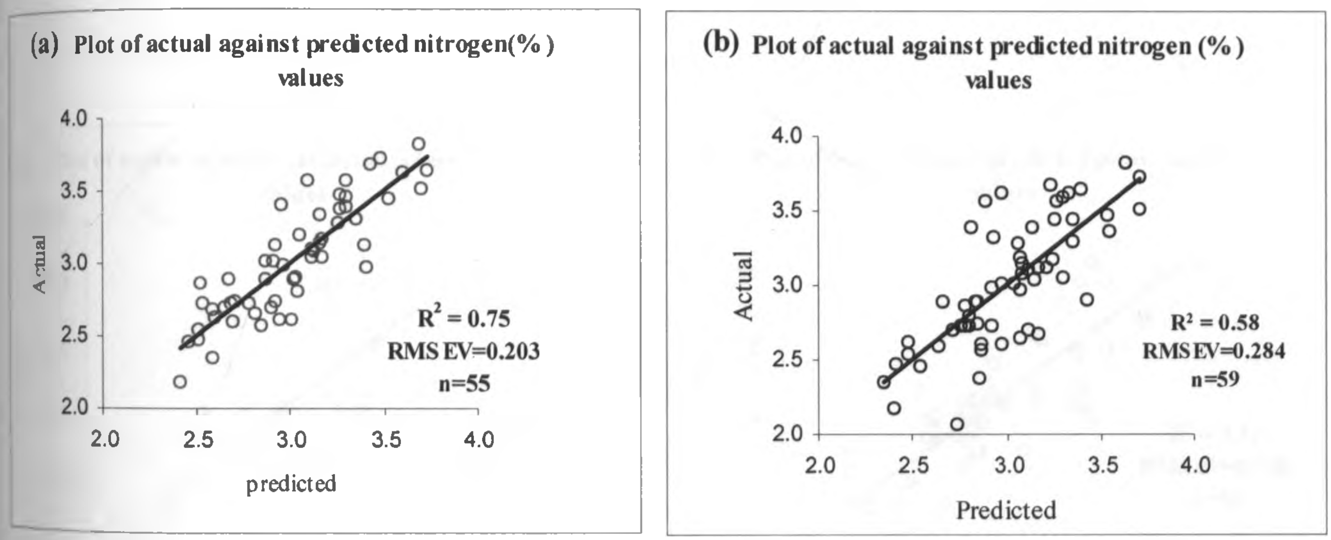


Figure 21: Predicted from spectral data against actual (reference data) (a) NIR (b) MIR

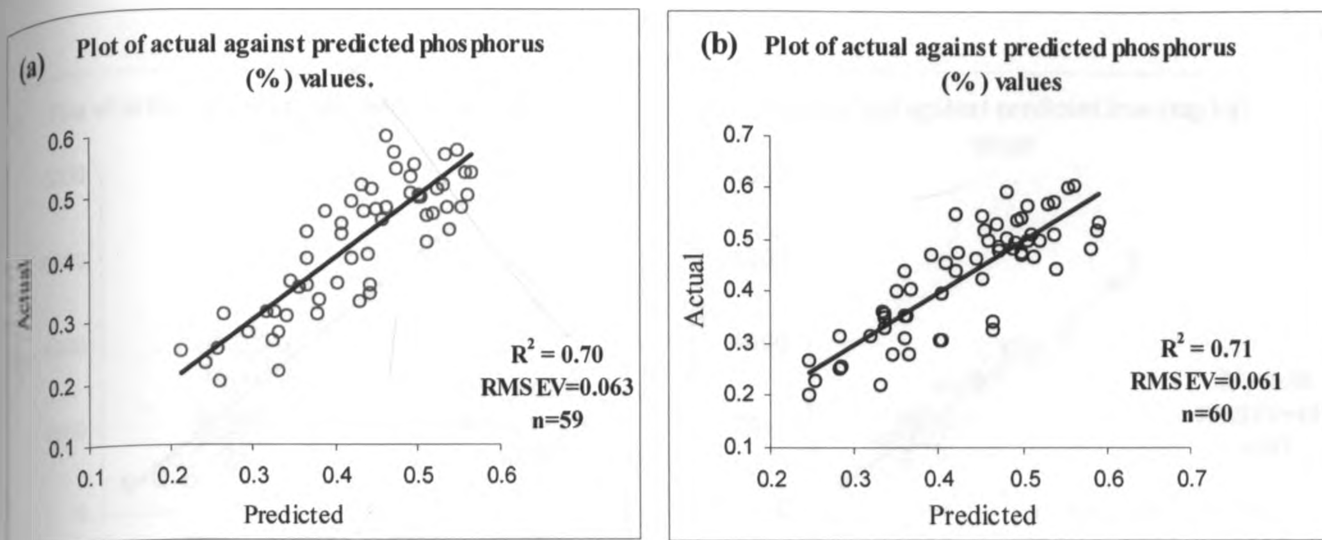


Figure 22: Predicted from spectral data against actual (reference data) (a) NIR (b) MIR

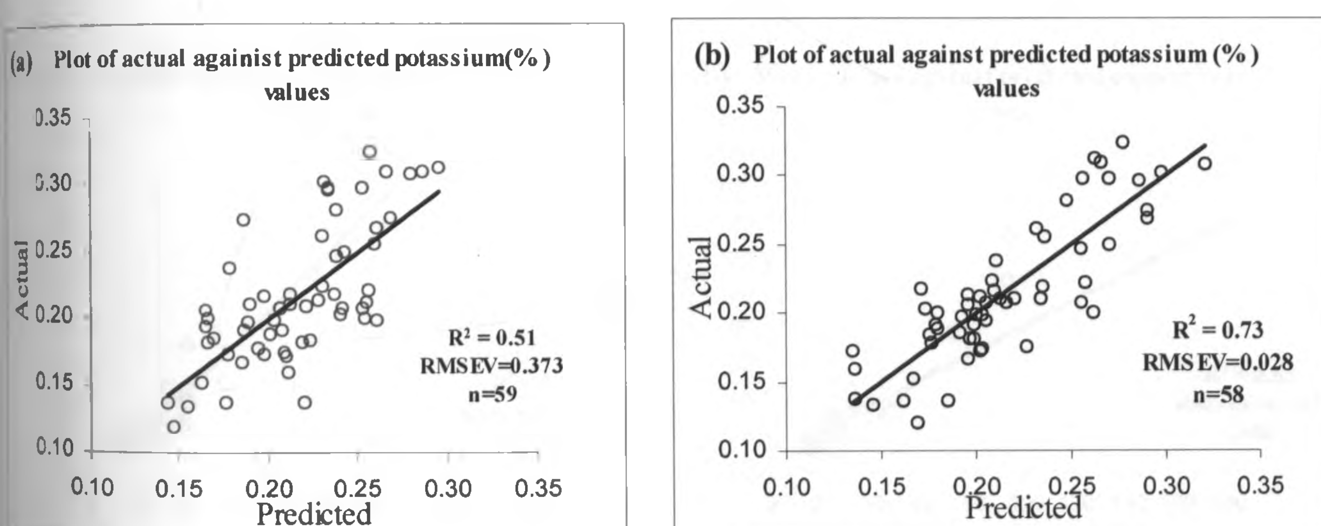


Figure 23: Predicted from spectral data against actual (reference data) (a) NIR (b) MIR

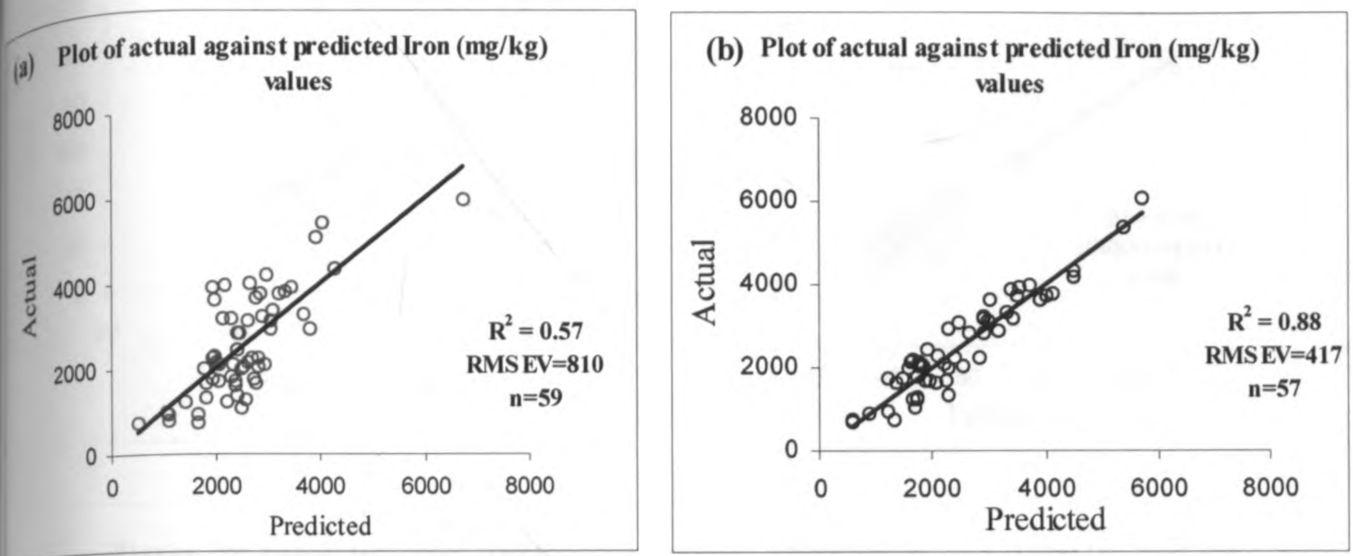


Figure 24: Predicted from spectral data against actual (reference data) (a) NIR (b) MIR

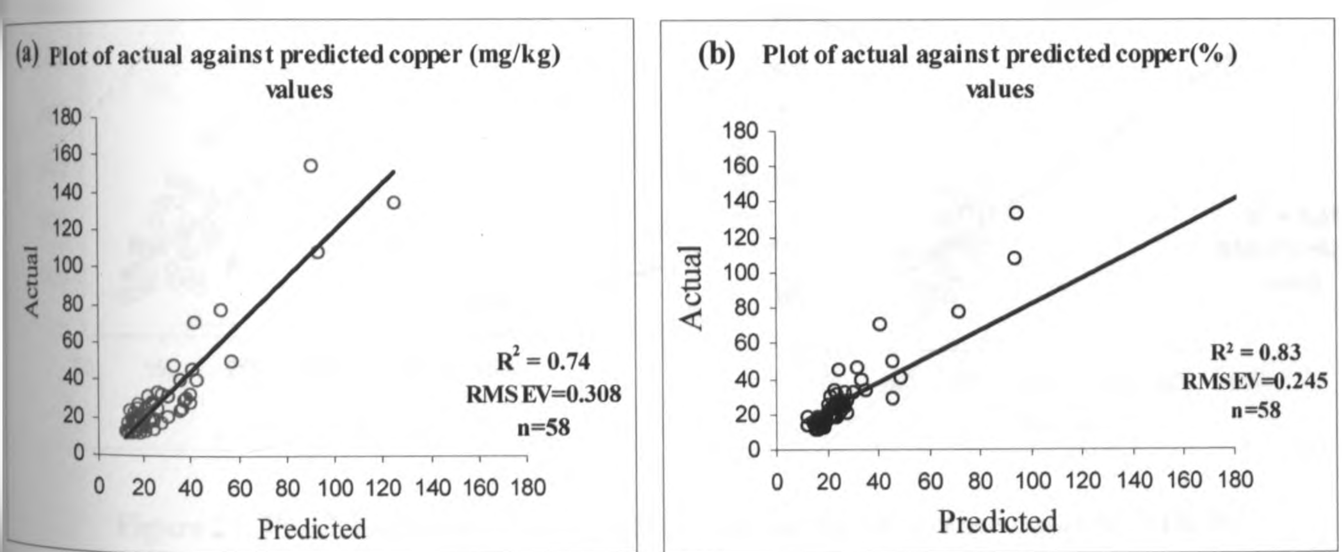


Figure 25: Predicted from spectral data against actual (reference data) (a) NIR (b) MIR

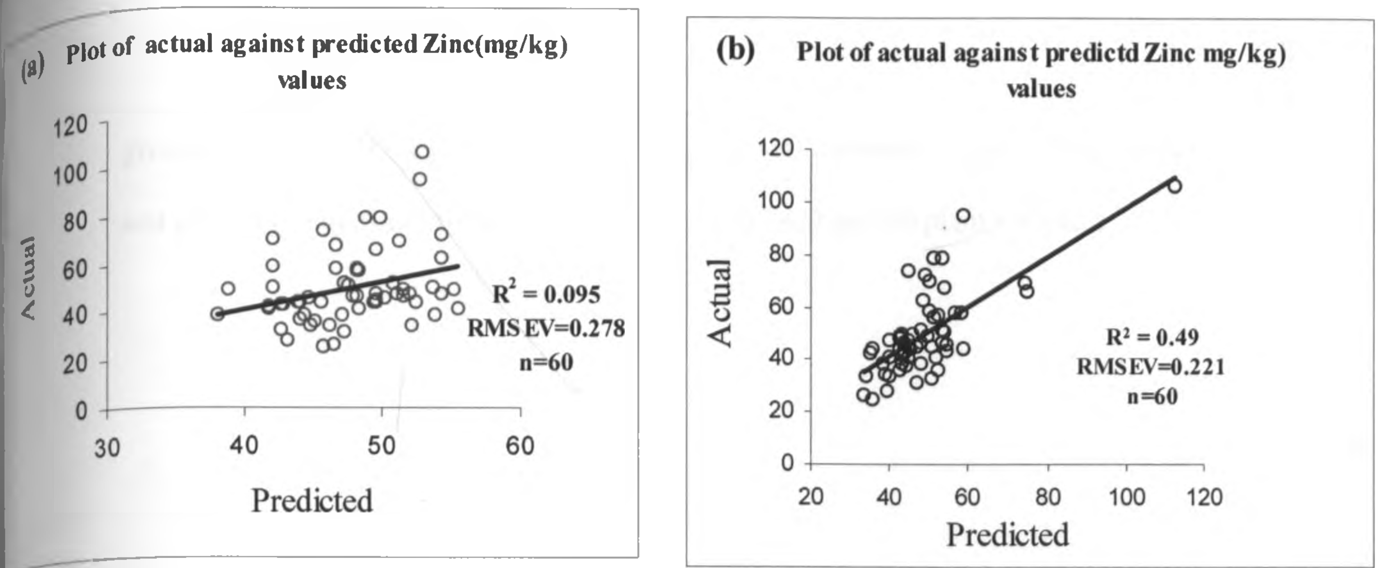


Figure 26: Predicted from spectral data against actual (reference data) (a) NIR (b) MIR

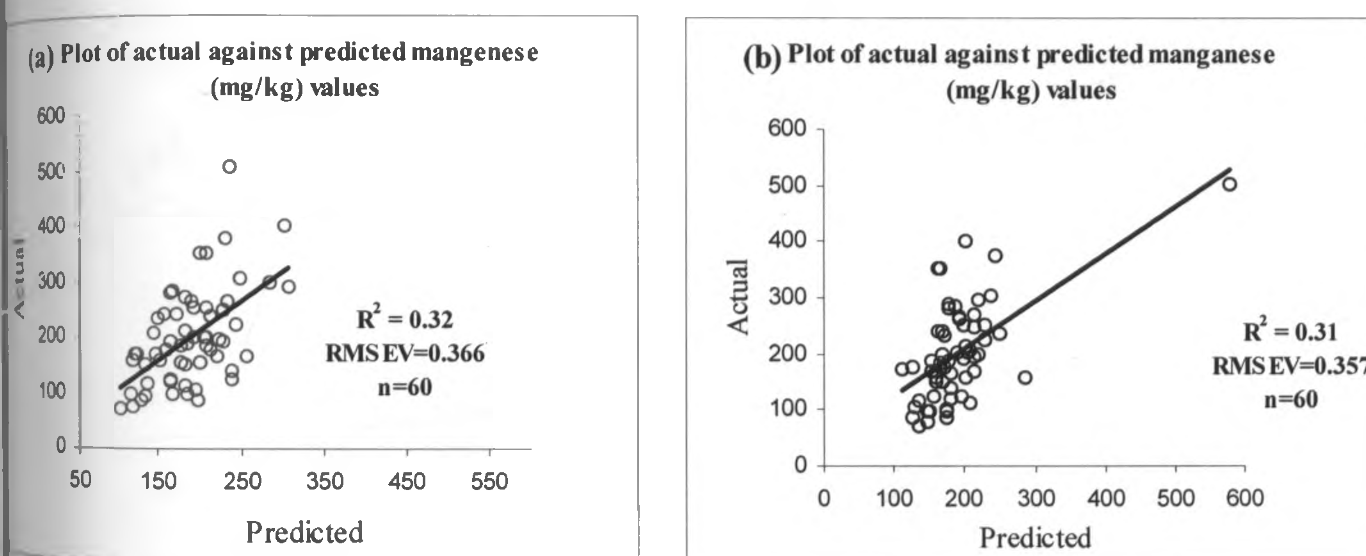


Figure 27: Predicted from spectral data against actual (reference data) (a) NIR (b) MIR

The relationship of groundnut plant above-ground biomass nutrient parameter evaluated and spectral information demonstrated how well the calibration models worked for the reference data. MIR spectral region yielded accurate prediction and was therefore used to characterize and diagnose soil/plant nutrient constraints of sampled groundnut farms. The calibration model for each soil parameter was used to predict the soil property in question for the whole data set (395 soil and 60 plant samples)

4.3. Characterization of soil nutrient status using mid infrared predictions

The average level of soil pH_w, TC, TN, Ext.P and Exch. K, were compared with the critical concentration level for optimum groundnut productivity. Critical concentration level is defined as the concentration that separates the zone of deficiency from the zone of adequacy (Okalebo et al., 2002).

(a) Soil pH_w

Data presented in Table 10 shows descriptive statistic for soil pH_w in AEZs for the topsoil. The mean soil pH_w for LM_1, LM_2, and LM_3 was 5.7, 5.7, 5.7 and 7.5 respectively and was within optimum recommended ranges of 5.3-7.3 (Figure 26) for groundnut production (Page et al., 2002). Eighty percent of groundnut farms ranged from slight acidity to near neutrality and within the recommended soil pH_w range.

The results indicated that there were significant difference, *p value* <0.01 at 95% level of confidence between soil pH_w means within AEZs. The difference in soil pH_w between AEZs could be due to differences in soil moisture regimes and soils types between AEZs. Conyers et al., (1995) observed that changes in temperature and water potential determine changes in microbiological activities which in turn determine changes in the hydrogen ions (H^+) budget. Soils in humid areas tend to be strongly weathered and leached of bases (Conyers et al., 1995).

Table 10: Descriptive statistics for soil pH_w

Soil variable	*Agro-zone*	*n*	*Mean*	*SD*	*Range*	*C V*
Soil pH_w	LM1	101	5.68	0.42	4.87–6.82	7.45%
	LM2	136	5.74	0.55	4.87–8.55	9.60%
	LM3	142	5.74	0.53	4.89–7.64	9.27%
	LM4/UM4	14	7.51	1.22	6.12–9.22	16.20%

n= sample size, SD= Standard deviation, CV= coefficient of variation.

Soil pH is important as a soil fertility variable in groundnut production. Low soil pH (below 5.2) affects availability of phosphorus and molybdenum (Mo) which are essential elements in biological nitrogen fixation (Gascho and Davis 1994; Jordan 2001). Soil acidity results in high concentration of hydrogen ions (H^+) in the soil that affects groundnut productivity. High concentrations of H^+ induce root injury and change the root membrane permeability and interfere with absorption and transport of both water and nutrients in groundnuts plant (Goldman, 1989). Groundnuts grown in acidic soils are bound to be restricted from utilizing water and nutrients because root proliferation and root function is limited by acid infertility. Low soil pH has been associated with a reduction in rhizobia population; especially in soils with low clay content (Mapfumo et al., 2000) which has an adverse effect on biological nitrogen fixation process that supplements nitrogen demands in groundnut production system.

Extremely and strongly acid soils could have high concentrations of soluble aluminum (Al), iron (Fe) and manganese (Mn) which may be toxic to the growth of groundnuts (Lindsay and Walthall, 1989; Brady and Weil, 2001). The availability of exchangeable bases (Ca, Mg and K) is sub-optimal at low pH (Fageria et al., 1990). Calcium element is essential for proper groundnut pod development and production of high quality seed (Cox et al., 1982; Gascho and Davis, 1994). Research studies have shown that low soil pH significantly influences groundnut seedling survival and early growth stages (Lemon, 1990). Acid soil infertility (low soil pH) in tropical soil has been cited by several authors as a major constraint for groundnuts growth as it affects nodulation and growth leading to reduced groundnut yield (Marziah et al., 1995). High soil pH_w (above 7.3) enhances soil Ca levels and optimizes the availability of other exchangeable bases and reduces Zn toxicity risk, but Mn deficiency is more likely at this soil pH level (Fageria et al., 1990).

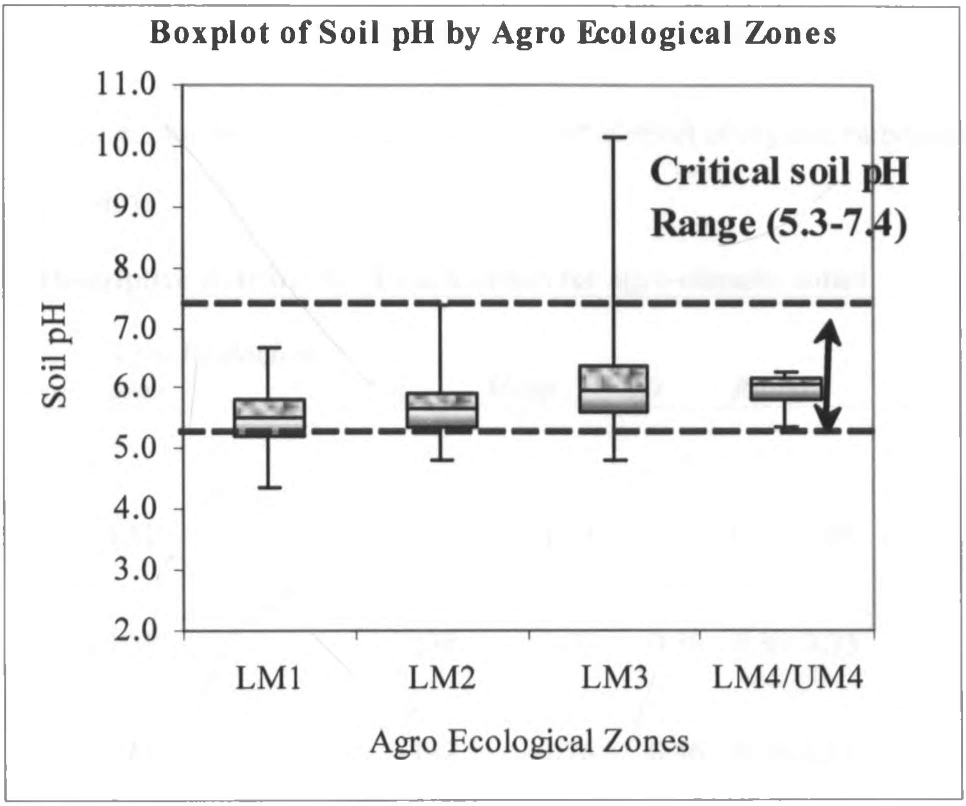


Figure 28: Mean ranges of soil pH_w in the agro- ecological zones

(b)Total Carbon

Agro-ecological zone LM_4/UM_4 had TC mean concentration level of 2.29 % while LM_3 had the lowest concentration of 1.18%. The mean TC concentration levels for LM_1 and LM_2 were 1.23 and 1.26 % respectively (Table 11). These were below the critical recommended level of 2% for cultivated areas. Thirty percent of the groundnut farms had the TC concentration levels above the critical concentration level. Giller et *al.*, (1997) observed that soil organic matter build-up in sandy soils may be practically difficult to achieve due to its rapid turnover and this leads to low levels of TC. High sand content in the soil could be associated with lower TC levels below the critical level. However, in plough layers an increase in the content of this fraction results in greater critical soil strength for root growth due to the favorable effect of organic carbon content (Lipiec et al., 2003).

Table 11: Descriptive statistics for Total Carbon for agro-climatic zones

Soil variable	*Agro Ecological zone*	*n*	*Mean*	*SD*	*Range*	*C V*
Total Organic (TC)	LM1	101	1.23	0.50	0.46–2.95	40.54%
	LM2	136	1.26	0.58	0.36–3.33	45.90%
	LM3	142	1.18	0.56	0.33–2.85	47.85%
	LM4/UM4	14	2.29	0.38	1.47–2.94	16.66%

The high CV value (> 40%) indicates high variation of within the AEZs. The difference in TC between the AEZs could be attributed to difference the land use practices that occur on the small-scale groundnut farms. Approximately 70% of groundnut farms farmers incorporated previous crop residue (maize strovers and weeds like black jack and *Amaranthus spp)* in the soil (Farmer, personal communication 2006) which could have led to accumulation of TC in the soil. The decomposition of the incorporated crop residue leads to accumulation of SOM (Brady and Weil, 2001). Several literatures have cited agricultural management practices to influence the amount of SOM. Tisdale et al., (1993) reported that increased tillage leads to decreased SOM because of higher rate of SOM decomposition.

Threshold values of TC (Karlen et al., 2001) have been set and chosen based on developed Kenyan national critical concentration levels. In Kenya the critical TC level of

2% is recommended for soils under cultivation (Okalebo et al., 2000; Nandwa 2003). Figure 29 illustrates ranges of TC concentration on groundnut farms. Most groundnut farms fell below the recommended 2% TC levels for cultivated farms (Figure 29) which is an indication of declining soil fertility.

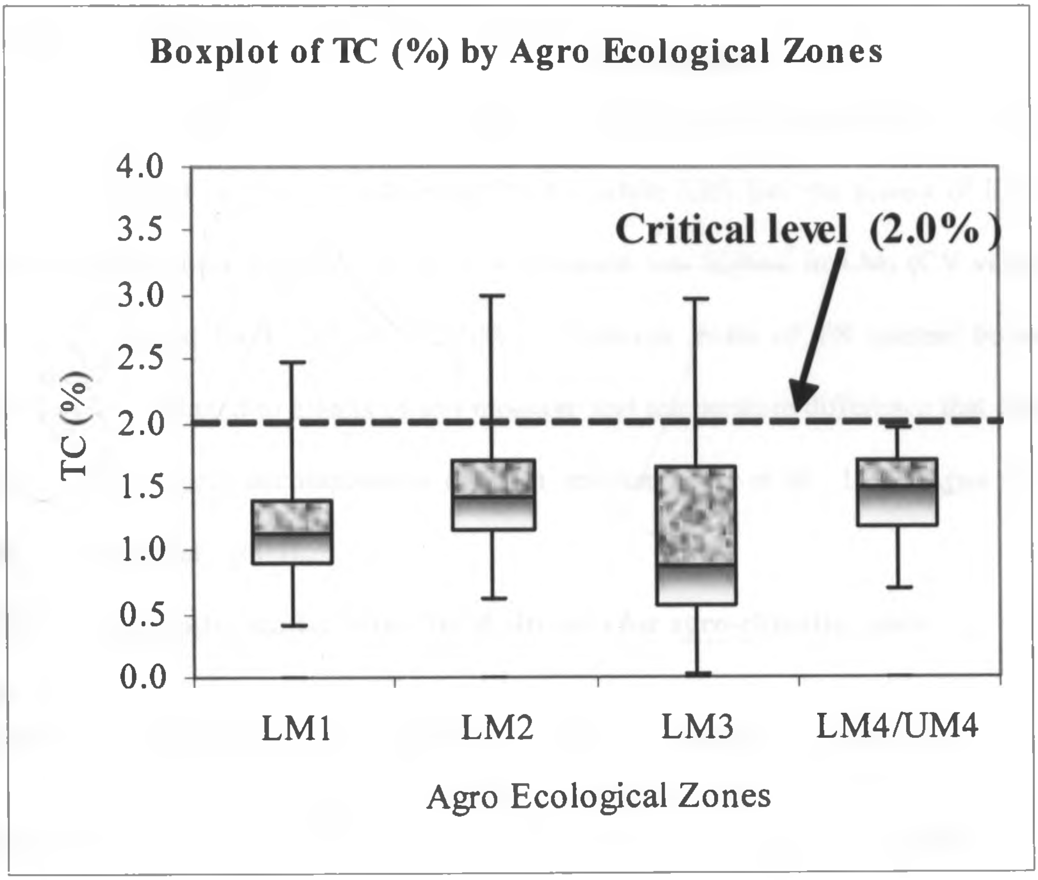


Figure 29: Mean ranges of total carbon in the agro- ecological zones

Total carbon (TC) is important in soil fertility due to its effects on soil physical and biological properties and has been used universally as a principle indicator of soil fertility (Alexander, 1977; Brady and Weil, 2001). It is also involved in the adsorption of basic cations like calcium (Alexander, 1977; Brady and Weil, 2001) which are important for groundnut nutrition. Other effects on soil quality associated with SOM; include increases in water holding capacity (Hillel et al., 1994), and storage and supply of nutrients for soil microbes that are important for biological processes such nitrogen fixation (Brady and Weil, 2001; Okito et al., 2004).

(c) Total nitrogen

Table 12 shows the descriptive statistics for TN (%) concentration levels. AEZs LM_1 and LM_2 had similar mean levels of 0.11% while LM_3 had the lowest of 0.10 % LM_4/UM_4 the highest level of 0.15%. The variation was highest in LM_3 (CV value of 44.5%) and lowest for LM_4/UM_4 (12.10%). Different levels of TN content between AEZs can be attributed to effects of soil moisture and temperature difference that causes rapid microbiological decomposition of plant residues (Fox et al., 1990; Ajwa et al., 1998; Agehara et al., 2005).

Table 12: Descriptive statistics for Total nitrogen for agro-climatic zones

Soil variable	*Agro-zone*	*n*	*Mean*	*SD*	*Range*	*C V*
Nitrogen(N)	LM1	101	0.11	0.04	0.03–0.23	37.69%
	LM2	136	0.11	0.05	0.03–0.25	42.42%
	LM3	142	0.10	0.05	0.02–0.24	44.47%
	LM4/UM4	14	0.15	0.02	0.13–0.19	12.10%

Levels of TN (%) were low compared to recommend critical values of 0.2% in 75% of groundnut farms sampled (Figure 30). Gascho (1992) reported similar results for soils that were deficient in nitrogen and responded well to N fertilization for optimum groundnut yields. Nitrogen is important and demand is high in early stages of groundnut growth since nitrogen fixation has not yet started (Gascho, 1992). During early growth stages a starter dose of N application has been reported to increase groundnut yield (Gascho 1992). When inoculated with effective strains of Rhizobia, groundnuts are independent of nitrogenous fertilizer because enough N is fixed through symbiotic relations with legume nodulating bacteria known as *Brayrhizobium spp* (Kvien et al 1986). Uptake of nitrogen is most intensive during reproductive stages of groundnuts and immobilization of N from leaves to developing fruits occurs during this stage (Kvien et al 1986; Cox and Sholar 1995).

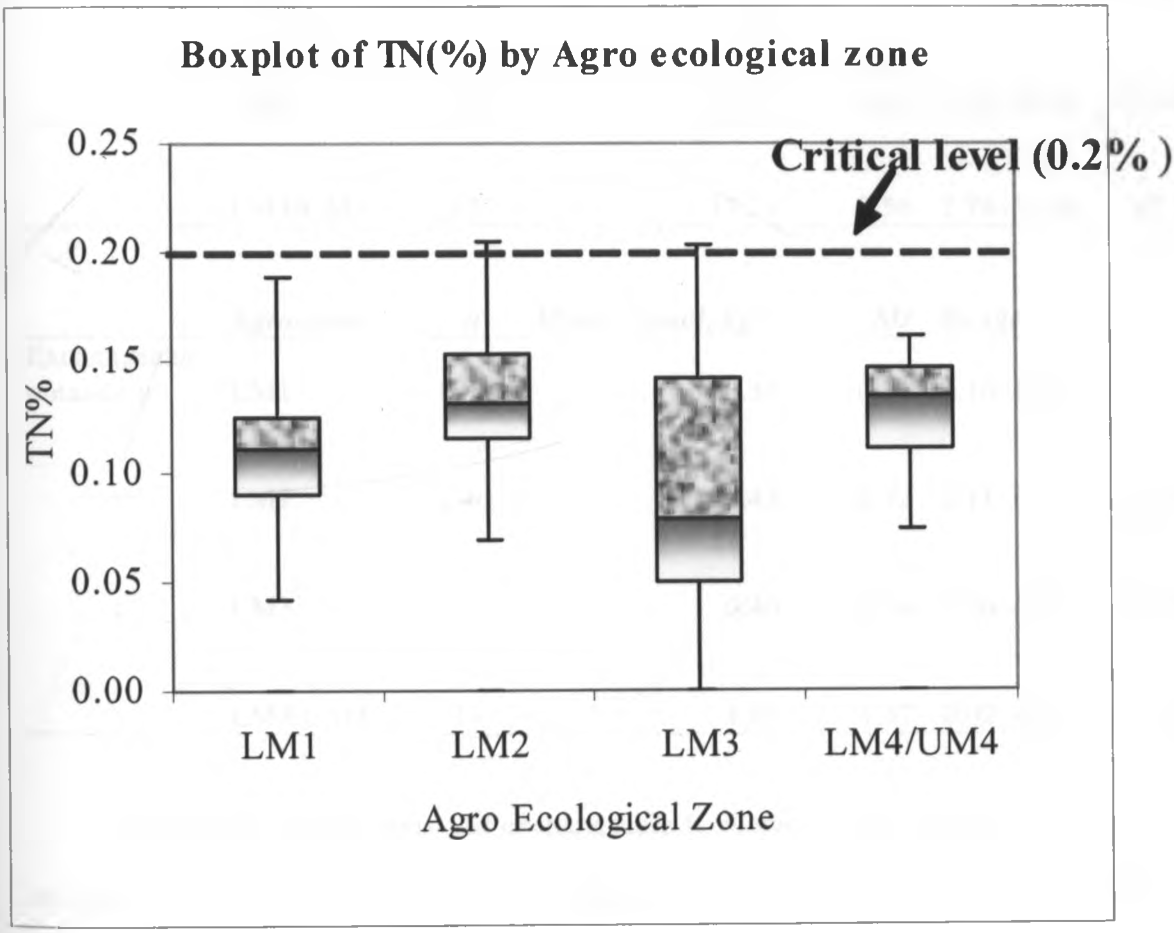


Figure 30: Ranges of total nitrogen in the agro- ecological zones

(d) Soil extractable phosphorus and exchangeable cations (K, Ca and Mg)

Table 13 shows the descriptive statistics for levels of extractable phosphorus and exchangeable potassium.

Table 13: Descriptive statistics for extractable phosphorus and exchangeable potassium

Soil variable	*Agro-zone*	*n*	*Mean (mg kg^{-1})*	*SD*	*Range*	*C V*
Extractable phosphorus	LM1	101	3.08	2.45	0.69–11.6	79.45%
	LM2	135	3.82	4.22	0.61–27.57	110.43%
	LM3	140	3.98	4.53	0.59–25.21	113.99%
	LM4/UM4	12	17.71	8.56	7.74–31.64	48.36%

	Agro-zone	*n*	*Mean (cmol$_c$ kg^{-1})*	*SD*	*Range*	*C V*
Exchangeable potassium	LM1	101	0.33	0.12	0.16–1.16	35.27%
	LM2	136	0.43	0.72	0.11–8.33	168.33%
	LM3	142	0.40	0.54	5.06–4.77	134.59%
	LM4/UM4	14	1.48	1.37	0.02–4.26	92.75%

Extractable phosphorous and exchangeable K showed a wide range of variation as shown in their CV values. The mean concentration of extractable P for LM_1, LM_2 and LM_3 were 3.1, 3.8, and 4.0 mg kg^{-1} respectively, which were below the critical level (5.0 mg kg $^{-1}$) for cultivated farms in Kenya (Okalebo et al., 2002). This is shown clearly in

Figure 31. Fifty percent of the groundnut farms fell below critical recommended level of 5.0 mg kg^{-1} for extractable phosphorus.

These results are in agreement to previous results reported in several literatures that indicated P as major limiting soil nutrient in Kenyan soils (Sanchez and Jama 1998). The limitation of P could be due to high fixation of P in soil (Lindsay and Walthall, 1989). Groundnuts preferably are grown on sandy soils with low amounts of clay and phosphorus fixation in such soil may not a problem (Lindsay and Walthall, 1989; Cox et al., 1982; Mengel and Kirkby 1982). Cox et al., (1982) indicated that groundnuts in most parts of the world are grown in sandy soils that are deficient in phosphorus.

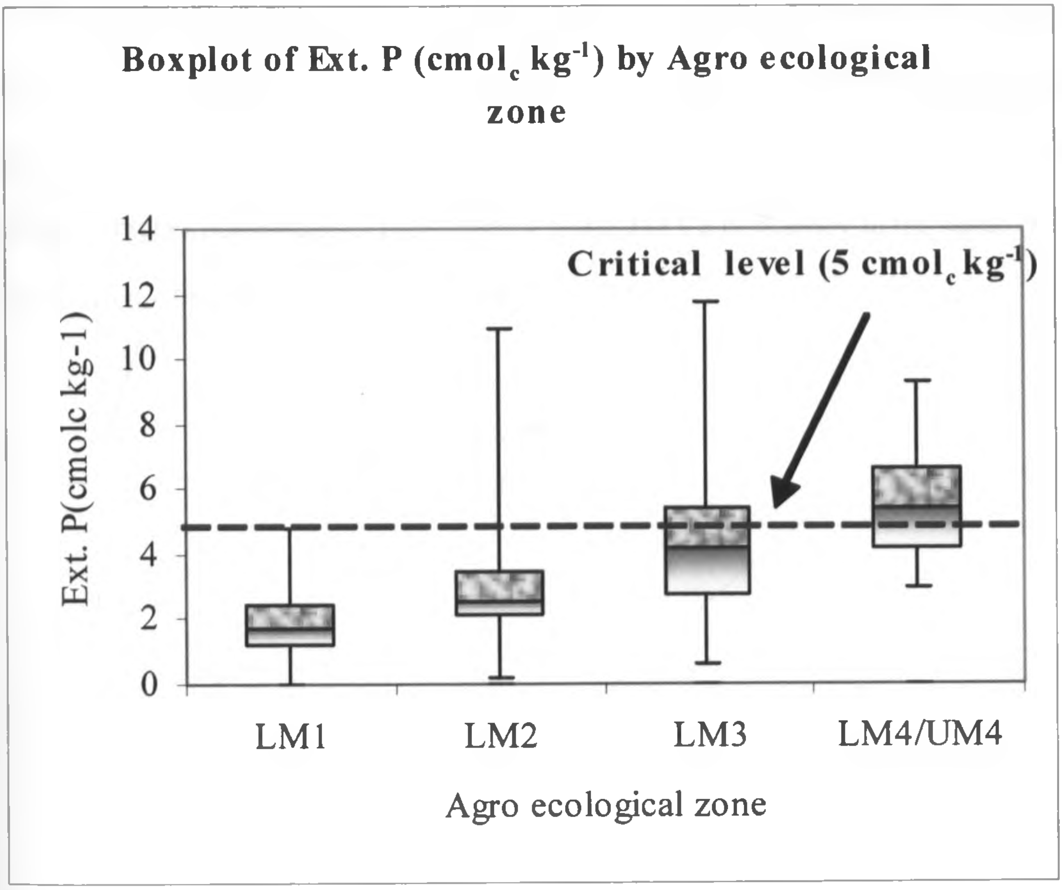


Figure 31: Mean ranges of extractable phosphorus in the agro- ecological zones

Mean exchangeable potassium was above the critical recommended level of 0.2 $cmol_c\ kg^{-1}$ across the agro-ecological zones (Okalebo et al 2002), though deficiency (Figure 32) was detected in some of the fields in all AEZs. Lemon (1990) reported that a lot of potassium in the upper horizons interferes with calcium uptake by groundnuts.

Potassium is significant to groundnut plants as it provides resistance to insect pests, diseases and water stress and helps the plant to economic use water (Cox et al., 1982). However, scientific findings have indicated that groundnut requires very little K for its growth and reproduction (Lemon 1990). This is because groundnut roots are able to efficiently obtain K from soil with low levels of available K (Weiss, 1983). Research has indicated that high levels of soil K in the pod zone are undesirable for optimum groundnut yield and result in pod rot and interfere with Ca uptake by pegs and pod hence result to higher percentage of pops (empty pods) and Ca deficiency in the seeds (Hallock and Garren, 1968; Csino and Gaines, 1986).

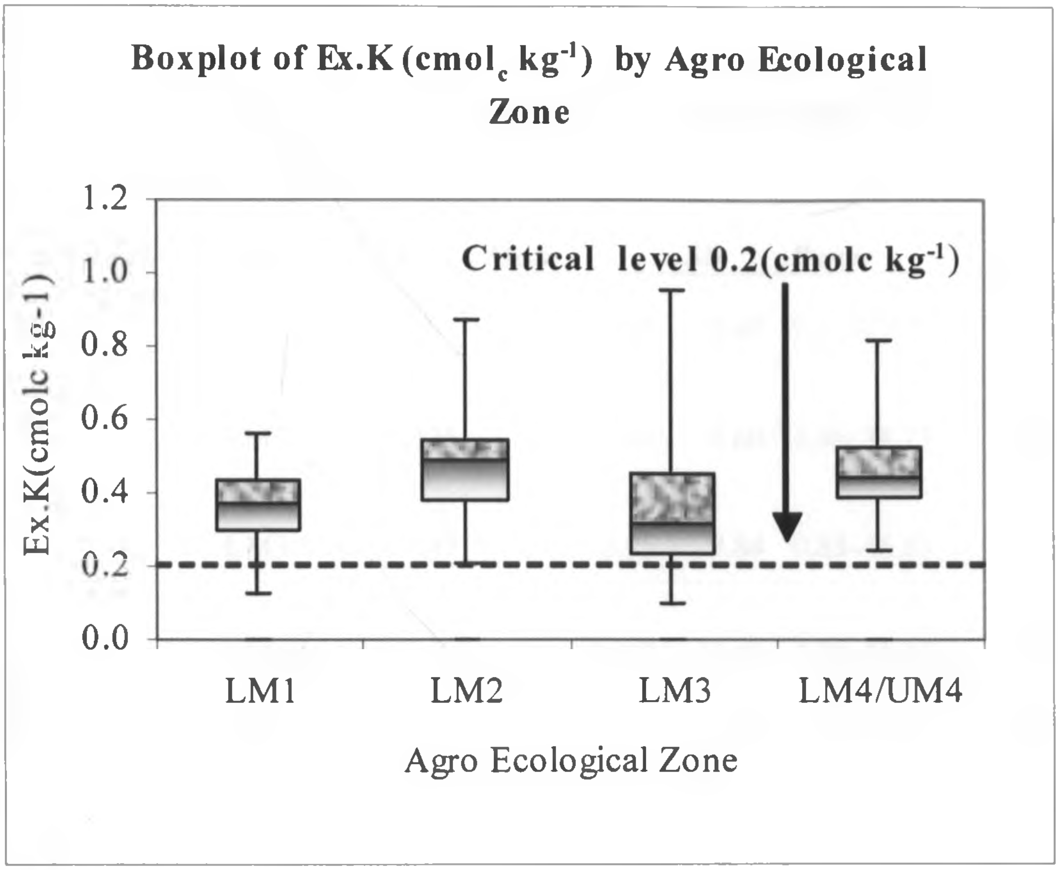


Figure 32: Mean ranges of exchangeable potassium in the agro- ecological zones

Table 14: Descriptive statistics for exchangeable cations (Ca and Mg)

Soil variable	*Agro-zone*	*n*	*Mean*	*SD*	*Range*	*C V*
Exchangeable calcium	LM1	101	4.55	2.49	1.1–14.52	54.87%
	LM2	136	6.13	6.60	1.06–38.73	107.52%
	LM3	142	6.25	7.84	0.83–45.83	125.32%
	LM4/UM4	14	28.07	18.18	5.59–59.36	64.75%
Exchangeable Magnesium	LM1	101	1.28	0.63	0.42–3.53	49.23%
	LM2	136	1.68	1.47	0.32–8.81	87.41%
	LM3	142	1.58	1.48	0.22–7.17	93.45%
	LM4/UM4	14	7.51	2.37	3.4–11.81	31.54%

Mean exchangeable calcium content was 4.55, 6.13, 6.25 $cmol_c\ kg^{-1}$ recorded in LM_1, LM2 and LM_3 respectively, which was quite low compared to the critical recommended level of 50 $cmol_c\ kg^{-1}$ (Okalebo et al., 2002). Calcium is a critical element in groundnut production and the results indicated that it was deficient in most of the groundnut farms. Calcium plays an important role in groundnut production and is strongly associated with rapid plant growth, structural integrity of stems that hold the pods and quality of groundnut seed produced (Dorner et al., 1989; Easterwood 2002).

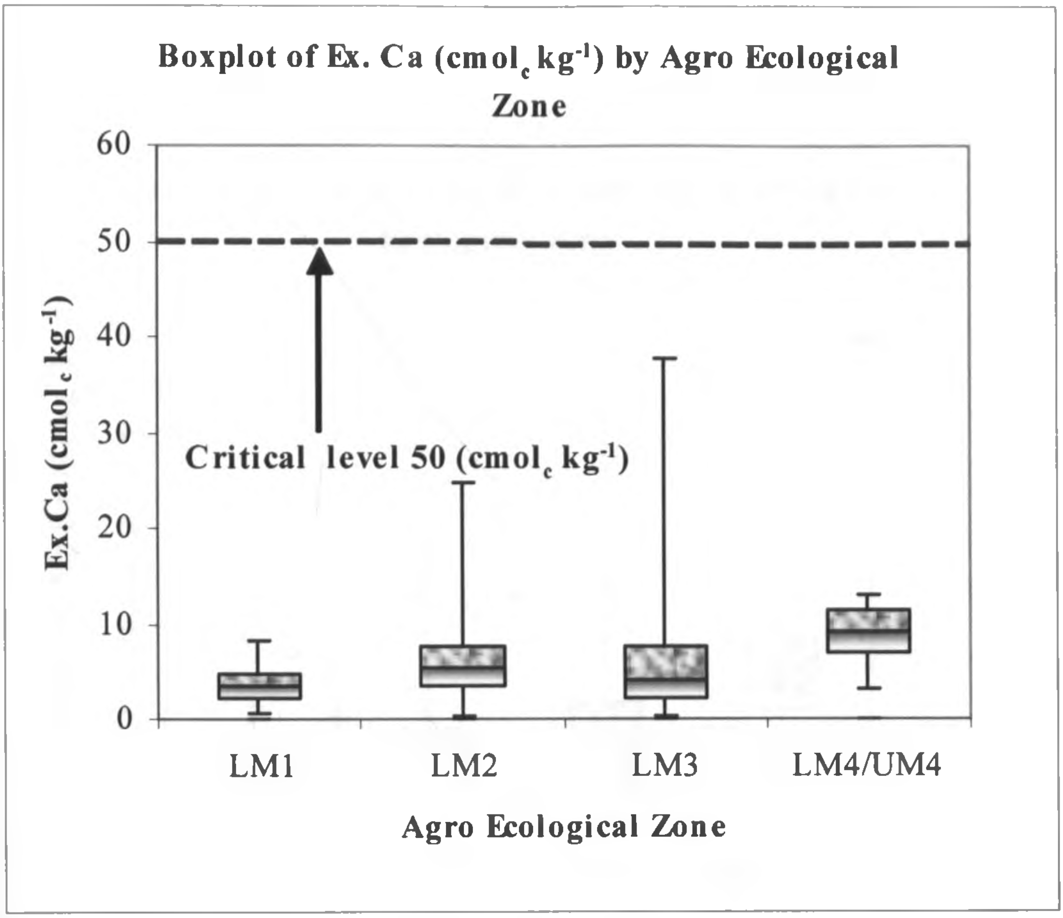


Figure 33 Box plot for ranges of exchangeable calcium in the agro- ecological zones

Exchangeable Mg means levels were; 2.37, 1.48, 1.47 and 0.63 $cmol_c\,kg^{-1}$ for LM_4/UM_4, LM_3, LM_2 and LM_1, respectively. Mg levels for LM_4/UM_4 were above the critical recommend level of 1.6 $cmol_c\,kg^{-1}$ with 65 % of groundnut farms falling above the critical concentration level (Figure 34). They were significant differences (p value <0.001) in mean levels. The CV values were high in LM_2 (87%) and LM3 (93%) across the AEZs. Variation of Mg concentration levels could be due to difference in precipitation between AEZs that result in leaching of exch. cations (Brady 1990) below rooting zone of groundnut (0-50cm). LM_1 receives high amount of rainfall is characteristic of compared to LM_2 and LM_3 (Jaetzold and Schmidt, 1982).

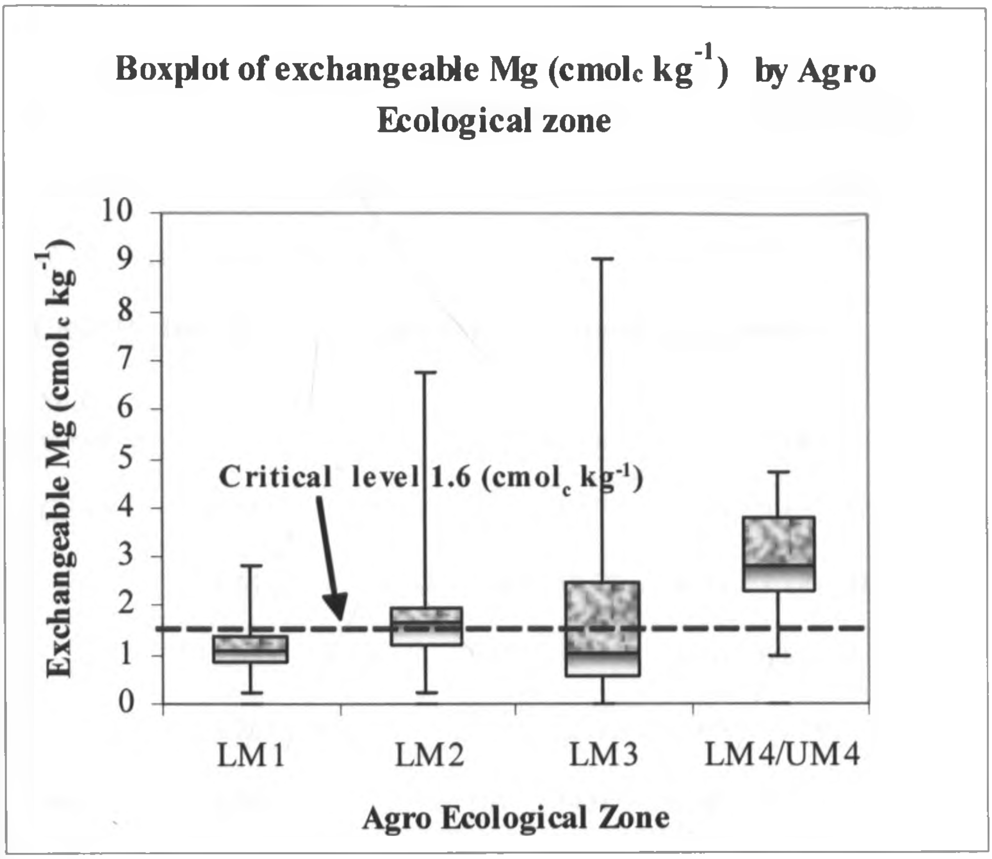


Figure 34 Box plot for ranges of exchangeable magnesium across the agro-ecological zones

Magnesium is an important element in groundnut production as it forms part of chlorophyll and provides energy rich compounds for groundnut growth and development (Mengel and Kirkby 1982). In addition, Mg helps groundnuts in the utilization of other plant nutrients, it necessities groundnuts stems in its role as a carrier of phosphorus in oil formation and has effects on seed viability (Dorner et al., 1989).

(e) Soil textural components

Most soils were sandy clay loam and clay loam. Mean ranges for clay content was 32.23, 30.79, and 30.47 % for LM_1, LM_2 and LM_3 respectively (Table 15). The sand content was higher compared to clay and silt fractions with values of 44.07, 47.16 and

48.19% for LM_1 LM_2 LM_3 respectively. There was high variation in the textural components (sand, silt and clay) as indicated by the high CV that ranged from 14.08 to 67.19% between the AEZs.

Table 15: Descriptive statistics for soil textural components

Soil variable	*Agro-ecological zone*	*n*	*Mean*	*S D*	*Range*	*C V*
Clay	LM1	101	32.23	8.65	9.12 – 50.55	26.83%
	LM2	136	30.79	8.39	7.18 – 48.71	27.26%
	LM3	142	30.47	8.20	6.81 – 44.27	26.90%
	LM4/LM4	14	25.89	3.65	17.18 – 29.08	14.08%
Sand	LM1	101	44.07	12.65	28.73 – 78.46	28.71%
	LM2	136	47.16	15.33	28.7 – 97.19	32.50%
	LM3	142	48.19	15.84	30.2 – 98.95	32.88%
	LM4/UM4	14	51.90	9.15	38.67 – 59.47	17.62%
Silt	LM1	101	21.77	9.13	2.8 – 39.43	41.92%
	LM2	136	20.24	8.44	0.74 – 33.91	41.71%
	LM3	142	20.36	8.58	0.38 – 39.67	42.16%
	LM4/LM4	14	11.60	7.80	3.1 – 24.36	67.19%

Mean clay content was 32%, the highest being in LM_1 soils. The LM_2 and LM_3 AEZs had 31 and 30% respectively. Mean sand content was higher compared to clay and silt, averaging 44, 47 and 48 % for LM_1 LM_2 LM_3 zones respectively. The textural classification was generally, clay loam for LM_1 and sandy clay loam for both LM_2 and LM_3. Mairura et al (2004) found similar textural ranges in soils from small-scale farms of central Kenya. Groundnuts require light-textured soils ranging from coarse and fine sands to sandy loams with good drainage. Fifty five percent of the groundnut farms had sandy clay loam soils which are fairly good for optimum groundnut yields (Weiss, 1983). However, in general there was a higher mean of sand content in the first horizon (0.—20 cm) with 49.3 % compared to the second horizon (20-50cm) that had a mean of 46.1 %. This could be an indication of textural discontinuities that could lead to the susceptibility of land to land degradation through soil erosion (Sanchez et al 2003) as a result of selective removal of fine particles.

The presence of the structural discontinuities also affects the groundnut productivity as it leads to the exponential decline in root growth with depth (Gerwitz and Page, 1974)

4.3 Nutrient content of above-ground groundnuts biomass.

(a) Macronutrients

Figure 35 shows the box plot of the macronutrients; nitrogen (N) phosphorus (P) potassium (K) in above-ground groundnut biomass. Nitrogen mean levels in above-ground groundnut biomass were 2.9 % for LM_1 and 3.0 % for the other AEZs. Groundnuts nutrient analysis performed at flowering have been considered suitable for judging nutrient status (Smith et al., 1994). The results indicated a deficiency of nitrogen in 75% of groundnut farms. Established nutrient critical range levels in groundnuts biomass are 3.9, 0.4 and 2.4 for N, P, K respectively (Gascho and Davis, 1994). The nitrogen mean were below the critical level of 3.9% an indication of nitrogen deficiency in the study area.

Comparison made between nitrogen content in above-ground groundnut biomass and total nitrogen levels in the soil indicated that TN in the soil was low (<0.2%) for 75% of groundnut farms. However, most researchers have reported that nitrogen is not much of a problem in groundnuts production (legumes systems) as it is presumed that the crop can meet its demands for nitrogen (Gascho and Davis, 1994, Lemon 1999) through biological nitrogen fixation. This is contrary to recorded results of N concentration levels in above-ground groundnut biomass. The results in this study indicated soil nutritional results indicated that groundnut farms were P deficient. Limited application of phosphate fertilizers in the groundnut farms to improved biological nitrogen fixation (Peoples et al., 1998) could attribute to low levels of N in the groundnut above-ground biomass. Nitrogen controls the efficient utilization of phosphorus and potassium by groundnut plants (Cox et al., 1970). However, most researchers have reported that excess of nitrogen results in too much of vegetative growth at the expense of groundnut pod production (Csino and Gaines, 1986).

Phosphorus concentration levels for above-ground groundnut biomass were 0.43, 0.41, 0.42 and 0.53 for LM_1, LM_2, LM_3 and LM_4/UM_4 respectively and slightly above the established critical amounts of 0.4 %. Though the means indicate a level of adequacy, 45% of the groundnut farms fell below the critical level and 55% of the farms indicated sufficient P levels in the above-ground groundnut biomass based on the critical level. This was contrary to the results of extractable P obtained from soil analysis that indicated P as being limiting.

Several scholars have observed the important role played by phosphorus in root and shoot growth and lengthening (Csino and Gaines, 1986). It stimulates the setting of pods, decreases the number of unfilled pods (pops) and hastens the maturity of groundnuts when in adequate amounts combined with calcium (Sumner et al., 1988). Phosphorus availability helps in increasing the efficiency of nitrogen use by plants (Csino and Gaines, 1986).

The mean concentration of potassium were not significantly different with (*P* <=0.205) among AEZs and mean concentration for LM_1, LM_2, LM_3, LM_4/UM_4 of 0.21, 0.21, 0.22, 0.23 % respectively. All the groundnut farms were below the critical level of 2.4%. Low levels K in the plant could have been due to high concentration of micronutrients that were found in the groundnut biomass as has been observed in other studied by Fageria et al., (1990).

Potassium is equally important as nitrogen and phosphorus in groundnut growth and development (Weiss, 1983). It is involved in providing resistance to insect pests, diseases, water stress and enhances water use efficiency (Weiss, 1983). Potassium also helps in improving the quality of the groundnut seed (Weiss, 1983).

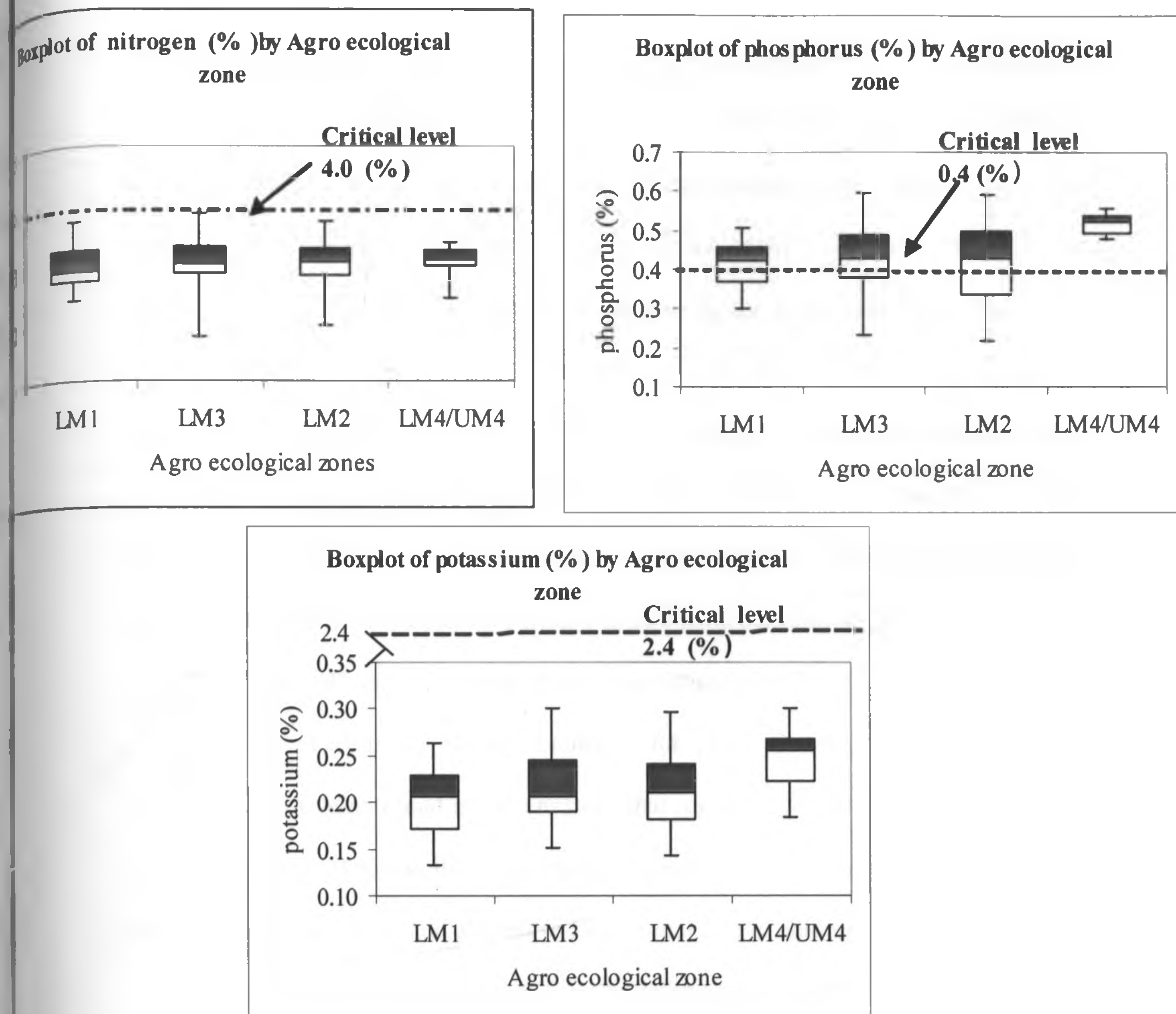


Figure 35: Box plot ranges plant macronutrients (a) nitrogen (b) phosphorus (c) potassium

Mean zinc concentration level for above-ground biomass was highest for LM_1, 45.8 mg kg^{-1} and 43.1, 44.2 and 39.8 mg kg^{-1} for LM_2, LM_3, and LM_4/UM_4 respectively. All groundnut farms indicated sufficiency levels above the critical recommended range of 20 mg kg^{-1}. However, zinc deficiency is widespread and groundnut yield is reduced by about half when the zinc level in the soil is lower than 0.08 $cmol_c$ kg^{-1}. But the results in this study indicated Zn was above the critical recommended limit. Zinc deficiency is likely to occur when soils are low in organic matter, under high levels of soil P, and when the soils are cool and wet during the vegetative phase of groundnut growth.

Copper concentration levels were above the critical level of 6 mg kg^{-1} an indication of sufficiency levels across the agro ecological zones as indicated in the box plot (Figure 36). Mean copper concentrations were 35.1 mg kg^{-1}, the highest for LM1 and 15.62 mg kg^{-1} the lowest for LM_4/UM_4 within the soils. Research finding have indicated that available Cu can vary from 1 to 200 parts per million (ppm) in soils and as a function of soil pH and soil texture (Rehm and Schmitt, 1989).

Copper (Cu) is an essential nutrient for plant growth. It is an important component of proteins found in the enzymes that regulate the rate of many biochemical reactions in plants. The specific role played in groundnuts by Cu include; enhancing seed production and formation and also plays an essential role in chlorophyll formation

Iron levels were quite high for the reference data and the result were not considered. However, groundnut is very susceptible to iron deficiency. Iron deficiency occurs in calcareous and alkaline soils with soil pH above 7.5 (Hartzok et al., 1971).

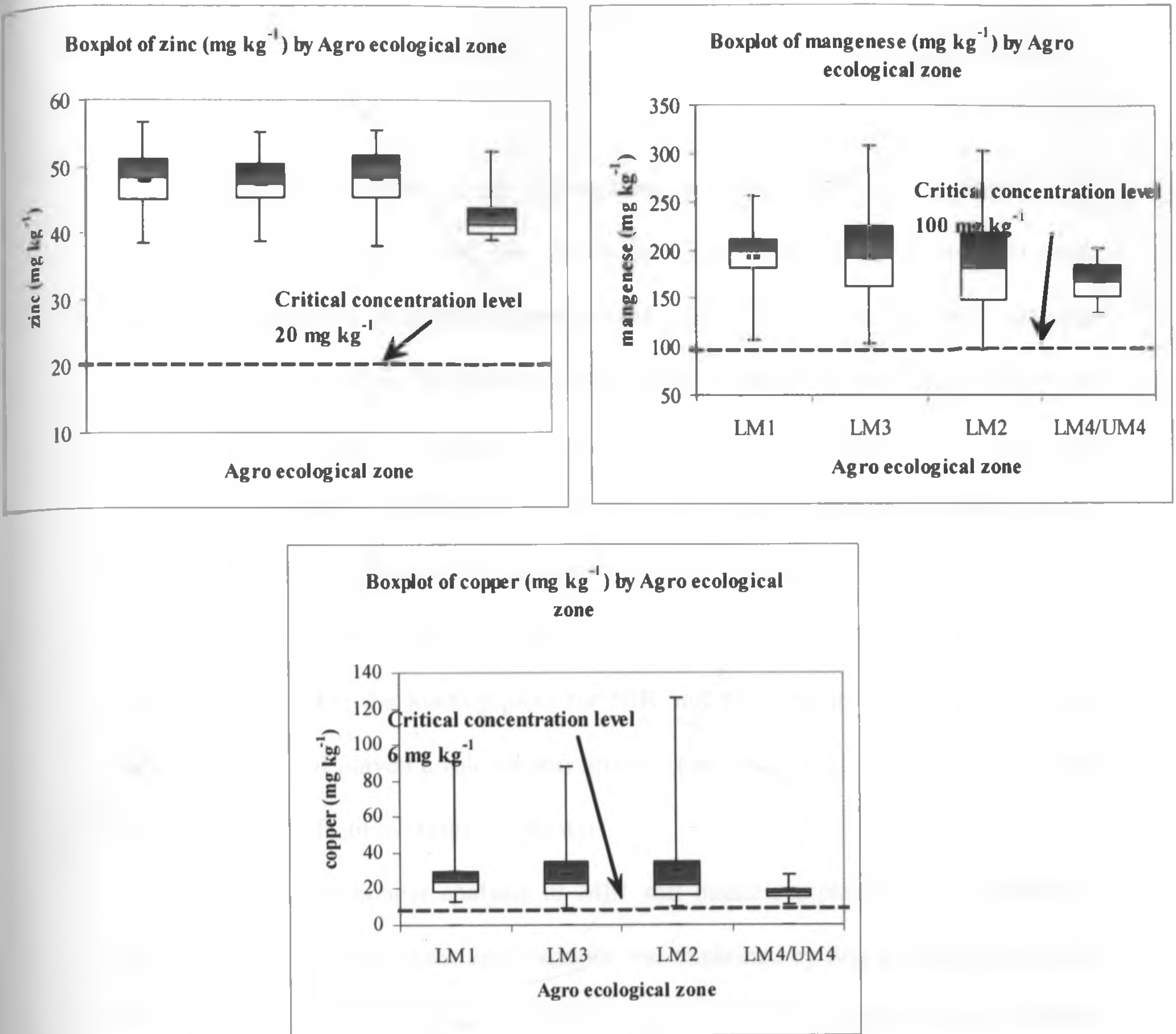


Figure 36: Box plot ranges plant micronutrients (a) Zinc (b) Manganese (c) Copper

4.3 Variation of soil nutrients

Analysis of variation of soil nutrients was done by combining the principle soil properties (soil pH, TC, TN, Est., Exch. K Ca and Mg and soil texture) using multivariate analysis - principle component analysis (PCA) for the soil reference data. The multivariate technique provided a holistic representation of variation of soil nutrients and took into account correlations among principle soil properties that had been analyzed. This method was followed as done by Sena (2002). Figure 37 shows loading plots for MIR dataset from PCA analysis. Torsternson et al., (1998) observed that no single soil property can provide an extensive picture of soil quality including the soil nutritional status. On the loading plots for NIR and MIR (figure 37) all soil nutrients were important and played a role on soil fertility status indicated by the location on the loading plot away from the origin of the axis.

Principal component analysis of MIR soil dataset, explained total variation of 80%. Fifty seven percent of the total variance was explained by first principle component (PC 1) and was due to the influence of TC which was closely located to the horizontal axis. Total nitrogen, Exch. Mg and silt had an influence on PC 1. Fox and Metla (2005) observed that PC 1 accounts for the largest amount of variation. Second principle component (PC 2) explained 23% of total variance and was influenced by Ext.P. Soil pH_w and Exch.K were important and had an influence on PC 2 as they were closely located to the vertical axis.

The total variation was explained by PC 1 and PC 2, while the remaining variability that was not explained by the two PCs; (20% for MIR and 26% for NIR)was considered redundant i.e. it contained no relevant information related to the combined influence of the principle soil properties on soil fertility (Fox and Metla 2005).

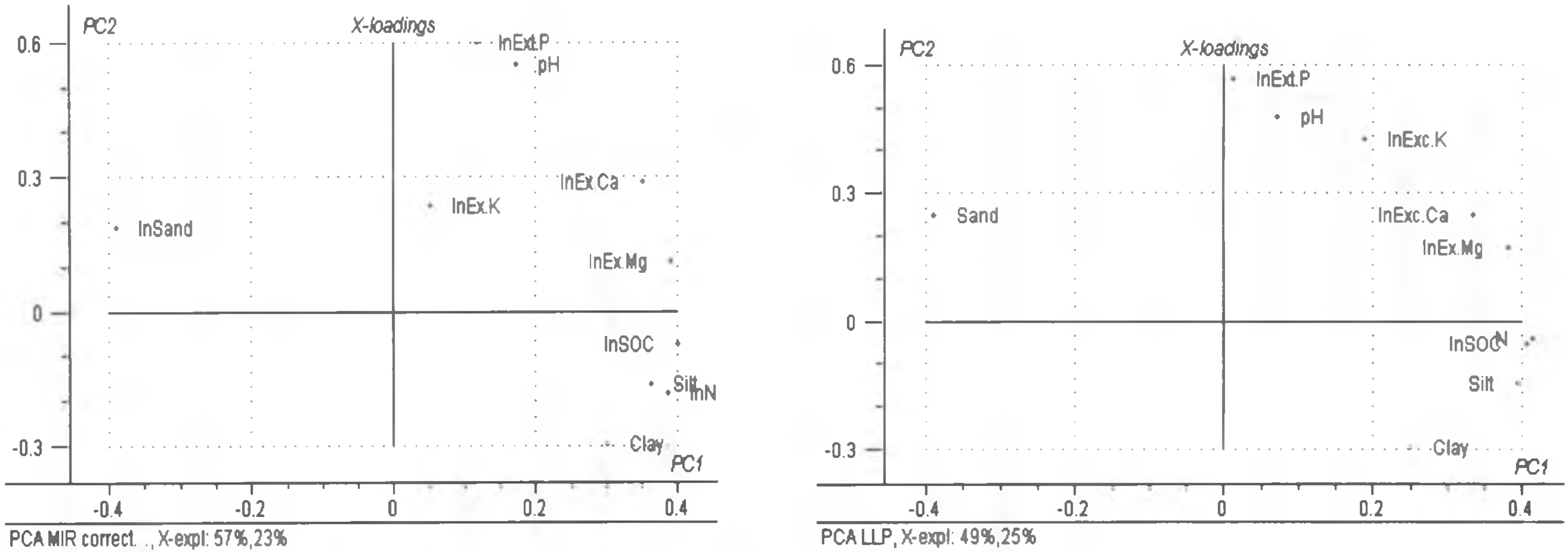


Figure 37: Loading plot for PCA analysis from Unscrambler (version 9.2) for MIR and NIR spectral regions

For the NIR soil reference data, PCA analysis showed that 74% of the total variance was explained by PC 1 and PC 2. First principle component accounted for 49% of the total explained variance which was due to the influence of TC. Exchangeable Ca and Mg, silt, clay and TN had loadings on PC 1. The second component explained 25% of the total variance and was due primarily to the influence of Ext. P and soil pH_w and to a lesser extent clay. On the loading plots, trends observed showed that sand and clay were negatively correlated. There was a positive correlation between levels of clay which tended to influence the concentration of exchangeable cations (Ca, Mg, and K) that increased with increasing clay content. Research findings have attributed this phenomenon to the increase of surface area on clay colloids and type of clay which influence cation exchange capacity (Greenland 1965).

Principle components (PCs) represented important soil fertility functional dimensions of principle nutrients on groundnut productivity. Therefore, soil fertility indicators (SFIs) were developed by renaming PCs. First principle component (PC 1) was renamed as soil fertility indicator 1 (SFI_1) and PC 2 as SFI 2. The advantage of synthesizing several soil fertility variables into one indicator, apart from simplicity, in the inter-correlation among the variables that can be utilized to provide more robust predictions than if they are treated individually.

To illustrate the functional dimension, a comparison of the strength an exponential relationship between SFIs and principle soil nutrients were evaluated based on r^2 value. Strong relationship existed between SFI_1 and TC, TN and Exch. Mg with r^2 values of 0.85, 0.80, and 0.85 respectively. Soil fertility is intimately linked to TC and has been universally accepted and taken in its own right as it is widely used as a soil quality indicator.

Moderately strong relationship existed between SFI_1 and Exch. Ca with r^2 value of 0.77. The relationship between SFI 2 and Ext.P was fair with r^2 values of 0.63, and 0.62 for soil pH_w while potassium had the lowest value of 0.5. Figure 38 (a) - (d) shows the relationship between the principle soil nutrients variables and the soil fertility indicator SFI_1 and SFI_2 (x-axis).

Using the SFIs concentration of the principal soil nutrients could be estimated using soil fertility score that give a holistic soil fertility status. The general trend observed in the graphs Figure 38 and 39) was that the concentration of principle soil nutrients increased in a non-linear trend as one moved from a negative fertility score to fertility score that is positive. The non-linear trend is useful because it is possible to identify sites (like the groundnut farms) that have high nutrient levels and that are not in need of amelioration from those that most probably do need amelioration. Figure 39 (e) – (f) shows concentration of nutrients by SFI_2

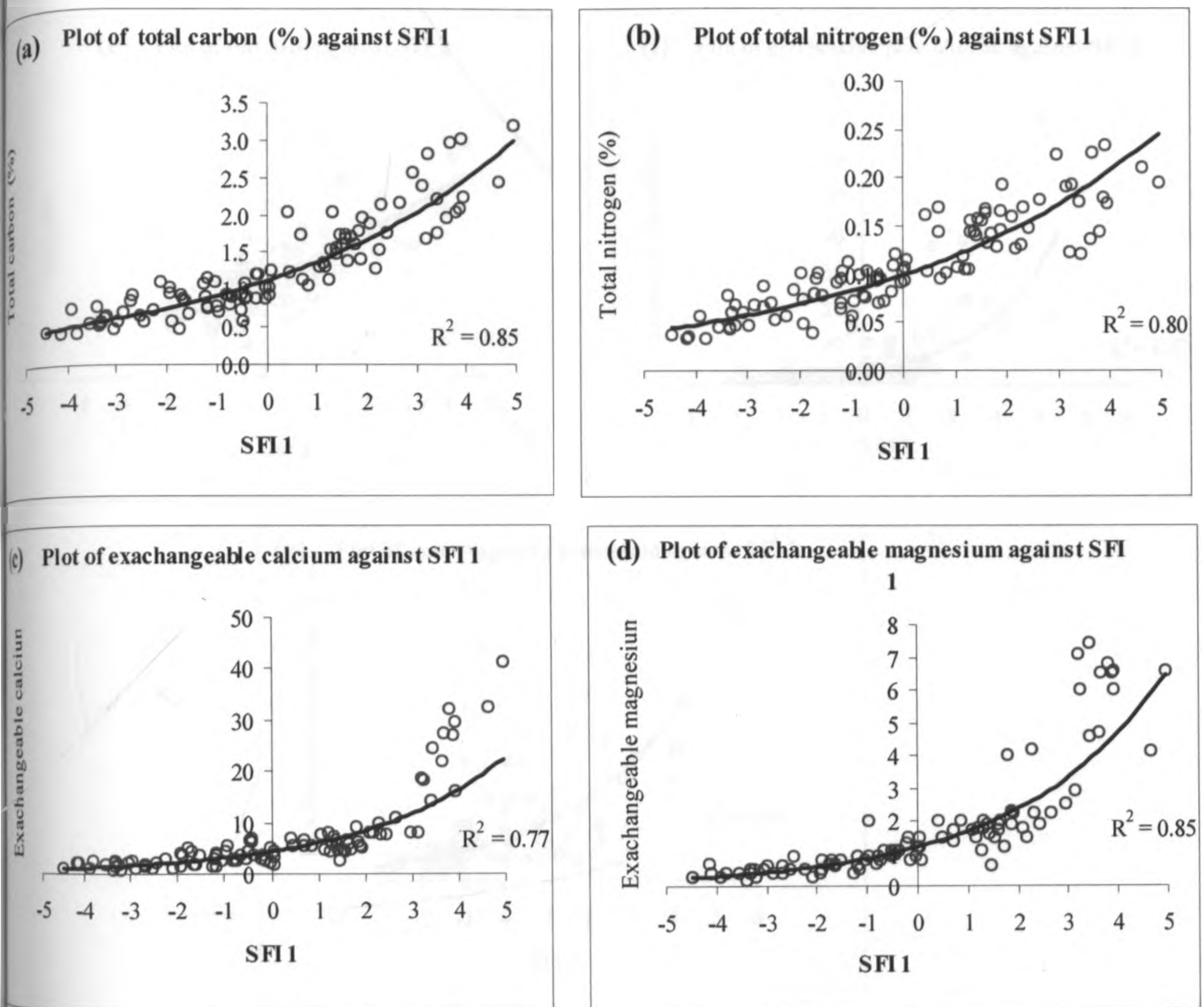


Figure 38: Soil fertility score (SFI 1) and soil nutrients; (a) total nitrogen (b) total carbon (c) Exchangeable magnesium (d) exchangeable calcium.

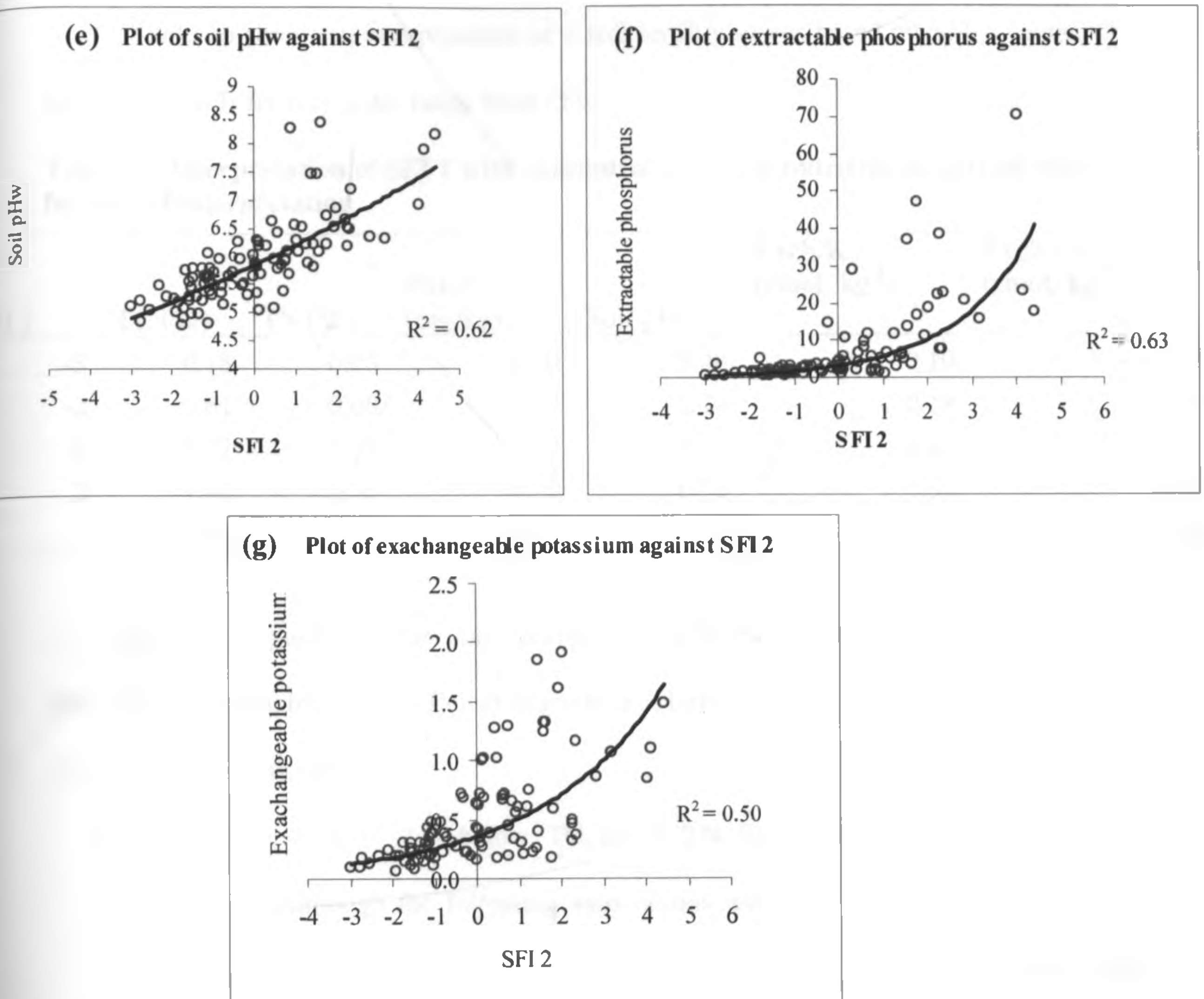


Figure 39: Soil fertility score (SFI 2) and soil nutrients; (e) Soil pHw (g) Extractable phosphorus (f) exchangeable potassium

4.4 Soil fertility scores

Table 16 shows an interpretation of a soil fertility scores based on SFI 1 values. On table 16 the SFI_1 fertility score range from -5 to + 5.

Table 16: Interpretation of SFI 1 with concentration of soil nutrients in normal units for ease of interpretation

SFI 1	TC (%)	TN (%)	Ext.P (mg/kg)	Soil pH	Exch.K ($cmol_c\ kg^{-1}$)	Exch Ca ($cmol_c\ kg^{-1}$)
-5	0.18	0.03	0.00	5.40	0.10	0.71
-2	0.61	0.08	0.97	5.70	0.18	0.83
0	1.27	0.11	3.52	5.80	0.42	6.23
2	1.93	0.16	4.70	6.70	0.55	9.64
5	2.90	0.20	10.15	7.30	0.83	21.39

An interpretation guide for the soil fertility scores based on SFI_1 which illustrate and distinguish which nutrient are deficient in groundnut farms

Interpretation of the table

1. When SFI 1 value is -2 or below, TC, Ext.P, TN, Exch.K and Ca levels are at very low levels. Although the following associations with SF1 were weak, there was a tendency for moderate acidity (<5.7), extremely deficient P levels (<1 mg kg^{-1}) and Exch.K levels in the deficient range (<0.2 $cmol_c\ kg^{-1}$). Exch. Ca levels below 4.0 $cmol_c\ kg^{-1}$ are generally considered to be critically low in tropical soils. These soils will need major rehabilitation of replenishment of Ext. P, TN and Exch. cations (Ca and K) for good groundnut production.
2. When SF1 1 falls below a value of 2, available phosphorus becomes deficient for groundnut production (Ext P < 7 mg kg^{-1}). An indication of the effect of acidity on availability of phosphorus. Between -2 and 2, P-replenishment is required with only

maintenance dressings of K. Above 2, soils have good potential for groundnut production and only maintenance dressings of P and K may be required. However the associations of P and K with SFI 1 were weak and it is better to examine SFI 2 for confirmation of these limitations. Organic matter levels may also need to be maintained.

3. When SFI 1 value is 5 and above, TC (2.90%), TN (0.20%) and Exch.K (0.83 $cmol_c$ kg^{-1}) are above the critical recommended levels and the soil pH (7.3) is near neutral and within the optimum range for groundnut productivity.

Table 17 shows an interpretation of a soil fertility scores based on SFI 2 values. On table 13 the SFI 1 fertility score range from -3 to +3

Table 17: Interpretation of SFI 2 with concentration of soil nutrients in normal units for ease of interpretation

SFI 2	Ext.P (mg/kg)	Soil pHw	Exch. K ($cmol_c$ kg^{-1})
-3	0.45	5.0	0.10
-2	1.50	5.2	0.23
0	4.19	6.0	0.43
2	10.93	6.5	0.60
3	15.70	7.2	0.85

1. When the score for SFI 2 is -3 extractable phosphorus, soil pH and exchangeable potassium are sub-optimal. There is an indication of acid infertility (<5.0) with phosphorus being quite deficient (0.45 mg kg^{-1}) as well as exchangeable potassium that is below the critical level of 0.2%. The groundnut farms that fell within this

range were 55%, and would therefore need major soil nutrient replenishment programme (application of phosphorus based and lime fertilizers for soil fertility replenishment) for this nutrients to improve groundnut yields.

2. Extractable phosphorus becomes moderate when SFI 2 score is 0 with a mean range of 5.2 mg kg^{-1}, slightly above the critical recommended level (5.0 mg kg^{-1}). Soil pH is within the optimum ranges recommended for availability of nutrients and for groundnut production. Exchangeable K is no longer deficient. Sixty percent of the groundnut farms fell in this category and would need liming to control soil acidity and phosphorus availability.
3. All nutrients; Ext.P, soil pH and exchangeable K are optimum for maximum groundnut productivity at soil fertility score of 3 for SFI 2. Management option for the groundnut farm will need to be maintained to the optimum levels of extractable P, Exch. K and soil pH.

4.5 Soil fertility indicators and soil reflectance spectra

The soil fertility indicators (SFIs) developed were calibrated against soil reflectance measured in the laboratory to evaluate the potential of soil reflectance spectra to predict soil fertility status. Excellent predictions from both MIR and NIR spectra with good cross validated statistics were obtained. Coefficient of determination (r^2) for SFI 1 and SFI 2 were 0.97 and 0.87 for MIR and 0.81 and 0.79 for NIR respectively. The lower values of the RMSEP, 0.42 and 0.60 for MIR and NIR has values 1.99 and 0.80 respectively further illustrated the goodness of the model. Figures 40 a and d illustrates this clearly. The cross validated statistic indicated soil reflectance from MIR calibrated well compared to NIR because of higher r^2 and lower RMSECV values. Even though the SFIs related quite well with spectral reflectance because of robust calibrations, higher r^2 values have been reported by other researchers for individual soil nutrient (Viscarra et al., 2005)

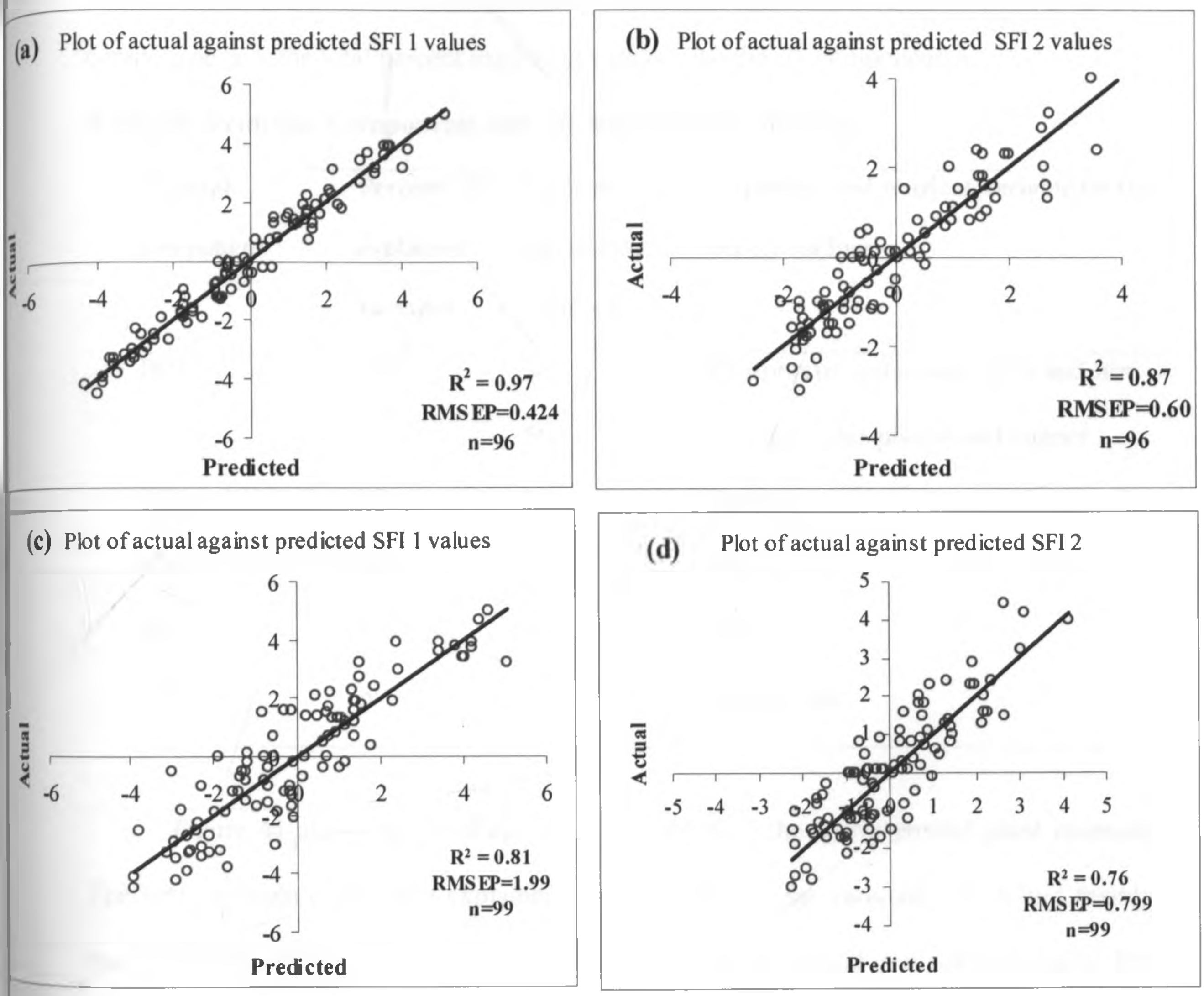


Figure 40: Calibrations of SFIs with spectra (a) SF1 1 and (b) SFI 2 for MIR, (c) SFI 1 and SFI 2 for NIR

4.6 Variation of above- ground groundnut biomass nutrients

Principle component analysis (PCA) conducted on biomass nutrients explained a total variation of 97 % by six principle components. Table 18 shows the principle components and the total percent explained variance for the six components.

Table 18: Principle Components and the main biomass loadings

Principle component	**Percent (%) explained variance**	**Percent (%) cumulative variance**	**Explained soil nutrient variable on the main Loadings**
PC1	34	34	Phosphorus, potassium, Zinc and Iron
PC2	22	56	Nitrogen, phosphorus and copper
PC3	15	71	Copper
PC4	12	83	Copper
PC5	8	91	Potassium
PC6	6	97	Phosphorus

Figure 41 shows the loading plot of the PCA of the above-ground plant biomass. The first principle component explained a total of 34% of the variation which was mainly due to the influence of total P, K, Zn and Mn in the above-ground groundnut biomass. The second principle component explained 25% and was mainly due to the influence of N and to a lesser extent K and Cu. General trends observed on the loading plot were; Zinc concentration was inversely related to P concentration and so was the relationship between Mn and K.

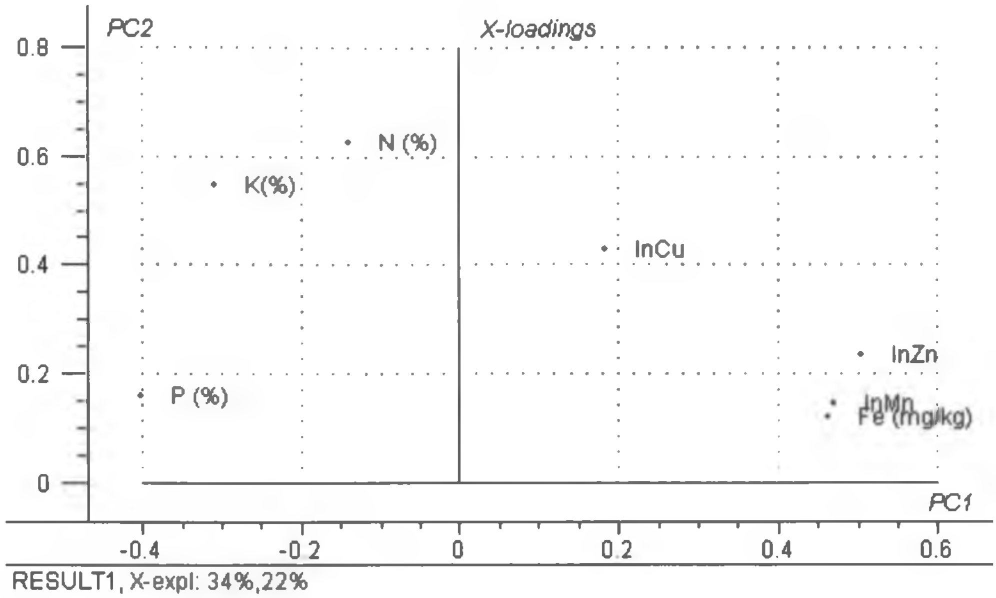


Figure 41: Loading plot for PCA analysis from Unscrambler (version 9.2) for MIR spectral regions

The two PCs represented important nutrient biomass functional dimensions of plant macro and micronutrients in above-ground groundnut biomass that play an important role in soil fertility. They gave a holistic representation of average biomass nutrient content. Therefore, the PCs were renamed as Biomass Nutrient Indicators (BNIs). The first principle component (PC 1) was renamed biomass nutrient indicator 1 (BNI 1) and PC 2 as BNI 2.

Using the BNIs concentration of groundnut, biomass nutrients could be estimated. The macronutrient N and K graphs, Figure 42 (a) and (b) show the concentrations increasing in a non-linear trend as the BNI score increases, from a negative score to a positive score.

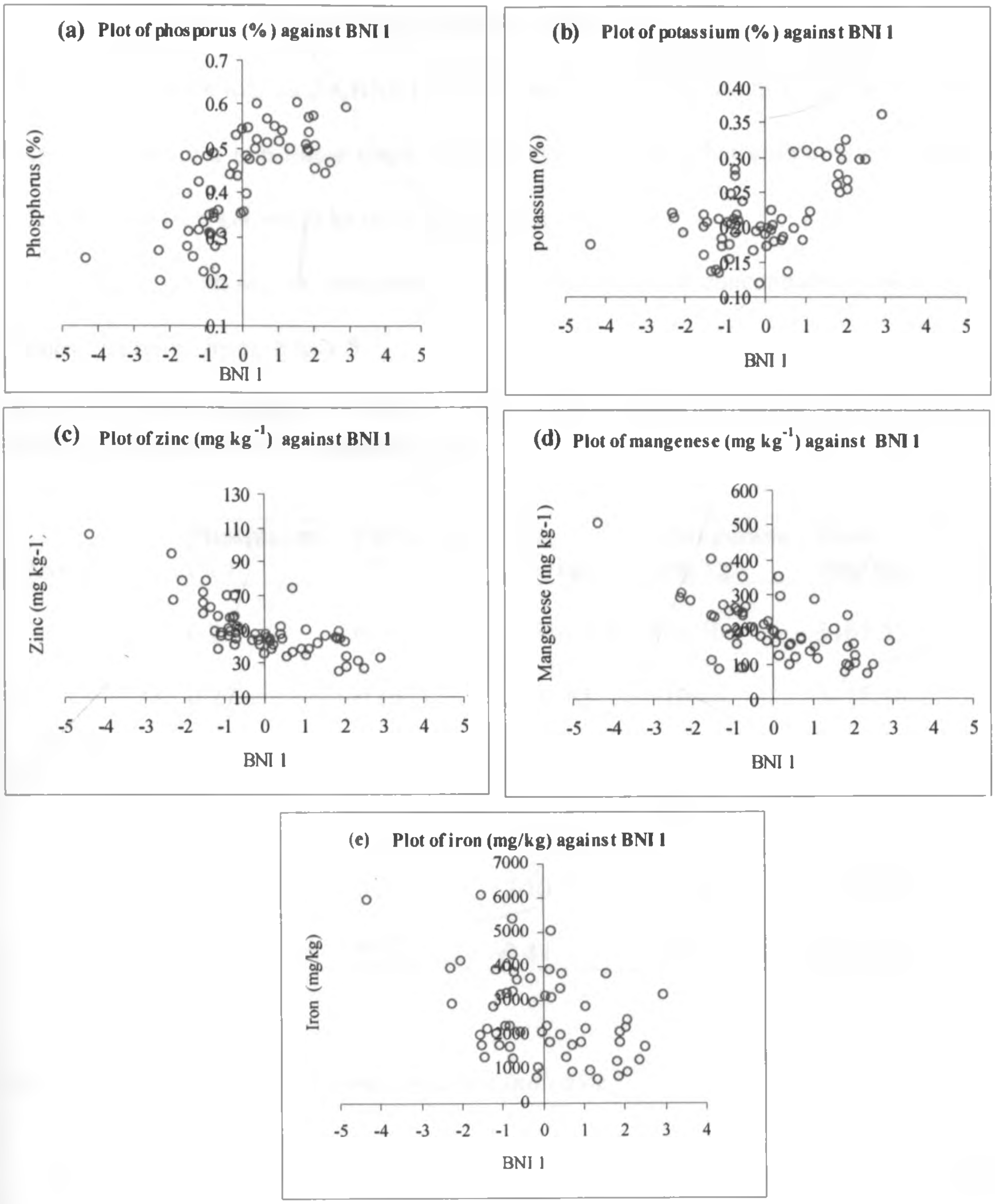


Figure 42: Biomass nutrient indicators (BNI 1) and plant macronutrients; (a) nitrogen (b) Total potassium (c) Total phosphorus

Trends observed for biomass micronutrients; zinc, manganese and iron (Figure 43 (a), (c) and (d) are that as the BNI 1 score increases the concentration of the micronutrients also decreases in a non-linear trend. This is due to the fact that high concentrations of the micronutrients are known to be toxic at certain level.

Table 19 shows an interpretation a biomass nutrient concentration based on BNI 1 values that range from -5 to + 5.

Table 19: Interpretation of BNI 1 with concentration of plant macro-nutrients in normal units for ease of interpretation

BNI 1	Phosphorus (%)	Potassium (%)	Zinc (mg/kg)	Manganese (mg/kg)	Iron (mg/kg)
-5	0.20	0.13	115442.68	456.50	5167.53
-3	0.27	0.16	5107.83	316.83	3725.48
-2	0.31	0.17	1074.41	263.95	3163.23
0	0.42	0.21	47.54	183.20	2280.50
2	0.55	0.26	2.10	127.15	1644.10
3	0.64	0.29	0.44	105.93	1395.98

Interpretive categories for biomass nutrient indicator.

1. When the BNI 1 score is -5 and below, P and K are very low below the critical levels of 0.4 % and 2.4 % respectively. The levels for soil micronutrients Zn, Fe and Mn are quite in the toxic levels. This could be a reason for low levels of P in the plant biomass as Zn is known to inhibit its uptake and the groundnut plants cannot absorb enough from the nutrients from the soil. Hence the soil needs a major K and P

replenishment for sufficient groundnut growth and rehabilitation to check the toxic levels of micronutrients.

2. When the BNI 1 score is 0 the levels of P are within sufficiency, at critical level 0.4%. However, when K concentration is 0.21 is slightly below the critical recommended limit of 0.24. The level of micronutrients Zn and Mn are within sufficiency levels above the critical level of 20 and 100 mg kg^{-1} respectively. Replenishment program that enhance the level of P and K while maintaining levels of the micronutrients should be considered at this BNI 1 score.
3. A biomass nutrient score of 2 and above indicate that the P and K levels are above the critical levels. However, Zn is below the critical level of 20 mg kg^{-1} are becoming deficient while Mn is still in the sufficiency levels. Amelioration is required for Zn

Using BNI 2, concentration of groundnut micronutrients (Zn, Cu and Mn) can be estimated. Trend observed on the graphs is that the concentration of micronutrients increased as one moved from a negative score to a positive score (-3 to +3). The non-linear relation for Cu indicates that high levels of Cu only occur at levels of SF2 >0.

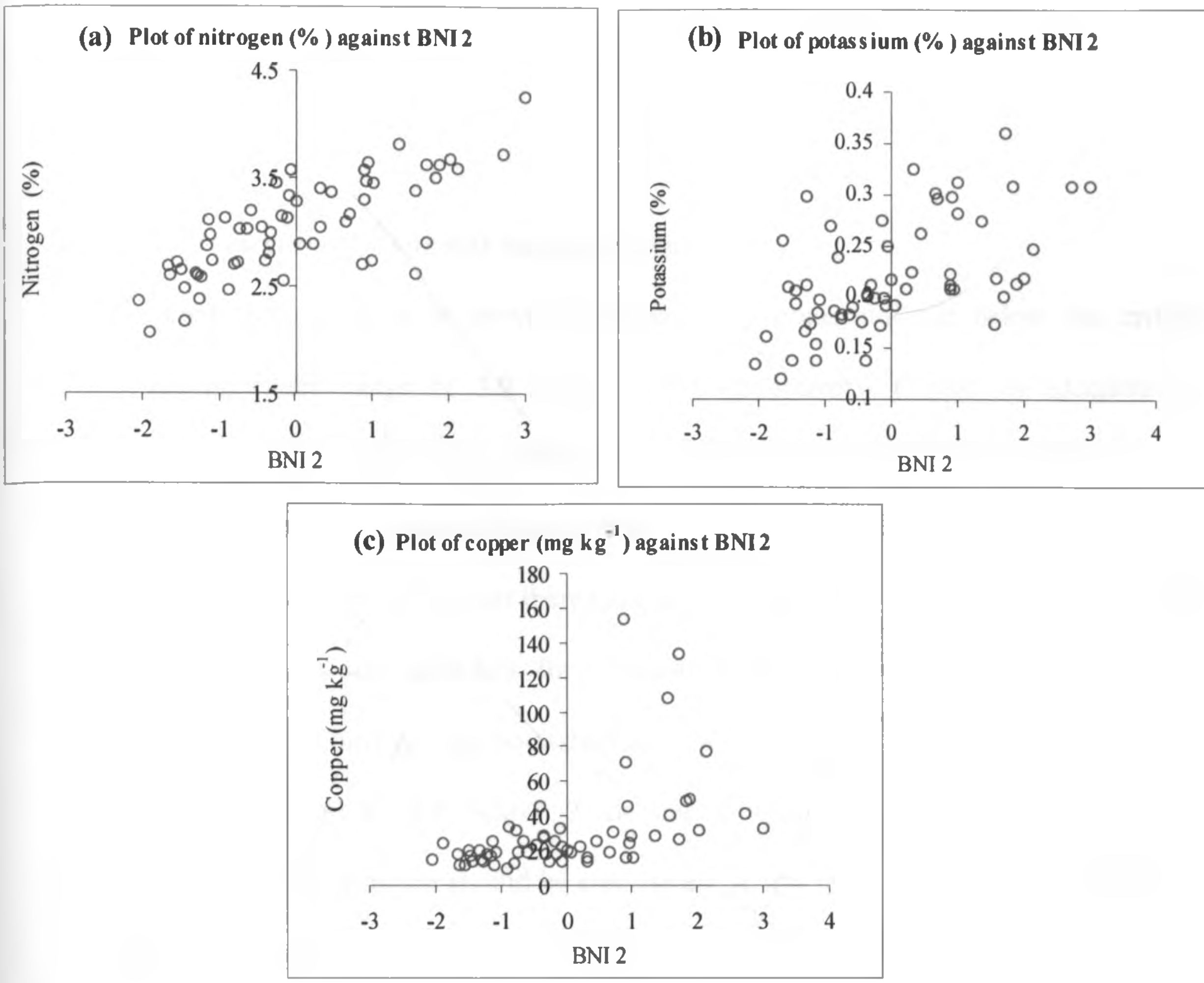


Figure 43: Biomass nutrient indicator 2 (BNI 2) and plant micronutrients; (a) Nitrogen (b) Potassium (c) Copper.

Table 20 shows an interpretation of soil fertility scores based on BNI 2 values that range from -2 to + 2.

Table 20: Interpretation of BNI 2 with concentration of groundnut micronutrients in normal units for ease of interpretation.

BNI 2	Nitrogen (%)	Potassium (%)	Copper(mg/kg)
-2	2.06	0.13	14.98
-1	2.50	0.17	15.00
0	2.80	0.21	33.17
1	3.12	0.30	24.17
2	3.50	0.31	48.23

Interpretive categories for biomass nutrient indicator

1. When BNI 2 score is above 0 nitrogen and potassium are below the critical recommended range of 3.9 and 2.4 (%) respectively. Copper is adequate for sufficient groundnut growth and above the critical concentrations of 6 mg kg^{-1}. A soil fertility program is required for replenishment of the soil macronutrient.
2. For a BNI 2 score of 2 means there is no input requirement for copper nutrients as the micronutrients are sufficient for optimum groundnut productivity. However the macronutrient nitrogen and potassium are low.
3. When the BNI 2 falls below -2 the micronutrients are becoming deficient and replenishment program should be considered. A soil fertility program is required for replenishment of the soil macro and micro nutrient.

4.7 Biomass nutrient indicators and soil reflectance spectra

The biomass nutrient indicators (BNIs) developed was calibrated against above-ground plant reflectance measured in the laboratory to evaluate the potential of soil reflectance spectra to predict biomass nutrient content. Good predictions from both MIR and NIR spectra with good cross validated statistics were obtained. Coefficient of determination (R^2) for BNI 1 and BNI 2 were 0.83 and 0.69 for MIR and 0.77 and 0.71 for NIR respectively. However, the NIR had a slightly higher R^2 value for BNI 2 compared to R^2 value for MIR. This could be attributed to the influence of N on BNI 2 which also yielded better prediction in the NIR region compared to MIR as presented in Figures 35 a and d. These results demonstrate the potential of IR as a utility for plant biomass nutrient analysis.

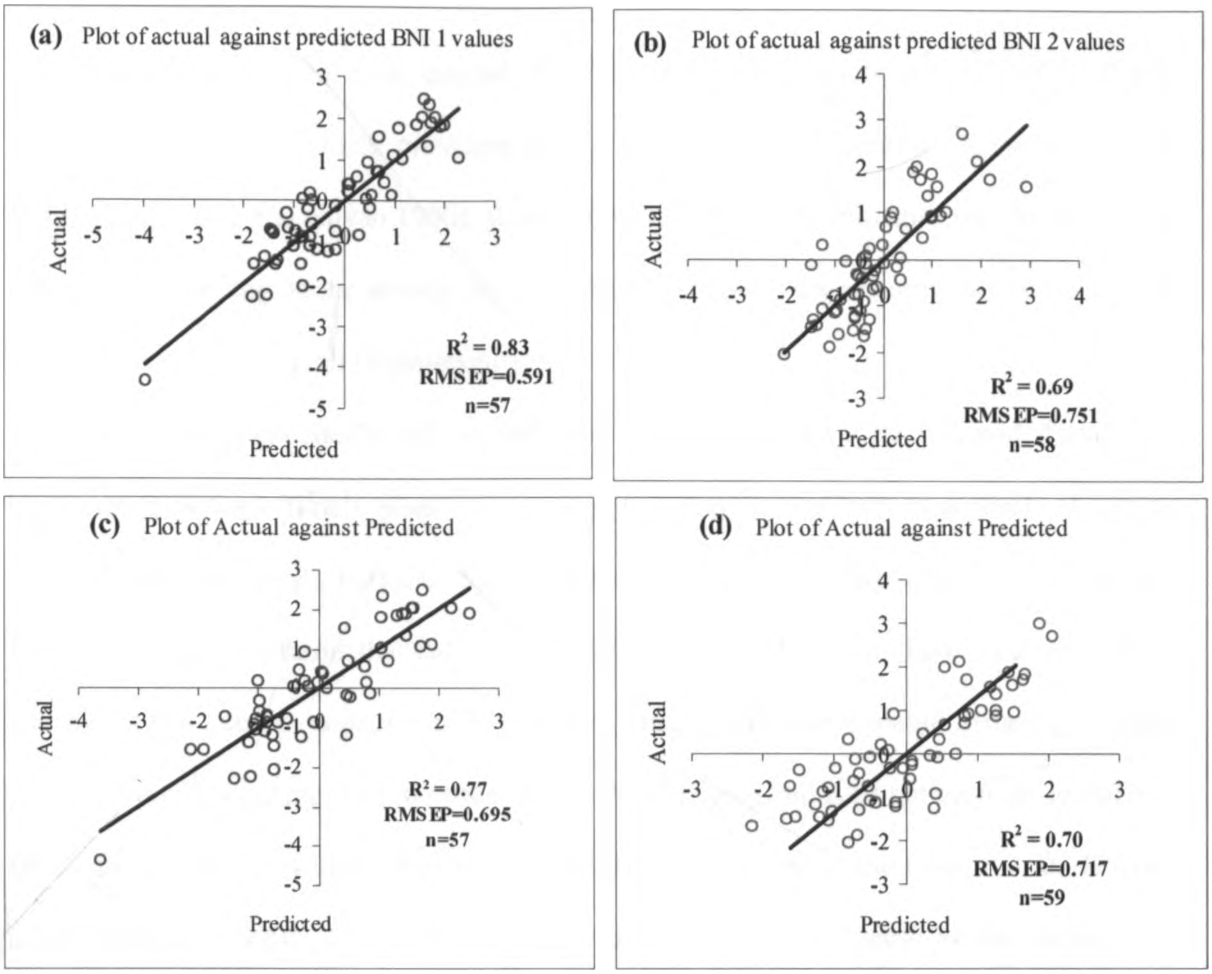


Figure 44: Calibrations of BNIs with spectra (a) BNI 1 and (b) BNI 2 for MIR, (c) BNI 1 and BNI 2 for NIR

4.7 Groundnut rosette prevalence on the groundnut farms

The mean percentage prevalence of groundnut rosette incidences was 5.8 % based on 70 groundnut farms sampled. Agro ecological zone LM_2 had the highest mean of rosette disease prevalence of 7.2% and mean percentages of 3.1, 5.6, and 5.2 for LM_1, LM_3 and LM_4/UM_4 respectively. This was quite low compared to results reported by Wangai et al., (2001), of groundnut rosette incidence in groundnut farmers at 32 % in western Kenya and 30% in the Rift Valley. Figure 45 shows the box plot of prevalence of groundnut rosette across agro ecological zones.

The disease is caused by the *groundnut rosette virus* (GRV) genus *Umbravirus* which is widely prevalent and is transmitted by the aphid *Aphis craccivora* Koch (Haciwa and Kannaiyan 1990). Rosetted plants produce significant lower kernel yields (34–90%) depending on the severity of the disease and often very severely infected plants do not produce any pods at all (Kannaiyan 1990).

The low prevalence could be attributed to tolerance of varieties provided and crop husbandry practices (timely planting, spacing, weeding) maintained as a result of farmer training (Agumba Singh, personal communication). The disease prevalence on the ground farms was highest in farms that had a low groundnut plant population. Low plant population was evident in nutrient depleted areas even in a single farm where malnourished groundnut plants occurred in patches (Field observation). Poor spacing and gaps between the groundnut farms due to poor growth could have been attributed to spread of the rosette virus (Haciwa and Kannaiyan, 1990). This facilitates easy movement of the disease vector (aphis) that spreads the rosette virus from one plant to the other (Wangai et al., 2001)

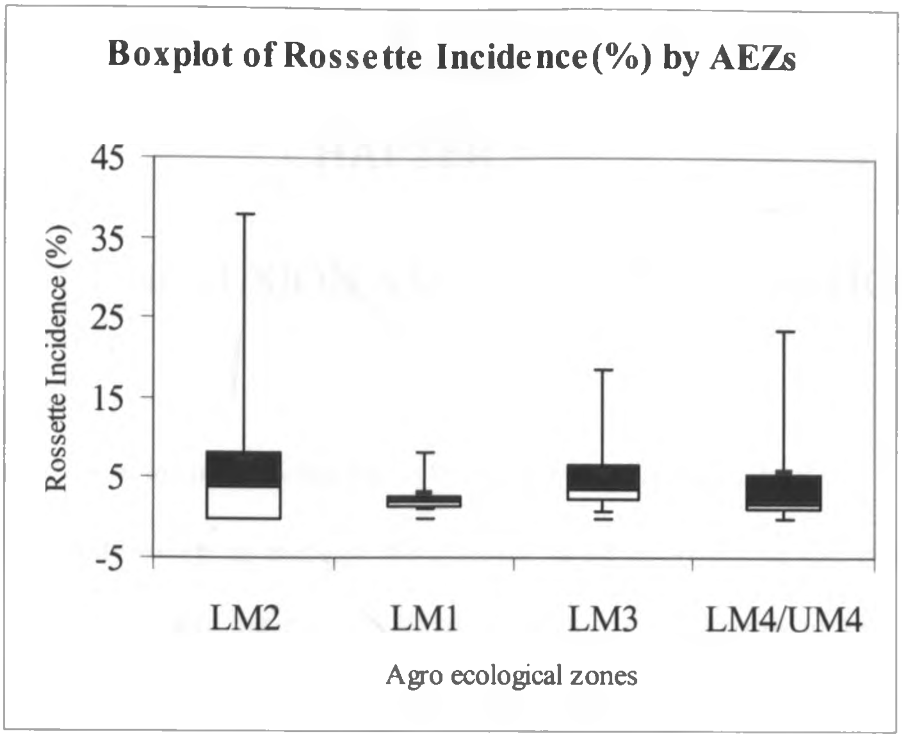


Figure 45: Box plot ranges groundnut disease prevalence (%) across agro ecological zones.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

1. Conclusions

(a) Evaluation of infrared technique as a soil fertility diagnostic tool

The study sought to evaluate the potential of IR in predicting soil nutritional status. The results demonstrated the utility of IR spectroscopy as a diagnostic tool for rapid nutrient assessment in small-scale groundnut production systems. Strong relationships existed among principle soil nutrients and soil reflectance for MIR and NIR. Robust calibration model were obtained for soil pH_w (r^2=0.85), TC (r^2=0.98), TN (r^2=0.97), Exch. Ca (r^2=0.95) and Mg (r^2=0.94) and particle size distribution (sand r^2=0.85) silt r^2=0.82 clay r^2 =0.81 for the MIR spectral region. Though calibration were robust for NIR spectral region for principal nutrients with lower r^2 compare to MIR, the MIR was superior based on the cross validated statistics. Extractable P and Exch.K had weak calibration models with r^2 values of 0.66 and 0.50 for MIR spectral region and 0.50 and 0.32 for NIR. Similarly the above-ground groundnut biomass (MIR) had more robust calibration models compared to the NIR spectral region, though Manganese (r^2 =0.33 and Zinc (r^2 = 0.09) for NIR had very weak calibrations and were equally poor for MIR spectral region.

Attenuated total reflectance (ATR) using the soil saturated paste performed well in prediction of TC and TN with r^2 values of 0.94 and 0.93 respectively. The calibration model for TC was not stable because of a bigger difference in r^2 values of calibration and validation models. Exchangeable K was fairly predicted with ATR (r^2=0.53) and better compared to values of NIR and MIR of 0.32 and 0.50 respectively. This demonstrated suitability of the developed simple protocol and potential for predicting soil parameters from soil pastes using ATR spectroscopic techniques

Given that plant and soil samples were collected from a broad diversity of small-scale groundnut farms, these results demonstrated the fundamental utility and potential IR spectroscopy as a rapid diagnostic screening tool for soil nutritional assessment in small-scale groundnut production systems. Large area assessment of soil nutritional status is quite appropriate for assessment of soil fertility degradation because of rapidity, cost-effectiveness and multi-nutrient analysis (from a single spectrum) (Shepherd and Walsh 2007). This is also an advantage to the small-scale groundnut farmers.

A spectrally –based soil fertility indicator was derived that provide rapid assignment of a soil sample to soil fertility classes that can help guide soil fertility management interventions. The soil fertility indicators (SFIs) which integrated soil nutrients, by use of soil fertility score different levels of soil nutrients were developed. At various soil fertility score it was possible to guide which soil nutrients are deficient and which are below the critical levels. Hence the score provided a kind of soil fertility management tool for identifying which nutrients are deficient and adequate levels for ease of management based on critical limits.

(b) Soil fertility status in small-scale groundnut farms

Soil nutritional status estimated from IR showed a clear indication of low soil fertility in the majority of the groundnut farms. The soil fertility was assessed in relation to groundnut production by comparing with critical recommended limit. For soil pH_w, 80 % of groundnut farms ranged from slight acidity to near neutrality and within the recommended soil pH_w range of 5.3-7.4. Thirty percent of the groundnut farms had the TC concentration levels above the critical concentration level of 2.0%., while levels of TN (%) were low compared to recommend critical values of 0.2% in 75% of groundnut farms. Exchangeable Ca and extractable P and total nitrogen were the main limiting nutrients in groundnut farms. All the farms had calcium levels below the critical recommended level of 50 $cmol_c\ kg^{-1}$ and 68% of the farms had deficiency in phosphorus. The biomass nutrient also indicated a serious deficiency in phosphorus and nitrogen in all groundnut farms based on the critical limit of 4.0 and 0.4 (%) respectively. However, exchangeable K was not limiting as earlier suggested based on the soil results. Above ground biomass indicated sufficient levels of micronutrients, Zn, Cu and Mn in 100 % of the groundnut farms. Given the soil nutritional status estimated using the IR there was a clear indication of soil fertility for groundnut production in the study area.

2. Recommendations

a) Future research works of spectroscopic techniques like IR offer the potential to quickly and inexpensively characterize soils relative to standard laboratory techniques. Future development of soil spectroscopy and expansion of IR should focus on improving on the predictability of extractable phosphorus and exchangeable potassium using soil water extracts. In addition, there is need to build capacity in Africa in this field of spectroscopy for ease adoption of the technique as a soil management tool and large scale assessment of soil fertility.
b) Based on the results obtained in this study, soil fertility replenishment will be required for successful small-scale groundnut production in western Kenya. Soil

fertility replenishment programs could focus on replenishment of the constraint soil nutrients and maintenance of the adequate ones.

c) Groundnut rosette prevalence and soil fertility status was assessed and there was no sufficient data to actually come up with solid conclusion of any relations. However, future works should focus on the role of soil fertility on the groundnut rosette prevalence. Spectral indices can be developed to predict groundnut rosette prevalence based on soil fertility indices and biomass fertility indices.

d) Further research should develop spectral indices of soil fertility and soil borne disease prevalence that can be used to assess and predict soil suppressive ability monitor effects of agronomic management. The ability of soil to be suppressive depends on the soil fertility status therefore the relationship between soil fertility and the soil suppressive ability should be studied. The main challenge is to design a single index that can be used to assess soil nutritional status and soil suppressive ability.

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