ASSESSMENT OF COAL MINE STOCKPILED SOIL QUALITY AND ITS IMPACT ON VEGETATION USING LABORATORY-BASED TECHNIQUES AND REFLECTANCE SPECTROSCOPY

BY

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DECLARATION

I declare that this thesis hereby submitted to the University of Limpopo for the degree of Doctor of Philosophy in Soil Science has not previously been submitted by me for a degree at this or any other university; I declare that the entirety of the work contained therein is my own, original work, that I am the sole author thereof (save to the extent explicitly otherwise stated); that reproduction and publication thereof by University of Limpopo will not infringe any third party rights. I also declare that all material contained herein has been duly acknowledged.

This dissertation includes four (4) original papers published and/or submitted in peer-reviewed journals. The development and writing of the papers (both published and unpublished) were the principal responsibility of myself, and for each of the cases where this is not the case, a declaration is included in the dissertation indicating the nature and extent of the contributions of co-authors.

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To my young sister, Sewela Rosinah Disego Mushia (02 August 1993 - 30 April 2016), you will forever be remembered.

ABSTRACT

Surface coal mining requires good and sound rehabilitation practices to re-establish productive land capability and land use after mine-closure. The vast majority of Mpumalanga's coal deposits are located below high quality and productive arable land. Impacts on soil and land, associated with surface coal mining can reduce the possibility to re-establish the pre-mining land capability and productive potential. Stockpiled soils are excavated from the ground during mining activities, and piled on the surface of the soil for rehabilitation purposes. These soils are often characterized by low Soil Organic Matter (SOM) content, low fertility, and poor physical, chemical and biological properties, limiting their capability for sustainable vegetation growth. The aim of this study was to assess coal-mine stockpile soil quality and its impacts on vegetation using laboratory techniques and Reflectance Spectroscopy.

Firstly, the impact of quality of coal-mine stockpile soils on sustainable vegetation growth and productivity was investigated. Soils were collected at three different depths (surface (0-25cm), mid (150-200cm) and deep (300-350cm)), as well as mixed (equal proportion of surface, mid and deep) from two stockpiles (named stockpile 1: aged 10 and stockpile 2:20 years) at the coal mine near Witbank in Mpumalanga Province, South Africa. Soils were amended with different organic and inorganic fertilizer. A 2 x 4 x 5 factorial experiment in a randomized complete block design with four replications was established under greenhouse condition. A grass species (*Digiteria eriantha*) was planted in pots with unamends and amended soils under the greenhouse condition at ambient temperatures of 26-28^{0}C during the day and 16.5-18.5^{0}C at night. Mean values of plant height, plant cover, total fresh biomass (roots, stems and leaves) and total dry biomass were found to be higher in the stockpile 1 than in stockpile 2 soils. On average, plants grown on soils with amendments yielded plant height that was 98.28% higher than plants grown on soil with no amendment. On average, height of plants grown on soil amended with poultry manure and lime was 44.65% higher compared to plants planted on soils amended with NPK + lime, compost and poultry manure. On average, mixed soils had better vegetation growth than soil from the individual depths. In total, dry biomass and plant height of plants

grown on mixed soils was 33.56% and 22.34% higher than plants grown on surface, mid and deep soils. Mixing soils changes texture, which might affect other physical properties like water availability, infiltration rate and aeration and, to some extent, chemical properties.

Secondly, the effect of soil amendments on enzyme activity of coal-mine stockpile soil was investigated. The activity of β-glucosidase, alkaline phosphatase, acid phosphatase and urease was analysed after harvest of grass species (*Digiteria eriantha*). The results show significantly high activity for β-glucosidase, alkaline phosphatase and urease when soils were amended with poultry manure + lime. Soils with no fertilizer yielded significantly low enzyme activity compared to soil amended with poultry manure+ lime, NPK + lime, sole application of poultry and in some instances compost application. β-glucosidase, urease and acid phosphatase mean values generally tend to decrease with an increase in soil depth. β-glucosidase activity for surface soil was found to be 18.06% higher than that of mid and deep soil. The stockpile depth plays a major role in biochemical activities of the soil; deep soils, in most cases, have decreased microbial biomass and enzyme activity due to oxygen and moisture availability. The results for the effect of organic and inorganic amendment on stockpile soil showed that on average, alkaline phosphatase activity following the application of poultry manure + lime was 17.69% higher than that of lime + inorganic fertilizers (NPK). On average, the acid phosphatase activity following the application of lime + NPK was 56.33% higher than that of poultry manure + lime, compost, soil with no fertilizer as well as sole poultry manure. Urease activity for soil with no fertilizer was found to be 84.70% lower than that of soil amended with poultry + lime. The increase in enzyme activity was attributed to change in soil pH due to application of amendments. A comparison of the two stockpiles indicated that, stockpile 2 (20-year old) had low enzyme activity compared to stockpile 1 (10-year old). The activity of β-glucosidase, acid phosphatase, alkaline phosphatase and urease was found to be 11.03%, 8.04%, 10.03% and 60.23% respectively, higher on stockpile 1, relative to stockpile 2 soils. When soils are stockpiled for a long period of time, microbial biomass is reduced and that affect enzyme activity because microbial biomass is considered as the primary source of enzymes in the soil.

Thirdly, the capability to estimate coal-mine stockpile soil properties using Reflectance Spectroscopy was investigated. Soil from coal-mine stockpiles were air dried, crushed, sieved and analysed using laboratory methods. The following soil properties: exchangeable calcium (Ca), sodium (Na), magnesium (Mg), potassium (K), soil pH, organic carbon (OC), phosphorus (P) and clay content were analysed as they are important for vegetation re-establishment during rehabilitation. Spectral reflectance of the soil samples was measured using FieldSpec 3 Portable Analytical Spectral Device (ASD®) spectrometer. Partial Least Square Regression (PLSR) was used to estimate various soil properties, in combination with various spectral transformation techniques such as untransformed reflectance spectra, First Derivative Reflectance (FD) and Log transformed spectra Log (1/R). To assess the performance of various predictive models, R^2 (Coefficient of Determination), Root Mean Squares Error of Validation (RMSEV) and Variable Importance in the Projection (VIP) values were computed. The results showed that pH and Ca were accurately estimated (R^2=0.79 and 0.69 and RMSEV=0.52 and 0.89cmol/kg respectively) using Log (1/R) reflectance as compared to other soil properties achieving R^2 less than 0.5. Ca has strong correlation with pH. Ca expressed in soil solutions is mostly related to pH, which is what was attributed to accurate prediction of both Ca and pH. Soil pH in most cases is directly influenced by calcium carbonate content in the soil. Although the performance of other soil properties was poor, they were highly correlated with pH and Ca except for K. K is soluble and mobile and is therefore subject to leaching in most soils resulting in low K concentrations. Low K concentrations results in higher variability and lower R^2 values.

Finally, the capability of Partial Least Square Regression and Reflectance Spectroscopy to estimate the effect of coal-mine stockpile soil on foliar nitrogen and phosphorus content was investigated. Grass samples were collected from coal-mine stockpile soils and the adjacent unmined soils at open-cast coal mine around Witbank area in Mpumalanga Province, South Africa. Samples were oven dried and analysed for foliar N and P concentration in the laboratory. Spectral reflectance of the dried grass samples were measured using Analytical Spectral Device (ASD) - FieldSpec 3. Partial Least Square

Regression (PLSR) was used to estimate N and P concentration, in combination with various spectral transformation techniques such as First Derivative Reflectance (FDR) and Log transformed spectra Log (1/R). The results show that stockpile soils appear to impact foliar N and P concentration as evidenced by low N and P concentration in the grass, sampled from stockpile soils compared to grass sampled from unmined soils. This was attributed to soil nutrient status of the study sites, as unmined sites had high soil nutrient content than stockpile soils. Foliar N concentration of grass sampled from stockpile soils and unmined soils can accurately be estimated without spectral transformation. FD yielded highest R^2 for N and P estimation in grass sampled from both stockpile soils and unmined soils.

Overall, the study shows that stockpiling affect soil quality, enzyme activity and vegetation growth. It further shows that soil amendments can improve soil quality and enzyme activity of coal-mine stockpile soils. Finally, Reflectance Spectroscopy can be used to estimate coal-mine stockpile soil properties, its quality and foliar N and P content as an indicator of vegetation nutrient stress.

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LIST OF ABBREVIATIONS/ACRONYMS

ASD	Analytical Spectral Devices, Inc.
COM	Chamber of Mines South Africa
CRA	Coaltech Research Association
D	Deep soils
FDR	First Derivative Reflectance
LOOCV	Leave-One-Out Cross Validation
M	Mid soils
MARS	Multivariate adaptive regression splines
MIR	Mid infrared
MRA	Multiple Regression Analysis
MX	Mixed soils
N	Nitrogen
NIR	Near Infra-Red
NN	Neural Network
OC	Organic Carbon
P	Phosphorus
PCR	Principal Component Regression
PLSR	Partial Least Squares Regression
R	Reflectance
RMSE	Root Mean Squares Error
RPD	Ratio of Prediction to Deviation
RS	Remote Sensing
S	Surface soils
SD	Standard deviation
SMLR	Stepwise Multiple Linear Regression
SOM	Soil Organic Matter
SWIR	Shortwave Infrared
VIP	Variable of Importance for Prediction
VIS	Visible

CHAPTER 1
GENERAL INTRODUCTION

1.1 Background of the Study

Mining may be described as an activity and occupation concerned with the extraction of minerals. These minerals include coal, petroleum oil, Baryte-limestone, quartz, lignite etc. The ever-increasing demand for minerals and energy as well as advancement in extraction techniques has increased the mining of minerals in South Africa (Whiteman, 1982; and Schobert, 1987). South Africa's economy is highly fossil fuel dependent, with the main source of electricity being coal accounting for about 90% of the country fuel use (Stats SA, 2015). Apart from the heavy domestic reliance on coal as a source of energy, South Africa is a significant participant in global coal markets (Botha, 2014). The majority of South Africa's reserves and mines are in the Central Basin, which includes the Witbank (eMalahleni), Highveld and Ermelo coalfields (COM and CRA, 2007). South Africa's economically recoverable coal reserves are estimated at between 15 and 55 billion tonnes and coal production in the Central Basin is likely to peak in the next decade (The Bench Marks Foundation, 2014).

Anthropogenic activities such as mining activities, specifically open-cast mining have resulted in drastic alternations of soil geochemical cycles that often lead to land degradation (Paterson *et al.,* 2016). It is imperative that mining process must ensure the restoration of productivity of the affected land (Ghose, 1989). Ghosh (1990) reported that every million tonne of coal extracted by surface mining methods cause the land damage of about 4ha. Opencast mining activities affect several physical, chemical and microbiological properties of soil as a result of excavation and storage of the soil (Strohmayer, 1999). The inability to preserve the quality of stripped soil (stockpiling) is one of the basic hindrances to restoration of mined land. The acute problem in preserving mine soil leads to large areas of land continually becoming infertile despite efforts for re-vegetation (Paterson *et al.,* 2016).

Several studies on stockpiled soil management have been done elsewhere to address the problem of soil quality after mining (Harris & Birch 1989; Jordan 1998; Tate & Klem, 1985; and Fresquez & Aldon, 1984). Most of these studies focused on assessment of stockpile soil properties using wet chemistry methods. There are limited studies focusing on assessing coal-mine stockpile soil properties using Reflectance Spectroscopy. In this study, Reflectance Spectroscopy was used to assess soil properties. The studies by Demattê *et al*. (2010) and Mashimbye *et al*. (2012) indicated that Near InfraRed (NIR) spectroscopy is among one of the less expensive, less labour intensive, effective, reliable and user-friendly technique for quantitative soil analysis.

Furthermore, the available studies do not address the relationship between stockpile ages, stockpile depth, vegetation growth and enzyme activity of coal-mine stockpiled soils. Hence, this study focused on generating information to address the problem of coal-mine stockpiled soil quality and its impact on vegetation growth and enzyme activities.

1.2. Motivation of the Study

The following considerations provided justification for the study:

- The challenges of coal-mine stockpiling and maintenance of its soil quality is critical for sustainability of mine land rehabilitation and it must be addressed;
- As part of potential rehabilitation plan, there is a need to continuously monitor and examine vegetation quality around stockpiled soils and the surrounding areas;
- Sustainable management and storage of coal-mine soils is critical to maintaining soil health; and
- The need to utilize low cost and time effective methods for improved assessment of stockpiled soils is required for environmental health and pollution reduction.

1.3. Aims and Objectives

The aim of the study was to determine if greenhouse studies, laboratory-based techniques and Reflectance Spectroscopy could provide reliable results for assessment of coalmine stockpile soil quality and its impacts on vegetation.

The main objectives of the study were, namely, to:

1. Evaluate the impact of quality of coal-mine stockpile soils on vegetation growth and productivity;
2. Evaluate the effect of soil amendments on enzyme activities of coal-mine stockpile soil;
3. Estimate coal-mine stockpile soil properties using Reflectance Spectroscopy; and
4. Estimate the effect of coal-mine soil stockpiling on foliar nitrogen and phosphorus content as indicators of vegetation quality using Partial Least Square Regression and Reflectance Spectroscopy.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

World population has doubled over the last fifty years and quadrupled over the past century (UN-DESA, 2013). During this period and in most parts of the world, productivity gains in agriculture have increased profoundly. However, the amount of land that can be brought into the agricultural system is physically finite, so the concern naturally emerges that a much larger world population cannot be fed. Access to food is a basic human need. It is acknowledged that poverty is a fundamental cause of food insecurity. Ensuring long term food security is a major challenge to many countries in the world (FAO, 2013). It is therefore critical for a country to retain its production capability to adhere to its food requirements. South Africa has only about 3 – 4% high potential agricultural land that is suitable for sustained food production. Much of this high potential agricultural land has however been lost to other competing land use prospects, with coal mining being one of the major competing land use (Van der Burgh, 2012).

Surface coal mining results in degradation of soil physical properties, significant loss of organic matter and nutrients and hence diminishes soil productivity (Akala & Lal 2001). Restoring the soil productivity and the establishment of sustained vegetative cover are primary objectives of mine soil reclamation. In the process of open-cast mining, the area is completely stripped of vegetation to remove overburden covering the coal seam. Soil loss is a regular occurrence at surface coal mines, especially older mines where soil management was not a management priority at the onset of mining operation (COM and CRA, 2007). In some areas, soil was not even stripped prior to mining as it was not a requirement to do so (Cogho, 2012). Adequate soil stripping, stockpiling and management of this resource at a surface coal mine is therefore of utmost importance. Without proper soil management, post-mining substrate might not only comprise soils and that might limit the ability of the substrate to support a good vegetation cover (Mentis, 2006). Soil generation (pedogenesis) is a lengthy process that spans over several years (Strohmayer, 1999).

2.2 Coal-Mine Soil Stockpiling

Soil is a vital natural resource, constituting a critical controlling component during the early stage of ecosystem development. Soil quality is defined as “the capacity of a soil to function within ecosystem boundaries to sustain biological productivity, maintain environmental quality and promote plant and animal health” (Doran & Parkin, 1994). Mining activities are invariably associated with the removal of fertile top soil organic layer enriched with vegetation cover (Fox, 1984) and hence has negative environmental consequences.

Surface coal mining requires good and sound rehabilitation practices to re-establish productive land capability and land use after mine-closure. The vast majority of Mpumalanga’s coal deposits are located below high quality productive arable land (Mentis, 2006). Impacts on soil and land associated with surface coal mining can reduce the possibility to re-establish the pre-mining land capability and productive potential. The result observed in practice, defined as the status quo, is that most surface coal mining companies in Mpumalanga aim to re-establish grazing land capability potential for the end land use option instead of the original arable land capability (Botha, 2014).

Stockpiling is a necessary part of civil engineering and mining operations, involving the removal of topsoil (the A and B-horizon of the soil). The topsoil is usually removed with heavy equipment and then stored in large, deep piles for the duration of the civil engineering or mining project. When the project is complete, the soil is re-spread to allow for the establishment of plants. The storage period for stockpiled soil ranges from a few months to several years. The depth of the stockpile and the length of time it is stored affect the quality of the soil (Strohmayer, 1999).

Soil takes centuries to develop from parent material and organic matter. In a study of soil development of six sites where surface mines existed between 5 and 64 years, the depth of the newly developed soil horizon in the 5-year-old site was 3cm compared to 35cm in the 55-year-old site (Strohmayer, 1999). If stockpiled soil is reapplied quickly after mining, with less compaction from mechanical traction, the production potential of vegetation on the stockpile remains high (Thomas & Jansen, 1985).

During the process of open-cast coal mining, topsoil is removed and stockpiled for future use. Stockpiled topsoil becomes highly degraded the moment this long-term structure is disturbed. Several studies conducted (Fresquez & Aldon, 1984; Harris & Birch, 1989; and Strohmayer, 1999) reveal that timeframe can lead to damage of most soil properties. The damage starts when topsoil is initially stripped from the ground. Changes that occur in soil include change in physical, chemical and biological properties, and loss or reduction of viable plant remnants and seeds (Strohmayer, 1999). For stockpiled soil to meet its goals of rehabilitation post mining-closure, quantification of soil physical and chemical properties that affect soil quality and crop production is necessary. Soil properties such as soil structure, microbial population and nitrogen can change rapidly when the soil is disturbed (Lad & Samant, 2015).

The natural process of soil development can take hundreds of years and stockpiled topsoil becomes highly degraded the moment the structure is disturbed (Birch *et al*., 1989). Studies reviewed herein lead to one timeframe where the most damage occurs. This timeframe is when topsoil is initially stripped from the ground. Changes that occur in soil include increased bulk density, decreased water holding capacity, chemical changes, reduced nutrient cycling, reduced microbial activity, and loss or reduction of viable plant remnants and seeds (Harris & Birch, 1989).

Soils are in practice stockpiled in three categories according to their clay content, topsoil and subsoil, and not grouped together as commonly prescribed in the soil guidelines of a mine (New Hope Group, 2014). The “A” and “B” horizons are usually stripped and stockpiled together, diluting the fertility status of the soil (COM and CRA, 2007), and increase fertility requirements post-closure. Mentis (2006) also described this impact as an effect of soil disturbance when bringing the subsoil, saprolite and fragmented rock to the surface. These components then form part of the mixture with topsoil that is used for the top layer on a post-mining surface. The result is that the mixture often cannot support plant life. Therefore, for good rehabilitation results to re-establish plant life, the contamination of soil, especially when bulk volume soil stripping is practised on a site, should be minimized or prevented (COM and CRA, 2007).

Several researches on stockpiled soils were conducted in other countries addressing challenges and problems faced in those respective countries. Ghose (1989) conducted a study that focused on the effect of open mining on soil fertility in India's largest open-cast coal project Eastern Coalfields Ltd. The study indicated that, for every million tonne of coal extracted by surface mining, approximately 4ha of a surface area is disturbed. Harris and Birch (1989) noted that when soil stockpiles in more than a meter deep, chemical effects such as accumulation of ammonium and anaerobic conditions occurred in the topsoil at the base of the pile. Other detrimental biological effects include absence of propagules and decrease in viability of buried seeds.

A study conducted in Wales and New Zealand by Williamson and Johnson (1990) reported that the soil pH and the mineral content of stockpiled soils are not affected, as long as the soil is not stored for long periods of time in deep stockpiles. The same study reported that soil biology of stockpiled topsoil is restored quickly once the soil is re-spread. Abdul-Kareem and McRae (1984) stated that, although there is a clear evidence of the effects due to storage and earthmoving equipment, the extent of deterioration of soil in stockpiles resulting from the equipment and storage has been greatly overestimated. The authors further indicated that there is no reason why soils should not continue to be stockpiled, although greater care must be given to minimize compaction and mixing of topsoil with subsoil.

A study conducted by Zelikman and Carmina (2013) demonstrated the possibility of using ground spectral-based approaches for digital quantification of some soil properties using the non-destructive NIRs (Near InfraRed) procedures. The study was also able to predict, soil moisture, hygroscopic water, carbonates and specific surface area at a reasonable level down the profile based on the spectral library containing laboratory and field in-situ collected spectra. Labovitz *et al.,* (1983) demonstrated that the metal content in the soil changed the leaf reflectance, especially in those parts of the spectrum used for chlorophyll content and leaf water absorption, and that variation in trace metal content was associated with leaf reflectance. Schellekens *et al.,* (2005) conducted a study that focused on changes of the leaf reflectance spectrum due to metal-induced stress from copper deposits.

2.3. Enzyme Activities of the Soil

Enzyme activity is a soil property that is chemical in nature, but has a direct biological origin. Since soil enzyme activities are very sensitive to pollution, enzymes have been suggested as potential indicator or monitoring tools to assess soil quality and health. Enzyme activities can effectively reflect the biological status of the soil (Sisa, 1993). Dick *et al*. (1996) suggested that soil enzyme analyses could be a good indicator of soil quality, because i) they are strongly linked to important soil properties such as organic matter, microbial activity or biomass, ii) they have the tendency to change earlier than other soil properties, and iii) they involve relatively simple methods as compared to other parameter assessment of soil quality. The enzyme activity depends on the contents of the organic and mineral colloids, metal types and chemical properties (Kucharski & Wyszkowska, 2004).

Soil enzyme activities are very sensitive to both natural and anthropogenic disturbances and show a quick response to the induced changes (Dirk, 1997; and Kumar *et al*., 2013). A study conducted by Fresquez *et al*. (1985) shows that soil stockpiling affected enzyme activity. Therefore, enzyme activities can be considered as effective indicators of soil quality changes resulting from soil stockpiling. Soil enzymes play a fundamental role in establishing biogeochemical cycles and facilitate the development of plant cover. It is an important aspect of the below-ground processes and give insight into the relative changes in below-ground system functioning as a plant community develops over time (Tabatabai *et al*., 2010). Enzyme activity in soil results from the activity of accumulated enzymes and from enzymatic activity of proliferating microorganisms (Kiss *et al.* 1975).

Soil enzymes mainly originate from soil microorganisms, which can indicate microbial activities in soil environment. Soil enzymes play an important role in organic matter decomposition and nutrient cycling. The activity of enzymes is affected by abiotic conditions (e.g., temperature, moisture, soil pH, and oxygen content), by the chemical structure of the organic matter and by its location in the soil strata (Deng &Tabatabai, 1994; and Pavel *et al*., 2004). Several studies show that soil enzyme activity data can be used as the foundation for the development of conceptual models that provide a more comprehensive understanding of key biochemical processes linking microbial populations and nutrient dynamics (Sinsabaugh & Moorhead, 1994; Schimel & Weintraub, 2003; and Akca & Namli, 2014).

Enzymes catalyse all biochemical reactions and are an integral part of nutrient cycling in the soil. Soil enzymes are believed to be primarily of microbial origin but also originate from plants and animals (Tabatabai, 1994). They are usually associated with viable proliferating cells, but enzymes can be extracted from both living and dead cells. Soil enzymes are considered to be indicative measures of soil fertility and bioremediation activities due to the fact that they participate in elemental cycling (Dick *et al.,* 1996).

Many studies have also suggested that soil enzymes can be used as indices of soil contamination, soil fertility and soil health (Martens *et al.,* 1992; Giusquiani *et al.,* 1994; and Saviozzi *et al.,* 2001). Soil enzyme activity is variable with substrate supply (Degens, 1998), providing useful linkage between microbial community composition and carbon processing (Waldrop *et al.,* 2000) and is sensitive indicators to detect the changes occurring in soils (Gonzalez *et al.,* 2007).

Criteria for choosing enzyme activities as biomarker to assess soil quality is based on their sensitivity to soil management practices, importance in nutrient cycling, organic matter decomposition and bioremediation activities. Among the parameters related to the biochemical and microbiological state of the soil, the most important are the indicators of the soil microbial activity, principally different enzymatic activities that are specifically related to the cycles of nitrogen (N), phosphorus (P), and carbon (C) (urease, phosphatase, and β-glucosidase, respectively) (Bandick & Dick, 1999).

Since enzyme activity is linked to several ecosystem processes including soil formation, organic matter transformation and bioremediation activities, it is important to understand the different physico-chemical factors affecting the enzyme activities (Kujur *et al*., 2012). Given the importance of enzymes in maintenance of soil quality, the present study was initiated to assess the impact of different soil amendments on enzyme activity, and to illustrate if soil enzyme activities can be used as indices for soil quality and health.

2.4 Reflectance Spectroscopy for Assessing Stockpile Soil

Remote Sensing (RS) has become an important tool to help facilitate effective environmental planning, as an alternative to conventional field based techniques that are labour intensive and time consuming. Reflectance Spectroscopy is another example of Remote Sensing that offers an opportunity to undertake pectral evaluation useful to characterize and discriminate soils (Demattê *et al.,* 2004) because various soil attributes absorb and reflect incident radiation differently. The differences between the intensity of both absorption and reflection at each wavelength are influenced by soil structural and chemical configuration. An inter-correlation between featureless and constituents with spectral features is the mechanism by which those harder to detect constituents are recognized and measured (Nanni & Demattê, 2006).

Several studies have shown that the spectral behaviour of soils is influenced by their physical, chemical, and mineralogical characteristics (Stoner & Baumgardner, 1981; Galvão *et al.,* 1997; and Demattê *et al.,* 2004). Reflectance Spectroscopy has been used for many years to assess grain, fertilisers and soil qualities (Ben-Dor & Banin, 1994; Faraji *et al.,* 2004; and Mohan *et al.,* 2005) and has proven to be a rapid and convenient means of analysing many soil constituents at the same time. NIR spectroscopy is an easy to use and less expensive technique that has the potential to replace traditional wet chemistry methods of soil analysis (Mashimbye *et al.,* 2012). Using traditional wet chemistry techniques for physico-chemical analysis may be restrictive due to high costs and labour when large amounts of samples have to be analysed. It is accepted that Near InfraRed (NIR) and Mid-InfraRed (MIR) spectroscopy are among less expensive and user-friendly techniques for quantitative soil analysis (Shepherd & Walsh, 2002; Brown *et al.,* 2006; Bellon-Maurel *et al.,* 2010; Bilgili *et al.,* 2010; and Bellon-Maurel & McBratney, 2011).

Adoption of spectroscopic techniques for soil analysis are gaining momentum nowadays. For example, Bilgili *et al.* (2010) evaluated visible-Near InfraRed reflectance (VNIR) spectroscopy for prediction of diverse soil properties related to four different soil series of the entisol soil group within a single field in northern Turkey. They obtained strong correlations for exchangeable Ca, Mg, cation exchange capacity, organic matter, clay, sand, and $CaCO_3$ contents. Bellon-Maurel *et al.* (2010) investigated the critical aspects to be conscious of when assessing NIR spectroscopy measurements for soil analysis.

A variety of statistical methods are used by researchers to extract soil attributes from the spectra. The statistical treatments that are used to enhance the extraction of soil attribute information from spectra include amongst others Principal Component Regression (PCR), Multiple Regression Analysis (MRA), Stepwise Multiple Linear Regression (SMLR), bagging PLSR and multivariate adaptive regression splines (MARS). Spectral transformations (mathematical treatments) are also applied to the spectra to maximize the extraction of information from spectra (Cho & Skidmore, 2006; and Ramoelo *et al.*, 2011).

The mathematical spectral treatments include first and second derivatives, straight line subtraction, vector normalization, and multiplicative scattering correction, to mention a few. It appears that the use of statistical methods and spectral transformation frequently have a favourable result for enhancing the extraction of soil information from spectra. For example, Janik *et al.* (2009) compared the performance of PLSR analysis for the prediction of a variety of soil chemical and physical properties from their MIR spectra using a combination of PLSR and neural networks (NN). While their study established that the PLSR-NN method outperformed the PLSR for the prediction of some soil properties, they cautioned that the use of PLSR-NN over the PLSR should be questioned against the backdrop of the trade-off of limited improvement and the added computational complexity. Primarily, PLSR is the most commonly used statistical spectral treatment technique for soil analysis. Bilgilli *et al*. (2010) assert that this is mainly because PLSR is superior to traditional methods in dealing with high dimensional multi-collinearity in the data.

PLSR is one of the most common multivariate statistical techniques for spectral calibration and prediction of soil properties, e.g., Chang and Laird, (2002); and McCarty *et al*., (2002). PLSR approach is known to minimize multi-colinearity and overfitting by decomposing independent variable into uncorrelated latent variables. The latter makes it useful for analysing spectrometer as compared to SMLR (Shepherd & Walsh, 2002).

Reflectance Spectroscopy has been successfully used to estimate leaf biochemical concentration, including nitrogen (N) and phosphorus (P) as indicators of vegetation quality (Cho & Skidmore, 2006; and Ramoelo *et al.* 2011). Often, this is achieved by using spectral transformation such as Log (1/R), first derivatives, second derivatives etc. The spectral transformation techniques are mainly used to enhance absorption features of foliar biochemical concentrations, while minimizing atmospheric, soil background, and water absorption effects, as well as data redundancy (Cho & Skidmore, 2006). Ramoelo *et al*., (2011) demonstrated that using water removed spectra (WR) and PLSR improves the estimation of foliar N and P in the controlled environment, due the capability of WR to minimize water absorption effect on the fresh leaf spectra. Continuum removal has also been successfully applied to enhance absorption features for foliar biochemical concentrations (Mutanga *et al*., 2005).

Reflectance Spectroscopy of natural surfaces is sensitive to specific chemical bonds in materials, whether solid, liquid or gas. The advantage of spectroscopy is that it is very sensitive to small changes in the chemistry and/or structure of a material (Clark, 1999). Using Remote Sensing, there is a significant progress in estimating foliar biochemicals, especially using spectroscopy approaches. A simple technique is to correlate vegetation index and a biochemical concentration of interest, e.g., N (Abdel-Rahman *et al*., 2010; and Ramoelo *et al*., 2012).

2.5 Conclusion

The review of literature presented in this chapter outlined the effect of open-cast mining on soil quality, properties of coal-mine stockpile soil, enzyme activity as indicator of soil health and the use of Reflectance Spectroscopy to estimate soil and vegetation properties.

Firstly, literature proves that open-cast mining severely alters the landscape, which reduces the value of the natural environment in the surrounding land and affect soil quality. During the process of open-cast coal mining, topsoil is removed and stockpiled for future use. Stockpiled topsoil becomes highly degraded the moment this long-term structure is disturbed.

Secondly, Soil properties do change during stockpiling. Changes that occur in soil include increased bulk density, decreased water holding capacity, chemical changes, reduced nutrient cycling, reduced microbial activity and loss or reduction of viable plant remnants and seeds.

Thirdly, Soil enzymes activity can be used as indicators of soil health. Soil enzyme activities are very sensitive to both natural and anthropogenic disturbances and show a rapid response to the induced changes.

Finally, Reflectance Spectroscopy has a potential to assess coal-mine stockpile soil and grass properties. Reflectance Spectroscopy is reliable, less tedious and cost effective technique to assess and predict properties of soil and grass. Clearly, the assessment of coalmine stockpile soil quality and its impact on vegetation using laboratory-based and Reflectance Spectroscopy techniques should to be investigated.

CHAPTER 3

IMPACT OF QUALITY OF COAL-MINE STOCKPILE SOILS ON VEGETATION GROWTH AND PRODUCTIVITY

3.1 Introduction

South Africa has only about 3-4% of high potential agricultural land that is suitable for sustained food production. Much of this land has however been lost to other competing land use prospects. Agricultural production is under tremendous pressure from new or expanding mining activities to facilitate current growth (Collett, 2013). Of the entire 3-4% of high potential agricultural land, 46.4% is found in Mpumalanga Province. At the current rate of coal mining, it is estimated that approximately 12% of high potential agricultural lands will be transformed while a further 13.6% is under prospecting by mines in Mpumalanga, South Africa (Van der Burgh, 2012).

Surface coal mining requires good and sound rehabilitation practices to re-establish productive land capability and land use after mine closure. The vast majority of Mpumalanga's coal deposits are located below high quality productive arable land. The impacts on soil and land associated with surface coal mining can reduce the possibility of re-establishing the pre-mining land capability and productive potential. The result observed in practice, defined as the status quo, is that most surface coal mining companies in Mpumalanga aim to re-establish grazing land capability potential for the end land use option instead of the original arable land capability (Botha, 2014).

Open-cast coal mining activities are leaving an unmistakable footprint on the landscape in the form of altered landscapes due to the creation of discard dumps. Valuable agricultural land is being degraded hence affecting long-term productivity (Chodak *et al*., 2011). Poor soil management in the operational phase of the mine could limit the re-establishment of pre-mining land-use or another sustainable land capability class post-closure (Strohmayer, 1999; Ghose, 2001; and Ghose, 2004). In this study, 10 to 20 years old coal-mine stockpile soils were used to evaluate their ability to support plant growth and to assess their quality and fertility status, as those soils will be used for rehabilitation during post mining phase.

Soil is a valuable resource as it is the growth medium used by vegetation and for food production. Adequate soil stripping, stockpiling, and management of this resource at a surface coal mine is therefore of utmost importance. Without proper soil management, post-mining substrate might not only comprise quality of the soils but can also affect re-vegetation (Mentis, 2006). If stockpiled soil is reapplied quickly after mining, with less compaction from mechanical traction, the production potential of vegetation on the stockpile remains high (Thomas & Jansen, 1985). Soil is a vital natural resource, constituting a critical controlling component during the early stage of ecosystem development. Soil quality is defined as the capacity of a soil to function within ecosystem boundaries to sustain biological productivity, maintain environmental quality, and promote plant and animal health (Doran & Parkin, 1994). Mining activities are invariably associated with the removal of fertile top soil organic layer enriched with vegetation cover and hence has environmental consequences (Fox, 1984).

Open-cast mining severely alters the landscape, which reduces the value of the natural environment in the surrounding land. The land surface is dedicated to mining activities until it can be reshaped and reclaimed. Topsoil stripping and stockpiling is an important and necessary practice of surface coal mining operations, as topsoil forms a critical element for the successful restoration of open pit mines (Ghose, 2001). Topsoil cannot always be placed directly onto mined out land. Therefore, it may be necessary to stockpile the resource for future use (COM and CRA, 2007).

Poor management of topsoil and stockpiles will lower the rehabilitation potential of the soils and increase rehabilitation costs. This, in turn, has an impact on the post-mining land capability and land use once mining has ceased. Improving the fertility and health of the stockpiled soils through amendment is critical for rehabilitation. Currently, there are limited studies of this nature as most of the studies are focused on rehabilitation rather than on good soil management practices during mining operation. The main objective of the study was to evaluate the impact of quality of coal-mine stockpile soils on vegetation growth and productivity

[1] This chapter is based on the work published in Sustainability Journal**: Mushia, N.M.; Ramoelo, A.; Ayisi, K.K**. The Impact of the Quality of Coal-Mine Stockpile Soils on Sustainable Vegetation Growth and Productivity. *Sustainability* **2016**, 8, 546.

3. 2 Objectives

The specific objectives were, namely, to:

1. Evaluate the effect of coal-mine stockpile soil depth on vegetation growth and productivity;
2. Evaluate the effect of coal-mine stockpile soil age on vegetation growth; and
3. Investigate the capability of different amendment of stockpile soils to support vegetation growth and productivity for rehabilitation purpose.

3.3 Hypotheses

1. Coal-mine stockpile soil depth has an effect on vegetation growth and productivity.
2. Coal-mine stockpile soil age has an effect on vegetation growth.
3. Amendment of stockpile soil has the capability to support vegetation growth and productivity for mine rehabilitation purpose.

3.4 Materials and Methods

3.4.1 Locality and Soil Sampling Process

Bulk soils were sampled from different depths of two soil stockpiles: stockpile 1 (10 years old) and stockpile 2 (20 years old) from a coal mine situated approximately 8 kilometres south of Witbank in Mpumalanga Province of South Africa. Stockpile soils are mixture of different soil types pilled together in a non-sequential form. There were no visible soil horizons. The depth of each stockpile soil was approximately 400cm. Sparsely scattered growth of different grass species were observed on the stockpile soils during the time of sampling. The climate of the area can be regarded as having warm, moist summers and cool to cold dry winters with frost. On average, 85% of the annual total rainfall of 750mm is received during the growing season (i.e., October to March).

3.4.2 Greenhouse Experiment: Set up and sampling

A 2x4x5 factorial experiment in a randomized complete block design (RCBD) with four replications was established under greenhouse condition (from January-May 2015) to minimise any unforeseen variations. The conditions inside the greenhouse were set at a temperature of 26-28^{0}C during the day and 16.5-18.5^{0}C at night, relative humidity of approximately 60%, photoperiod of 8-12 hour light/24 hour and the evapotranspiration of 3.5-4.0mm/day. The indoor temperature was set to mimic the temperature of the surrounding area in summer. The factors studied were as follows: Factor 1 (age of the stockpile soil) at 10 years old and 20 years old; Factor 2 (stockpile soil depth), sampled as follows: surface soil (0-25cm); mid soil (150-200cm); deep soil (300-350cm) and mixed soil (mixture of equal amounts of surface, mid and deep). The mixed soil treatment was carried out to simulate the condition of the soil during rehabilitation process at the mines. The third factor was soil amendments namely: poultry manure, no fertilizer, lime + poultry manure, compost and lime + mineral fertilizers (NKP).

Soils were amended with organic amendments and mineral fertilizers according to fertilizer recommendations for smut finger grass (*Digiteria eriantha*) using method by FSSA (2007). One litre (13cm diameter top x 11cm depth x 9.6cm diameter at the base) plastic pots perforated at the base were filled with the amended soils for planting in the greenhouse. Prior to application, poultry manure was air dried and analysed for nutrient content (Total N=5.8 %, P=2.5%, K=2.8 %, Ca=12.15 % and pH=8.9) (Non-Affiliated Soil Analysis Working Group, 1990). The chicken manure was applied two weeks before planting at a rate of 16g/pot, which is equivalent to 3.2t/ha. 80 g/pot or 16t/ha of compost was applied two weeks before planting. Statistically, there was no significant differences in soil pH from the different depths sampled. Lime ($CaCO_3$) was applied three months before planting at a rate of 10g/pot or 2t/ha. The reason for applying lime months before planting was to allow enough time for the lime to be released into the soil. Application of inorganic fertilizers (NPK) Superphosphate [Ca (H_2PO_4) 2]. (10.5% P), Potassium chloride [KCl] (50%K) was done a week after planting (Unagwu *et al*., 2012). Superphosphate was applied at 0.55g/pot or 110kg P/ha, Potassium chloride was applied at 0.3g/pot or 60kg K/ha for soils with clay% <20 and 0.39g/pot or 78kg K/ha for soil with clay% >20. 0.6g/pot or 120kg N/ha of LAN was applied when plants were four weeks old and the other 0.6 g/pot was applied when plants were twelve weeks (Huang *et al*., 1994). Smuts finger (*Digiteria eriantha*) seeds were subsequently sown in the pots following the soil amendments on 10th January 2015 in a greenhouse. A total of 160 pots were arranged into 2x4x5 factorials with four replicates (Morrison, 2001). The decision to use this grass specie to evaluate soil fertility and quality of stockpiled soils was based on the fact that this grass is one of the species commonly used for post mine rehabilitation in South Africa (Truter *et al*., 2009). It is also an important source of forage for livestock and wildlife (Rethman & Tanner, 1995).

3.4.3 Soil Chemical Analysis

Prior to soil amendment, the sampled soils from surface, mid, deep and mixed were analysed for physical and chemical properties. The soils were first air-dried and screened through a 2mm sieve for analysis. A particle size analysis was performed on the <2mm soil fraction using the pipette method (Soil Analysis Working Group, 1990). Exchangeable cations, cation exchange capacity, soil organic carbon and exchangeable aluminium (Al), as well as pH (H_2O) were determined according the procedures of Non-Affiliated Soil Analysis Working Group (1990). Textural classes of the soil are as follows; stockpile 1: Surface (sandy clay loam), mid (sandy loam), deep (clay loam) and mixed (loam). Stockpile 2; Surface (loamy sand), mid (silt loam), deep (sandy loam) and mixed (sandy loam) (Table 3.1). Sampled soils were amended according to their respective treatments: (poultry manure + lime, poultry manure, compost, no amendments and mineral fertilizers + lime. Ten seeds of *Digiteria eriantha* were sown in each pot and thinned out to five plants after seedling emergence. Plants were watered four times a week for the first 6 weeks and, thereafter, were watered daily until the experiment was completed.

Table 3.1. Pre-Sown Soil Fertility Results

	Stockpile 1 (10 years)				Stockpile 2 (20 years)			
	Soil Depth							
‡ Soil Properties	Surface	Mid	Deep	Mix	Surface	Mid	Deep	Mix
Na cmol(+) kg^{-1}	0.07	0.08	0.07	0.08	0.03	0.04	0.05	0.06
K cmol(+) kg^{-1}	0.18	0.11	0.07	0.17	0.11	0.06	0.05	0.07
Ca cmol(+) kg^{-1}	0.74	0.47	0.33	0.68	0.54	0.77	0.72	0.66
Mg cmol(+) kg^{-1}	0.45	0.42	0.27	0.49	0.27	0.58	0.28	0.46
CEC cmol(+) kg^{-1}	5.80	3.46	3.94	5.11	4.68	2.83	5.54	4.27
pH (H_2O)	5.67	5.25	5.19	5.88	5.49	5.99	5.20	5.68
Org C (%)	0.45	0.34	0.18	0.53	0.70	0.25	0.30	0.82
Al cmol (+) kg^{-1}	0.72	0.84	1.12	0.69	0.79	0.77	1.07	0.93
P-Bray 1 (mg $kg^{-1)}$	8.99	7.07	6.68	8.35	6.76	6.04	4.93	7.03
Clay %	25.32	16.14	30.05	21.84	14.44	11.32	10.39	12.94
Silt %	23.10	15.90	45.68	32.01	7.38	50.19	35.66	32.18
Sand %	51.28	67.96	24.27	45.98	78.18	38.49	53.95	54.88

‡ *Surface soil (0-25 cm) (S); mid soil (150-200 cm) (M), deep soil (300-350 cm) (D) and mixed soil (mixture of equal amounts of surface, mid and deep) (Mx)*

3.4.4 Data Collection

The following growth parameters were measured on 30th May 2015 as indicators of vegetative growth: plant height, plant cover, total fresh biomass (roots, stems and leaves) and total dry biomass (Maas, 1998). Plant height was measured using measuring tape from the base of the plant to the tip of the topmost leaf of the plant (BBIRD Grassland Protocol, 1997). Plant cover was measured by visual scoring of the grass cover around the pot (BBIRD Grassland Protocol, 1997). Total fresh biomass was determined at the end of the experiment where the plants were removed from the pots and soil on the roots were thoroughly washed off under a tap and a sieve to remove bound soils and retrieve any broken root fraction. The whole plant was weighed to determine total fresh biomass. Grass samples were oven dried at 60°C for 48hours until constant weight and were weighed with Mettler PE 6000 balance with 0.01g readability for total dry biomass (Anash *et al.*, 2010).

3.4.5 Statistical Analysis

Data were analysed using standard procedure for analysis of variance (ANOVA) of a factorial arrangement of a randomised complete block design (Gomez & Gomez, 1984). Differences between treatment means were separated using the Duncan's Multiple Range Test (DMRT) procedure at 0.05 and 0.01 probability levels. Pearson's correlation coefficient was done to determine the relationships among various variables at 95% probability level ($p<0.05$). All data were analysed using the statistical package, STATISTIX 10.0.

3.5 Results

The mean values of plant parameters at different depths and soil amendments are recorded in Tables 3.2 and 3.3 respectively. There were significant differences ($P \leq 0.05$) in plant height, fresh biomass, dry biomass and plant cover in relation to depth and soil amendments. Mixed soils produced higher mean values for all measured plant parameters (Table 3.2).

Table 3.2. The Effect of Different Depths of the Stockpile on Plant Parameters

	Measured plant parameters			
‡ Soils	Height (cm)	Fresh biomass (g)	Dry biomass (g)	Plant cover (%)
MX	18.72^{a}	28.33^{a}	12.96^{a}	70.80^{a}
S	16.55^{b}	23.91^{b}	9.28^{b}	62.00^{b}
M	14.21^{c}	22.19^{b}	8.07^{c}	61.00^{b}
D	12.85^{d}	17.34^{c}	7.34^{c}	45.90^{c}
P (≤0.05)	*0.00**	*0.00**	*0.00**	*0.00**

*‡ $^{a, b, c, d}$ indicates significant difference. Means in the same column followed by the same letter are not significantly different from each other at the 5% probability level, *Significant at p≤0.05.*
‡ MX = Mixed soil; S = Surface soil; M = Mid soil; D = Deep soil.

Considering the impact of soil amendment, there was significant improvement in most of the plant parameters measured when soils were amended, relative to those sown on unamend soil (Table 3.3). The application of poultry manure+ lime consistently increased height, fresh and dry biomass as well as plant cover compared to the plants sown on unamend soils. Compost and poultry manure application improved height, fresh biomass and dry biomass. Plants sown on soil with no fertilizer showed significantly low growth rate. Among the different soil amendment treatments, the poultry manure + lime and lime + inorganic fertilizer were superior in increasing the parameters measured.

Table 3.3: The Effect of Soil Amendments on Plant Parameters

	Measured plant parameters			
‡ Amendments	Height (cm)	Fresh biomass (g)	Dry biomass (g)	Plant cover (%)
P+L	23.47^{a}	28.33^{a}	14.55^{a}	85.16^{a}
NPK+L	20.04^{b}	23.91^{a}	12.19^{b}	78.44^{b}
C	14.53^{d}	17.34^{b}	8.97^{d}	57.50^{c}
P	17.09^{c}	22.19^{a}	10.92^{c}	73.28^{c}
NF	0.28^{e}	1.80^{c}	0.44^{e}	5.30^{d}
P (≤0.05)	*0.00**	*0.00**	*0.00**	*0.00**

*‡ $^{a, b, c, d}$ indicates significant difference. Means in the same column, followed by the same letter are not significantly different from each other at the 5% probability level, *Significant at p≤0.05.*
‡ Height=Plant height, Amendments= Soil amendments, NF= No Fertilizer, P+L= Poultry manure + lime, NKP+L= Inorganic fertilizer + lime, C= Compost, P= Poultry manure.

Figures 3.1 and 3.2 presents the combined effects of soil depth and amendments on plant height and total dry biomass. The results show that there was no significant difference ($p<0.05$) in plant height at different depth when the grass is sown on soils with no fertilizer (Figure 3.1). The results in Figure 3.1 also showed significant difference in plant height in response to soil depths when soil was amended with lime + poultry, compost, lime + inorganic fertilizer and poultry manure. Plants sown on soil with no fertilizer showed no significant ($p<0.05$) for dry biomass on different depths of stockpile (Figure 3.2). Correlation statistics indicated significant correlations among all measured plant parameters (Table 3.4).

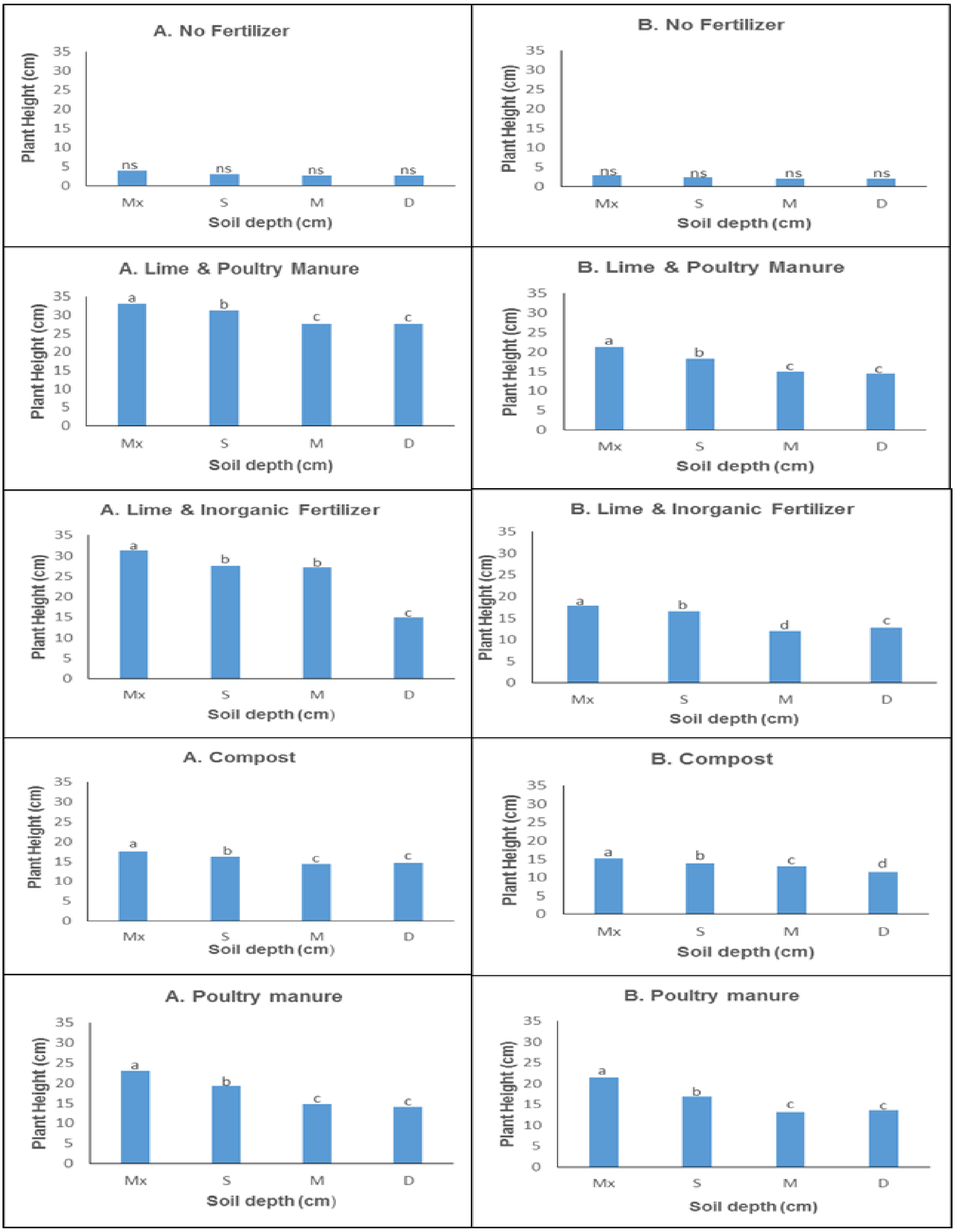

Figure 3.1. Effect of Soil Depth and Amendments on Plant Height

a, b, c indicates significant difference. Means with the same letter are not significantly different from each other at the 95% probability level.

** Significant at p d' 0.05. A = Stockpile 1, B = Stockpile. ‡ MX = Mixed soil; S = Surface soil; M = Mid soil; D = Deep soil.*

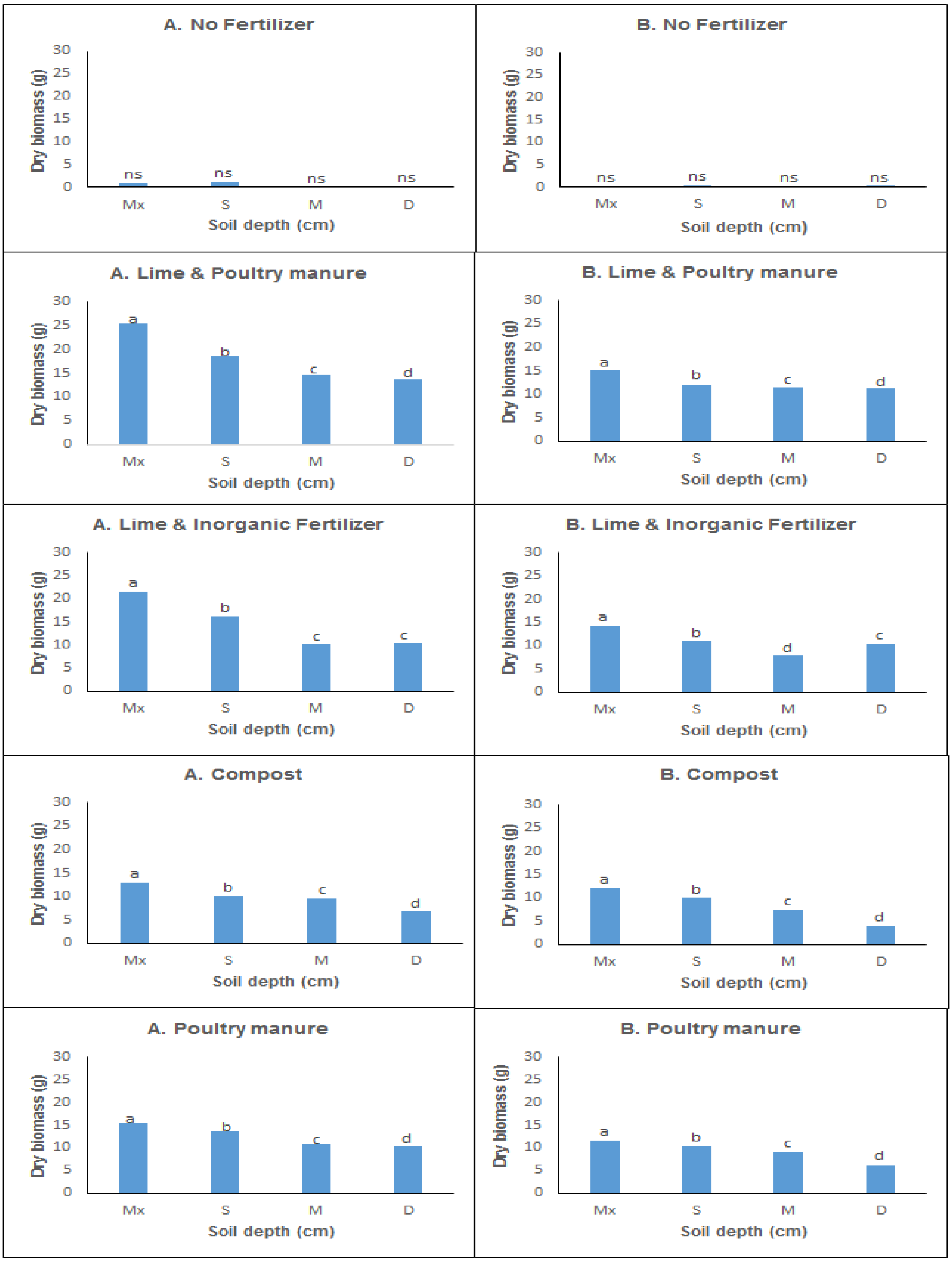

Figure 3.2. Effect of Soil Depth and Amendments on Total Dry Biomass

*a, b, c indicates significant difference of mean. Means with the same letter are not significantly different from each other at the 95% probability level (e.g., a, b). * Significant at p d' 0.05. A = Stockpile 1, B = Stockpile 2. ‡ MX = Mixed soil; S = Surface soil; M = Mid soil; D = Deep soil*

Table 3.4. Correlations Coefficients (R^2) between Selected Parameters Measured from Plants Parameters Grown on Stockpile Soils

	Height	Fresh biomass	Dry biomass	Cover
Height	1.00			
Fresh biomass	0.97*	1.00		
Dry biomass	0.96*	0.99*	1.00	
Cover	0.93*	0.97*	0.95*	1.00

** = significant at P<0.05*

3.6 Discussion

3.6.1 Effect of Soil Stockpile Age on Vegetation Growth

Stockpiling of soil mounds during mineral extraction has been shown to affect the chemical and physical properties of the soil (Harris *et al.,* 1989; and Johnson *et al*., 1991). Plant parameters measured from plants grown on soils from stockpile 1 (age 10 years) produced higher mean values compared to those planted on stockpile 2 (age 20 years). This can be attributed to the fact that when soils are stored for a long time nutrients released by microbiological activity is continually lost due to leaching and erosion, nutrient cycle is broken down and soil ultimately become unproductive (De & Mitra, 2002; and Ghose, 2004). According to Kundu and Ghose (1997), as the age of soil stockpile increased, the concentrations of suitable plant growth nutrients in soil gradually decreased. Their study revealed that K was 54.70% lower in soil after ten years, relative to 36.84% after one year of top soil stockpiling and pH was 7.21% lower after ten years, relative to 2.20% after one year of top soil stockpiling.

3.6.2. The Effect of Stockpile Soil Depth on Plant Parameters

Mixed soils tend to have higher vegetation growth as indicated by measured parameters than all other soils from different depths (surface, mid and deep). The higher vegetation growth is an indication that mixing stockpile soils can improve productivity of the soil. There was no significant increase in organic carbon percentage, soil pH and other soil elements and a decrease in exchangeable aluminium when the soils were mixed. The higher mean values of all plant parameters measured on plants grown on mixed soils can be attributed to the change in soil texture that affects other physical properties like water availability, infiltration rate and aeration, and, to some extent, chemical properties (Rice, 2002; and Garg & Kumar, 2012). Mixed soil of stockpile 1 was classified as loam soil (Table1). According to NRCCA (2010) and Shaxson and Barber (2003), the average water holding capacity (inch/foot) of loam soil is two times higher than that of sandy clay loam (surface soil).

The same applies to sandy loam and loamy sand. Sandy loam soil has water holding capacity two times higher than that of loamy sand (Shaxson & Barber, 2003; and NRCCA, 2010). Stockpile 2 mixed soil was classified as sandy loam whereas surface soil was classified as loamy sand. According to Bierhuizen (1959), soil with high water holding capacity is favourable for plant growth since plants receive enough water for cell elongation, leaf expansion and fresh biomass.

Using deep and mid soils as a growth media resulted in low vegetation growth as most plant parameters measured were statistically lower compared to plants grown on mixed and surface soils. According to Harris and Birch (1989), when soil is stockpiled more than a meter deep, chemical effects, such as accumulation of ammonium and anaerobic conditions, occur at the base of the pile. Mid and deep soils used in this study were stockpiled deeper than 1 meter. Deep soils in this study were found to have aluminium content of more than 1.0cmol (+) kg^{-1}. High concentration of Al^{3+} content in the soil inhibits shoot growth by inducing deficiency in Ca, Mg and P and hormonal imbalances in plants (Roy & Bhadra, 2014). Tate and Klem (1985) concluded that the depth of stockpiles should be restricted to the rooting depth of covering vegetation and further indicated that, if plant cover can be maintained with roots extending throughout the depth of the stockpile, nutrient cycling processes and microbial activity can continue while the stockpile is stored. Soils used in the experiments were stockpiled to a maximum depth of approximately 4 meters. There was higher plant growth rate in surface soils in both stockpiles as compared to mid soils and deep soils that can be attributed to high organic carbon on surface soils. According to NSW (2010), microbes decompose organic matter in the soils releasing nitrogen, phosphorus and other range of elements for use by plant roots. The report further indicates that soil organic carbon decreases with soil depth and that disturb soils loses more labile organic carbon that well managed soils.

3.6.3. Effect of Soil Amendments on Vegetation Growth

Soils disturbed by surface mining are always hostile to planted tress due to changes physical and chemical properties (Chodak *et al.,* 2011). Surface coal mining results in degradation of soil physical properties as well as significant loss of organic matter and nutrients, and thus diminishes soil productivity (Akala & Lal, 2001). Restoring the soil productivity and the establishment of sustained vegetative cover are primary objectives of mine soil reclamation. The soil used in the study was acidic with pH ranging from 5.2-5.9. This can be attributed to high rainfall within the area that resulted in losses of exchangeable bases from the soil with a consequent effect of soil acidification (Mentis, 2006).

Most of the stockpile soils had deficiencies in essential soil elements confirming the findings by Ussiri and Lal (2005) that physical and chemical properties of mine soils tend to inhibit soil-forming processes and plant growth. This is usually due to lack of nutrients associated with SOM, including nitrogen (N) and phosphorus (P). Soils with no amendments had low plant growth rate compared to soils amended with fertilizers. This is consistent with the finding of Mohapatra and Goswami (2012) that stockpile soil tends to have reduced essential nutrients for plant absorption.

The mean values of plant parameters measured in this study increased with addition of soil amendments. Poultry manure and lime tend to have higher mean values for all measured plant parameter in both stockpile soils. This confirms the findings by (Hue, 1992; and Haynes & Mokolobate, 2001) that organic waste applications have been shown to raise soil pH and increase plant growth in acid soils. According to Stevenson and Vance (1989), manures contain humic type substances with many functional groups such as carboxyl and phenolic groups that are able to consume protons at their natural pH values. These substances are formed during the decomposition process and are relatively stable against further decomposition. Their capacity to consume protons therefore controls the buffer characteristics of these materials and therefore their ability to neutralize soil acidity. Addition of agricultural lime increases soil pH, and at pH5.5 most of toxic elements bind to other essential elements in the soil solution and reduce their availability for plant uptake (Vogel 1981). When soils were amended with lime and inorganic fertilizer, vegetation growth parameters increased but not similar to poultry manure + lime. According to Ayeni and Adetunji (2010), poultry manure has Ca and Mg that are not usually supplied by inorganic fertilizer except as impurities. The studies by Adeniyan and Ojeniyi (2006) and Adediran *et al*., (2005) reported that poultry manure composed micro and macronutrients. Because of the more balanced nutrition given by poultry manure, their studies found that poultry manure at 10t ha^{-1} gave higher maize yield than NPK fertilizer at 400kg ha^{-1}. In this study, 3.2t ha^{-1} of poultry manure yielded high vegetation growth than a combination of application of 240kg N ha^{-1}, 110kg P ha^{-1} and 78kg K ha^{-1}.

Poultry manure normally adds cations in the soils (especially Ca). Addition of large quantities of cations to a soil results in accumulation of cations in soil solution with a consequent displacement of H^+ from exchangeable sites into solution (Samuel *et al*., 1985). Displacement of H^+ from exchangeable sites into solution contributes to availability of essential nutrients for plant absorption. Poultry manure alone had good influents on plant parameters as compared to compost. Poultry manure has high Ca content that contributes to high $CaCO_3$ content of the manure, which explains why poultry manure was an effective amendment for increasing vegetation growth. Addition of compost to soils increased productivity better than no fertilizer application. Compost increases soil pH and adds nutrients to the soil (Chang *et al*., 2005). Addition of compost improves the cation exchange capacity of soils, enabling them to retain nutrients longer. It will also allow crops to more effectively utilize nutrients, while reducing nutrient loss by leaching (USCC, 2001). Wong *et al.* (1998) found out that addition of compost to acid soils increases soil pH and ameliorates soil acidity. They attributed this effect primarily to the proton consumptive ability of the added organic materials.

3.7. Conclusion

- The depth of the stockpile affects the quality of the soil at replacement. Soil stored in depth higher than 1m had an effect on plant growth. They yielded low grass growth in terms of measured plant parameters (plant height, dry biomass etc.). Mixed soil (as would happen in the rehabilitation process) yielded better grass growth, relative to three soils sampled separately at different depths.
- Without addition of lime and fertilizers, stockpiled soil could not support vegetation growth as evidenced by low plant growth on soil without fertilizer. Poultry manure + lime is essential for plant growth and productivity of stockpile soils.
- Soil amendments in particular agricultural lime and mineral fertilizers helps in reducing soil nutrients stress, but are often expensive; something which will make soils rehabilitation difficult.

Since the process of stockpiling and reapplying stockpile involves additional expense and effort, a careful analysis of results from sites with stockpile soil applications would provide the necessary information for cost-benefit analysis and would indicate possibilities for improvement in the efficiency of the process of stockpiling.

CHAPTER 4
THE EFFECT OF SOIL AMENDMENTS ON ENZYME ACTIVITIES OF COAL-MINE STOCKPILE SOIL

4.1 Introduction

Coal is the world's most abundant and widely distributed fossil fuel and it remains the primary energy source for several countries world-wide (Botha, 2014). In South Africa, coal mining makes a significant contribution to economic activity, development of sustainable job opportunities and foreign exchange earnings. The coal mining sector contributes 1.8% of South Africa's GDP (Stats SA, 2015). Coal extraction is essentially mined by two methods, namely, underground and opencast methods, both of which are very destructive processes. During coal extraction, the topsoil is usually removed with heavy equipment and then piled in large, deep piles for the duration of mining project (Strohmayer, 1999). Unfortunately, highly potential agricultural lands, ecologically sensitive environments and surroundings are compromised for this development, often resulting in loss of ecosystem value (CRA, 2012).

Soil is a vital natural resource that plays a critical controlling component during the early stage of ecosystem development. Soil quality is defined as "the capacity of a soil to function within ecosystem boundaries to sustain biological productivity, maintain environmental quality and promote plant and animal health" (Doran & Parkin, 1994). Mining activities in most cases alters the soil subsystem areas and an assessment of these changes is essential to determining soil quality. There is growing recognition for the need to develop sensitive indicators of soil quality in promoting appropriate soil management strategies for long-term sustainability of terrestrial ecosystems (Kujur & Patel 2012).

The assessment of soil enzyme activities is simple, requires low labour costs compared to other biochemical analysis (Ndiaye *et al*., 2000), and the results are correlated to other soil properties (Klose *et al*., 1999; Moore *et al*., 2000; Ndiaye *et al*., 2000; and Tra´sar-Cepeda *et al*., 2000). Furthermore, it has been reported that any change in soil management and land use is reflected in the soil enzyme activities, and that they can anticipate changes in soil quality before they are detected by other soil analyses (Ndiaye *et al*., 2000). Previous studies with soils from various regions have shown that enzyme activities are sensitive to soil changes due to tillage (Kandeler *et al*., 1999; Acosta-Martı´nez; and Tabatabai, 2001); cropping systems (Bandick & Dick, 1999; Klose *et al*., 1999; Ndiaye *et al*., 2000; and Ekenler & Tabatabai, 2002); and land use (Staben *et al*., 1997; Gewin *et al*., 1999; and Acosta-Martı´nez *et al*., 2003). Therefore, enzyme activities can be considered as indicators of soil quality changes resulting from soil stockpiling.

Several researchers have studied the effect of fertilization on soil fertility by investigating soil enzymatic activity (Martens *et al*., 1992; Giusquiani *et al*., 1994; Baldrian, 2009; Banerjee *et al*., 2012; and Frincu *et al*., 2015). Martens *et al*. (1992) reported from a long-term study that the addition of organic matter maintains high levels of soil phosphatase activity. Giusquiani *et al*., (1994) observed in field experiment that phosphatase activity increased when the compost manure was added at rates between 90 and 270t ha^{-1}. Frincu *et al.,* (2015) reported that soil enzymes are often used as indicator of soil fertility because they are very sensitive and respond to changes in soil management more quickly than other soil variables. All these studies (viz., Martens *et al*., 1992; Giusquiani *et al*., 1994; Baldrian, 2009; Banerjee *et al*., 2012; and Frincu *et al*., 2015) were mainly concentrated on the static effect of soil type and fertilization on soil microorganism and enzymatic activity, but few, if any, have been conducted on the effects of chemical and organic amendments on the dynamic changes of enzymatic activity in coal-mine stockpile soils. This study therefore examines the effects of different amendments on the variation of soil enzymatic activity at different depths of stockpile soils.

Among the parameters related to the biochemical and microbiological state of the soil, the most important are the indicators of the soil microbial activity, principally different enzymatic activities that are specifically related to the cycles of nitrogen (N), phosphorus (P), and carbon (C) (urease, phosphatase, and β-glucosidase, respectively). These were the enzyme activities assessed in this study. This study will provide information on the effect of soil amendment material for coalmine stockpile soils, and their potential for rehabilitation process.

4.2 Objectives

The objectives of this study were, namely, to:

1. Evaluate the effect of amendments on coal-mine stockpile soil enzyme activities;
2. Evaluate the effect of coal-mine stockpile soil depth on enzyme activities; and
3. Evaluate the effect of coal-mine stockpile soil age on enzyme activities.

4.3 Hypotheses

1. Inorganic and organic amendments have effect on coal-mine stockpile soil enzyme activity.
2. Coal-mine stockpile soil depth has effect on enzyme activity.
3. Coal-mine stockpile soil age has effect on soil enzyme activity.

4.4. Materials and Methods

Soil sampling process, greenhouse experiment (experiment set including experimental design, sampling and fertilizer applications) and soil chemical analysis is similar to the one used in the previous chapter (See Chapter 3 for more information). The same treatment in Chapter 3 was further analysed for enzyme activities.

4.4.1 Soil Enzyme Analysis

Prior to amendment and planting, the soil used for this experiment were analysed for activity of urease, acid and alkaline phosphatase, and β-glucosidase (Table 4.1). The same analysis was conducted on soils at the end of the experiment to evaluate the effect of soil amendments on enzyme activities.

For soil urease activity analysis, 5g soil was taken in an Erlenmeyer flask (100ml) and 2.5ml urea solution was added. The flask was incubated at 37^{0}C for 2 hours. After incubation, 50ml of KCl solution was added and the flask shaken for 30 minutes. Solution was filtrated and the filtrate was analysed for ammonium content. The method described above was used to prepare a blank but with 2.5ml distilled water. Urea solution was added at the end of the incubation and before KCl addition. For ammonium estimation, 1ml of the clear filtrate was taken into an Erlenmeyer flask (50ml), then added 9ml of distilled water, 5ml of Na salicylate/ NaOH solution and 2ml of dichloroisocyanide solution and allowed to stand at room temperature for 30 minutes and optical density was determined at 690nm (Tabatabai & Bremmer, 1972).

The soil alkaline phosphatase activity was measured by putting 1g soil in Erlenmeyer flask (50ml) and treated with 0.25ml of toluene, 4ml of MUB (Modified Universal Buffer, pH of 11 for alkaline phosphatase) and 1ml of p-nitrophenyl phosphate (PNP) solution made in the same buffer. After stopping the flask, contents were mixed and incubated for 1 hour at 37^0C. After incubation, 1ml of $CaCl_2$ (0.5M) and 4ml of NaOH (0.5M) were added. The solution was mixed and soil suspension was filtered through whatman no. 2v folded filter paper. For control preparation, 1ml of PNP solution was added after the addition of 1ml $CaCl_2$ (0.5M) and 4ml of NaOH (0.5 M). Soil suspension was filtered and optical density was measured at 400nm (Alef & Nannipieri, 1995).

For soil acid phosphatase activity, the same method of Alef and Nannipier (1995) used for alkaline phosphatase was used with addition of Modified Universal Buffer, pH of 6.5 instead of Modified Universal Buffer, pH of 11. Optical density was measured at 400nm.

β-glucosidase activity was determined using 1g of air-dried soil (<2mm) with p-nitrophenyl-b-d-glucopyranoside (PNG, 0.05M) as substrate. This assay is based on the release and detection of p-nitrophenyl (PNP). Two millilitres of 0.1M maleate buffer at pH 6.5 and 0.5ml of substrate was added to 0.5g of sample and incubated at 37^0C for 90min. The reaction was stopped with tris-hydroxymethyl aminomethane (THAM), that is, according to Tabatabai (1994). The amount of PNP was determined in a spectrophotometer at 398nm (Tabatabai, 1994). The enzyme activities were assayed in duplicate with one control, to which substrate was added after incubation and subtracted from a sample control value.

Table 4.1. Enzyme Activity Analyses for Stockpile Soils Prior to Planting and Amendment with Organic and Inorganic Amendments

	Stockpile 1 (10 years)					Stockpile 2 (20 years)				
	Soil Depth									
‡ Enzyme activity	Surface	Mid	Deep	Mix	*P* (≤0.05)	Surface	Mid	Deep	Mix	*P* (≤0.05)
Gase (mg PNF kg^{-1} h^{-1})	14.47^{b}	14.38^{b}	12.16^{c}	24.14^{a}	0.00	12.48^{b}	9.55^{c}	8.16^{d}	16.23^{a}	0.00
aPase (mg PNF kg^{-1} h^{-1})	22.64^{a}	18.03^{b}	18.44^{b}	23.12^{a}	0.00	18.55^{b}	12.67^{c}	8.33^{d}	20.99^{a}	0.00
Pase (mg PNF kg^{-1} h^{-1})	12.91^{b}	11.11^{c}	9.65^{d}	14.65^{a}	0.00	6.61^{a}	4.95^{b}	3.46^{c}	6.79^{a}	0.00
Urease (mg $NH4^{+}kg^{-1}$ h^{-1})	19.66^{b}	16.10^{c}	16.55^{c}	21.62^{a}	0.00	9.46^{b}	6.20^{c}	6.56^{c}	13.02^{a}	0.00

‡ $^{a, b, c, d}$ *indicates significant difference*. *Within rows, means followed by the same letter are not significantly different (P = 0.05) using Duncan's multiple range test.* Surface *soil (0-25 cm) (S); mid soil (150-200 cm) (M), deep soil (300-350 cm) (D) and mixed soil (mixture of equal amounts of surface, mid and deep) (Mx). Gase= beta-glucosidase, Pase= Alkaline phosphatase, aPase= Acid phosphatase.*

4.4.2 Statistical Analysis

Data were analysed using analysis of variance (ANOVA) in a randomised complete block design (Gomez & Gomez 1984). Differences between treatment means were separated using the Duncan's Multiple Range Test (DMRT) procedure at 0.05 and 0.01 probability levels. Pearson's correlation coefficient was done to determine the relationships among various variables at 95% probability level ($p<0.05$). All data were analysed using the statistical package, STATISTIX 10.0.

4.5 Results

Table 4.1 reported the mean values of enzyme activity from different depth of coal-mine stockpile soil before planting. The results show that mixed soil has significantly high mean values for activity of β-glucosidase, urease and alkaline phosphatase, followed by surface soils. There was no significant difference for acid phosphatase activity between mixed soil and surface soil. After planting, mixed soil showed the same trend of having significantly high mean values for activity of β-glucosidase, urease and alkaline phosphatase, followed by surface soils (Table 4.2). There was no significant different ($P<0.05$) for alkaline phosphatase on soils from surface, mid and deep. On average, the alkaline phosphatase activity from surface, mid and deep soils was 30.3% lower than that of mixed soil (Table 4.2). β-glucosidase, urease and acid phosphatase mean values generally tend to decreases with an increase in soil depth. There were no significant differences among β-glucosidase, urease and alkaline phosphatase between mid and deep soils. β-glucosidase activity for surface soil was found to be 18.06% higher than that of mid and deep soil (Table 4.2).

Table 4.2: The Effect of Different Depths of Coal-Mine Soil Stockpile on Enzyme Activities

	Enzyme activity			
‡ Soils	β-glucosidase	Acid Phosphatase	Alkaline Phosphatase	Urease
MX	98.21^{a}	95.47^{a}	48.33^{a}	100.46^{a}
S	90.07^{b}	93.82^{a}	33.55^{b}	93.29^{b}
M	79.12^{c}	68.16^{c}	32.39^{b}	79.02^{c}
D	73.46^{c}	53.76^{d}	35.04^{b}	65.71^{c}
P (≤0.05)	*0.00**	*0.00**	*0.00**	*0.00**

*‡ $^{a, b, c, d}$ indicates significant difference. Means in the same column, followed by the same letter are not significantly different from each other at the 5% probability level,*Significant at p≤0.05.‡ MX = Mixed soil; S = Surface soil; M = Mid soil; D = Deep soil.*

The results for the effect of organic and inorganic amendment on stockpile soil were recorded in Table 4.3. β-glucosidase activity following application of poultry manure+ lime yielded significantly ($P<0.05$) high mean values than lime + inorganic fertilizers (NPK), compost, no fertilizer as well as poultry manure. On average, the β-glucosidase activity following the application of poultry manure + lime was 62.7% higher than that of lime + inorganic fertilizers (NPK), as well as single application of poultry manure (Table 4.3). β-glucosidase activity for soil with no fertilizer was 86.15% lower than soil amended with poultry manure + lime. β-glucosidase activity for soil amended with compost was 77.79% lower than soil amended with poultry manure + lime and 60.33% higher than soil with no fertilizer (Table 4.3). The application of poultry manure + lime significantly ($P<0.05$) increased alkaline phosphatase activity more than other soil amendments. Similar to β-glucosidase, there was no significant difference in alkaline phosphatase recorded between soils amended with poultry manure and lime + inorganic fertilizers (NPK).

On average, the alkaline phosphatase activity following the application of poultry manure+ lime was 17.69% higher than that of lime + inorganic fertilizers (NPK), as well as single application of poultry manure. Alkaline phosphatase activity following the application of compost was found to be 72.62% lower than that of soil amended with poultry manure + lime. There was significant difference in alkaline phosphatase activity between soil amended with compost and soil with no fertilizer. Alkaline phosphatase activity for soil with no fertilizer was found to be 51.93% lower than that of soil amended with compost. There was significant difference ($P<0.05$) in alkaline phosphatase activity between soil amended with lime + NPK and soil with no fertilizer. Alkaline phosphatase activity for soil with no fertilizer was found to be 84.70% lower than that of soil amended with lime + NPK (Table 4.3).

Application of lime + NPK yielded significantly high mean values for acid phosphatase compared to poultry manure + lime, compost, no fertilizer as well as poultry manure. On average, the acid phosphatase activity following the application of lime+ NPK was 56.33% higher than that of poultry manure + lime, compost, soil with no fertilizer as well as sole poultry manure. There was no significant difference ($P<0.05$) for acid phosphatase for soil amended with compost and no fertilizer. The application of poultry manure + lime yielded significantly high mean values ($P<0.05$) for urease, followed by lime + inorganic fertilizers (NPK) as well as sole poultry manure. There was no significant difference for urease recorded between soils amended with poultry manure and lime + inorganic fertilizers (NPK). Similar to acid phosphatase compost application and soil with no fertilizer showed no significant difference in urease and yielded low mean values compared to inorganic fertilizers (NPK), poultry manure + lime and sole poultry manure. Urease activity for soil with no fertilizer was found to be 84.70% lower than that of soil amended with poultry + lime (Table 4.3).

Table 4.3: The Effect of Soil Amendments on Enzyme Activities

	Enzyme activity			
‡ Amendments	β-glucosidase	Acid Phosphatase	Alkaline Phosphatase	Urease
P+L	166.67[a]	52.02[b]	89.13[a]	147.91[a]
NPK+L	101.34[b]	67.41[a]	76.66[b]	105.07[b]
P	103.53[b]	49.89[b]	74.57[b]	103.08[b]
C	37.02[c]	34.19[d]	24.40[c]	33.10[e]
NF	23.09[d]	36.36[d]	11.73[d]	33.44[e]
P (≤0.05)	*0.00**	*0.00**	*0.00**	*0.00**

*‡ [a, b, c, d] indicates significant difference. Means in the same column, followed by the same letter are not significantly different from each other at the 5% probability level, *Significant at p≤0.05. ‡ P+L= Poultry manure + lime, NKP+L= Inorganic fertilizer + lime, C= Compost, P= Poultry manure, NF= No fertilizer*

Table 4.4 shows results for effect of stockpile on enzyme activities. Stockpile 1 soil yielded higher mean values of all the enzymes assessed compared to stockpile 2 soil. The activity of β-glucosidase, acid phosphatase, alkaline phosphatase and urease was found to be 11.03%, 8.04%, 10.03% and 60.23% high on stockpile 1, relative to stockpile 2 soils.

Table 4.4. The Effect of Age of Coal-Mine Soil Stockpile on Enzyme Activities

	Enzyme activity			
‡ Stockpile	β-glucosidase	Acid Phosphatase	Alkaline Phosphatase	Urease
Stockpile 1	89.67[a]	82.34[a]	57.04[a]	104.21[a]
Stockpile 2	80.76[b]	76.21[b]	51.84[b]	65.03[b]
P (≤0.05)	*0.00**	*0.00**	*0.00**	*0.00**

*‡ [a, b, c, d] indicates significant difference. Means in the same column followed by the same letter are not significantly different from each other at the 5% probability level, *Significant at p≤0.05.*

Table 4.5 showed the association between the different enzymes studied. There was significantly high positive correlation among soil enzymes (Table 4.5). Correlation coefficient ranged from 0.86 to 0.95. The highest correlation was observed between alkaline phosphatase and acid phosphatase and the lowest between acid phosphatase and urease.

Table 4.5. Correlations Coefficients (R^2) between Enzyme Activities of Stockpile Soils after Planting

	Acid Phosphatase	Alkaline Phosphatase	β-glucosidase	Urease
Acid Phosphatase	1.00			
Alkaline Phosphatase	0.95*	1.00		
Beta-glucosidase	0.87*	0.90*	1.00	
Urease	0.86*	0.88*	0.89*	1.00

* = significant at *P<0.05*

4.6. Discussion

4.6.1. Effect of Age of Coal-Mine Stockpile on Enzyme Activity

Stockpiling of soil mounds during mineral extraction has been shown to affect the soil biological, chemical and physical properties mainly as a result of anaerobic conditions within the heaps, but also due to machineries used during the stripping and stockpiling of the soil (Rai *et al*., 2014). Enzyme activities are sensitive to both anthropogenic and natural disturbance; they show quick response to any soil induced change (Dirk, 1997). Soils from stockpile 1 (10 years old) yielded high mean values for all analysed enzyme activity compared to soils from stockpile 2 (20 years old). These findings can be attributed to the fact that when soils are stockpiled for a long period of time microbial biomass is reduced (Strohmayer, 1999). According to Hu and Cao (2007), enzyme activity in soil is associated with microbial biomass because microbial biomass is considered as the primary source of enzymes in the soil.

4.6.2. The Effect of Stockpile Soil Depth on Enzyme Activity

Enzyme activity was high in mixed soil. This improvement in soil enzyme activities can be attributed to change in soil texture when soils are mixed. Change in soil texture affects other physical properties like water availability, infiltration rate and aeration and, to some extent, chemical properties and biological properties (NRCCA, 2010; and Garj & Kumar, 2012). Activities of β-glucosidase, alkaline phosphatase, acid phosphatase and urease in all soil depths have shown improvement after planting, relative to pre-planting (Table 4.1 and Table 4.2). This is consistent with the findings by Widdowson *et al*., (1982) that soil biology of stockpiled topsoil is restored quickly once the soil is re-spread. Surface soils yielded high activity for β-glucosidase, acid phosphatase and urease compared to mid and deep soils. According to Strohmayer

(1999), soil stockpile depth plays a major role in biochemical activities of the soil. This study is consistent with the findings by Fresquez *et al*., (1985) that reported that soil enzyme activities decreases with increase in depth of the stockpile soil. Abdul-Kareem and McGae (1984) reported a decrease in microbial biomass and enzyme activity from 0.3m depth until 2m depth of stockpile soils. Alkaline phosphatase was not significantly different between surface, mid and deep soils. This can be attributed to pH of the soil. The pH of the soil in this study was found to be less than 6. The study conducted by Turner (2010) reported that alkaline phosphatase was found to be predominant in soils that are less acidic (>6). Soil pH affects ionic and hydrogen bonds, which are important to enzyme shape and therefore enzyme activity (Reece *et al*., 2010).

4.6.3. Effect of Soil Amendments on Enzyme Activities

Soil enzyme activities are very sensitive to both natural and anthropogenic disturbances and show a quick response to the induced changes (Dirk, 1997). The study conducted by Fresquez *et al*., (1985) shows that soil stockpiling affected enzyme activity. Any change in soil management and land use is reflected in the soil enzyme activities, and they can anticipate changes in soil quality before detection through other soil analytical methods (Ndiaye *et al*. 2000). Treatment involving poultry manure + lime showed significantly high mean value of 166.67mg p-Nitrophenol kg^{-1} h^{-1} for β-glucosidase activity, followed by treatment with NPK+ lime and poultry manure (Table 3). According to Acosta-Martinez and Harmel (2006), significant increase of β-glucosidase activity due to poultry litter application represents limiting steps of cellulose degradation of soil and recycling of the nutrients from poultry litter. Hota *et al*., (2014) reported that application of lime in combination with organic manure has favourable effect on soil microbial biomass and that organic manure is more pronounced when applied with lime rather than their sole application. Naramabuye (2004) reported that the application of lime and poultry manure increase soil pH, relative to sole application of poultry manure. A study conducted by Chao *et al*., (2015) reported that soil enzyme activities increase along the gradient of soil pH, indicating that the influence of organic amendments on soil enzyme activities observed in their study could mainly be due to the effect of soil pH.

The results for β-glucosidase activity (23.09mg p-Nitrophenol kg^{-1} h^{-1}) without fertilizer application in this study were lower than the findings by Chang *et al*. (2014) who recorded 39.3mg p-Nitrophenol kg^{-1} h^{-1} for β-glucosidase on soil with no fertilizer treatment. Similar to the results for β-glucosidase activity (23.09 mg p-Nitrophenol kg^{-1} h^{-1}) without fertilizer application, Chang *et al*., (2014) recorded high enzyme activity of 57.2mg p-Nitrophenol kg^{-1} h^{-1} for β-glucosidase on soil with compost application as compared to this study where 37.02mg p-Nitrophenol kg^{-1} h^{-1} was recorded. This inconsistency can be attributed to the type of soil used in the studies as the soil in the study conducted by Chang *et al*., (2014) whereas the soil in this study was disturbed by stripping and stockpiling. Acid phosphatase was found to be higher than alkaline phosphatase when no fertilizer was applied.

The findings of this study are consistent with finding by Hota *et al.* (2014). While in their study, the activities of acid and alkaline phosphatase are closely related to soil pH with acid phosphatase dominating in acid soil. The study by Chaitanya *et al.* (2013) recorded a high alkaline phosphatase activity of 52.78 mg p-Nitrophenol kg^{-1} h^{-1} at harvesting stage compared to 11.73mg p-Nitrophenol kg^{-1} h^{-1}, which was recorded in this study at the same growth stage from soils with no fertilizer treatment. This can be attributed to the nature of soil and soil pH as the soil in this study had pH less than 6 and their study soil pH was 7.8.

Application of lime and poultry manure significantly increased alkaline phosphatase activity, followed by NPK + lime and sole application of poultry manure. This is due to the fact that alkaline phosphatase is dominant in alkaline soils (Turner, 2010). According to Dick *et al.* (1988), application of lime has positive effect on phosphatases as it increases soil pH, which can limit enzyme mediated reaction rates by affecting maximum activities of the enzymes and solubility of substrate. NPK + lime yielded high alkaline phosphatase activity than acid phosphatase activity. This contradicts the findings by Laxminarayana (2013) who reported high acid phosphates compared to alkaline phosphatase when soil was treated with NPK + lime.

Sole application of poultry manure significantly increased alkaline phosphatase better, relative to application of compost. According to Naramabuye (2004), poultry manure contains substantial amount of $CaCO_3$ compared to compost. Upon addition of poultry manure to the soil, $CaCO_3$ is dissociated releasing CO_3^{2-} into the soil that combines with protons forms H_2CO^3 thereby increasing soil pH. Significantly high value of 147.91mg $NH_4^+kg^{-1}$ h^{-1} for urease activity was obtained from soil amended with poultry and lime combination. The study by Fernandes *et al*., (2005) reported that application of organic amendments stimulates urease activity. According to Klebanovich and Moroz (1998), application of organic fertilizers and lime decreases soil acidity and increases urease activity. In this study, urease activity value of 105.07mg $NH_4^+kg^{-1}$ h^{-1} was recorded under application of NPK + lime, which was found to be lower than 204mg $NH_4^+kg^{-1}$ h^{-1} recorded by Klebanovich and Moroz (1998). Compost and no fertilizer yielded low values for urease activities 33.10 and 33.44mg $NH_4^+kg^{-1}$ h^{-1} respectively compared to values recorded by Chang *et al*. (2007), who recorded 55.2 and 50.1mg $NH_4^+kg^{-1}$ h^{-1} respectively. This difference can be attributed to soil types, duration of the study and the rate of application of amendments.

4.7. Conclusion

Soil quality depends on physical, chemical, microbial and biochemical properties. Soil enzyme activity has a great potential as an indicator of soil quality as it is sensitive to change. The study unearthed the following findings:

- Deep stockpile soils had low enzyme activity compared to surface and mixed soils, at the depth >1 meter biological activity becomes low due to the environmental condition that favours mostly anaerobic organisms;
- Mixing of stockpile soils generally showed the great potential to increase soil enzyme activity;
- Duration of soil stockpiling can have influence on soil enzyme activity; when soils are stockpiled for a long period of time, microbial biomass is reduced;
- Soil amendments have potential to improve enzyme activity of stockpile soils;
- Poultry manure and lime showed a great potential in improving urease, alkaline phosphatase and β-glucosidase activities of stockpile soils; and
- Increasing soil pH by adding lime or using poultry manure can increase enzyme activity.

Information obtained from the study can be useful in providing guidance about selection of most effect soil amendment material to improve enzyme activity and nutrient cycle of coalmine stockpile soils.

CHAPTER 5
ESTIMATING COAL-MINE STOCKPILE SOIL PROPERTIES USING REFLECTANCE SPECTROSCOPY

5.1. Introduction

Open-cast coal mining has been associated with various negative environmental impacts such as soil, water, air pollution as land degradation (Maczkowiack *et al*., 2012; and Cogho, 2012). Open-cast coal mining may lead to adverse changes in soil textural and structural attribute. In view of the increasing open-cast coal mining activities in South Africa that affect soil quality and have adverse effects on soil flora and fauna, it is of utmost importance to monitor the physical and chemical characteristics of coal-mine stockpiled soils (O'Beirne *et al*., 2013). This will not only pave the way for greater understanding of the direction of improving soil fertility and bioremediation, but also as a prerequisite for assessing the process of soil reclamation, thus leading to the vegetation development/succession with respect to time (COM and CRA, 2007).

During the process of open-cast coal mining, topsoil is removed and stockpiled for future use. Stockpiled topsoil becomes highly degraded the moment this long-term structure is disturbed. Several studies conducted (Fresquez & Aldon, 1984; Harris & Birch, 1989; and Strohmayer, 1999) reveal that timeframe can lead to damage of most soil properties. The damage starts when topsoil is initially stripped from the ground. Changes that occur in soil include change in physical, chemical and biological properties, and loss or reduction of viable plant remnants and seeds (Strohmayer, 1999). For stockpiled soil to meet its goals of rehabilitation post mining-closure, quantification of soil physical and chemical properties that affect soil quality and crop production is necessary. Soil properties such as soil structure, microbial population and nitrogen can change rapidly when the soil is disturbed (Lad & Samant, 2015), making traditional laboratory methods impractical due to time and cost of the sampling and analytical procedures.

There are several studies conducted on physical and chemical properties of stockpiled soils using wet chemistry methods (Harris & Birch, 1989; Kundu & Ghose, 1997; and Strohmayer, 1999). Soil samples are collected at targeted stockpiles and analysed in the laboratory for physical and chemical properties. In recent times, the need for well managed top soil stockpiling process has increased as the soil will be required for post-mining rehabilitation (COM and CRA, 2007). Consequently, the use of wet chemistry methods for analysing and assessing the effect of topsoil stockpiling will be restrictive in terms of the costs and labour involved. It is desirable to investigate reliable, less tedious and cost effective techniques to assess and predict properties of coal-mine stockpiled soils.

Remote Sensing (RS) has become an important tool for environmental applications. Spectral evaluation has proven to be useful, particularly to characterize and discriminate soils, for several purposes in survey (Demattê *et al.,* 2004). Several studies have shown that the spectral behaviour of soils is influenced by their physical, chemical, and mineralogical characteristics (Stoner & Baumgardner, 1981; and Galvão *et al.,* 1997). Reflectance Spectroscopy has been used for many years to assess grain, fertilizers and soil qualities and has proven to be a rapid, convenient means of analysing many soil constituents at the same time (Bellon-Maurel *et al.,* 2010; Bilgili *et al.,* 2010; and Bellon-Maurel & McBratney, 2011). NIR spectroscopy is an easy to use and less expensive technique that has the potential to replace traditional wet chemistry methods of soil analysis (Mashimbye *et al.,* 2012). Using traditional wet chemistry techniques for physical and chemical analysis may be restrictive due to high costs and labour when large amounts of samples are involved. It is accepted that Near InfraRed (NIR) spectroscopy and Mid-InfraRed (MIR) spectroscopy are among less expensive and user-friendly techniques for quantitative soil analysis (Shepherd & Walsh, 2002; and Bilgili *et al.,* 2010).

A variety of statistical methods are used by researchers to extract soil attributes from the spectra, which include, amongst others, Principal Component Regression (PCR), Multiple Regression Analysis (MRA), Stepwise Multiple Linear Regression (SMLR), bagging Partial Least Square Regression (PLSR) and multivariate adaptive regression splines (MARS). Spectral transformations (mathematical treatments) are also applied to the spectra to maximize the extraction of information from spectra (Cho & Skidmore, 2006; and Ramoelo *et al.,* 2011).

The mathematical spectral treatments include first and second derivatives, straight line subtraction, vector normalization, and multiplicative scattering correction, to mention a few. It appears that the use of statistical methods and spectral transformation frequently have a favourable result for enhancing the extracting of soil information from spectra. For example, Janik *et al*., (2009) compared the performance of PLSR analysis for the prediction of a variety of soil chemical and physical properties from their MIR spectra using a combination of PLSR and neural networks (NN). While their study established that the PLSR-NN method outperformed the PLSR for the prediction of some soil properties, they cautioned that the use of PLSR-NN over the PLSR should be investigated against the backdrop of the trade-off of limited improvement and the computational complexity. Primarily, PLSR is the most commonly used statistical spectral treatment technique for soil analysis. Biligili *et al*., (2010) asserted that this is mainly because PLSR is superior to traditional methods in dealing with high dimensional data and multicollinearity problem. In this study, PLSR was used to estimate coal-mine stockpile soil properties.

Many studies have been conducted to estimate soil properties using Reflectance Spectroscopy on agricultural soil, soil salinity and soil pollution (Bellon-Maurel *et al.,* 2010; Bilgili *et al.,* 2010; Bellon-Maurel & McBratney, 2011; and Mashimbye *et al.,* 2012), no studies were found to estimate coal-mine stockpile soil properties using spectroscopy and spectral transformation. Evaluation of the potential of spectroscopy in estimating coal-mine stockpile soil properties could be critical for understanding the effects of stockpiling on properties of coal-mine soils.

5.2 Objectives

The objectives of the study were, namely, to:

1. Determine the ability of Reflectance Spectroscopy to estimate soil properties.
2. Determine the ability of spectral transformation techniques to enhance estimation of soil properties.
3. Investigate what spectral regions and bands are dominant in estimating properties of coal-mine stockpiled soil.

5.3. Hypotheses

1. Soil properties can be estimated using Reflectance Spectroscopy.
2. Spectral transformation techniques can enhance estimation of soil properties.
3. No spectral regions and bands are dominant in estimating properties of coal-mine stockpile soils.

5.4. Materials and Methods

5.4.1. Locality and Soil Sampling

Soil samples were collected from three open-cast coal mines located approximately 8 kilometres south of Witbank in Mpumalanga Province of South Africa. The climate of the area can be regarded as having warm, moist summers and cool to cold dry winters with frost. On average, 85% of the annual average rainfall of 750mm falls in the growing season (i.e., October to March).

Fifty samples were collected with soil auger from selected three stockpiles with age >6 at depth 0-25cm using a line transect sampling method at every 25 m interval (Bhatti *et al.,* 2005). Soils were a mixture of different soil types and origins. They ranged from red freely drained to dark black high clay content soils (Soil Classification Working Group, 1991). The depth of the stockpiles was approximately 4-5m deep (Figure 1). Sparsely distributed grass species was growing on stockpile soils at the time of sampling. The soils showed signs of sheet erosion during sampling. There were signs of non-homogenous mixture of soils. Soils were not stockpiled according to soil type or horizon. Geographical Positioning System (GPS) co-ordinates were recorded at every sampling point. At total of 150 samples were collected and taken for spectral analysis.

Figure 5.1. Stockpile Soils

5.4.2. Spectral Data Collection

A FieldSpec 3 Portable Analytical Spectral Device (ASD®) spectrometer (manufactured by Analytical Spectral Devices, Inc.) was used to acquire spectral signatures of the same soil samples that were used for laboratory analysis. Spectral data were collected in a darkroom to ensure stable atmospheric and uniform illumination conditions. The instrument covers the visible to short-wave infrared wavelength range (350-2500nm). The spectrometer has a sampling interval of 1.4nm for the region 350 to 1000nm and 2nm for the region 1000 to 2500 nm with a spectral resolution of 3 and 10nm, respectively. A halogen lamp (Lowel Light Pro, JCV 14.5V-50WC) was used as a source of light. The lamp was fixed at a nadir position 20cm above the target. To prevent contamination of one sample by another, each sample was placed on a separate black paper background before making spectral signature measurements. Soil was spread on 16cm dimension plate to completely cover the plate's surface. The soil was flattened 3cm above the plate using a sterile ruler to form an even surface. Reflectance calibration was done using a white reference. The white reference is a calibrated white spectralon with a near 100% diffuse (Lambertian) reference reflectance panel made from a sintered poly-tetra-flourethylene based material. Calibration was done before taking measurements of each of the samples. Spectral signatures were taken at a height of approximately 15cm above the target at approximately 15º off nadir to minimize the effect of bidirectional reflectance. Each sample was rotated five times when the spectra were measured to minimize bidirectional reflectance effects (Mashimbye *et al*. 2012).

5.4.3. Soil Physical and Chemical Analysis

Soil samples collected were analysed in the laboratory for the following: exchangeable calcium (Ca), Sodium (Na), magnesium (Mg), potassium (K), soil pH, organic carbon (OC), phosphorus (P) and clay content. The soils were air-dried, ground with pestle and mortar and screened through a 2mm sieve for analysis. A particle size analysis was performed on the <2mm soil fraction using the pipette method to determine clay percentage of the soils. Soil pH was determined in deionized water with a 1:1 (w/v), soil: water ratio the mixture was centrifuged and analysed using a method by Non-Affiliated Soil Analysis Working Group (1990). OC was determined by a dry combustion procedure using a LECO CHN 1000 Auto-Analyzer. The exchangeable Ca, Mg, K, Na and cation exchange capacity (CEC) were extracted with 1M ammonium acetate at pH7.0 and determined by atomic absorption spectrophotometry. Available P was determined using Bray-1 methods (Non-Affiliated Soil Analysis Working Group, 1990).

5.4.4. Data Analysis

Descriptive statistics of selected physical and chemical properties of the soils were computed. Mean values, standard deviation as well as spearman correlation statistics were computed using Statistica 12.0 (Statsoft, 2013). Predictive models were computed using untransformed individual reflectance, First Derivative Reflectance (FD), Log transformed spectra Log (1/R). Commonly used spectral transformation techniques such as Log transformed spectra Log (1/R) and first derivative were computed. Log (1/R) was determined by calculating a log function of the spectral reflectance's reciprocal (Hruschka, 1987; Yoder & Pettigrew-Crosby, 1995; and Fourty

& Baret, 1998). The first derivative of the spectral reflectance was derived using a first-difference approach. This approach calculates differences in reflectance between adjacent wavebands (Dawson & Curran, 1998).

5.4.5. Estimation of Soil Physical and Chemical Properties Using Reflectance Spectroscopy and PLSR

Hundred and fifty soil samples were used for regression. The total numbers of samples were split into 70/30 proportion, 70% for calibration and 30% for validation and evaluation of the models. To optimize the accuracy of the prediction models, the data were subjected to spectral pre-treatments called Mean Centering (MC).

Partial Least Square Regression (PLSR) was used to analyse the data as this technique is commonly used regression technique (Viscarra Rossel, 2008). Regression predictive models for Clay%, pH, organic C, exchangeable Ca, Mg, Na, K and P using soil samples collected from open-cast coal-mine stockpiles were computed. Soil reflectance data in the wavelength range between 350 and 2500nm were used for the analysis.

PLSR was computed using the ParLeS version 3.1 software (Viscarra Rossel, 2007, 2008). In this study, PLSR was used to derive calibrated and validated models for selected coal-mine stockpile soil properties. PLSR is a method that specifies a linear relationship between a set of dependent variables, Y, and a set of predictor variables, X (Farifteh *et al.,* 2007). The general idea of the PLSR is to extract the orthogonal or latent predictor variables, accounting for as much of the variation of the dependent variables as possible (Viscarra Rossel, 2008). PLSR generates model evaluation statistics such as the R^2, adjusted R^2 (R^2adj), Root Mean Squares Error (RMSE), Mean Error (ME), Ratio of Prediction to Deviation (RPD), and Standard Deviation of the Error distribution (SDE). The model accuracy and efficiency were assessed in the validation set on the basis of Coefficient of Determination (R^2), Root Mean Square Error of Validation (RMSEV), and Residual Predictive Deviation (RPD) (Williams, 2001). The R^2 values indicate the strength of statistical correlation between measured and predicted values (Farifteh *et al.,* 2007). Additionally, the PLSR models were tested with the Residual Predictive Deviation (RPD), which is the ratio of the standard error of performance to the standard deviation of the reference data (Williams, 2004). Interpretation of the RPD differs amongst authors and applications.

The six level interpretations of RPD given by Viscarra Rossel *et al*., (2006) were adopted as follows: RPD<1.0 indicates very poor models/predictions, and their uses are not recommended; 1.0< RPD <1.4 indicates poor models/predictions, where only high and low values are distinguishable; 1.4< RPD <1.8 indicates fair models/predictions, which may be used for assessment and correlation; 1.8< RPD <2.0 indicates good models/predictions, where quantitative predictions are possible; 2.0< RPD <2.5 indicates very good, quantitative models/predictions; and RPD >2.5 indicates excellent models/predictions. Generally, an optimal model should have lower RMSEV and higher R^2 and RPD. Variable Importance in the Projection (VIP), with a threshold of 1, was used to determine the important wavelengths used in the PLSR calibration (Viscarra Rossel *et al.,* 2010). Generally, wavelengths with VIP scores greater than 1.0 are highly influential; values between 0.8 and 1.0 indicate moderately influential variables; and values lower than 0.8 represent less important variables (Eriksson *et al.,* 2001; and Gosselin *et al.,* 2010).

5.5. Results

5.5.1. Descriptive Statistics of Coal-Mine Stockpile Soil Properties

Results of the descriptive statistics of selected of coal-mine stockpile soil properties are presented in Table 5.1. Clay% of the samples ranges from 1.30 to 34.00. pH range from 3.96 to 8.62 with the mean value of 5.46. Organic carbon was found to range from 0.02% to 1.65% and P ranged from 0.55mg/kg to 16.95mg/kg. Ca ranged from 0.12cmol/kg to 7.08cmol/kg. Mg ranged from 0.12cmol/kg to 9.28cmol/kg, K ranged from 0.05cmol/kg to 15.16cmol/kg and Na ranged from 0.01cmol/kg to 1.19cmol/kg. Figure 5.2 illustrate the relationship between concentration of soil properties and raw (original) spectra. For Clay%, spectra reflectance is high when soil percentage of clay is low. Spectral reflectance of pH increases with an increase in pH values. The highest correlation between Ca and spectra is approximately R^2=0.5 at the wavelength between 1700nm-1800nm. P, Mg, K and Na shown the same trend spectral reflectance increased with in concentration of P, Mg, K and Na in the soil. Low concentration of OC in the soil yielded high spectral reflectance.

Table 5.1. Coal-Mine Stockpile Soil Properties

Variable	Mean	Min	Max	Std. Dev	Median	Skew
Clay (%)	17.90	1.30	34.00	8.80	16.50	166.78
Na (cmol/kg)	0.16	0.01	1.19	0.24	0.06	0.04
K (cmol/kg)	0.81	0.05	15.16	2.44	0.18	62.24
Ca (cmol/kg)	1.53	0.12	7.08	1.50	0.70	4.81
Mg (cmol/kg)	1.41	0.12	9.28	1.85	0.45	14.77
P (mg/kg)	4.32	0.55	16.95	3.89	3.04	82.91
pH	5.46	3.96	8.62	1.08	5.29	1.08
OC (%)	0.43	0.02	1.65	0.38	0.37	0.007

n= 150, Skew= Skewness coefficient, Std.Dev= Standard deviation, OC= Organic Carbon

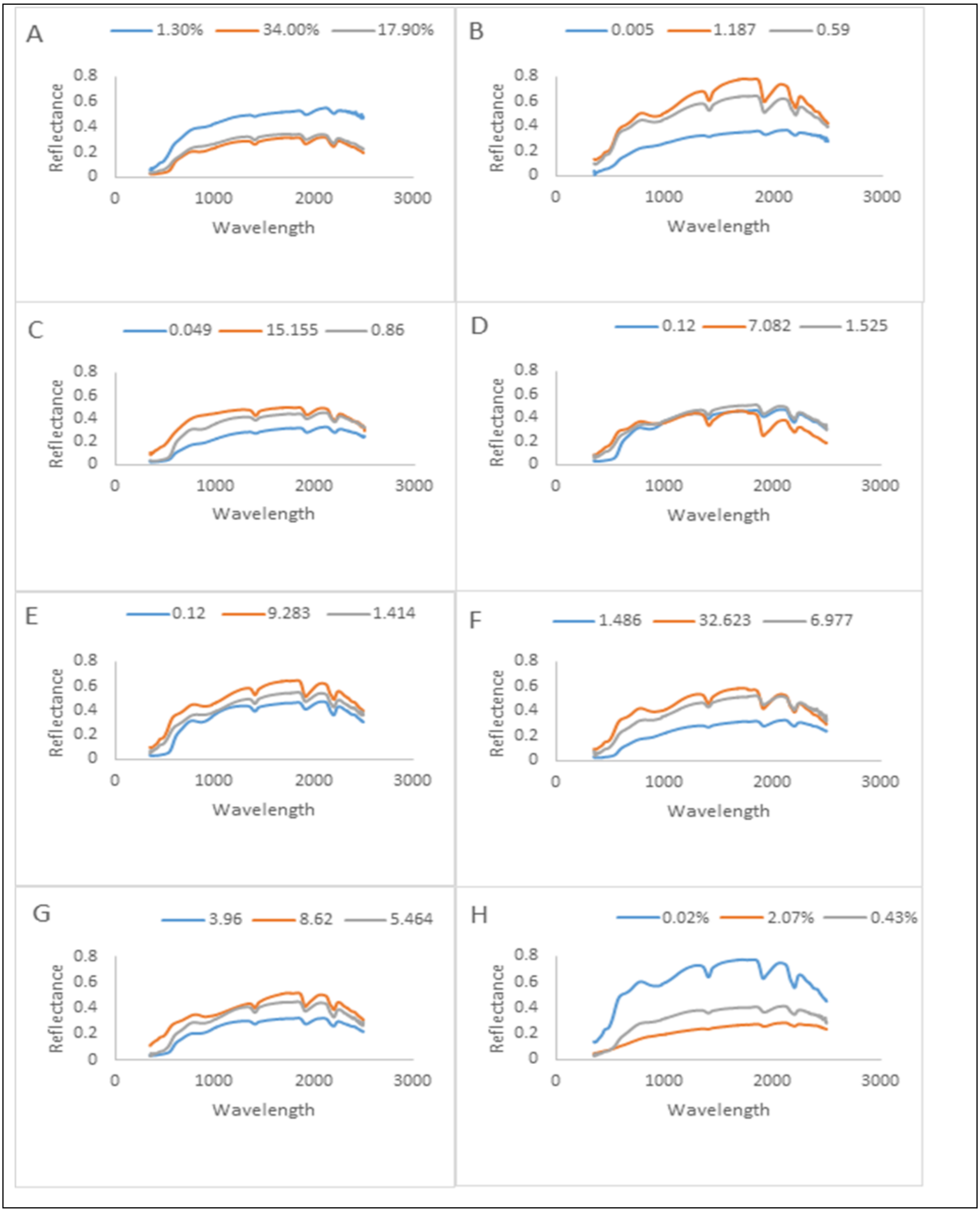

Figure 5.2: Descriptive statistics (showing low (Blue), moderate (Grey) and high (Orange) content of each soil property) of the original spectral reflectance of stockpile soils

A= Clay (%),B = Na (cmol/kg), C = K (cmol/kg), D = Ca (cmol/kg), E = Mg (cmol/kg),F = P (mg/kg),G= pH (H2O), H = OC (%)

Table 5.2 reports on spearman correlation matrix of coal-mine stockpile soil properties. Clay% significantly correlated ($p<0.01$) with all other measured soil properties except pH. K had significant correlation with clay and P but not with other soil properties. The relationship between soil spectra and laboratory analysis is presented in Figure 5.1. To illustrate the spectral dependence of the relation between original soil reflectance and measured soil properties, the correlogram have been calculated (Figure 5.3). The correlogram reports the coefficient of correlation (r) between soil reflectance and soil properties. They have been calculated from reflectance spectra convoluted with a median filter (size 50nm). The highest correlation was found between soil pH and the spectral, followed by Ca and Mg. The highest correlation soil pH, Ca and Mg and raw spectra was found near 520nm-560nm and the R^2 was found to be approximately 0.56, 0.54 and 0.52 respectively.

Table 5.2. Correlation Matrix of Selected Coal Mine Stockpile Soil Properties

	Clay %	Na	K	Ca	Mg	P	pH	OC
Clay %	1.00	0.46**	0.35**	0.28**	0.39**	0.47**	0.21	-0.35**
Na		1.00	0.07	0.62**	0.70**	0.59**	0.52**	-0.38**
K			1.00	-0.22	-0.17	0.43**	-0.19	-0.04
Ca				1.00	0.87**	0.38**	0.87**	-0.39**
Mg					1.00	0.44**	0.69**	-0.44**
P						1.00	0.38**	-0.38**
pH							1.00	-0.46**
OC								1.00

OC= Organic Carbon, ** Significant at $p<0.01$.

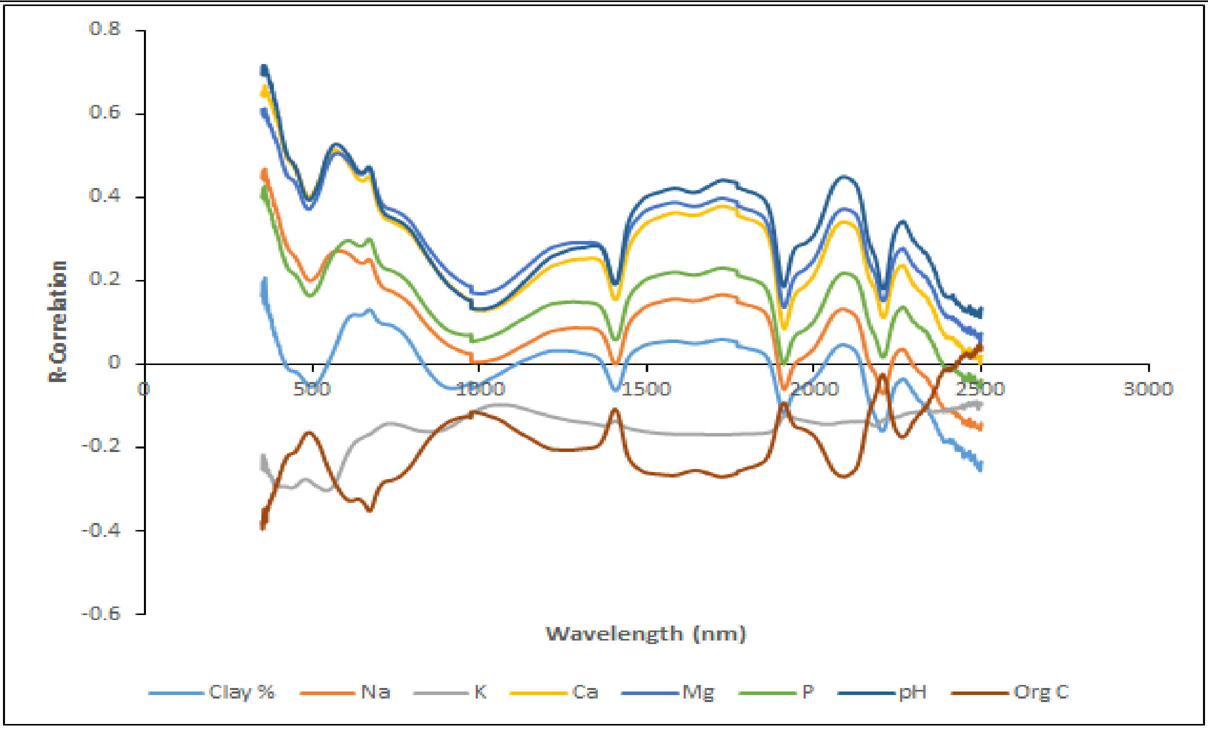

Figure 5.3: Correlogram of Reflectance Spectra and Soil Physical and Chemical Properties

5.5.2. Spectral Features

The spectral features of all 150 soil samples are depicted in Figure 4. The spectral reflectance is typical of soil spectra as it follows the basic shape similar observed by other researchers. The spectra show prominent absorption around 1400, 1900 and 2200nm. The absorption features shown by spectra are associated with the bending and stretching of the O-H bonds of free water at 1400, 1900nm and lattice minerals around 2200nm. The highest reflectance found around 1721-1849nm and the lowest reflectance was found around 356nm.

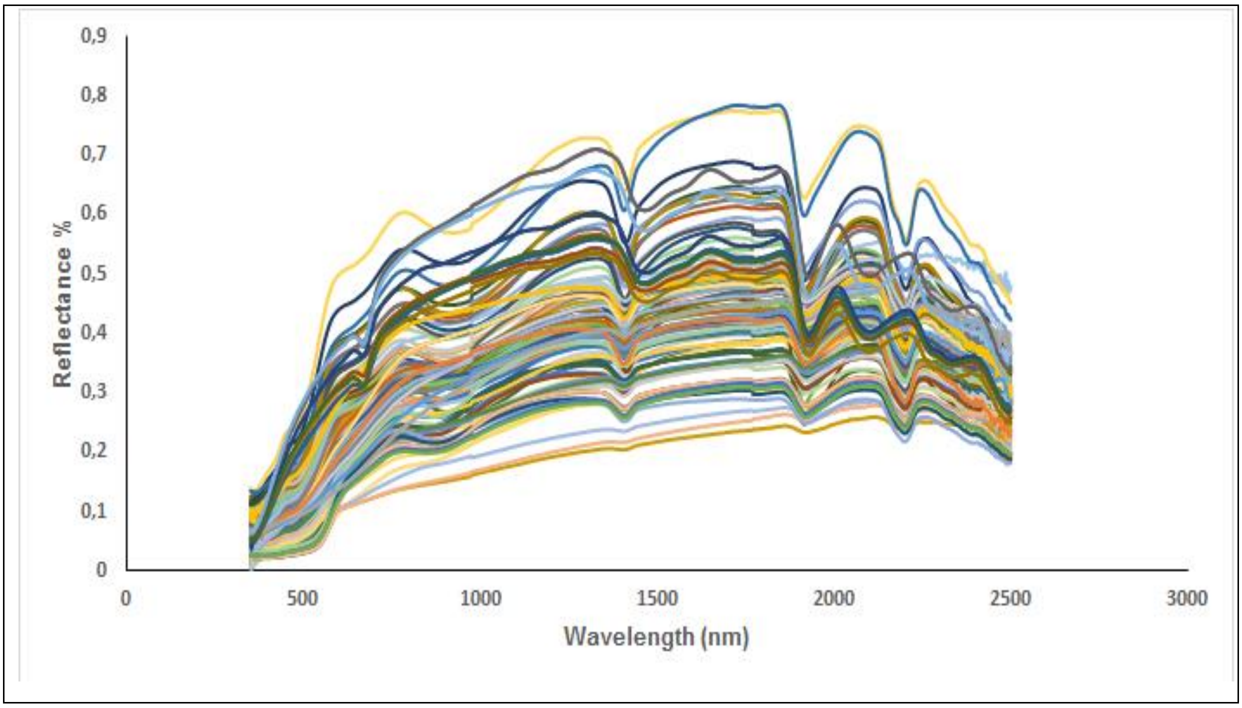

Figure 5.4. Untransformed Spectral Reflectance of All the Soil Samples

5.5.3 Soil Physical and Chemical Properties Estimation Using PLSR and Various Spectral Transformation Techniques

Soil properties that were estimated with high accuracy were pH and Ca based on R^2 values ranging from 0.5 to 1.0 and RPD values of more than 1.5 (Table 5.3). The extent of prediction is graphically presented in Figure 5.5. Other soil properties were poorly predicted by the model based on low RPD values that were found to be less than 1.5 (Table 5.3). Log (1/R) transformation spectra yielded higher estimation accuracy (R^2= 0.79, RPD=2.08, RMSEV=0.52) for pH compared to untransformed spectra (R^2= 0.77, RPD=2.01, RMSEV=0.53) and first derivative spectra (R^2=0.64, RPD=1.53, RMSEV=0.70) (Table 3). In relation to Ca, Log (1/R) transformation spectra yielded high estimation accuracy (R^2=0.69, RPD=1.79, RMSEV=0.89cmol/ kg) compared to untransformed spectra (R^2=0.64, RPD=1.65, RMSEV=0.97cmol/ kg) and first derivative transformation (Table 5.3), Mg, K, CEC, Clay content, OC and Na were poorly predicted (Table 5.3).

Table 5.3. Performance of PLSR Models for Predicting Various Soil Properties Using Different Spectral Transformation

Spectra	Variable	R^2	RMSEVRPD		Factors
No transformation	Clay%	0.40	6.44	1.18	6
	Na	0.23	0.21	1.14	3
	K	0.23	2.31	1.12	6
	Ca	0.64	0.97	1.65	6
	Mg	0.49	1.41	1.37	5
	CEC	0.37	5.14	1.16	5
	pH	0.77	0.53	2.01	3
	OC	0.23	0.41	1.14	4
First Derivative	Clay%	0.29	7.33	1.03	4
	Na	0.24	0.21	1.15	4
	K	0.28	2.20	1.17	4
	Ca	0.63	1.02	1.57	4
	Mg	0.46	1.50	1.29	4
	CEC	0.37	5.17	1.25	5
	pH	0.64	0.70	1.53	5
	OC	0.14	0.44	1.07	7
Log (1/R)	Clay%	0.47	6.14	1.23	7
	Na	0.27	0.21	1.17	4
	K	0.28	2.18	1.18	5
	Ca	0.69	0.89	1.79	7
	Mg	0.48	1.42	1.37	7
	CEC	0.33	5.39	1.39	7
	pH	0.79	0.52	2.08	7
	OC	0.16	0.44	1.06	4

OC= Organic Carbon

Variable Importance for Projection (VIP) plot and regions for estimation of coal-mine stockpile soil properties shows the highest VIP scores for clay are centred near 574nm for untransformed spectra, 1910nm for FD and 2332nm for Log (1/R) transformed spectra (Table 5.4). K, Ca, Mg, P, pH and OC spectral domains used by the PLSR prediction model are centred near 674, 1071, 673, 976, 1900, 549nm for untransformed spectra. Na was found to have VIP of less than 1 for untransformed spectra. Clay%, Na, K, Ca, Mg, P, pH and OC had highest VIP scores near 2192, 975, 2480, 2475, 2490,986 and 2497nm wavebands for FD. Clay%, K, Ca, Mg, P and pH had highest VIP scores near 882, 2093, 2480, 2479, 567 and 2499nm wavebands for Log (1/R) transformed spectra (Table 5.4). Na and OC were found to have VIP of less than 1 for Log (1/R) hence were not recorded in Table 5.4.

Table 5.4: Highest Variable Importance in the Projection (VIP) Values of Each Estimated Soil Property

Spectra	Variable	VIP	λ (nm)	Region
No transformation	Clay%	10.71	574	VIS
	K	3.61	674	VIS
	Ca	3.71	1071	NIR
	Mg	3.50	673	VIS
	P	23.27	976	NIR
	pH	4.88	1900	SWIR
	OC	1.02	549	VIS
First Derivative	Clay%	9.29	1910	SWIR
	Na	7.81	975	NIR
	K	16.95	2480	SWIR
	Ca	21.60	2475	SWIR
	Mg	17.83	2490	SWIR
	P	23.27	976	NIR
	pH	2.14	986	NIR
	OC	4.88	2497	SWIR
Log (1/R)	Clay%	6.34	2332	SWIR
	K	2.59	2093	SWIR
	Ca	3.91	2480	SWIR
	Mg	4.53	2479	SWIR
	P	5.81	567	VIS
	pH	7.93	2499	SWIR

VIS=visible region, NIR= Near InfraRed region, SWIR= Short wavelength infrared, Soil properties with VIP score of <0.8 are excluded from the table

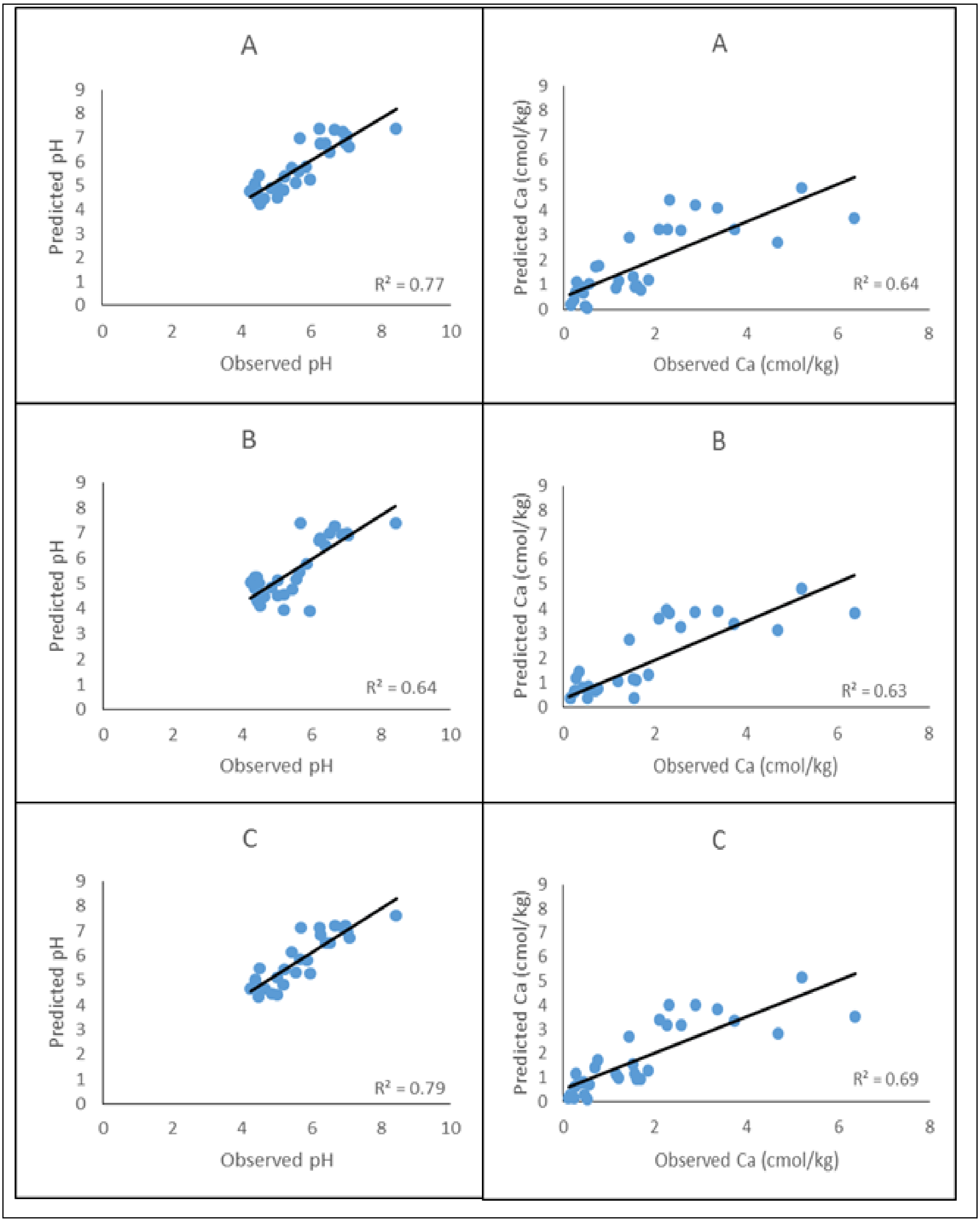

Figure 5.5: Scatterplots of Highest Predicted Soil Properties, i.e., pH and Ca from untransformed and transformed spectral using partial least significant regression (PLSR). *A= No transformation, B= First derivatives, C= Log (1/R) transformation.*

5.6. Discussion

The study intended to evaluate the performance of PLSR and Reflectance Spectroscopy in estimating various properties of coal-mine stockpiled soils. The specific objectives were, namely, to: (1) determine the ability of Reflectance Spectroscopy to estimate soil properties; (2) determine the ability of spectral transformation techniques to enhance estimation of soil properties; and (3) investigate what spectral regions and bands are dominant in estimating properties of coal-mine stockpiled soil.

This section explains the findings of this study.

5.6.1. Untransformed Soil Spectral Characteristics

The spectra of all soil sample shows prominent absorption around 1400, 1900 and 2200nm, these findings are consistent with the findings by Viscarra Rossel *et al*. (2006). The spectra show prominent absorption features that are associated with the bending and stretching of the O-H bonds of free water at 1400, 1900nm and lattice minerals around 2200 nm (Shepherd & Walsh, 2002; Viscarra Rossel *et al.,* 2006; and Mashimbye *et al.,* 2012). The results for organic carbon in this study are consistent with the findings by Stoner and Baumgardner (1981) that show that increasing soil organic carbon (SOC) lowered albedo across the whole visible, ShortWave InfraRed and Near-InfraRed (Vis–NIR–SWIR) reflectance spectrum. For clay content, there was variation in respective to textural reflectance. Soils with low clay content showed high reflectance than soils with high clay content.

The results of this study are contrary to previous studies (Stoner & Baumgardner, 1981; Baumgardner *et al.,* 1985; and Gosselin *et al.,* 2010), which suggest that, as soil grain size decreases, surface component decreases and volume component increases indicating an increased reflectance with decreased grain size (surface becomes smoother). The studies (viz., Stoner & Baumgardner, 1981; Baumgardner *et al*., 1985; and Gosselin *et al*., 2010) concluded that reflectance should decrease as soil particle size increases; this is due to the increasing number of optical traps causing loss of radiation. The reason for high reflectance of soils with low clay content in this study can be attributed to the fact that soils in the study area were disturbed and that soils' high clay content increases the potential for aggregate formation. Macro aggregates physically protect organic matter molecules from further mineralization caused by microbial attack making soil to have high organic matter and low reflectance (Schreier, 1977; and Rice, 2002). Ca showed high reflectance in the visible region and concave shape. According to Melfi *et al*. (1979), this concave shape of the spectra in the visible to Near-InfraRed region is due to crystalline iron in the soil. Na, K, Mg, P and pH have shown similar trend in reflectance, high concentration of each element have shown high reflectance. According to Zornoza *et al*. (2008), these properties are principally controlled by clay and organic matter type and content, which have functional groups with variable charges responsible for the adsorption of the different cations and water.

5.6.2. Soil Parameters Estimation Using Reflectance Spectroscopy vs PLSR

Ca and pH are stockpile soil properties that were accurately predicted in this study. According to Bonnet *et al*. (2015), Ca has strong correlation with pH, and Ca expressed in soil solutions is mostly related to pH resulting in accurate prediction of both Ca and pH. A study conducted by Leluva (2007), revealed that there is an overlap of wavelength regions associated with soil pH and Ca prediction. Soil pH in most case is directly influence by calcium carbonate content in the soil. OC, P, Na, K, Mg and clay content were poorly predicted. RPD of their models were less than 1.4 (Viscarra Rossel *et al.,* 2006). The poor predictive models are presumably due to the nature of soils used in the study area. For instance, K can be highly mobile in the soil solution. Stockpile soils structure gets destroyed during stripping, which enhances leaching with a consequent reduction of soil elements (Ghose, 2004). According to Janik *et al.* (1998), spectroscopy is unlikely to provide quantitative data where the property being predicted is unrelated to soil chemistry or for soil solution chemistry where concentrations are low. Ca and pH properties are related to Mg, P, Na, clay and OC from the correlation matrix table in the results section, which means that there might be no need to estimate more variables using spectroscopy, rather few and key properties could be of interest and used to understand the physio-chemical makeup of the stockpiled soils.

The results of pH estimation are consistent with those reported by Bonnet *et al.* (2015) and Islam *et al*. (2003). Bonnet *et al.,* (2015) reported R^2 of 0.70 and RPD of 1.64. This study recorded R^2 values of (0.77 and RPD=2.01 untransformed spectra, 0.64

and RPD=1.53 FD and 0.79 and RPD=2.08 Log (1/R) respectively). Terhoeven-Urselmans *et al.* (2010) also recorded correlation coefficients of 0.80, RMSE=0.75 and RPD=2.21 for pH using MIR spectroscopy and first derivatives transformation. For pH, the Log (1/R) transformation yielded higher estimation accuracy. Log (1/R) is transformation known as diffusion reflectance that enhances absorption of features for soil properties (Mashimbye *et al.,* 2012).

Ca was among the most accurately estimated soil property, especially using Log transformation spectra (R^2=0.69, RPD=1.79). The R^2 found in this study were lower than that reported by Shepherd and Walsh (2002) and Chang *et al.,* (2001) (R^2=0.75) but are consistent with the one reported by Mashimbye *et al*., (2012) from the South African soils (R^2=0.62). In this study, Log transformation was important in estimating Ca. This demonstrates the potential to estimate Ca from soil properties using Reflectance Spectroscopy.

Organic carbon was poorly predicted with untransformed spectra yielding (R^2=0.23 and RPD=1.14) as compared to FD and Log (1/R) transformation. The performance of Log (1/R) (R^2=0.16, and RPD=1.06) and FD (R^2=0.14 and RPD=1.07) yielded results that contradicts finding by Peng *et al*. (2014). Peng *et al*., (2014) reported (R2=0.60 and RPD=1.59) untransformed spectra, (R^2=0.52, and RPD=1.43) Log (1/R) and (R^2=0.55 and RPD=1.47) FD. Other studies on OC contents estimation using Vis-NIR spectra (Islam *et al.,* 2003; Viscarra-Rossel, 2007; and Urselmans *et al.,* 2010) found the R^2 values in a range of R^2=0.57 to 0.91. The predictive performance of the soil organic carbon models in this study was found to be poor according to the evaluation standard of Viscarra-Rossel *et al*. (2006). The poor predictive performance is attributed to the nature of soil used. Stockpile soils were found to have low organic carbon content (mean value = 0.43 %). According to Nicholas (2004), it is unlikely for spectroscopy to provide quantitative data where the property being predicted has low concentration in the soil solution.

For the soluble Mg, this study found that the R^2 using PLSR was poor compared to that obtained by (Janik *et al.,* 1998; Mashimbye *et al.,* 2012; and Peng *et al.,* 2014). The performance of PLSR and original spectra was higher than those of FD and Log (1/R) but comparably lower than what was achieved by Janik *et al*. (1998) (R^2= 0.76), Genu and Demattê (2011) (R^2 =0.68) and Mashimbye *et al*. (2012) (R^2=0.78). The difference in results can be due to soil stockpiling as soil nutrients are leached during stockpiling resulting in low concentrations of soluble nutrients (Ghose, 2004).

In this study, Na was poorly estimated using Reflectance Spectroscopy. The R^2 for exchangeable Na ranged from 0.23 to 0.29. The results of this study are comparable to those of Janik *et al.* (1998), who recorded R^2 of 0.33. The R^2 value obtained in this study is higher than that recorded by Bikindou *et al*., (2012) and Chang *et al*. (2001). Bikindou *et al*., (2012) and Chang *et al*., (2001) reported R^2 of 0.12 and 0.09 respectively. The reason for poor prediction can be attributed to low Na concentrations in the soil that could have been caused by leaching. According to Ghose (2004), stockpiled soils experience excessive leaching and lose of basic exchangeable cations.

Predictive models for K were poor (R^2 = 0.23 to 0.28). This is consistent with previous studies. Janik *et al.,* (1998) reported an (R^2= 0.34) using MIR and PLSR. According to Janik *et al.* (1998), spectroscopy is unlikely to provide quantitative data where the property being predicted is low in concentration. In this study, the mean value of K was found to be 0.860cmol/kg, which is low to moderate according to Nicholas (2004). The low concentration of K in the soil is attributed to the fact that K is affected by its high mobility in the soil solution, which easily varies K content, thus providing less certain prediction results (Bonnet *et al.,* 2015). Regarding P, the PLSR predictive models were poor. While the R^2 values for untransformed spectra, FD and Log (1/R) were 0.30, 0.33 and 0.29 respectively. The R^2 for P obtained in this study is lower than those obtained by Genu and Demattê (2011); Dhawale *et al*. (2013); Franceschini *et al*. (2015), which were R^2 of 0.70, 0.84 and 0.79 respectively.

The differences are presumed to be due to the use of different statistical techniques and different instruments. In this study, Analytical Spectral Device (ASD) FieldSpec 3 spectrometer and PLSR were used while Genu and Demattê (2011); Dhawale *et al.* (2013). Franceschini *et al.,* (2015) used airborne hyperspectral sensor and PLSR, P4000 dual type spectrophotometer instrument and PLSR and Infra-Red Intelligent Spectroradiometer (IRIS) sensor and Multiple Linear Regression Analysis respectively. Clay% was poorly estimated in this study at R^2 0.47. Gomez *et al.*

(2008); Lee *et al.* (2009); and Franceschini *et al.,* (2015) obtained R^2 = of 0.83, 0.85 and 0.80 using cross validation method and PLSR respectively. The differences are presumed to be due to the use of different instruments and statistical methods.

5.6.3. Spectral Bands and Region Important in Estimation Soil Properties

The spectral regions critical for estimating Ca and pH are presented in this section. The best performing bands for field-based predictions of pH and soluble Ca were found to be in SWIR and the findings were related to that of Mashimbye *et al*. (2012). The VIP scores for prediction models for soil pH show that the most important spectral bands used by the PLSR prediction model are centred near 1900nm for untransformed spectra, 986nm for FD and 2499 for Log (1/R) transformed spectra.

A study conducted by Paz-Kagan *et al*., (2015) mapping the Spectral Soil Quality Index (SSQI) using airborne imaging spectroscopy at Schäfertal Site, Germany recorded that the highest VIP scores for pH are associated with absorption bands near 1000 and 1900nm. Those wavelengths are consistent with the wavelengths recorded in this study. The other wavelength recorded in this study that is associated with soil pH was found near 2499nm. According to Clark (1999), the wavelength near 2500nm are associated with carbonates in the soil, hence, in this study, high pH and low Na concentration were recorded. The VIP scores for prediction of Ca models show that the most important spectral domains are found in SWIR region near 2475 and 2480nm. The wavelengths found in this study are consistent with the findings by Lee *et al*. (2011) that show that for Ca, the wavelengths near 2460nm were identified by PLSR analyses. High VIP scores for Ca are found near 2475nm and 2480, which is around 20nm to the known Ca absorbance waveband.

5.7. Conclusion

The aim of the study was to evaluate the feasibility of Reflectance Spectroscopy to estimate physical and chemical properties of the stockpile soils. Spectral reflectance for dried, crushed and sieved soil samples were measured under controlled conditions using ASD Fieldspec 3 spectrometer leading to the following observations:

- PLSR predictive models for clay content, Ca, Mg, K, Na, pH and OC were found to be poor;

- Ca and pH were accurately predicted;
- The results showed that PLSR can be used to predict soil pH and Ca of coal-mine stockpile soils;
- The most important bands were for Ca and pH were found in the NIR and SWIR;
- Predictive models using PLSR can be efficiently used as a tool for estimation of soil pH and Ca for coal-mine stockpile soils;
- This study is one of the few if not the only study to use Reflectance Spectroscopy-PLSR to estimate properties of coal-mine stockpile soils and it shows that a potential to use Reflectance Spectroscopy to assess pH and Ca in stockpile soils.

The findings of this study would be useful to provide information on use of Reflectance Spectroscopy to estimate properties of coal-mine stockpile soils. Further research with a large number of sample and different study sites will be required to quantify the findings of this study.

CHAPTER 6

ESTIMATING THE EFFECT OF COAL-MINE SOIL STOCKPILING ON FOLIAR NITROGEN AND PHOSPHORUS CONTENT USING PARTLIAL LEAST SQUARE REGRESSION AND REFLECTANCE SPECTROSCOPY

6.1. Introduction

In open-cast mines, coal evacuation is done by open excavation of the land and approaching the coal strata by excavating the entire earth mass lying above the coal starta (Ghose, 2004). This process of topsoil stockpiling in most cases results in drastic alternations in soil geochemical cycles and often lead to land degradation, with adverse changes in soil textural and structural attributes (Abdul-Kareem & McRae, 1984). Other effects of topsoil stockpiling are reduction in succession of most of the pre-existing vegetation. Plant fragments from pre-existing vegetation are lost or greatly reduced. The seed bank is also reduced, and what does remain must compete for the reduced nutrients with microbes (Strohmayer, 1999). These microbes become highly competitive as the base of stockpiles become anaerobic. In addition to a loss in the breakdown of organic matter, stockpiling causes many other deleterious changes including a marked drop in the earthworm population that, in turn, affects soil nutrients, bulk density and water holding capacity (Johnson *et al.,* 1991; and Rai *et al.,* 2014).

The process of topsoil stockpiling affects the physical, chemical and biological properties of the soil. Consequently, these soils have lower soil aggregate stability, lower infiltration rates, reduced water holding capacity, and a greater capacity to resist root extension (Chapman *et al.,* 1994), all of which inhibit the potential for plant growth. The soil chemical properties of the soil also deteriorate when topsoil is stockpiled. Oxygen becomes limiting and anaerobic environment is created. As a result, large quantities of nitrogen are lost to the atmosphere as gaseous N_2 or N_2O, through the process of de-nitrification. Loss of nitrogen and other nutrients by leaching also occurs, thus reducing available nutrients for vegetation growth and thereby inducing stress (Davies *et al.,* 1995).

Estimation of foliar biochemicals provides information that enables the assessment of ecosystem functioning, for example, nutrient cycling, gas exchange and plant productivity (Ollinger *et al.,* 2002). Foliar biochemicals such as nitrogen (N) and phosphorus (P) are primary indicator of physiological processes such as photosynthesis, leaf respiration and growth rates (Gusewell, 2004). Therefore, leaf N and P can be used as an indicator of vegetation stress or status (Ramoelo *et al*. 2015).

To estimate foliar N and P various techniques have been used for different ecosystems including agriculture (Bogrekci & Lee, 2005; and Mutanga *et al*., 2005). Several researchers (Mutanga & Kumar, 2007; Skidmore *et al.,* 2010; and Ramoelo *et al.,* 2011) have used spectroscopy and Remote Sensing techniques to estimate foliar biochemical. Spectroscopy is among less expensive, rapid and user-friendly techniques for quantitative foliar biochemical analysis as compared to traditional wet chemistry techniques that maybe restrictive due to high costs and labours (Bogrekci & Lee, 2005). The premise to estimate leaf N and P is based on the assumption that is a positive relationship between leaf N and chlorophyll concentrations (Yoder & Pedigrew, 1995). To achieve the latter, vegetation indices based on the red edge band correlated with leaf N to develop a simple leaf predictive models (Ramoelo *et al.,* 2012, 2015). The red edge band is a region of the spectra that shows an abrupt change between red and Near-InfraRed, and it is known to relate to leaf N and chlorophyll. The other approach is to integrate Remote Sensing indicators and environmental variables to improve the estimation of leaf N and P (see Ramoelo *et al.,* 2012; 2013; 2014). In spectroscopy, the use of absorption features are commonly used (Curran 1989; and Ramoelo *et al.,* 2013).

Most of the spectral absorption features that have been identified and used for N estimation are located in the Near InfraRed (NIR) and ShortWave InfraRed (SWIR). For example, N has absorption features centred at 430nm, 460nm, 640nm, 660nm, 910nm, 1510nm, 1940nm, 2060nm, 2180nm, 2300nm, 2350nm, dominating in the SWIR region (Curran, 1989). The main leaf biochemicals absorbing in the SWIR region (1000-2500 nm) include lignin, cellulose, starch and proteins (Curran, 1989; Kokaly and Clark, 1999; and Kumar *et al.,* 2001). For estimating leaf P, absorption features for starch are often used (Knox *et al.,* 2012; and Ramoelo *et al.,* 2013). Leaf P does not have a well-defined absorption features because it often occurs in small quantities within the plant. Most of the studies conducted focused on estimation of foliar N and P growing on undisturbed soils, few if not none has focused of the effect of soil stockpiling on grass quality.

6.2 Objectives

Specific objectives were, namely, to:

1. Determine if nutrient content of grass sampled from stockpile and unmined sites differ;
2. Determine the ability of spectral transformation to enhance prediction of foliar N and P;
3. Investigate what spectral bands are important in predicting N and P; and
4. Investigate what spectral regions are more dominant in predicting N and P of grass sampled from coal-mine stockpile and unmined soils.

6.3. Hypotheses

1. There is no difference in nutrient content of grass sampled from unmined and mined soils.
2. Spectral transformation can enhance prediction of foliar N and P can be determined
3. No spectral bands are important for prediction of foliar N and P.
4. No spectral regions are dominant in predicting foliar N and P of grass sampled from coal-mine stockpile and unmined soils.

6.4. Materials and Methods

6.4.1. Locality

Grass samples were collected from an open-cast coal mine and its adjacent unmined site located approximately 8 kilometres south of Witbank in Mpumalanga Province of South Africa. The climate of the area can be regarded as having warm, moist summers and cool to cold dry winters with frost. On average, 85% of the annual average rainfall of 730mm falls in the growing season (October to March).

6.4.2. Grass Sampling

Grass samples were collected from coal-mine stockpile soil and the unmined plot adjacent to the mining site (Table 6.1). The following dominant grass species were identified: *Cynodon dactylon*, *Eragrostis plana*, *Eragrostis. Curvula*, *Panicum coloratum* and *Aristida bipartite*. A line transect sampling design was used to collect field data (Fewster *et al.,* 2005) at 25 meter intervals. Site discrimination was based on the nature of soils in the study sites, e.g., stockpile (anthropogenic soils) and unmined (natural soils). Geographical Positioning System (GPS) co-ordinates were recorded at every sampling point. A total of 100 samples were collected at each site.

Table 6.1. Soil Properties of the Study Sites

Properties	Coal-mine stockpile soil site	Unmined soil site
Na cmol(+) kg^{-1}	0.07	0.04
K cmol(+) kg^{-1}	0.18	0.74
Ca cmol(+) kg^{-1}	0.74	4.83
Mg cmol(+) kg^{-1}	0.45	1.79
pH (H_2O)	5.67	6.4
Org C (%)	0.45	2.86
Al cmol (+) kg^{-1}	0.72	0.37
Total N (%)	0.04	0.18
P (mg/kg)	8.99	23.47
Clay%	18.34	22.6

OC= Organic Carbon

6.4.3. Chemical Analysis

The dried grass samples were sent to the laboratory for chemical analysis. N was analysed using the acid digestion method, using sulphuric acid to retrieve foliar N concentration and P was determined using the acid digestion technique were perchloric and nitric acids were used for foliar P concentration retrieval (Giron, 1973; and Grasshoff *et al*. 1983). Chemically analysed N and P are henceforth referred to as observed N and P content.

6.4.4. Spectral Measurements

An Analytical Spectral Device (ASD) FieldSpec spectrometer was used to acquire spectral signatures of the same grass samples that were used for laboratory analysis. Spectral data were collected in a darkroom to ensure stable atmospheric and uniform illumination conditions. The instrument covers the visible to short-wave infrared wavelength range (350-2500nm). The spectrometer has a sampling interval of 1.4nm for the region 350 to 1000nm and 2nm for the region 1000 to 2500 nm with a spectral resolution of 3 and 10nm, respectively. Darkroom conditions were used to eliminate diffuse light conditions and to ensure that light conditions are similar to allow comparison. A halogen lamp (Lowel Light Pro, JCV 14.5V-50WC) was used as a source of light. The lamp was fixed at a nadir position 20 cm above the target.

To prevent contamination of one sample by another, each sample was placed on a separate black plastic background before making spectral signature measurements. Grass sample was spread on the plate to completely cover the plate's surface. The grass was flattened on top to form an even surface. Reflectance calibration was done using a white reference. The white reference is a calibrated white spectralon with a near 100% diffuse (Lambertian) reference reflectance panel made from a sintered poly-tetra-flourethylene based material. Calibration was done before taking measurements of each of the samples. Spectral signatures were taken at a height of approximately 15cm above the target at approximately 15º off nadir to minimize the effect of bidirectional reflectance. Each sample was rotated five times when the spectra were measured to minimize bidirectional reflectance effects (Ramoelo *et al.,* 2011; and Mashimbye *et al.,* 2012).

6.4.5. Data Analysis

Descriptive statistics of grasses from stockpiles and unmined areas were computed. Mean values of N and P, standard deviation as well as analysis of variance of the same elements were computed using Statistix 10.0. Predictive models were computed using untransformed individual reflectance, First Derivative Reflectance (FD), Log transformed spectra Log (1/R). Commonly used spectral transformation techniques such as Log transformed spectra Log (1/R) and first derivative were computed. Log (1/R) was determined by calculating a Log function of the spectral reflectance's reciprocal (Hruschka, 1987; Yoder & Pettigrew-Crosby, 1995; and Fourty & Baret, 1998). The first derivative of the spectral reflectance was derived using a first-difference approach. A first-difference transformation of the reflectance spectrum calculates differences in reflectance between adjacent wavebands. More details on this can be found in Dawson and Curran (1998).

6.4.6. Regression Analysis and Bootstrapping

Total number of 200 samples was used for regression. Partial Least Square Regression (PLSR) was used to due to its popularity to this type of analysis (Ehsani *et al*., 1999; Martens & Naes, 2001; and Viscarra Rossel, 2008). To compare the retrieval accuracy of foliar N and P using the various spectral transformation techniques, a bootstrapping approach was used (Efron, 1983). The advantage of bootstrapping is that it can be used efficiently when only a limited number of samples are available.

Bootstrapping was used as an alternative to the split method since it iteratively resamples the data set to be used for model development, making it a good technique for assessing model accuracy (Verbyla & Litvaitis, 1989). In this study, PLSR was integrated with bootstrapping to derive calibrated and validated models. To integrate PLSR and bootstrapping, bagging-PLSR was implemented using the Parles 3.1 software (Viscarra Rossel, 2007, 2008).

Using bagging-PLSR, independent or predictor variables were mean-centred to normalize them prior to further statistical analysis. The Leave-One-Out Cross Validation, as defined by the lowest root mean square error (RMSE), was used to determine the optimal number of factors or latent variables to be used for model development (Cho *et al*., 2007; Darvishzadeh *et al*., 2008; and Viscarra Rossel, 2008). This Optimal number of factors was then used for model development and validation with the number of bootstraps equalling 1000. The retrieval accuracy was defined by the bootstrapped mean of the Coefficient of Determination (R^2) and the RMSE. The confidence interval at a 95% confidence level was calculated for both R^2 and RMSE (Ramoelo *et al.,* 2011). The importance of a given waveband in the estimation of foliar N and P concentration of grass samples was assessed by the variable Importance in the Projection (VIP) score (Wold *et al.,* 2001). The VIP gives a summary of the importance of an X-variable (waveband) for both y and X, and is calculated using the weighted sum of squares of the PLS-weights (w), with the weights calculated from the y-variance of each PLS factor. A large VIP score, like PLS regression coefficient (βw), indicates an important X-variable (waveband). VIP scores provide a measure of importance of each explanatory variable or predictor (Wold *et al.,* 2001), and as a measure of performance when multi collinearity exists among variables, as evaluated by Chong and Jun (2005) through computer simulation experiment.

6.5 Results

6.5.1. Descriptive Statistics and Spectral Features

Figure 6.1 shows original reflectance of grass samples from coal-mine stockpile site and unmined sites. The reflectance increases in the red/infrared boundary near

700nm. The reflectance is nearly constant from 1100 to 1300nm and then decreases for the longer wavelengths. Results of the descriptive statistics of foliar N and P from grass sampled from coal-mine stockpile soils and unmined site are presented in Table 6.2. Grass samples from unmined site had significantly higher mean values for N and P as compared to those from coal-mine soil stockpile site. There was significant difference ($p<0.05$) between mean values of measured N and P from both study sites. N concentration was 10.50mg/g for grass sampled from coal-mine stockpile soil site and 17.20mg/g for grass sampled from unmined soil site. N concentration for grass sampled from stockpile soil was 38.95% lower, relative to grass from unmined site. P concentration was 0.66mg/g for grass sampled from coal-mine stockpile soil site and 1.32mg/g for grass sampled from unmined site. P concentration for grass sampled from stockpile soil was 50.00% lower, relative to grass from unmined site. The results show that there is high concentration of N than P on grass samples from both stockpile soils and unmined soils.

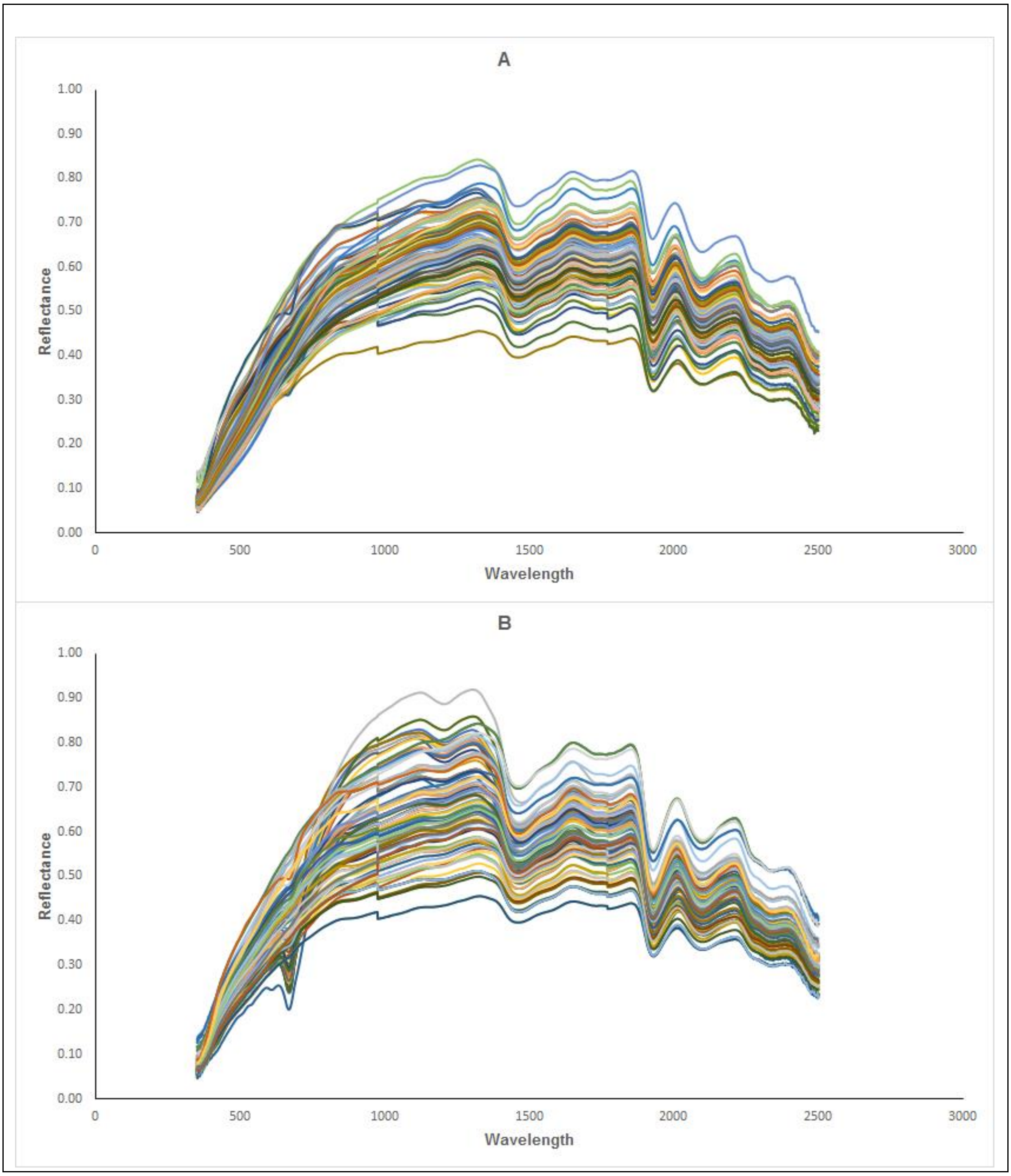

Figure 6.1: Untransformed Spectral Reflectance of All the Grass Samples; *A= Soil Stockpile Site, B= Unmined Site*

Table 6.2: Descriptive Statistics of Foliar N and P from Stockpile Site and Unmined Site

Measured Variable	Sampling site	Mean	C.V	Min	Max
N (mg/g)	Unmined	17.20[a]	26.94	1.03	25.80
	Stockpile site	10.5[b]	21.93	0.58	17.30
P (≤0.05)		0.00			
P (mg/g)	Unmined	1.32[a]	41.35	0.70	2.68
	Stockpile site	0.66[b]	20.00	0.38	0.97
P (≤0.05)		0.00			

‡ a, b indicates significant difference. Within rows, means followed by the same letter are not significantly different (P=0.05) using Duncan's multiple range test. SD=Standard derivative, C. V=coefficient of variance, Min=Minimum, Max=Maximum. n=100

6.5.2. Estimating Grass Foliar N and P Concentration Using PLSR and Various Transformation Techniques

Predictive models of foliar N and P concentration were examined using Partial Least-Squares Regression (PLSR). PLSR analysis yielded accurate prediction for foliar N from both soil stockpile and unmined sites (Table 6.3; Figure 6.2). All models for foliar N possessed a high Coefficient of Determination (R^2). FD yielded highest predictive models for foliar N in both sites (soil stockpile site R^2=0.88, RMSE=0.087, unmined site R^2=0.93, RMSE=0.071).

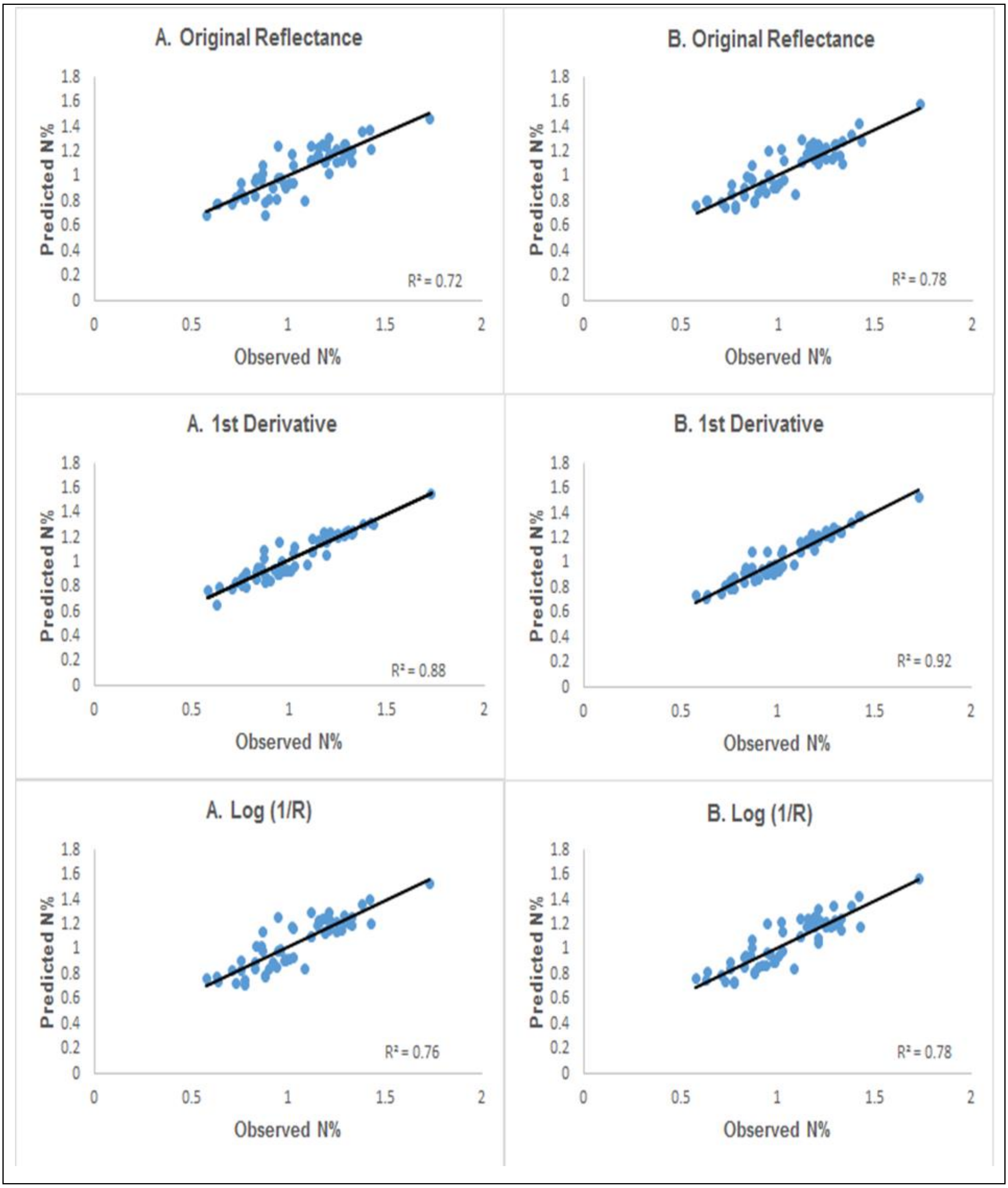

Figure 6.2: Scatterplots of Measured and Predicted Values for Foliar N Based on PLSR Prediction; *A= Soil Stockpile Site, B= Unmined Site*

Table 6.3. Performance of PLSR Models for Estimating Foliar N and P Concentration Using Different Spectral Transformation from Coal Mine Stockpile Soil and Unmined Sites

		Stockpile soil site					Unmined soil site				
Spectra	variables	R^2	RMSE	95% LCI	95% UCI	No. of factors	R^2	RMSE	95% LCI	95% UCI	No. of factors
R	N (%)	0.72	0.120	0.102	0.147	8	0.78	0.112	0.092	0.132	6
	P (mg/kg)	0.47	94.84	80.19	116.02	8	0.55	87.53	74.02	107.08	8
FD	N (%)	0.88	0.087	0.074	0.106	5	0.93	0.071	0.060	0.087	5
	P (mg/kg)	0.71	74.26	62.79	98.45	7	0.87	55.14	46.63	67.46	6
Log (1/R)	N (%)	0.76	0.113	0.095	0.138	7	0.78	0.108	0.091	0.132	7
	P (mg/kg)	0.49	93.43	79.01	114.30	8	0.59	84.65	71.58	103.56	7

FD= 1st derivative, R= Original reflectance.

There was high foliar N and P concentration predictive models for grass sampled from unmined site as compared to soil stockpile sites (Table 6.3). Original spectra and Log (1/R) spectra of grasses sampled from coal-mine stockpile soils showed poor prediction for foliar P (R^2=0.47, RMSE=94.84 original spectra; R^2=0.49, RMSE=93.43 Log (1/R)). FD yielded accurate predictive model for foliar P from grasses sampled from stockpile soils (R^2=0.71, RMSE=74.26). Grasses sampled from unmined site yielded accurate predictions for foliar P concentration. FD yielded the highest predictive model for foliar P, followed by Log (1/R) transformation (Table 6.3; Figure 6.3).

Variable Importance for Projection (VIP) and regions for estimation of foliar N and P concentration VIP scores revealed the highest for N are centred near 1978nm for original reflectance, 1770nm for FD and 672nm for Log (1/R) transformed spectra for grass sampled from stockpile soils. For grasses sampled from unmined soils, the highest VIP scores for N are centred near 676nm for original reflectance, 1770nm for FD and 924nm for Log (1/R) transformed spectra. For P concentration, the highest VIP scores are centred near 1001nm for original reflectance, 976nm for FD and 676nm for Log (1/R) transformed spectra for grasses sampled from stockpile soils. For grasses sampled on unmined soils, the highest VIP scores for P are centred near 1197nm for original reflectance, 1770nm for FD and 1079nm for Log (1/R) transformed spectra (Table 6.4).

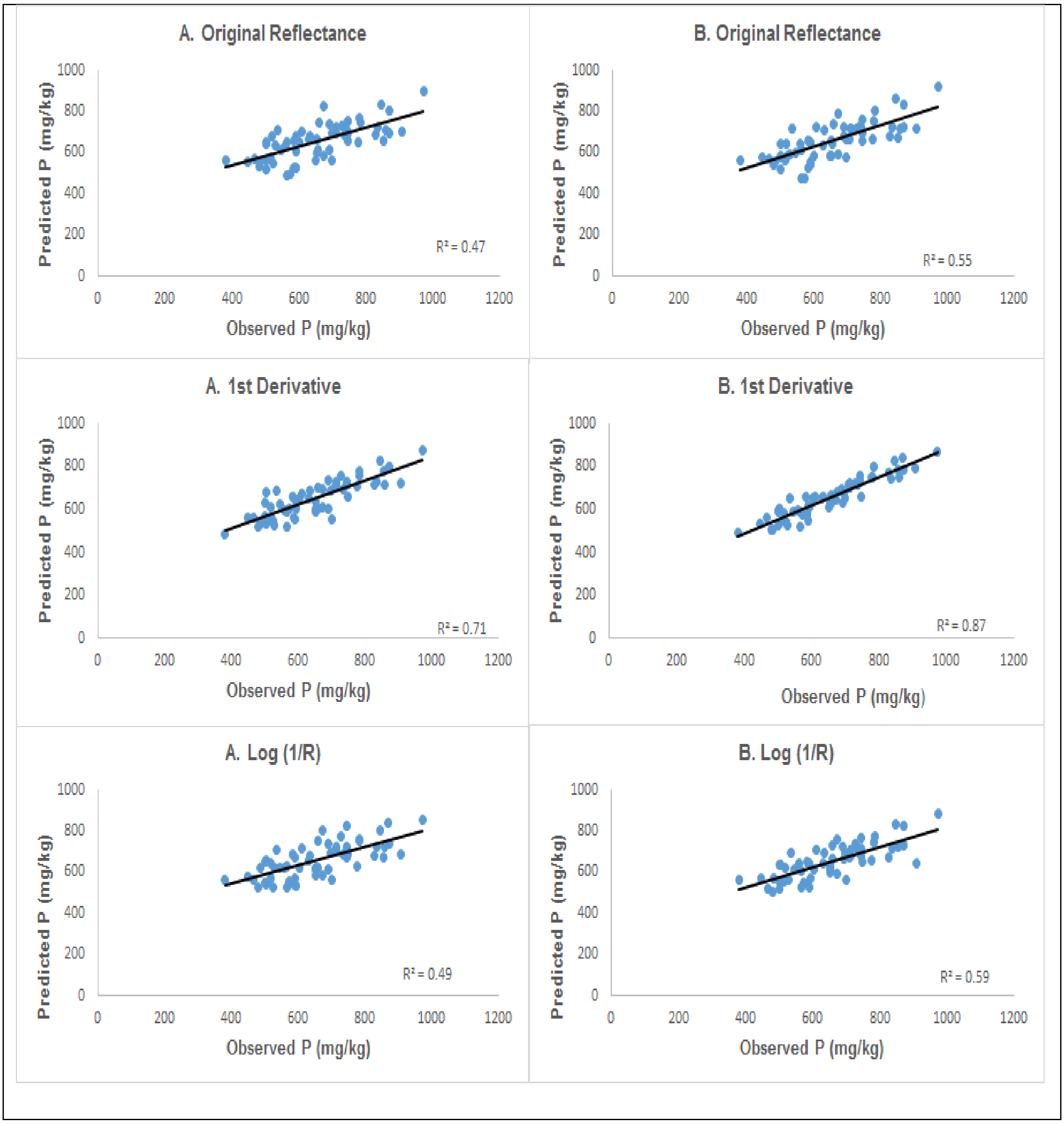

Figure 6.3: Scatterplots of Measured and Predicted Values for Foliar P Based on PLSR Prediction; *A= Stockpile Soil Site, B= Unmined Soil Site*

Table 6.4. Highest Variable Importance in the Projection (VIP) Scores for Foliar N and P Estimation

		Stockpile soil site			Unmined soil site		
Spectra	variables	VIP	λ (nm)	Region	VIP	λ (nm)	Region
R	N (%)	1.54	1978	SWIR	3.63	676	Visible
	P (mg/kg)	6.93	1001	NIR	9.59	1197	NIR
FD	N (%)	17.72	1770	SWIR	28.91	1770	SWIR
	P (mg/kg)	19.47	976	NIR	16.91	1770	SWIR
Log (1/R)	N (%)	2.97	672	Visible	2.57	924	NIR
	P (mg/kg)	7.64	676	Visible	8.04	1079	NIR

FD= 1st derivative, R= Original reflectance;

6.6 Discussion

The study was initiated to estimate the effect of coal-mine stockpile soils on foliar N and P concentration using PLSR and Reflectance Spectroscopy. The specific objectives were, namely, to: (1) determine if nutrient content of grass sampled from stockpile and unmined sites differ; (2) determine the ability of spectral transformation to enhance prediction of foliar N and P; (3) investigate what spectral bands are important in predicting N and P; and (4) investigate what spectral regions are more dominant in predicting N and P concentration of grass sampled from coal-mine stockpile and unmined soils.

6.6.1. Foliar N and P Content

Foliar nutrient contents are widely recognized as an effective measure of the nutritional status of plants because leaves are the primary sites of physiological activities including photosynthesis, respiration, transpiration, gas exchange and nutrient storage (Dogan *et al.*, 2010; and Demirayak *et al.,* 2011). The results from chemical analysis of foliar N and P show that grass sampled from stockpile soils have low mean values than those sampled from unmined soils. According to Davies *et al.* (1995), the chemical properties of the soil deteriorate when topsoil is stockpiled. Oxygen becomes limiting and anaerobic environment is created. As a result, large quantities of nitrogen are lost to the atmosphere as gaseous N_2 or N_2O, through the process of de-nitrification. Loss of nitrogen and other nutrients by leaching also occurs, reducing available nutrients for vegetation growth. The mean value for foliar N from grass sampled from stockpile soils was low according to threshold set by Paarlahti et al., (1971) and Reinikainen *et al.* (1998). The authors indicated that threshold (mg/g) of (< 12) poor, (12 to13) adequate and (13 to18) is optimal foliar N concentration. The mean value for foliar N from grass sampled from unmined site was optimal according to threshold set by Paarlahti *et al.* (1971) and Reinikainen *et al.* (1998). According to Moilanen *et al.* (2010), the more fertile the site, the higher the foliar N concentration. The mean value for P concentration from grass sampled from stockpile soils was also low according to threshold set by Paarlahti *et al.* (1971) and Reinikainen *et al.* (1998). They indicated that threshold (mg/g) of (<1.3) poor, (1.3 to 1.6) adequate and (1.6 to 2.2) optimal foliar N concentration. The mean value for foliar P from grass sampled from unmined site was adequate according to threshold set by Paarlahti *et al.* (1971) and Reinikainen *et al.* (1998).

6.6.2. Original Reflectance Characteristics

The spectral reflectance is typical of vegetation spectra as it follows the basic shape as observed by other researchers (Card *et al.,* 1988; Curran, 1989; Elvidge, 1990; and McLellan *et al.,* 1991). The wavelength regions in which the grass components have strong absorption features shows that the reflectance increase around 550nm (green) and is low around 400-450nm (blue region) and near 660-680nm (red region). This is attributed to pigments absorption (Kokaly *et al.,* 2007). In this study, reflectance increased above 700nm-1300nm, which is consistent with finding by (Curran, 1989, and McLellan *et al.,* 1991). The high reflectance results from an increased amount of light scattering at cell-wall interfaces because of a change in the index of refraction, the absence of pigment absorptions, and the weakening of overtone absorption of water in leaves at those wavelengths. The absorption feature near 700nm is the results of electron transitions in chlorophyll (Curran, 1989). There was a strong absorption feature around 1900nm in both grass sampled from unmined and coal-mine stockpile soil sites. This is attributed to the bending and stretching of the O-H bond in water and other chemicals (Curran, 1989).

6.6.3. Foliar N and P Concentration Estimation Using PLSR and Various Spectral Transformation Techniques

Foliar nitrogen concentration was estimated with high accuracy on grass sampled from unmined and coalmine stockpile soils. The RMSE for N concentration prediction were found to be low ranging from 0.071 to 0.120. Low RMSE values verify reliability of the models (Liu *et al.,* 2003). The original reflectance for estimation of foliar N concentration had R^2= 0.72 for grasses sampled on stockpile soils and R^2= 0.78 for grasses sampled on unmined soils. The R^2 found in this study is higher than the R^2 recorded by Ramoelo *et al.,* (2011). Ramoelo *et al.,* (2011) recorded R^2 = 0.60 (original reflectance) for N from Savannah grass species using NIR-PLSR. This difference can be attributed to the kind of grass species and the time of sampling. In this study, the sampling took place in the beginning of summer.

The findings of this study are consistent with those of Pellissier *et al.,* (2015) and Wang *et al.* (2015). Pellissier *et al.,* (2015) recorded R^2=0.76 using field based imaging spectrometer and PLSR while Wang *et al.* (2015) recorded R^2=0.75 using PLSR. The study by Ramoelo *et al.,* (2011) recorded R^2=0.59 for FD and R^2=0.62 for Log (1/R) using PLSR. In this study, R^2=0.88 and 0.92 were recorded (for FD from grasses sampled from coal-mine stockpile soils and unmined soils respectively) using PLSR. The R^2 results recorded in this study are consistent with the findings by Kawamura *et al.* (2010) and Serbin *et al.,* (2012) who recorded R^2=0.90 using FD and PLSR on pasture canopy and R^2= 0.89 using PLSR- leave-one-out (LOO) cross-validation procedure for glasshouse leaf nitrogen concentration respectively. Curran *et al*. (2001) recorded R^2=0.96 using FD and stepwise regression. Log (1/R) for N concentration prediction yielded R^2=0.76 and 0.78 for grass sampled from coal-mine stockpile soils and unmined soils respectively. The R^2 recorded in this study is higher than that recorded by Ramoelo *et al.* (2011). Ramoelo *et al.,* (2011) recorded R^2=0.62 (Log (1/R)) for N concentration estimation using PLSR from savannah grass and Serrano *et al.,* (2002) recorded R^2 range (0.39-0.45) from data collected using Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) analysed using multiple stepwise regression. The study conducted by Ramoelo *et al*., (2011) recorded high R^2 value for N estimation based on Log (1/R) transformation as compared to FD and original reflectance. Yoder and Pettigrew-Crosby (1995) showed Log (1/R) performed accurately estimating N concentrations, compared to reflectance.

Similar results were also attained by Fourty and Baret (1998). They argued that by transforming reflectance to absorbance Log (1/R) values, the accuracy of biochemical estimates was improved. Log (1/R) is likely to be used instead of the original reflectance because of the linear relation between the absorbing components and its contribution to the Log (1/R) value at the wavelength absorbed (Hruschka, 1987). But, in this study, FD performed better that Log (1/R), this can be attributed to the fact that FD explore information that is often suppressed by other standard analytical methods. The study conducted by Ruano-Ramos *et al*., (1999) showed no significant difference between Log(1/R) and FD values as it recorded R^2= 0.97 (Log (1/R)) and R^2=0.98 (FD).

Grass P concentration for grass sampled from stockpile soils was poorly estimated, with the original reflectance recording Coefficient of Determination of R^2= 0.47 and that of Log (1/R) transformation as R^2=0.49.

The findings of this study are consistent with findings by Ramoelo *et al.* (2011). Ramoelo *et al.* (2011) recorded R^2= 0.47 (Log (1/R)) for P concentration from Savannah grass species using NIR-PLSR. Poor prediction of grass foliar P was recorded by several researchers, e.g., Brogrekci and Lee (2005); Serusi (2010); Knox *et al.* (2012); and Özyigit and Bilgen (2013). They recorded R^2= (0.34 to 0.43) using different statistical methods. For grass sampled on unmined soils, original reflectance and Log (1/R) yielded fairly predictive models. The R^2 values were 0.55 and 0.59 respectively. The findings are consistent with findings by Chadwick and Asner (2016). They recorded R^2 = 0.53 using PLSR from data collected through airborne high fidelity imaging spectroscopy (HiFIS). FD yielded accurate prediction for grasses sampled from coal-mine stockpile and unmined soils. R^2 = 0.71 and 0.87 were recorded respectively. The Coefficient of Determination found in this study is higher than that found by Ramoelo *et al*. (2011) (R^2=0.17) using FD and PLSR. R^2=0.71 from grass sampled coal-mine stockpile soils is consistent with recorded by Wang *et al*. (2015) (R^2 = 0.69), which was Coefficient of Determination obtained using support vector regression. Curran *et al*., (2001) recorded R^2 = 0.78 using FD method. Mutanga and Skidmore (2003) recorded R^2 = 0.76 using continuum removed derivative reflectance method. The findings of Curran *et al*. (2001), Mutanga and Skidmore (2003) were consistent with of the findings of this study.

FD yielded high model prediction accuracy than Log (1/R) and original reflectance in both grass N and P content estimation (Table 6.3). This can be explained by the ability of FD to eliminate background signals and calculates differences in reflectance between adjacent wavebands (Demetriades-Shah *et al*., 1990; and Tsai & Philpot, 1998). Foliar N concentration was accurately predicted in both study sites compared to P. In this study, the total concentration of phosphorus was low compared to N concentration. According to Seastedt (1988), the total concentration of phosphorus in plants is low. Detection of phosphorus concentrations from spectra has not been studied to the same extent as compounds such as nitrogen, cellulose, and water (Curran, 1989; and Kokaly & Clark, 1999). Features that would be directly linked to phosphorus would likely be undetectable due to the overlaps from features found in higher concentrations within plants, e.g., water, cellulose, and nitrogen (Kokaly *et al.,* 2009). Foliar N and P concentration for grass sampled from unmined soils were highly predicted than those of grass sampled from coal-mine stockpile soils. This can be attributed to soil nutrient status of the study sites. Unmined soils have high nutrients content that stockpile soils (Table 1). According to Vogel (1981), stockpile soils are often deficient in N and P, especially when associated organic materials were removed and buried during stockpiling.

The study shows that the pre-processed spectra obtained better predictive results compared with the raw spectral reflectance. Similar results have been reported in many studies, which also confirmed the effects of pre-processing methods (Log (1/R) and first derivative) on improving the biochemical component estimations of plants (Bogrekci & Lee 2005; Rossel 2008; Serusi, 2010; Ramoelo *et al.,* 2011; and Özyigit & Bilgen, 2013).

6.6.4. Spectral Bands and Regions Important in Estimation of Foliar N and P Concentration

The spectral regions critical for estimation of foliar N and P concentration of grass samples are presented in this section. The best performing bands for predictions of foliar N concentration of grass sampled from stockpile soils were found to be in these regions: visible (672nm) for Log (1/R) transformation and ShortWave InfraRed (1770nm) for FD (1978nm) for original reflectance. For grass sampled from unmined soils, the highest VIP scores for prediction of N concentration were found to be in the visible (676 nm) for original reflectance, Near InfraRed (924nm) for Log (1/R) and ShortWave InfraRed (1770nm) for FD.

For dried leaf, wavelengths that are most relatable to nitrogen concentration occurred in association with the absorption spectra of plant pigments, i.e., the red-edge position (670–780nm). The 672 and 676nm wavelengths that yielded high VIP scores for N concentration are found near 660nm, which is a known wavelength for N concentration absorption (Curran, 1989; and Kumar *et al.,* 2001). Lamb *et al.* (2002) reported that leaf reflectance in red-edge range of wavelengths (690–740nm) could be used to predict leaf nitrogen concentration and total nitrogen content of ryegrass (*Lolium multiflorum Lam*). This shows that red region absorption changes due to the nitrogen content of plants. The wavelength 1770nm yielded high VIP score using FD and PLSR. This is consistent with the finding by Kawamura *et al*. (2010). Their study recorded that, the wavelength 1770nm yielded high VIP for N concentration prediction using FD and PLSR. According to Clark and Lamb (1991), 1620 to 1845nm wavebands are associated with C-H, C-N, and N-H groups that are related mainly to fibre components and protein (Clark & Lamb 1991). The waveband 924nm (Log (1/R)) yielded high VIP score and this is the waveband is found near known absorption waveband for N concentration (910nm). This waveband is associated with C-H stretch (Curran, 1989). The waveband 1978nm (original reflectance) also yielded high VIP score. This waveband is found near a known waveband for N concentration estimation (1980nm) (Curran, 1989). According to Mitchell *et al.* (2012), waveband 1980nm is associated with N–H asymmetry.

For foliar P concentration, the highest VIP scores for original reflectance for grass sampled from stockpile and unmined soils were found near 1001 nm and 1197nm respectively. The dominant regions for foliar P concentration estimation were found to be NIR region for original reflectance. This can be attributed to internal cellular structure of the leaves (Zhai *et al.,* 2013). One thousand and three (1003) nm waveband is found near waveband 982nm recorded by Kawamura *et al.,* (2010). In their study, waveband 982nm yielded high VIP score for P concentration estimation on pasture using FD and PLSR. Waveband 1197nm is consistent with the waveband recorded by Kawamura *et al.* (2010). The authors recorded that waveband 1197 nm yielded high VIP score for P concentration estimation. The wavebands 950 to 1360nm are associated with C-H and O-H biochemical groups (Thenkabail *et al.* 2004; and Kawamura *et al.* 2010). For FD, high VIP scores were recorded near 976nm and 1770nm for grass sampled on stockpile soils and unmined soils respectively. These findings are consistent with the findings by Kawamura *et al.* (2010), they recorded 978nm and 1770nm using FD and PLSR for foliar P estimation on pasture.

For Log (1/R), the highest VIP score were recorded near 676nm and 1079nm for grass sampled on stockpile soils and unmined soils respectively. The waveband 675nm is consisted with the waveband (676nm) selected by Özyigit and Bilgen (2013) for estimation of P concentration in rangeland plants. Their study found that significant relationships existed between phosphorus levels and red region wavelengths. The spectral reflectance in the visible (VIS) wavelengths (400–700nm) depends on the absorption of light by leaf chlorophyll and associated pigments such as carotenoid and anthocyanins (Babar *et al.* 2006). The waveband 1079nm is consistent with the waveband (1079nm) recorded by Kawamura *et al*. (2010). In the study by Kawamura *et al*. (2010), the waveband 1079nm yielded high VIP score for P concentration prediction on pasture. The VIP peaks centred around 1079, 1197 and1770nm wavelengths, are commonly selected for prediction of each pasture nutrients properties (Kawamura *et al.* 2010). These VIP wavebands are within ±10 nm of wavebands used to predict herbage nutrient concentrations with NIRS in the laboratory (garcía-Ciudad *et al.* 1999).

6.7. Conclusion

The following conclusions are drawn from this study:

- The results show that NIRS-PLSR can be used to estimate foliar N and P;
- Foliar N concentration of grass sampled from stockpile soils and unmined soils can accurately be estimated using original reflectance;
- Top soil stockpiling appear to impact foliar N and P concentration as evidenced by low N and P concentration in the grass species, sampled from stockpile soils, relative to those from unmined soils;
- Foliar P was poorly estimated without spectral transformations;
- FD yielded highest co-efficient of variance value for both foliar N and P estimation. This is due to its effectiveness in eliminating background signals and the ability of FD to explore information that was often suppressed by other standard analysis methods;
- The highest VIP bands were found in the SWIR for foliar N estimation in grass sampled from both study sites using FD transformation; and
- For foliar P estimation, the highest VIP bands were found at NIR for grasses sampled from stockpile soils; and for grasses sampled from unmined soils, the highest VIP bands were found at SWIR both using FD transformation.

CHAPTER 7
GENERAL CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

This study investigated coal-mine stockpile soil quality and its impact on vegetation growth using greenhouse study, laboratory-based techniques and Reflectance Spectroscopy.

The key conclusions of the study are as follows:

- The depth of the stockpile affected the quality of the soil. Soil stored in depth deeper than 1.0m had effect on plant growth through reduced grass biomass production. When the soils were mixed, as would happen in a rehabilitation process, the resultant effect on grass growth was higher as compared to any of the three soils sampled separately at different depths (Chapter 3);
- Without addition of lime and fertilizers, stockpiled soil could not significantly support vegetation growth and productivity. Soils with no fertilizer treatment yielded very low grass biomass (Chapter 3);
- The duration of stockpile affected soil quality and vegetation growth. As the age of the soil stockpile increases, the concentration of suitable plant growth nutrients decreases (Chapter 3);
- Deep stockpile soils had low enzyme activity compared to surface and mixed soils. A depth greater than 1.0 meter, biological activity becomes low due to the environmental condition that favours mostly anaerobic organisms (Chapter 4);
- Mixing of stockpile soils generally showed the great potential to increase soil enzyme activity (Chapter 4);
- Duration of soil stockpiling can have influence on soil enzyme activity. When soils are stockpiled for a long period of time, microbial biomass is reduced (Chapter 4);
- Soil amendments have potential to improve enzyme activity of stockpile soils (Chapter 4);

- Reflectance Spectroscopy can predict coal-mine stockpile soil properties. Soil Ca and pH were accurately predicted by Partial Least Square Regression and Reflectance Spectroscopy (Chapter 5);
- Predictive models using Partial Least Square Regression can be efficiently used as a tool for estimation of soil pH and Ca for coal-mine stockpile soils (Chapter 5);
- Top soil stockpiling affects foliar N and P concentration as indicated by low N and P concentration in grass sampled from stockpile soils as compared to samples from unmined soils. Reflectance Spectroscopy and Partial Least Square Regression can be used to estimate foliar N and P (Chapter 6);
- Overall, coal-mine stockpiling affect soil and vegetation quality. Soil properties deteriorate during stockpiling, the deterioration in soil properties affect nutrient cycling. Enzyme activity can be used as a rapid method of soil health indicator;
- Since the process stockpiling and reapplying stockpile involves additional expense and effort, a careful analysis of results from sites with stockpile soil applications would provide the necessary information for cost-benefit analysis and would indicate possibilities for improvement in the efficiency of the process of stockpiling; and
- In order to achieve site stabilization, minimize degradation, and facilitate the long-term recovery of these mining sites with an aesthetically pleasing landscape, an understanding must exist that the successful recovery of these sites is dependent on soil quality. Soil stockpiling is a valuable technique, but restoration plans must be guided by research such as this one so that soil that is re-spread back is productive.

7.2 Knowledge Contribution

The study contributes knowledge with regard to:

- Proper soil stockpiling and management during open-cast mining process;
- The ability of Reflectance Spectroscopy to timely estimate selected parameters of stockpile soils;
- Literature with regard to coal-mine stockpile soil quality and characteristics in relation to vegetation growth and soil health;

- Application of soil amendments to improve grass biomass and coal-mine stockpile soil enzyme activity;
- Effect of coal-mine stockpile soil on foliar biochemicals (N and P); and
- Use of enzyme activity as well as grass as an indicator soil coal-mine stockpile soil quality.

7.3. Recommendations

This study recommends that:

- Pre-mining soil survey must be carried out to obtain soil information that will assist in soil stripping;
- Soil must be stockpiled according to their characteristics (similar or related soil forms, similar physical properties etc.). Mixing topsoil and subsoil during stripping is likely to result in poor vegetation growth as the subsoil might end up at the top and used as a top soil during rehabilitation;
- Depth of stockpile must be maintained at around 1.0-meter deep as deep soils tend to have less oxygen, which, in turn, affects biological activities;
- Duration of the stockpile should be limited to less than 6 years. In situations where soils can be re-spread immediately after striping, this must be carried out to avoid nutrient loss;
- Grass samples for estimation of foliar N and P concentration should be collected during summer and winter as vegetation nutrient levels varies in response to season;
- Microbial diversity of the stockpile soils need to be investigated to understand the role played by microbes in enzyme activity; and
- Further research with a large number of soil samples and different study sites is required to enhance the findings of this study.

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