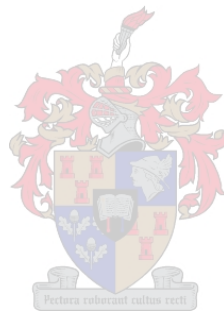


AN EVALUATION OF LIME REQUIREMENT METHODS FOR SELECTED SOUTH AFRICAN SOILS

by

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*Thesis presented in fulfilment of the requirements for
the degree of Master of Science in Agriculture
at
University of Stellenbosch*

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March 2017

Declaration

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Abstract

A laboratory study was conducted to evaluate seven widely used methods to predict soil lime requirement (LR) using 20 acidic South African top and sub-soils with a wide range of properties. The LR methods which were evaluated against a standard CaCO_3 incubation LR procedure, included: the original Eksteen method with organic matter correction factor (OMCF), commonly used in the Western Cape; two modifications of the Eksteen method, namely: (i) Eksteen-KCl method, involving the use of 1 M KCl exchangeable acidity instead of titratable acidity at pH 7, and (ii) Modified-Eksteen method, where a correction factor was applied to titratable acidity that was derived from soil data obtained in this study; the Cedara method, most commonly used in KwaZulu-Natal; the ARC-SGI method, developed primarily for Free State soils by the ARC- Small Grain Institute in Bethlehem; the Shoemaker-McLean-Pratt single buffer (SMP-SB) method most commonly used in the North East and North Central regions of the USA; the Adams and Evans single buffer (AE-SB) method most commonly used in the South East and Mid-Atlantic regions of the USA.

The original Eksteen method, although highly correlated with incubation LR, was found to be a relatively inaccurate predictor of LR. The Eksteen-KCl and Cedara methods were found to be highly correlated with incubation LR, yet consistently underestimated LR. The modified-Eksteen method was found to be highly correlated with incubation LR, and was a good predictor of LR. The ARC-SGI method was a considerably poorer predictor of LR, and tended to grossly overestimate LR. The SMP-SB method was found to be highly correlated with incubation LR, and was shown to be reasonably accurate to achieve a target pH_{KCl} of 5.5. Recalibration of the SMP-SB soil-buffer pH with incubation LR resulted in considerable increases in accuracy. The AE-SB method was found to be highly correlated with incubation LR, yet tended to overestimate LR. Recalibration of the AE-SB soil-buffer pH with incubation LR resulted in a sufficient increase in accuracy.

A correlation study was conducted to investigate the relationship between soil properties and both incubation LR and LR methods. It was revealed that soil properties other than soil pH, which are useful indicators of LR are: soil C > variable charge > $\text{CEC}_{\text{pH}7}$ > clay + silt. Soil C was found to be a significant contributor to LR due to its association with exchangeable Al and due to its high pH dependent acidity. Titratable acidity was found to be the soil property that most strongly related to soil LR. Variable charge was also shown to exhibit significant relationships with soil parameters that most strongly influence LR. For these reasons, a multiple regression equation was developed that utilised only titratable acidity and variable charge. The multiple regression equation was able to predict 96.76% of the variation observed for incubation LR, and was 97.86% accurate in predicting the LR for each specific soil to obtain a target pH_{KCl} of 5.5. Regarding the relationship between soil properties and LR methods, it was revealed that the local methods, except the ARC-SGI method, were most strongly influenced by exchangeable acidity and Al, and had significant relationships with soil C. The American

direct buffer methods were strongly correlated with essentially all of the soil properties studied. This is indicative of the ability of these methods to directly determine the amount of acidity that may originate from various sources in the soil, in order to make a sufficiently accurate LR. It is therefore recommended that the application of direct buffer methods be further developed for use on South African soils in order to further improve the accuracy of LR determination in South Africa. The existing method that was found to most accurately predict LR on a wide range of soils was the modified-Eksteen method.

Uittreksel

'n Laboratorium studie was uitgevoer om sewe metodes te evalueer, wat algemeen gebruik word om kalkbehoefte (KB) te bepaal, op 20 suur Suid-Afrikaanse bo- en ondergronde wat oor 'n wye reeks eienskappe beskik. Die KB metodes wat geëvalueer was, teenoor 'n standaard CaCO_3 inkubasie KB prosedure, was: die Eksteen metode met organiese materiaal korreksie faktor (OMKF) wat algemeen in die Wes-Kaap gebruik word; ingesluit was twee veranderinge tot die oorspronklike metode, naamlik: (i) die Eksteen-KCl metode, wat die gebruik van 1 M KCl uitruilbare suur bewerkstellig, i.p.v. titreerbare suur by pH 7, en (ii) die gemodifiseerde Eksteen metode, waartoe 'n korreksie tot die titreerbare suur data toegepas is soos verkry in die studie; die Cedara metode, wat algemeen in KwaZulu Natal gebruik word; die ARC-SGI metode, wat primêr vir Vrystaatse gronde ontwikkel is deur die LNR Klein Graan Instituut in Bethlehem; die Shoemaker-McLean-Pratt enkel buffer (SMP-SB) metode, wat algemeen in die Noord-Oostelike en sentrale Noordelike streke van die V.S.A gebruik word; die Adams en Evans enkel buffer (AE-SB) metode, wat algemeen in die Suid-Oostelike en mid-Atlantiese streke van die V.S.A. gebruik word.

Dit was gevind dat die oorspronklike Eksteen metode 'n relatiewe onakkurate voorspeller vir KB-bepaling was, alhoewel 'n sterk verwantskap gevind was tussen dié metode en die inkubasie KB metode. Die Eksteen-KCl en Cedara metodes het sterk gekorreleer met die inkubasie KB, maar het in meeste gevalle die KB om 'n teiken pH te bereik onderskat. Die gemodifiseerde Eksteen metode het 'n sterk verwantskap met die inkubasie KB getoon, en was oor die algemeen 'n goeie voorspeller van KB om 'n teiken pH te bereik. Die ARC-SGI metode was veral 'n hoogs onakkurate voorspeller van KB, en het daartoe geneig om KB drasties te oorskat. Die SMP-SB metode het 'n sterk verwantskap met die inkubasie KB getoon, en was gevind om bevredigend akkuraat te wees in die geval van KB bepaling om 'n teiken pH te bereik. Kalibrasie van die SMP-SB grond-buffer pH met inkubasie KB het 'n toename in akkuraatheid tot gevolg gehad. Die AE-SB metode het 'n sterk verwantskap met die inkubasie KB getoon, maar het daartoe geneig om KB te oorskat. Kalibrasie van die AE-SB grond-buffer pH met inkubasie KB het egter 'n bevredigende toename in akkuraatheid tot gevolg gehad.

'n Korrelasie studie was uitgevoer om die verhouding tussen grondeienskappe en beide inkubasie en KB metodes te ondersoek. Dit was bevind dat grondeienskappe anders as grond pH wat KB bepaal die volgende insluit: grond C > veranderlike lading > $\text{KUK}_{\text{pH } 7}$ > klei + slik. Dit was bevind dat grond C die grootste bydrae tot KB gehad het, a.g.v. C se assosiasie met uitruilbare Al en die groot bydrae daarvan tot pH veranderlike suurheid. Titreerbare suur was bevind om die grondeienskap te wees wat die sterkste verwantskap met KB het. Veranderlike lading het ook sterk verhoudings met grondeienskappe wat KB sterk beïnvloed getoon. Vir hierdie redes was 'n veelvoudige regressie formule ontwikkel wat slegs titreerbare suurheid en veranderlike lading in ag neem. Die veelvoudige

regressie model was in staat daartoe om 96.76% van die variasie te beskryf om 'n KB te bepaal vir 'n spesifieke grond om 'n teiken pH_{KCl} van 5.5 te bereik. Rakende die verhouding tussen grondeienskappe en KB metodes, was dit bevind dat plaaslike metodes – behalwe die ARC-SGI metode – die meeste deur uitruilbare suur, Al en C beïnvloed was. Die Amerikaanse direkte buffer metodes het sterk verwantskappe met feitlik alle geëvalueerde grondeienskappe getoon. Hierdie bevindinge toon dat die bestudeerde direkte KB metodes daartoe in staat is om alle suurheidsbronne in ag te neem tydens die voorspelling van KB. Dit word daarom aanbeveel dat die toepassing van sogenaamde direkte buffer metodes verder ontwikkel word vir gebruik op Suid-Afrikaanse gronde, om sodoende die akkuraatheid van KB bepaling te verhoog. Die bestaande metode wat bevind was om oor die algemeen die meeste akkuraat te wees op 'n wye reeks gronde, was die gemodifiseerde Eksteen metode.

Acknowledgements

As with most of one's accomplishments during a limited lifespan, a work such as the one presented here, is only possible through the assistance and cooperation of many others besides the one whose sole name appears on the cover page. It would be considered impractical to thank and acknowledge every person who played a part in this work, as the length of this thesis may then be considered too long.

Firstly, my thanks are extended to my parents, who – with their capacity to reproduce and the exertion of their influence on my thinking throughout my life – made this thesis possible to manifest in the way that it has. I respect and appreciate them for absolutely everything they have ever done for me.

Then, an incredible amount of thanks are extended to my major supervisor Dr. A.G. Hardie, for providing me with unlimited intellectual freedom, and for always finding time to offer support and work out any problems I encountered while I was at Stellenbosch University. To my co-supervisor, Dr. P.J. Raath, a substantial amount of gratitude is extended towards for initiating this study and supplying the financial means for the thesis to realise. In addition, I would like to thank him for always keeping my mind focussed on the practical aspects of theoretical thought, his assistance kept the project grounded.

Then, I am short of any suitable words to describe the degree of gratitude I experience as of writing this for the support and joy selflessly offered by the staff members at the Department of Soil Science at Stellenbosch University. I am considerably grateful for absolutely everything we have shared, and in particular I would like to thank Nigel Robertson, Herschell Achilles, Uncle Matt Gordon, Aunty Delphine Gordon, The Eagle (Dr. E. Hoffman), Dr. A. Rozanov, Dr. C. Clarke, Tannie Annatjie and my fellow post-graduate students. An incredible amount of gratitude is also extended to the laboratory team at Bemlab for all the assistance they have provided regarding the analysis of the project soils. The friends I have made at Bemlab whilst working there, specifically Wakkie, Carlo, Anna, Sister Martha, the entire water and microbiology laboratory staff, Jack, Stefan, Johan, Karien, Oom Koos, Anel, Braam, and Michelle, I am eternally grateful to have had the pleasure of meeting you. Thank you for all your support, and that you continuously believed in my abilities.

To everyone that has supported me during field work, specifically J.P. Nel, John Morrison, Francis Yeatman, Adela Jansen at Pathcare for arranging accommodation and the means to travel, the Genis family in Paulpietersburg, and a considerable amount of people that would make the list too long, I am incredibly grateful for your assistance and support.

Then, last but definitely not least, a substantial amount of gratitude is extended to all my friends, for providing me with an immense amount of support and pressuring me to endure and finish on time. In particular, I would like to sincerely thank my partner, Suné Bothma, for pulling me through the last stretch and supporting me when times were dark. I will never have the words to sufficiently thank you.

Then, in the circumstance that I have overlooked anyone, I would like to thank you in particular as well, as your effort is indeed represented in this thesis.

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Chapter 1

Introduction

Large expanses of soils in South Africa's vital agricultural regions are considered to be moderately acidic at best. As such, soil acidity is a problem that causes constraints on the optimal production of crops in South Africa. However, the South African agricultural industry is rife with speculation as to which lime requirement (LR) method used in various parts of the country is most accurate. In addition, there is very little evidence available in the literature regarding evaluations and verifications of the most commonly used South African LR methods. Indirect methods, which consist of using multi-variate models, are mostly used for the determination of LR on South African soils. These indirect methods make use of routinely analysed soil properties in order to recommend supposedly accurate LRs. Soil properties usually selected to determine the LR of a soil by use of these indirect methods are generally soil pH, carbon and clay content, exchangeable acidity and acid saturation. In addition, there are persons and consultants in the South African industry that acquire the services of some American soil testing laboratories, which serve to determine the LR of South African soils in some cases. However, the application of these methods on soils from South Africa have also not yet been evaluated in any manner. Furthermore, there is very little information available regarding the relationship between soil properties and other factors that affect the LR of a soil. Thus, it is very difficult to make an educated decision regarding the accuracy of a LR determined for a specific soil.

For these reasons, Bemlab (PTY) LTD, an independent analytical laboratory that offers an agricultural testing service, funded this study to evaluate the accuracy and precision of some commonly used LR methods. This was done in order to determine a more suitable means to quantitatively determine LR for various agricultural regions throughout South Africa in a manner that would most easily be implemented for routine laboratory testing. In addition, two rapid American buffer methods were also selected to evaluate the practical application of such methods on South African soils. Prior to the adaption of a LR method, several methods are generally evaluated in laboratory and/or greenhouse studies, by use of a commonly accepted reference method. These procedures are commonly also referred to as correlation studies, due to predicted LRs by use of a respective method being related to a selected reference method. These evaluations allow for a representative and large number of soils to be evaluated for a given region. Such a process thus allows for the selection of the most accurate method, one that provides the best index of a soil LR, for a specific region. Generally, the next step is calibration of the LR method to agricultural soils. In this case, laboratory results are related to actual field responses. As such, field recommendations may then be made from these results.

The primary aim of this thesis was to evaluate the range and scope of the Eksteen method, the Cedara method, the ARC Small Grain Institute (Bethlehem) method, and two rapid American buffer

procedures, namely the Shoemaker-McLean-Pratt and the Adams and Evans single buffer methods using a variety of acidic South African soils. Data obtained from this evaluation may serve to indicate the most suitable LR method for a given type of soil, as well as indicate limitations associated with a given method on soil types outside of its practical range. A secondary aim was to determine the relationship between soil properties and the inherent LR of a soil in order to reach a specified target pH. Data obtained from such an investigation may serve to identify the most pivotal factors that influence the inherent LR of soil in order to obtain a specific target pH. As such, this information is important in order to develop models that can serve as reference to evaluate predicted LRs.

This thesis is divided into five parts. Chapter II serves as a review of the literature pivotal to the study. Chapter III presents a general chemical and physical description of the soils that were selected for the abovementioned investigations. Chapter IV presents the results obtained from the laboratory incubation study that was designed to evaluate the respective methods. Chapter V presents results regarding the relationship between soil properties that are commonly determined in routine soil analysis and the LR as determined by incubation. Further, this chapter investigates the relationship between these soil properties and LRs as predicted by each respective method. Finally, Chapter VI summarises the general findings of the study and provides recommendations for future research regarding the topic.

Chapter 2

Review of the Literature

2.1 **Introduction**

Soil acidity and the amelioration thereof has received much more attention from early investigators of plant growth than did alkaline soils (Millar, 1955). Scientific investigations into the optimal amelioration of acid soils had their beginnings in the early agricultural research (Shaw, 1953). McLean (1973) defined the lime requirement (LR) of a soil as “the amount of lime or other base needed to neutralise the undissociated and dissociated acidity in range from the initial acid condition to a selected neutral or less acid condition.” In some situations, the index selected to which the soil is to be neutralised is the pH value that is most favourable for plant growth (McLean, 1973). Other workers, such as Kamprath (1970) and Reeve and Sumner (1970) have reported that exchangeable Al was a valid criterion for the measurement of LR on highly weathered, leached Oxisols and Ultisols. In other situations, the definition of LR can be altered on the basis of economic considerations, such as that of Hesse (1971), where LR is related to the amount of liming material needed to obtain maximum economic return. Due to the difficulties in identifying factors contributing to acidity and LR, it is not surprising that many methods that aim to determine LR are available. This may be attributed to the circumstance that many of the independent variables that are measured are interrelated (Curtin, *et al.*, 1984). Uncertainty therefore still remains as to which method may be the most accurate in order to determine the LR of a soil.

This literature review consists of four sections with the aim of presenting information required to develop an understanding of the concept of soil LR, along with an understanding of the rationale behind methods used to determine LR. The first section covers an overview of the fundamentals of soil acidity and the related soil properties that influence LR. The second section presents a general historical overview of the development of LR methods, along with approaches that were used to improve such methods. The third section of the review consists of a summary of previous evaluations and findings of the LR methods that will be evaluated in the study. Finally, the fourth section describes procedures that are used to evaluate LR methods, along with a sub-section on how lime recommendations are calculated through use of the methods selected for the study.

2.2 **Soil Acidity**

The unfavourable influence of soil acidity on crop production and plant growth in general, is due to a variety of causes, any of which may enjoy greater importance for any particular situation (Townsend, 1973). The increased understanding of acid soil reaction has allowed scientists to refine LR methods that have been based on sound scientific principles. An overview pertaining to the factors that influence

acidic soil reaction and biotic responses to the qualities of such a soil is necessary, in order to identify and describe inaccuracies of commonly used LR methods.

2.2.1 Soil Acidification

Soil acidification is a natural, slowly occurring phenomenon that results from geological evolution through the process of pedogenesis. Soil acidity as a concept can be understood in two differing ways: i) relatively, as the ratios of acids and bases present in the soil solution and that occupy the cation exchange sites on the surfaces of soil colloids; ii) and absolutely, as the quantity of acids stored within a given mass or volume of soil (Fey, *et al.*, 1990). For the natural weathering process from which acidic soils are derived, the presence of carbonic acid (H_2CO_3) in rain provides protons (H^+) and removes basic cations in the leachate (Sumner & Noble, 2003). This is especially prevalent in high rainfall areas, due to the relative ease with which base cations leach from soils, leaving them acidic (Rengel, 2003). Soils can also become acidic due to parent material being acidic or containing base cations in small quantities (Fageria & Baligar, 2008). Acidification of the soil environment due to deposition of acid rain is also important in some parts of the world (Rengel, 2003). Mostly, natural acidification of soils results from specific processes linked to the surface biomass, such as the production of CO_2 by microbial and root respiration as well as the production of organic acids by microbes and plants (Bloom, *et al.*, 2005). Nevertheless, the relationship between the abovementioned master variables and many secondary variables is significantly more complex than can be described concisely (Fey, *et al.*, 1990).

Considering that soil acidification is a naturally occurring process in many soil environments, anthropogenic contributions such as agricultural practices and pollution from industrial, mining, and other human practices, have accelerated the process (McBride, 1994). According to Fey *et al.* (1990), the rate of soil acidification may potentially be the highest in agriculture due to the liberal use of ammoniacal fertilisers and the production of legumes. Basic cation levels can also be altered through various agricultural management practices that increase water infiltration and concomitant leaching. The major processes which accelerate agricultural soil acidification include: i) net H^+ excretion by plant roots due to excess uptake of cations over anions; ii) removal of alkalinity in farm products such as grain, hay, meat, and wool; iii) accumulation of organic anions in the form of soil organic matter; iv) mineralisation of organic matter, nitrification of ammonium, and subsequent leaching of nitrate; v) input of acidifying substances such as NH^+ -based fertilisers (Tang & Rengel, 2003). Nevertheless, the resultant decrease in soil pH associated with agricultural practices may be sufficient to cause moderate to severe Al^{3+} and Mn^{2+} toxicity (Sumner & Noble, 2003). This in turn affects the long-term economic feasibility of farming practices, and in some cases may lead to permanent dilapidation of the resource base (Sumner & Noble, 2003).

2.2.2 Forms and Measurement of Soil Acidity

According to Coleman and Thomas (1967), the dominant sources of acidity present in most soils are: i) dissociated and undissociated hydrogen ions (H^+) associated with layer silicate clays or Al or Fe oxides; ii) ionisable H^+ that originates from acidic functional groups of soil organic matter such as carboxyl and phenolic groups; iii) various forms of soil Al, including exchangeable aluminium (Al^{3+}), hydroxy-Al [$Al(OH)^{2+}$] and polymeric Al hydroxides; iv) soluble H^+ resulting from acidic precipitation, soluble organic acids or from acid-forming reactions in soils, e.g. oxidation of ammonium-based fertilizers. However, considering the abovementioned sources of acidity, soil acidity can holistically be understood as being comprised of mainly two forms, namely active acidity and reserve acidity.

Active acidity consists of H^+ in the soil solution, and is the first form of acidity to react with the input of a base such as liming material. This form of acidity is associated with the solution phase of the soil. Active acidity is commonly measured, through use of a glass membrane electrode along with a reference electrode inserted into the soil solution, as the H^+ ion activity. Active acidity therefore is expressed as pH measurements made in the soil solution and is thus a measure of the acid intensity of the soil (McBride, 1994). If a soil pH value is below 7.0 the soil is considered acidic, whereas if the pH value is above 7.0 the soil is considered alkaline. Soil reactions are essentially controlled by soil pH and result in the chemical transformation of many soil elements (Plaster, 2009). These include important reactions within soil systems such as ion exchange, dissolution and precipitation of minerals, redox, adsorption and complexation reactions (McBride, 1994; Menzies, 2003). Soil pH therefore has a regulatory effect on the availability of plant nutrients (Plaster, 2009), as well as on microbial activity (Robson & Abbott, 1989).

Reserve acidity is defined as H^+ and Al^{3+} ions adsorbed by soil components, as well as other constituents that may be able to generate hydrogen ions (Fageria & Baligar, 2008). This form of acidity is associated with the solid phase of the soil, specifically humus and clay colloids. It is also the form of acidity that primarily serves to replenish active acidity that has reacted with the input of a base material, and is thus a measure that represents the buffer capacity of a soil (Plaster, 2009). Reserve acidity can be slow to react chemically to a change in the concentration of active acidity in the soil solution due to slow ionic diffusion through micro pores of soil particles and slow dissociation of Al^{3+} complexes (McBride, 1994). Reserve acidity originates from the following sources: i) organic acid dissociation; ii) hydrolysis of Al^{3+} -organic complexes; iii) exchangeable H^+ and Al^{3+} , released as acidity by cation exchange and hydrolysis; iv) non-exchangeable forms of acidity on minerals that can build up at low pH values on surfaces of variable charge minerals (McBride, 1994). It should be noted that reserve acidity can be further distinguished as two distinct forms, namely exchangeable and residual (non-exchangeable) acidity.

Exchangeable acidity is defined as that which is extractable by the cation of a neutral, unbuffered salt, such as KCl, NaCl, CaCl₂ (Thomas, 1982). Exchangeable acidity therefore theoretically describes the amount of acidity present at the pH of a soil, and varies with the nature of the soil and the percentage base saturation as a proportion of the total acidity (Coleman & Thomas, 1967). According to Brady and Weil (2008), exchangeable acidity is generally highest for smectites, intermediate for vermiculites, and the lowest for kaolinite at a given pH value. Coleman and Thomas (1967) found that monomeric Al³⁺ almost entirely contributes to exchangeable acidity. Yuan (1959) made a modification to previously used exchangeable H⁺ methods to distinguish between exchangeable H⁺ and Al³⁺ extracted by this method. Due to this modification, it was observed that H⁺ dominated over Al³⁺ in exchangeable acidity for soils where organic matter was an important contributor to cation exchange capacity (CEC). However, Coleman and Thomas (1967) argued that this observation might have been more apparent than real, as much of the exchangeable H⁺ observed by Yuan might have been due to the hydrolysis of Al³⁺ held in non-exchangeable form by organic matter. Protons produced by the decomposition or dissociation of organic matter are unstable in mineral soils due to reaction with layer silicate clays, which results in the release of exchangeable Al³⁺ and siliceous acid (Coleman & Thomas, 1967). Residual acidity, also known as non-exchangeable acidity, is defined as acidity that is not displaced, or extremely slowly displaced, by a concentrated neutral salt solution. Residual acidity has also been more ponderously termed “titratable but non-exchangeable acidity” (Bohn, *et al.*, 1985). This form of acidity can be determined by using a buffered salt solution in order to raise the pH to a specified value. On the contrary, it can simply also be calculated by subtraction of salt exchangeable acidity from total acidity (Coleman & Thomas, 1967). Residual acidity is primarily associated with weak acid groups on humus, organically complexed Al, and strongly retained Al-hydroxy cations on mineral surfaces (McBride, 1994). This form of acidity is generally far greater than either the active or neutral salt exchangeable acidity (Brady & Weil, 2008).

Together, the abovementioned forms of soil acidity can be regarded as total or potential acidity. Total acidity is that which is neutralised at a designated pH that represents a pH attained when a soil is treated with excess CaCO₃, which would cause dissolution of CaCO₃ to cease. It was originally proposed by Bradfield and Allison (1933) that soil acidity be determined directly at a pH of 8.2. A pH value of 8.2 was determined as the pH that represents a base saturated soil which had reached equilibrium with a surplus CaCO₃ at the partial pressure of CO₂ existing in the atmosphere at a temperature of 25⁰C. Total acidity at pH 8.2 therefore gives an indication of the potential amount of acidity that must be neutralised in order to obtain a pH between the original soil pH and a pH of 8.2 (Coleman & Thomas, 1967). The value of this form of acidity is generally much higher than that of exchangeable Al due to inclusion of non-exchangeable residual H⁺ associated with carboxyl groups and Fe and Al hydrated oxides (Sanchez, 1974). This residual acidity component may be 1000 times greater than the active acidity component in sandy soils, and even 50 000 to 100 000 time greater in a soil with high clay and organic matter

contents (Brady & Weil, 2008). According to Kamprath (1972), these non-exchangeable components have no detrimental effect on plant growth in highly weathered soils, and are therefore of no practical value (Sanchez, 1974). It should also be noted however, that the amount of liming material needed to at least partly neutralise residual acidity is commonly in the range of 5 to 10 tons per hectare for 15 cm of top soil (Brady & Weil, 2008). It is therefore of economic importance to make use of a proper replacing cation and buffer pH to determine extractable acidity.

In order to evaluate the efficacy of buffers to determine soil acidity, principles involved with the displacement of acidity by a cation in a strongly buffered solution should first be considered. The quantity of acidity displaced by the cation in the buffer solution is influenced by the cation used, the strength of the buffer, the pH to which the solution was buffered, extraction time and the intensity of leaching (Wiid, 1963). Through manipulation of any one or more of these factors, differing values for extractable acidity may be obtained, depending on the fraction of the pH dependant acidity that is being measured (Coleman, *et al.*, 1959). Nõmmik (1983) evaluated the effect of replacing cation, duration of soil-extractant contact, and soil-extractant ratio on amount of titratable acidity determined. It was found that Ca as replacing cation was more effective at displacing H^+ and Al^{3+} than K. Increasing the duration of soil-extractant contact increased the average amount of acidity determined by 4.4% for a 2 hour contact period, compared to a 1 hour contact period. Allowing for an overnight contact period, increased the average measured acidity by 9.7%. Further, increasing the soil-extractant ratio from 1:2.5 to 1.5 resulted in an average increase in measured acidity of 9.8%. A study done by Hargrove and Thomas (1984) evaluated the extractability of Al from Al-organic matter by using K^+ , Ca^{2+} , and La^{3+} as replacing cations. It was found that the order of effectiveness for extracting the bound Al^{3+} was in the order of $La^{3+} > Ca^{2+} > K^+$. According to the authors, these results are important to acid soils in which organic matter is altered through various management practices, and justified greater emphasis on the role of organic matter in soil acidity.

As mentioned earlier, total soil acidity is usually regarded as the quantity of acidity that must be neutralised in order to obtain a pH of close to 8.2. The $BaCl_2$ -TEA method has been found to be the rapid buffer method that most closely resembles the titration method used by Bradfield and Allison (Thomas, 1982). According to Shoemaker *et al.* (1961) however, the $BaCl_2$ -TEA buffer does not react with all of the extractable Al present in the soil system. Also, the adoption of $BaCl_2$ -TEA or any other complex chemical as pH buffers only places emphasis on a pH value alone, thus disregarding specific effects that may be exerted upon the soil complex by these chemicals (Shaw, 1953). Adams and Evans (1962) reported that their buffer measured slightly more acidity than what was measured by extraction with 1 M NH_4OAc buffered at pH 7.0. The 1 M NH_4OAc acidity buffered at pH 7.0 is calculated by subtracting total bases from the CEC determined at pH 7.0. However, according to Shoemaker *et al.* (1961), buffers weaker than $BaCl_2$ -TEA would be expected to extract less acidity.

2.2.3 Buffering Capacity

The buffering capacity of a soil describes the degree to which a soil resists changes in pH due to acidification or the addition of bases. Soil buffering is important for two primary reasons (Brady & Weil, 2008). Firstly, buffering ensures stability in the soil pH, which prevents fluctuations that might have a negative effect on soil biota. Secondly, buffering capacity strongly influences the quantity of amendments needed to bring about a desired change in soil pH. Thus, the greater the buffer capacity of a soil, the greater the LR tends to be. According to Goulding and Blake (1998), soils generally exhibit buffering capabilities in the following order: i) dissolution of carbonates and other basic minerals; ii) replacement of exchangeable base cations by H^+ and Al^{3+} on the exchange complex, and; iii) dissolution of Al, followed by Fe bearing minerals. The order of these processes tend to respectively buffer soil pH at values of about 7.0, 6.0 – 5.0, and 4.0 – 3.0.

For soils in the pH range of 5.0 – 7.0, buffering is predominantly described in terms of the equilibrium that exists between active, salt exchangeable, and residual acidity (Brady & Weil, 2008). The most important ways in which highly weathered soils can exhibit buffering capabilities over a wide range of pH values are through reversible charge surfaces, such as Al- and Fe oxides and hydroxides, kaolinite, and amorphous Al-silicates such as allophane (Bloom, *et al.*, 2005). A decrease in pH results in a more positive net charge, whereas an increase in pH results in a more negative net charge (Bloom, *et al.*, 2005). The surface hydroxyls present on these minerals thus resultantly protonate or deprotonate in response to pH fluctuations. These surfaces are primarily amphoteric and can simultaneously be basic or acidic, depending on the pH (Bloom, *et al.*, 2005). It has also been shown that clay has a weak buffer capacity in relation to organic matter (Curtin & Rostad, 1997). However, the greater the clay content of a soil, the more acidic cations may be adsorbed on exchange sites (McLean, 1973). Acidic groups associated with organic matter such as carboxyl (pKa 2 – 7) and phenolic (pKa 6 -10) functional groups serves as the main buffering components in organic matter (Bloom, *et al.*, 2005). The contribution of organic matter to buffering capacities in highly weathered can also be significant, even at low quantities (Coleman & Thomas, 1967). The ionisation of carboxyl and phenolic groups are generally complete at pH values of 8 and 11, respectively (Bloom, *et al.*, 2005). Carboxyl groups are strongly acidic enough to ionise appreciably when the soil pH is below 7, along with some contribution from polyphenols and substituted phenols (Coleman & Thomas, 1967). However, the greater the organic matter content of a soil, the more acidic cations may accumulate on exchange sites (McLean, 1973). Protons originating from the abovementioned organic matter and mineral sources due to deprotonation can react with any bases added to the soil.

2.2.4 Cation Exchange in Soil Buffering

The degree of cation saturation is an important factor when considering the potential LR of a soil. Base saturation, for example, tends to increase with a general increase in soil pH (Brady & Weil, 2008). Percentage base saturation is an indication of exchangeable bases such as Ca, Mg, Na and K that occupy the cation exchange sites of soil (McBride, 1994). In acidic soils, available exchange sites are primarily occupied by acidic cations such as Al^{3+} and H^+ . Thus, a low base saturation indicates acidic soil conditions, whereas a percentage base saturation approaching 100 will resultantly indicate neutrality or alkalinity (Brady, 1974). Acid saturation (exchangeable acidity divided by exchangeable bases plus exchangeable acidity), is therefore the complement of base saturation. Adams and Evans (1962) used an acid saturation vs. pH_w relationship from 348 red-yellow podzolic soils as the basis of their LR method. This relationship was used to describe the general buffering capacity of a group of soils; however no constant relationship existed between pH and acid saturation for all soils. The specific pH value in relation to the percentage base saturation is primarily determined by at least two factors, namely the nature of the colloid and the particular bases present on the colloidal complex (Brady, 1974).

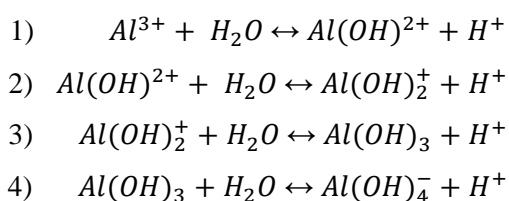
The nature of the colloid is an important factor that results in soils exhibiting different buffering capacities. This can be explained by the differing ability of various colloidal materials to furnish H^+ to the soil solution, resulting in differences in charge density (Brady, 1974). According to Brady and Weil (2008), smectite clays are able to hold on to calcium more strongly, due to a higher charge density, compared to kaolinite at a given percentage base saturation. This results in smectite clays that must be raised to approximately 70% base saturation before calcium will exchange significantly to supply the needs of plants, whereas kaolinite clays exchange calcium more readily at a notably lower base saturation. In addition, by using $BaCl_2$ -TEA as extractant, Mehlich (1942a) found kaolinite - which acts as a weak acid - to only be 65% base saturated at pH 7.0, whereas montmorillonite was 95% base saturated at pH 7.0. Base saturation values for organic material were found to be intermediate between the values for kaolinite and montmorillonite for almost the entire pH range. Comparing pH values found when various colloids are about 50% base saturated, reveals that organic colloids would have pH values of 4.5 to 5.0, the silicate clays 5.2 to 5.8, and the hydrous oxides 6.0 to 7.0 (Brady, 1974). It is thus for the factors highlighted above that the LR of two soils with differing colloidal properties would be somewhat different (Brady & Weil, 2008).

The pH value at which base saturation is determined, also plays a pivotal role in the degree of base saturation. According to Sanchez (1976), determining base saturation based on $BaCl_2$ -TEA buffered at pH 8.2 or using 1 M NaOAc at pH 7.0 makes the soil seem more acid than it is if the field pH is lower than the pH of the extractant. Sanchez (1976) cited work done by Buol in 1973 where the base saturation of 88 soils were compared and was found that 35% base saturation at pH 8.2 was equal to 55% base saturation at effective cation exchange capacity (ECEC). This phenomenon is attributed to essentially

all the variable charge being considered as extractable acidity (Sanchez, 1974). Variable charge is an important component to be considered in order to determine LR. Variable charge is indicated by the difference in CEC and ECEC, where CEC refers to the value obtained through analysis with 1 M NH₄OAc buffered at pH 7 and ECEC is the sum of exchangeable cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, and Al³⁺) (Rengel, 2003). According to Sumner (1994), soils that contain variable charge minerals in their subsoil would be able to consume more alkali when compared to soils that predominantly contain permanent charged minerals.

2.2.5 Aluminium Buffering

Due to the association of Al with both the mineral and organic fractions of a soil, Al transformations can make a significant contribution to the buffering capacity of a soil. The amount of soluble Al in acidic soils may be determined by the dissolution of inorganic compounds, adsorption onto inorganic minerals, or through reactions with organic matter (Ritchie, 1989). According to Bohn *et al.* (1985), H⁺ ions are subsequently released due to monomeric Al hydrolysis according to the following sequence of reactions:



The Al³⁺ ion is predominant below pH 4.7, Al(OH)₂⁺ between pH 4.7 and 6.5, Al(OH)₃ between pH 6.5 and 8.0 and Al(OH)₄⁻ above pH 8.0. The Al(OH)₂⁺ species is of minor importance and exists only over a narrow pH range (Bohn, *et al.*, 1985). The hydrolysis of monomeric Al illustrated above usually becomes significant at pH values above 4.0, and at pH 4.9 more than 80% of the total Al is hydrolysed (Ritchie, 1989). The H⁺ ions that originate from Al hydrolysis can lower the pH of the soil solution, as well as react with soil minerals to further break them down (McBride, 1994). The abovementioned reaction products of Al hydrolysis may either remain in the soil solution, be adsorbed as monomers to CEC sites, be adsorbed and polymerised on the surfaces of clay minerals, or be adsorbed and then complexed by organic matter (McLean, 1976; Brady & Weil, 2008). The Al³⁺ that has been adsorbed and polymerised can affect the actual LRs of soils due to its acidic nature, as well as affect the predicted LRs due to its effects on the buffers used in LR methods (McLean, 1976).

Aluminium forms rather stable complexes with soil organic matter, primarily through reaction with carboxyl groups and to a lesser extent with phenolic groups (Hargrove & Thomas, 1984). However, the presence of Al and Fe on the exchange sites of organic matter causes the organic matter to exhibit greater weakness as an acid, resulting in a lower contribution to the ECEC of the soil, especially at low pH values (Coleman & Thomas, 1967). Further, the amount of complex formed between Al and organic

matter is dependent on both the pH and Al^{3+} concentration in the soil solution. Schnitzer and Skinner (1963) have reported that Al was primarily hydroxylated in organic matter as $\text{Al}(\text{OH})_2^+$.

2.2.6 Biotic Reaction to Acidic Soil

Plant growth-limiting factors associated with soil acidity result from complex interactions involving the physical, chemical, and biological properties of a soil (Fageria & Baligar, 2008). However, the major effects of soil pH on biota are biological in nature (Foth & Turk, 1972). The effect of pH on the availability of nutrients is arguably the greatest general influence pH has on biota in the soil environment. Soil pH tends to significantly affect the level of toxicity of certain elements. When the pH of a soil is low, appreciable amounts of Al, Fe, and Mn become soluble to such an extent that they may become extremely toxic to soil biota (Brady, 1990). The cause of poor crop growth on acid soils is commonly a direct result of Al toxicity (Sumner & Noble, 2003), particularly below pH_w 5.5. Due to the accumulation in roots, Al damages membrane canals through which Ca is normally absorbed, resulting in the restriction of cell wall expansion which causes roots to grow improperly (Brady & Weil, 2008). Roots that grow under such conditions tend to become short, stubby, and unbranched (Plaster, 2009). The root tips, along with lateral roots, often also turn brown (Brady & Weil, 2008). Thus, the major limiting factors that are associated with poor root penetration on acid soils are the lack of Ca^{2+} and/or excess Al^{3+} (Sumner & Noble, 2003). As previously mentioned, leaching of basic cations such as Ca and Mg cause soils to become acidic. Resultantly, a fairly definitive relation exists between soil pH and the concentrations of these two nutrients in exchangeable form. This general relationship holds true for soils in arid environments, except under conditions where substantial concentrations of sodium have been adsorbed (Brady, 1990). In addition, Ca^{2+} and Al^{3+} antagonism is considered to be the most important factor that affects the Ca uptake of plants below pH 5.5 (Fageria & Baligar, 2008). Plants that are exposed to Al toxicity often also show signs of P deficiency (Brady & Weil, 2008). P availability also decreases in acid soils due to the resultant formation of insoluble metal phosphates. This is due to the increased activities of Fe, Al, and Mn, especially when soil pH is below 5.0 (Brady, 1990). In contrast however, as the pH of a soil is increased, the solubility of these elements decrease due to precipitation reactions that take place. Around neutrality, the availability of these metals may decrease to such an extent that certain plants may suffer from iron and manganese deficiency (Brady, 1990). The availability of Mo however, tends to increase as the pH of a soil is increased. At low pH values, Mo forms insoluble compounds with Fe, rendering it unavailable (Foth & Turk, 1972). Trace metals such as Cu and Zn have reduced availability in both highly acid and alkaline soils (Townsend, 1973). In general, optimal nutrient availability is found near a soil pH of 6.5.

Some organisms are unable to tolerate even the smallest variations in pH, whereas others are able to tolerate wider ranges of soil pH. Studies have shown that the actual concentrations of H^+ or OH^- are not as important, except under the most extreme circumstances (Foth & Turk, 1972). It is rather the

associated conditions prevailing at a specific pH value that is of most importance. Most soil microorganisms and plants prefer a near-neutral pH in the range of 6.0 to 7.0 due to the favourable availability of most soil nutrients (Hartel, 2005). The proportion of fungi to bacteria and actinomycetes is generally greater in acid than neutral soils; acid soil thus favours the development of fungi, but is unfavourable to the development of other forms (Foth & Turk, 1972). Generally, actinomycetes prefer a soil reaction of 7.0 to 7.5, bacteria in the range of 6.0 to 8.0, and the fungi from 4.0 to 8.0 (Foth & Turk, 1972). The pH of the microbial cytoplasm approximates to neutral, and therefore most soil microorganisms thrive at pH values near 7.0 (Gray & Williams, 1971). However, the occurrence of a microbe in a soil with a certain gross pH does not necessarily mean that it is functioning at that pH value. Conditions are not always similar in micro-environments in relation to that of the bulk soil environment. This may be attributed to localised changes in pH, influenced by soil organisms and plant roots in conjunction with the chemico-physical properties of soil particles (Gray & Williams, 1971). Localised differences in pH may also be due to the ability of negatively charged colloids to attract H⁺, resulting in a higher concentrations of these around such colloids (McLaren, 1960).

Many bacteria, such as *Rhizobia* bacteria that are involved in transformations within the N cycle, are also adversely impacted by toxic levels of Al³⁺ and Al(OH)²⁺ that are prevalent at low soil pH (Brady & Weil, 2008). In addition, soil reaction also has a strong effect on the activity of soil borne pathogens along with the antagonistic interaction between beneficial organisms and pathogens. Liu and Baker (1980) demonstrated that an increase in soil pH resulted in an increased rate of infection of radishes by *Rhizoctonia solani*. The alteration of pH was thought to have affected the antagonistic activities of *Pseudomonas* sp. and *Trichoderma harzianum* in the soils (Liu & Baker, 1980). Both *Gaeumannomyces graminis* var. *tritici* and indigenous antagonists are sensitive to soil pH and mineral nutrition (Duffy, *et al.*, 1997). According to Cook and Baker (1983), microbially-mediated take-all decline (*Gaeumannomyces graminis* var. *tritici*) usually occurs after three wheat crops in soils that are slightly acidic with a pH value of 5.5, but tends to be delayed until the sixth or seventh crop rotation when soil pH has been increased to 7.0 through liming. Duffy *et al.* (1997) also reported that take-all severity was decreased through increased effectivity of *T. koningii* as bio control agent in soils with a lower pH or available phosphorous content.

2.3 Historical Overview of Lime Requirement Methods

The problem of determining the LR for a given soil is one that has been studied extensively, resulting in numerous methods that have been suggested which are variously used (Townsend, 1973). Methods that are currently in use are therefore the result of the historical evolution of approaches to LR determination and theory over time. In order to understand the concepts behind the use of contemporary methods, a historical overview pertaining to the development of LR methods essentially follows.

2.3.1 Standard Liming Practices

References to the use of liming materials date back to the first and second centuries B.C. (Barber, 1967). The taste of water that percolated through an acidic soils as a means of detecting soil acidity has been mentioned in literature (Millar, 1955). In the first century A.D., Pliny the Elder extensively documented the use of marl, of which according to him greatly enriched the soils of the Gaelic Provinces and the British Isles (Gardner & Garner, 1953). He also described the type of marl most suitable to a specific soil; a sandy marl for wet soils, and a rich unctuous marl for dry soils (Gardner & Garner, 1953). Through the writings of Ruffin in the early and mid 19th century, the use of lime in the U.S.A. was promoted by reporting that marl applications improved crop yields on his farms (Barber, 1967). According to Dierolf (1986), lime had been used for centuries by European farmers and knowledge of its benefits were carried over to new colonies from previous experience and writings based on the principles of plant growth and nutrition. Agricultural experiment stations situated in several North American states began research on lime – primarily burned lime, gas lime, or marl – between 1880 and 1902 (Barber, 1967).

2.3.2 Early Qualitative Methods

The first use of litmus paper as an indicator of acidity was in 1856 by Thaer (Millar, 1955). In a study done by Dr. H. J. Wheeler, it was reported that soils benefitted more from liming that tested more acid on litmus paper than did soils testing neutral or near neutral (Dierolf, 1986). Use was also made by H. J. Wheeler of the theoretical principal that humus is soluble in acidic solutions. A dilute solution of NH_4OH was shaken in soil, resulting in a yellow-brown colour, the intensity of which was indicative to some extent as to the degree of acidity (Millar, 1955). Another qualitative chemical method that was employed was the pH determination by means of a glass electrode (Shaw, 1953). However, this method is only indicative of the H^+ concentration of the soil solution, thus the concentration of soil acidity cannot quantitatively be determined (Millar, 1955). In addition, complicated calculations in conjunction with additional data, or the intuitive judgement of technicians that are familiar with the soils of the area, are needed to predict the LR based on pH measurements (Shaw, 1953). Further, determining the soil pH is questionable due to the effect that the ionic strength of solutions has on pH measurements (Millar, 1955). It was for these reasons that the need arose to develop chemical methods for the quantitative determination of LR (Shaw, 1953).

2.3.3 Soil-Lime Titrations

The pioneering era of quantitative determination of soil LR emerged between the late 19th and early 20th century. The earliest of these methods were based on reaction of soil with excess CaCO_3 (Shaw, 1953). According to Shaw (1953), Tacke (1897) was arguably the first to investigate this method. The method consisted of suspending excess CaCO_3 with a soil and aspirating the evolved CO_2 for 3 hours at room temperature. The amount of CO_2 that evolved in the reaction was determined as the amount of acidity

present in the soil (Stephenson, 1918). In 1900 however, Wheeler, Hartwell, and Sargent investigated the possibility of utilising evolved CO_2 as a measure to determine the LR of a given soil (Shaw, 1953). Unfortunately, the researchers were unable to identify a reasonable period of time wherein which the elimination of CO_2 would cease and be observed.

Veitch (1902) developed a refined lime-water procedure based on the procedure developed by Tacke, which consisted of a series of CaO equilibrations followed by boiling. The method was designed to raise the pH of the soil to a neutral value. Therefore, the smallest amount of lime-water that caused a faint but permanent pink colour in the presence of phenolphthalein was determined as a soil's apparent acidity equivalent. Nevertheless, the method was shown to have poor reproducibility (Stephenson, 1918) and was considered to be too laborious (Shaw, 1953).

A method in which a neutral salt solution consisting of NaCl mixed with soil was first proposed by Hopkins, Pettit and Knox in 1903 (Veitch, 1904). Their method was based on the author's theory that the mineral acids would bind with mineral bases. The method consisted of shaking the acidic soil together with 5 *N* NaCl solution for three hours. The results obtained were dependent upon liberation of mineral acid from exchange sites, which amounts to free acidity (Stephenson, 1918). A standard fixed base was then titrated with the liberated mineral acid to a phenolphthalein end point. In order to determine LR, the titration result was multiplied by 3 to determine the amount of alkali needed to neutralise 100 g of soil (Veitch, 1904). Hopkins *et al.* (1903) conducted trials in which they added quantitative amounts of lime to the soil as recommended by the method, and found that all of the acidity was neutralised.

Jones (1913) proposed a method similar in type to that of Hopkins *et al.* (1903) in which CaOAc used to extract acidity (Stephenson, 1918). Acetic acid, formed through reaction of mineral acids, was titrated with 0.1 *N* NaOH until a pink colour was achieved in the presence of phenolphthalein. It was shown by Stephenson (1918) that the method proposed by Jones recommended more lime than the method proposed by Hopkins *et al.* (1903). However, the method was further shown to underestimate LR in relation to other methods (Stephenson, 1918), due to the method being regarded as merely an equilibrium H^+ replacement, which is further vitiated by the initial alkalinity of the salt (Shaw, 1953).

Truog (1916) proposed a method where 0.4 *N* $\text{Ba}(\text{OH})_2$ was used to determine active acidity. The soil was treated with an excess $\text{Ba}(\text{OH})_2$ and allowed to react with constant stirring for just a minute. This was followed by the passing of a CO_2 current for approximately two minutes with continued stirring, allowing excess $\text{Ba}(\text{OH})_2$ to change to carbonate. After evaporation to dryness, the excess $\text{Ba}(\text{OH})_2$ was derived from carbonate determination, from which the quantity of acidity was calculated.

Pierre and Worley (1928) titrated soil suspensions with 0.1 *N* $\text{Ba}(\text{OH})_2$ that were held in collodion bags in order to determine the amount of lime needed to bring soils to a definite pH (Dunn, 1943). After

allowing the suspensions to come into equilibrium after three days with intermittent shaking, pH determinations were made on a clear diffusate (Dunn, 1943).

Dunn (1943) investigated soil-lime titrations in order to develop a more satisfactory titration method for determining the LR of a soil. He proposed a method where differing amounts of 0.04 *N* Ca(OH)₂ was added to flasks containing soil and 100 mL of distilled water. The suspensions were allowed to stand for three days, allowing for thorough shaking twice a day. pH measurements were made using a glass electrode, and a titration curve was constructed. The titration curves were compared to field and laboratory trials, where increments of CaCO₃ or Ca(OH)₂ were added to the soils for several months. It was found that the titration curves underestimated the field LRs, but were accurate enough to bring field soil pH values within 0.5 pH units of the target pH.

Liu *et al.* (2004) investigated the time consuming titration method of Dunn (1943) in order to determine if it may be simplified. The original method was modified by only applying three additions of 0.022 *M* Ca(OH)₂ to a 1:1 soil-water mixture, with a 30 minute time interval between additions, during which pH was determined. It was found that the three-addition modification to the original method predicted 80% of the soil acidity as measured by the original three day incubation method by Dunn (1943). The method was further modified by Liu *et al.* (2005), where it was proposed that the 1:1 soil-liquid mixture should contain 0.01 *M* CaCl₂ instead of distilled water. The modified version required only two pH measurements, one after addition of 0.01 *M* CaCl₂, followed by another after addition of 0.022 *M* Ca(OH)₂ and a 30 min shaking period.

2.3.4 Soil-Lime Potentiometric Titrations

The first investigations into the quantitative determination of soil acidity through means of potentiometric titration with Ca(OH)₂ were done by Sharp and Hoagland (1916). Calcium hydroxide was added to soil suspensions until an alkaline reaction was obtained. MacIntire (1920) reported at a 1917 meeting on a collaborative effort that compared various methods that were proposed at the time. The LRs predicted by the methods evaluated were assessed through use of soil-lime incubations. It was reported that the acetate method developed by Jones (1913) had offered the best possibility for obtaining a coefficient of lime determination (Shaw, 1953), although no data was made available by the laboratories that performed the evaluation (MacIntire, 1920).

Bjerrum and Gjalbaek (1919), as cited in Shaw (1953), made a striking contribution to the field when they developed titration/buffer curves through potentiometric titration. Simultaneously, they also established the relationship between the partial pressure of CO₂ and pH values of solutions saturated with CaCO₃ (Shaw, 1953). Jensen (1924) and Christensen and Jensen (1926), as cited in Shaw (1953), respectively used Ca(OH)₂ and CaCO₃ to obtain soil-buffer pH curves. The most well-known titration procedure is that of Bradfield (1942), as cited in (Coleman & Thomas, 1967). Increments of Ca(OH)₂ were added to soil suspensions, followed by aeration to precipitate excess Ca(OH)₂ as CaCO₃. It was

found that the titration curves levelled off at pH 8.2 with the intersection of horizontal lines corresponding to Ca saturation (Coleman & Thomas, 1967).

2.3.5 Buffer Methods

Schofield (1933) developed a soil-buffer method which required two separate titrations. A solution containing lime water and p-nitrophenol was added to a soil sample. After about 16 hours on a shaker, followed by filtration, both the original and soil solutions were titrated with HCl using bromocresol green as indicator. The difference in volume titrated between the two solutions was equal to the milli-equivalents lime taken up by the soil.

Mehlich (1939) highlighted the need for a rapid and accurate method of analysis in order to simultaneously determine base exchange capacity, base and hydrogen saturation, and LR on a large number of soils. In order to achieve this rapid analyses of soils, a TEA-acetate-barium hydroxide buffer at pH 8.15 was proposed. It was reasoned that due to the greater exchange power of barium, base exchange, and acid and base saturation determination would be best accomplished using barium hydroxide. After adding the barium solution, soil samples were shaken for 30 minutes and filtered, and additionally washed with 50 mL Ba^{2+} solution. Base exchange was determined by subtracting titration values from the original buffer and the soil-buffer solution. Titratable acidity was determined through electrometric titration with 0.2 M HCl to pH 6.0. Mehlich (1942b) proposed an improved buffer containing BaCl_2 -TEA buffered at pH 8.2. pH 8.2 was selected, because barium adsorption attains a maximum at this pH (Mehlich, 1942b). Also, BaCl_2 -TEA was selected, since the CO_2 in the air does not influence values obtained during titration. Due to the modifications of this method, base exchange and titratable acidity could be determined on one aliquot of extract.

Brown (1943) was arguably the first to propose the combined use of a glass electrode and the concept of buffer pH depression as means of determining exchangeable H^+ present in soils. Exchangeable H^+ was determined by adding soil to a neutral normal NH_4OAc solution in a 1 to 10 ratio. After allowing the mixture to stand for 1 hour with intermittent shaking, pH was determined. The depression in pH of the mixture was then read off a titration curve as milli-equivalents of acid. Woodruff (1948) proposed a buffer method that required only one pH measurement. The buffer contained CaOAc , p-nitrophenol, and MgO . The buffer was based on the idea that the equilibrium pH of the soil-buffer mixture had a linear relationship to the total exchangeable H^+ (Brown & Cisco, 1984). It was found that the titration curve of the buffer was linear from pH 7.0 to 6.0.

Shoemaker *et al.* (1961) proposed a buffer method that was composed of a more dilute mixture of TEA, p-nitrophenol, K_2CrO_4 , and CaOAc than what was used in the Woodruff procedure. For soils in Ohio, it was observed that the Woodruff buffer recommended only half the actual LR, whereas the Mehlich TEA buffer recommended too high a LR for soils that have been partly limed. The authors stated that the new proposed buffer is much weaker than the popular Woodruff and Mehlich buffers, and is thus

able to indicate a pH change more readily, without reacting with as much acidity as the other two buffers (Shoemaker, *et al.*, 1961). This method would recommend a quantity of lime in excess of that based solely on the assumption that H^+ were the only acidic component in soils (Brown & Cisco, 1984). Consequently, the buffer is able to accurately determine the quantity of lime needed to neutralise soils with appreciable quantities of exchangeable Al. The titration curve of the buffer was linear in the pH range of 7.5 – 4.8.

Adams and Evans (1962) developed a buffer method that was specifically designed for red-yellow podzolic soils that contained low amounts of 2:1 type clays, organic matter, and low cation exchange capacities (Sims, 1996). The buffer solution contains lower amounts of p-nitrophenol than the SMP single buffer method, and is able to detect extremely small differences in LR (Sims, 1996). In contrast to the Woodruff method, the Adams and Evans method has a higher concentration of p-nitrophenol, and contained K-borate instead of CaOAc. The method is further based on a pH-base unsaturation relationship of Ultisols, which is included in the calculation of field LR. The titration curve of the buffer was linear in the pH range of 8.0 – 7.0.

Yuan (1976) was the first to develop the double buffer method in order to take into consideration both the acidity and buffering capacity for a given acidic soil. The buffer consisted of trisaminomethane, imidazole, chromate, and pyridine in a 0.2 M $CaCl_2$ solution. Determination of the LR was based on two separate pH measurements in buffer solutions of the same composition, but initially adjusted to pH 6.0 and 7.0. The acidity to be neutralised was determined by the buffering capacities of a soil, which in turn was defined by dividing the difference in soil acidity neutralised by the two buffer system by the difference of the two equilibrium soil-buffer pH values.

Mehlich (1976) developed a buffer that was designed for the rapid estimation of unbuffered salt exchangeable acidity, along with LR. The buffer consisted of sodium glycerophosphate, acetic acid, TEA, NH_4Cl , and $BaCl_2$. The buffer acidity values as related to pH were calibrated against the unbuffered salt exchangeable acidity. Instead of basing LR on the attainment of a certain pH value, recommendations were made to neutralise a part of the exchangeable acidity. The buffer showed a linear relationship in the range of pH 6.6 to 3.8.

McLean *et al.* (1978) applied the double buffer concept developed by Yuan (1974) to the original SMP single buffer method. The initial buffer pH values for the two buffer solutions were adjusted to pH 6.0 and 7.5. The authors found the new double buffer system to be more promising, especially on soils that have low LRs where the SMP single buffer method was known to lack accuracy. It was stated, however, that the original single buffer method was still the most satisfactory when simplicity of measurement and reasonably accurate results for soils that have a wide range of LRs were taken into consideration.

Nõmmik (1983) proposed a modified buffer method to determine LR and titratable acidity on Swedish soils. The buffer, similar to the buffer of Yuan (1976), consisted of a mixture of trisaminomethane,

imidazole, chromate, and pyridine, which resulted in a linear pH-acidity relationship in the pH range of 7.0 to 5.4. It was found that the method correlated strongly with both the SMP single buffer method, and the Yuan double buffer method.

Brown and Cisco (1984) did a study to investigate the modifications made by Woodruff in the mid 1960's on his original buffer method. The buffer was originally modified to more accurately take into account the contribution of Al, however, Woodruff failed to publish work supporting the change. The new Woodruff buffer was found to be slightly more accurate than the SMP single buffer, however, the authors cautioned that the method should not be adopted on Ultisols and Oxisols prior to being properly calibrated. According to personal communication with Woodruff, as cited by Brown and Cisco (1984), the buffer was originally developed for acid soils that a LR below 10 tons/ha.

Huluka (2005) modified the Adams and Evans buffer due to the hazardous nature of p-nitrophenol. p-nitrophenol was substituted by monobasic potassium phosphate, which has a similar buffering compared to p-nitrophenol. The modified Adams and Evans buffer was shown to be as effective as the original buffer, based on soil-buffer pH made on 407 soil samples. Sikora and Moore (2008) developed a buffer aimed at reproducing similar values as to those obtained through use of the original Adams and Evans buffer. The new buffer consisted of boric acid, 3-(N-morpholino)propanesulfonic acid, and 3-(N-morpholino)ethanesulfonic acid hydrate. The new buffer was compared to the original Adams and Evans buffer on 222 South Carolina soils and 41 North American Proficiency Testing Program soils. It was found that the Moore-Sikora soil-buffer pH was strongly related to those of the Adams and Evans buffer method, however, soil-buffer pH values were lower for the Moore-Sikora compared to the Adams and Evans method. This resulted in a higher LR of 0.34 Tons/ha on average.

Sikora (2006) developed a method aimed at reproducing soil-buffer pH values similar to those obtained through use of the original SMP single buffer method, however, without the hazardous chemicals contained in the original SMP buffer. The p-nitrophenol and chromate was substituted with imidazole and 2-(N-morpholino) ethanesulfonic acid monohydrate. The author found that the new buffer produced soil-buffer pH values similar to that of the SMP buffer on 255 Kentucky soils. It was concluded that the Sikora buffer would be suitable to use on soils to which the SMP buffer is suited.

Hoskins and Erich (2008) modified the original Mehlich (1976) buffer method. Due to the hazardous nature of BaCl₂, Hoskins and Erich (2008) substituted Ba with Ca in the Mehlich buffer. The modified buffer exhibited identical buffering capabilities compared the original buffer. The buffer was shown to exhibited extended linearity over the pH range of 6.6 – 3.0.

2.3.6 South African Methods

The method used to estimate LR in South Africa prior to 1923 was based on the total lime content of a soil as was determined through HCl extraction (Smuts, 2001). This method was found to significantly overestimate the LR of a soil.

Eksteen (1969) proposed a method based on the relationship between the fundamental ratio of extractable Ca and Mg to extractable acidity, termed the R-value $[(Ca+Mg)/H]$, and pH. The method was developed for top soils low in organic matter and a Ca:Mg ratio of approximately 5 (Eksteen, 1969). This method is most commonly used in the winter rainfall region of the Western Cape, South Africa. The principle on which the method is based, is that for every plant or crop, there exists an optimum balance between basic cations and soil acidity (Smuts, 2001). The abovementioned R – value was further related to pH_{KCl} through soil-lime incubation trials, where it was found that R – values of 5 and 10 respectively corresponded to pH values of 5.0 and 5.5. Table 3 - 1 indicates R – values corresponding to specific crops along with target pH values.

Kotzé and Joubert (1979) developed a method based on the relationship of exchangeable acidity and exchangeable Ca and Mg. The method embodied a regression equation based on the amount of lime needed to neutralise a portion of exchangeable acidity that would result in a pH_{KCl} of 5.5.

The Fertiliser Advisory Service at Cedara developed a method based on calculating LR by acid saturation (Manson, 1996). Acid saturation was determined by expressing 1 M KCl exchangeable acidity as a percentage of the total exchangeable cations. The acid saturation concept has been found to be a useful indicator of LR, at least in highly buffered soils (Farina & Channon, 1991).

Table 2 – 1. pH_{KCl} and R value requirements of different crops (Eksteen, 1969)

Crop	Critical pH_{KCl}	R – value
Potatoes	4.1	1.5
Wheat, lupins, seradella, kikuyu	4.5	3
Trifoliums, barley, vegetables	5.0	5
Fruit, vines	5.5	10
Lucerne, medics	6.0	15

Van Zyl (2001) developed a LR method based on the regression analysis of the relationship between the change in acid saturation due to a change in pH_{KCl} . The method was developed based on data obtained from both field and incubation liming trials on four soils.

Smuts (2001) modified the original Eksteen (1969) method due to the efficacy of the method being doubted on certain soils. Furthermore, although Smuts (2001) claimed that the Eksteen method used for the calculation of LR was accurate for a majority of soil types in the Western Cape, some modifications were proposed that could be made to the Eksteen method to address some of the limitations associated with the method. The most prominent modification was adjustment of the standard R-value: pH calibration curve (which predicts R-values of 5 and 10 for pH values of 5.0 and 5.5 respectively). The use of an organic matter correction factor (OMCF) was also suggested to ensure that the method does not over-predict the LR for soils with noticeable organic matter contents. However, none of the proposed changes were evaluated through use of any reference methods.

2.4 Previous Evaluations of Lime Requirement Methods

2.4.1 South African Methods

No contemporary evaluations of LR methods that are used throughout South Africa have been undertaken or published. Smuts (2001) addressed some shortcomings to the Eksteen (1969) method, however, proposed modifications to the method were not evaluated by any means. There have been no other comparisons made between the Eksteen, Cedara, or ARC Small Grain Institute method (van Zyl, 2001) in terms of precision over recent years.

2.4.2 SMP Single Buffer Method

McLean *et al.* (1966) evaluated the SMP single buffer method using soil-lime incubations as reference method. Strong correlations were found between the SMP single buffer method LR and incubation LR, where it was concluded that the SMP single buffer was reasonably accurate for soils requiring more than 4.9 tons/hectare. McLean *et al.* (1966) noted however, that the vertical change in buffer pH in the range of 7.5 to 6.9 would be too great to indicate adequate lime for acid soils with low CEC values.

van Lierop (1983) evaluated the SMP buffer method on acidic organic soils in an eight month incubation study. It was observed that the SMP buffer method was somewhat less precise than the Mehlich buffer for determining the LR of organic soils with a potential LR of more than 20 tons/hectare. However, the SMP buffer was as precise as any other buffer method to accurately determine the LR for soils with potential LRs below 20 tons/hectare. This was attributed to the low buffering capacity of the SMP buffer, as it was observed that the SMP buffer exhibited greater sensitivity to change in pH for a given LR.

Aitken *et al.* (1990) evaluated a number of laboratory procedures used to determine LR, which included the SMP buffer. It was found that a better linear regression fit was obtained when the target pH was closer to the initial buffer pH of 7.5. This was ascribed to the relatively large proportion of soil acidity with which the buffer reacts at pH 7.5, while the LR to obtain a pH of 5.5 would only neutralise a comparatively small proportion of soil acidity. Thus, for soils with a low LR and/or buffer capacity,

use of an alkaline buffer at pH 7.5 would neutralise acidity in the buffering region above pH 7.0. According to the authors, the use of buffers with pH values below 7.0 would be more suitable for these soils.

Machacha (2005) found that the SMP buffer method showed a high correlation ($r = 0.80$) between LR as predicted by the buffer method compared to incubation LR. However, the standard error was quite large ($SE = 0.37$), which according to the author indicated a weak predictability of the method.

Godsey *et al.* (2007) evaluated the SMP buffer method with a two month soil-lime incubation study. A significant correlation ($r^2 = 0.60$) was found between the predicted SMP buffer LR and the incubation LR. It was found however, that the SMP buffer method overestimated LR at low values ($LR < 4.5$ tons/hectare), or underestimated LR at relatively high values ($LR > 4.5$ tons/hectare).

Wolf *et al.* (2008) compared the SMP buffer to the modified Mehlich of Hoskins and Erich (2008) with a three month soil-lime incubation study. A strong correlation ($r = 0.87$) was found between the LR predicted by the SMP buffer method to raise the soil pH_w to 6.5 and the incubation LR. However, it was concluded that the modified Mehlich buffer method was a more accurate predictor of LR for soils from Pennsylvania than the SMP single buffer.

Viswakumar *et al.* (2010) compared the SMP single buffer method with the Sikora single buffer method in a one month soil-lime incubation study. A strong correlation ($r^2 = 0.92$) was found between the two buffers, which indicated that no significant difference between the two methods was found. It was also noted that both the SMP and Sikora single buffer methods accurately predicted LR for soils with a potential LR of more than 4 meq/100g soil, whereas the accuracy decreased for soils with lower LRs.

2.4.3 Adams and Evans Single Buffer Method

Adams and Evans (1962) reported that their method generally underestimated the LR of three soils used for evaluation of the method, compared to the predicted incubation LR. It was suggested that the buffered solution did not measure all of the acidity at lower pH values. However, the difference between the buffer method and incubation LR decreased as the potential LR increased. McLean *et al.* (1966) evaluated the Adams and Evans along with other buffer methods, although no data was published for the Adams and Evans method. It was noted, however, that the Adams and Evans buffer indicated LR values were generally lower than those for the SMP method, especially on for soils with a high LR. On the contrary, the Adams and Evans buffer indicated LR values were considerably higher than those predicted by the Woodruff buffer.

Fox (1980) compared the Adams and Evans buffer method to a soil-lime incubation method, and reported a strong correlation ($r = 0.919$) between the two methods. It was found that the Adams and Evans buffer method overestimated the LR for soils with a low potential LR (< 4.87 meq/100g soil), and underestimated the LR for soils with a high LR (> 4.87 meq/100g soil).

Edmeades *et al.* (1985) evaluated the suitability of the Adams and Evans buffer method to estimate field LR. A significant correlation ($r = 0.77$) was found between the Adams and Evans buffer method and the field LR. However, it was found that the method underestimated the field LR in all cases. From the data reported, it can be observed that the Adams and Evans buffer method recommended less lime than the SMP single buffer method in all but one instance.

Dierolf (1986) evaluated the Adams and Evans buffer method by use of soil-lime incubations and field trials. It was found that the Adams and Evans buffer method was very highly correlated with incubation LR, but largely underestimated incubation LR. It was further shown the Adams and Evans buffer method underestimated field LR, with the problem shown to be the liming factor used in the method, along with the inherent underestimation of the Adams and Evans buffer method LR.

Machacha (2005) evaluated the suitability of the Adams and Evans buffer method on soils in the eastern region of Botswana. It was found that the Adams and Evans buffer method showed a poor correlation ($r = 0.56$) with the actual incubation LR. The method tended to overestimate the LR of soils with a low potential LR, whereas it underestimated the LR of soils with a high potential LR. It was further noted that there was an uneven distribution of data points along the regression line, being indicative of poor accuracy on the soils used in the study.

Kissel *et al.* (2007) evaluated the precision and accuracy of determining LR with the single-addition titration method proposed by Liu *et al.* (2005) in comparison to the Adams and Evans buffer method. It was found that the Adams and Evans buffer method recommended slightly less lime than the single-addition titration method for soils with LRs below 2.22 tons/ha. Further analysis found that the Adams and Evans buffer method was less accurate and precise than the evaluated titration procedure.

2.5 Methods for Evaluating Lime Requirement Methods

2.5.1 Reference Methods

According to McLean *et al.* (1966), the order of testing soils for LR with respect to increased duration of time needed for completion can be listed as follows: pH measurement < titration < incubation trials < field trials. Before the development of rapid LR tests, early researchers had to primarily rely on field trials in order to determine the LRs for soils (McLean, 1973). However, in addition to prolonged periods of time required for completion, researchers are also limited by locality to specific soils with a set range of variables than can be studied. It is for this reason that more rapid laboratory tests have been developed in order to study LR on soils with a wider range of variables. Although field trials are not used as frequently as less time consuming methods, they are still tantamount for correlating laboratory test results with actual field responses (Edmeades, *et al.*, 1985; Peters, *et al.*, 2012; Sims, 1996)

Examples of reference methods commonly used include lime-soil incubation trials as described by Shoemaker *et al.* (1961), buffer methods such as the BaCl₂-TEA method as described by Peech (1965),

and the $\text{Ca}(\text{OH})_2$ titration method as described by Liu *et al.* (2005). Incubation trials can last anything from one up until 17 or more months, whereas buffer and titration methods can take one to two days to complete. Considering that long term lime-soil incubation trials are a more attractive method short of field trials, some pitfalls may be encountered with this method. It should be noted that microbial activity is intensely stimulated under the ideal conditions prevalent under incubation conditions. This can be attributed to soil conditions being at or near field water capacity and room temperature (Dierolf, 1986). In order to overcome the problem associated with microbial activity, Dunn (1943) added 100 mL distilled water to which three drops of chloroform was added to 10 g of soil in a four day incubation trial. In a ten week incubation trial, Nõmmik (1983), 10 ppm dicyandiamide was added to the soil with the intent of suppressing nitrification.

The accumulation of salts is another consideration necessary for incubation trials, as nitrates of Ca, Mg, and K in particular tend to accumulate in the soil due to intense microbial activity (McLean, 1973). These salts should preferably be leached out, or otherwise taken into account, lest they suppress the soil pH (McLean, 1973). Aside from the options of measuring pH in a salt solution or leaching the soil, other methods have been proposed in order to overcome the effects of salt accumulation. Greenhouse pot trials planted with a crop have been used by workers such as Brown and Cisco (1984). It was postulated that the effect of water leaching salts from the soil and crop uptake of nutrients would serve as a prevention of salt accumulation.

A liming factor usually accompanies LR recommendations that were based on laboratory analysis, by means of any of the abovementioned reference methods. Some methods, such as that developed by Adams and Evans (1962) incorporates a liming factor of 1.5, whereas the Eksteen (1969) method incorporates a factor of 4. These factors are usually implemented due to the reduced effectiveness of pulverised agricultural limestone compared to laboratory grade CaCO_3 that is used in incubation studies. Also taken into consideration is the incomplete mixing of a liming material with the soil in the field.

2.5.2 Calculation of Studied Methods' Lime Requirements

2.5.2.1 Eksteen Method

Calculation of the Eksteen method LR requires two steps, firstly a laboratory analysis, and secondly a set of calculations based on the resultant laboratory analysis. In the laboratory step, an acidic extracting solution is used to determine base cations in order to account for any residual lime that might be present in the soil sample, however 1 M NH_4AOc is currently most commonly used in industry. Titratable acidity is determined by using 0.5 M K_2SO_4 as extracting solution, that is weakly buffered at pH 7 with potassium acetate through addition of 0.1 M NaOH. After extraction, the filtrate is titrated with 0.1 M NaOH until a pink colour is achieved in the presence of phenolphthalein. The formula that is used to calculate the LR of a soil through the procedure described above was derived as follows:

$$R = \frac{(Ca+Mg)}{H}$$

where H is titratable acidity determined at pH 7; addition of liming material (x), which concomitantly contains base cations and acid neutralising carbonate, would manipulate the R – value as follows:

$$R = \frac{(Ca+Mg)+X}{H-X}$$

$$RH - RX = (Ca + Mg) + X$$

$$RX + X = RH - (Ca + Mg)$$

$$X(R + 1) = RH - (Ca + Mg)$$

$$X = \frac{RH - (Ca+Mg)}{R+1} \times F$$

where Ca, Mg, and H is expressed in cmol_c/kg and X as the amount of liming material required in tons per hectare for 15 cm soil depth, and F is a field calibration liming factor. According to Smuts (2001), F usually has a value of 4 for soils containing low amounts of organic matter and with CEC values below 7 cmol_c/kg. The field calibration factor (F) is also based on the following assumptions according to Smuts (2001):

- i) Lime dissolution is considered to be 100% effective at pH values below 5.0. Only approximately 50% of liming material reacts at pH values between 5.0 and 5.5.
- ii) A liming material purity of 70% is assumed
- iii) An average bulk density of 1500 kg/m³ is assumed, and not the regularly used 1333 kg/m³.
- iv) A 75% mixing efficiency is taken into consideration, as liming material is seldom uniformly mixed with the soil.

According to Smuts (2001), the Eksteen method's accuracy is doubted for sandy soils, soil with high organic matter contents (>1% organic carbon) and for strongly structured soil containing high Mg concentrations (e.g. low Ca:Mg ratios). The result is over-liming of sandy soils and soils containing high amounts of organic matter, while structured soil with low Ca:Mg ratios tend to be under-limed. The proposed reasons for these limitations are that the Eksteen method does not take into consideration the buffer capacity of a soil, pH dependant acidity of organic matter and the lower neutralising capacity of magnesium.

Modifications to the Eksteen method have resultantly been proposed. Conradie (1994) proposed correction factors to be used for predicted LR based on the carbon content of the soil, as can be seen from Table 2 – 2.

Table 2 – 2. Correction factors to adapt the Eksteen determined lime requirement of soils with different levels of organic carbon (Conradie, 1994)

Carbon Content (%)	Fraction of predicted lime requirement to be applied (%)
0 – 1	100
1 – 2	80
2 – 3	60
3 - 4	40

In certain circumstances where the Mg content of a soil exceeds that of the Ca content, it has also been considered, assuming an optimal Ca:Mg ratio of 4, that the Eksteen method be adapted as follows (van Schoor, *et al.*, 2000):

$$X = \frac{RH - 1.25Ca}{R+1} \times F$$

These adaptations have been found to sufficiently extend the applications of the Eksteen method to soils high in organic matter and soils with appreciable quantities of Mg (Smuts, 2001). Nevertheless, it was argued by Smuts (2001) that these adaptations were empirical in nature which reflected pragmatic solutions to practical problems associated with the application of the Eksteen method on soils for which the Eksteen method was not developed. For this reason some modifications were proposed by Smuts (2001) that could be made to the Eksteen method to address some of the abovementioned limitations. The most prominent modification is the adjustment of the standard R-value: pH calibration curve (which predicts R-values of 5 and 10 for pH values of 5.0 and 5.5 respectively). The use of an organic matter correction factor (OMCF) was also suggested to ensure that the method does not over-predict the LR for soils with noticeable organic matter contents.

The first step towards deriving the OMCF was to account for pH dependant acidity included in total acidity extracted as specified by the procedures of Eksteen (1969). This was done by defining pH dependant acidity in terms of the difference between the acidity as determined by the Eksteen method, which is weakly buffered to pH 7, and acidity determined in 1 M KCl, which is assumed to be at field pH (Smuts, 2001). pH dependant acidity was expressed on a unit pH basis through the following manipulation:

$$\Delta H = \frac{(\text{Total extractable acidity at pH 7}) - (\text{Total neutral salt extractable acidity})}{7.0 - \text{field pH as measured in 1M KCl}}$$

where ΔH is the mean pH dependant acidity in $\text{cmol}/\text{kg}/\text{pH}$ unit. The mean pH dependant acidity for the population of soils with less than 1% carbon was determined to be $0.3 \text{ cmol}/\text{kg}/\text{pH}$ unit. For soils containing more than 1% carbon, the mean pH dependant acidity was corrected for by subtracting the mean pH dependant acidity value from the average value determined for soils containing less than 1% carbon, resulting in a value of $0.411 \text{ cmol}/\text{kg}/\text{pH}$ unit. This value was further divided by the mean carbon content of the soils containing more than 1% carbon (2.031 %), resulting in an OMCF value of 0.202 indicating the mean pH dependant acidity contribution of organic matter for every percentage of soil carbon at any specific soil pH. Resultantly, the acidity extracted as specified by the Eksteen method is corrected for as follows:

$$H_{\text{OMCF}} = H - \{(7.0 - \text{field pH}_{\text{KCl}}) \times \%C \times \text{OMCF}\}$$

It was noted that this correction should only be applied to soils containing more than 1% carbon. However, LRs as predicted after implementation of this correction factor were not evaluated by use of any reference method.

2.5.2.2 Cedara Method

Determination of Cedara method's LR requires two steps, firstly a laboratory analysis and secondly, a set of calculations. In the laboratory step, 1 M KCl exchangeable acidity (Al+H), Ca, and Mg are determined using 2.5 mL of soil in 25 mL of extracting solution, to which a 10 min stirring time was allowed. In the calculation step, LR is calculated as follows:

$$X = [\text{Exch. (Al+H)} - (\text{Total Cations} \times \text{PAS}/100)] \times F$$

where exchangeable acidity and total cations (Ca, Mg, K, Al, H) is expressed in cmol/L and X as the amount of liming material required in tons per hectare for 20 cm soil depth with a CCE of 75%, where PAS refers to a crop "permissible acid saturation". F is a factor indicating the amount of lime required to neutralise 1 cmol/L of exchangeable acidity, and is assumed to be 4.0 where the crop PAS is 20% or higher (Manson, 1996). In situations where the crop PAS is less than 20%, F is calculated as follows:

$$F = 5.0 - \text{PAS}/100 \times 4.0$$

According to the formula indicated above, F increases from 4.0 to 5.0 as PAS concomitantly decreases from 20% - 0%. This is explained by the proportionally higher amount of lime required to achieve such low acid saturation levels, resulting from a stronger buffering capacity at these lower acid saturation levels (Manson, 2000). The Cedara computerised fertiliser advisory service uses F values for different levels of PAS as is indicated in Table 2 - 3.

Table 2 – 3. F-values for different levels of permissible acid saturation (Manson, 2000)

PAS	F - value
1	4.96
5	4.8
10	4.6
15	4.4
20	4.0
> 20	4.0
Established Pasture	2.0
Established Fruit and Nuts	2.0

LRs are generally rounded to the nearest 0.5 tons/ha unless the calculated LR is between 0 and 1.0 tons/ha, where 1.0 tons/ha is recommended (Manson, 2000).

2.5.2.3 ARC – Small Grain Institute (Bethlehem) Method

The ARC method requires two steps to calculate the LR of a soil. Firstly, a laboratory analysis where pH_{KCl} and clay content is determined. In the second step, the values obtained through laboratory analysis are then used in a calculation in the following manner:

$$X = (\Delta pH \times 8.324) + (0.0459 \times \text{Clay } \%) - 1.037$$

where ΔpH is the desired change in pH_{KCl} and X the amount of liming material required in tons per hectare, assuming a CCE of 75.3%. There is, however, no indication as to what depth the liming material needs be applied. In addition, Table 2 - 4 serves as a guideline from which LR may also be determined based on achieving a specific change in pH and acid saturation.

Table 2 – 4. Lime requirement (ton/ha) determination for varying levels of acidity and clay contents (van Zyl, 2001)

% Clay	$\Delta pH > 0.5$	$\Delta pH: 0.5 - 0.4$	$\Delta pH: 0.4 - 0.3$	$\Delta pH: 0.3 - 0.2$	$\Delta pH < 0.2 - 0.1$
	$\Delta \text{ Acid Sat} > 32$	$\Delta \text{ Acid Sat: } 32 - 25$	$\Delta \text{ Acid Sat: } 25 - 15$	$\Delta \text{ Acid Sat: } 15 - 10$	$\Delta \text{ Acid Sat} < 10$
5 – 10	3.9	3.0	2.2	1.4	0.5
10 – 15	4.1	3.3	2.5	1.6	0.8
15 – 20	4.4	3.5	2.7	1.9	1.0
20 – 25	4.6	3.8	2.9	2.1	1.3
25 – 30	4.8	4.0	3.2	2.3	1.5
30 – 35	5.1	4.2	3.4	2.6	1.7

2.5.2.4 Shoemaker-McLean-Pratt Single Buffer Method

A complete discussion on the procedure of the SMP LR method can be found in Sims (1996). The SMP method requires two steps in order to recommend a LR for a given soil. Firstly, 5 mL of deionised water must be added to 5 g of soil in order to determine pH_w with a standardised pH meter. After measurement of pH_w values, 10 mL of the SMP buffer solution is added to the soil-water mixture. The soil-buffer mixture must constantly be shaken for 10 min at 250 oscillations per min. The pH of the soil-buffer mixture, recorded as the soil-buffer pH, must be determined after the mixture has been allowed to stand for 30 min. The second step requires one to select and record the LR based on the soil-buffer pH of Table 2 – 5.

2.5.2.5 Adams and Evans Single Buffer Method

A complete discussion on the procedure of the Adams and Evans LR method can be found in Sims (1996). In order to calculate the LR using the Adams and Evans single buffer, two principal steps need be employed. The first step involves 10 mL of deionized water is added 10 g of air-dry, sieved soil, which is briefly stirred with a glass rod. After 10 min, pH_w is measured on a standardised pH meter and recorded. 10 mL of the Adams and Evans buffer solution is added to the soil-water mixture, which is stirred intermittently for 10 min. The soil-buffer mixture is allowed to stand for 30 min and stirred prior to pH measurement, after which the pH of the solution is measured to the nearest 0.01 pH unit.

The second step involves a set of calculations. The first calculation involves a calculation to estimate acid saturation from the pH_w measurement recorded in the first step. It is based on the relationship between pH_w and acid saturation established by Adams and Evans, and is calculated as follows:

$$\text{Soil pH} = 7.79 - 5.55 (\text{Acid-Sat}_1) + 2.27 (\text{Acid-Sat}_1)^2$$

The same equation is used to determine the acid saturation at the pH value to which the soil will be limed, where acid saturation is denoted as (Acid-Sat_2) in this case. Secondly, the pH determined from the soil-buffer solution is then used to determine the exchangeable acidity as was measured through use of the buffer solution as follows:

$$\text{Exch. Acidity (cmol/L)} = 8(8.00 - \text{Soil-Buffer pH})$$

Based on the values obtained from the above mentioned equations, LR may be calculated as follows:

$$X = (\text{Exch. Acidity}/\text{Acid-Sat}_1) \times (\text{Acid-Sat}_1 - \text{Acid-Sat}_2) \times 1.5 \times 2.24$$

where X is the amount of liming material required in tons per hectare for 20 cm soil depth. A liming factor of 1.5 is included to account for incomplete mixing and reaction of lime with the soil.

Table 2 – 5. Calibration to determine lime requirement of the surface 20 cm of soil using the SMP single buffer method (Sims, 1996)

Soil-buffer pH	Quantity of liming material in tons/ha required to reach target pH				
	Mineral Soils				Organic Soils
	7.0	7.0	6.5	6.0	5.2
	Pure CaCO ₃	←	Ag-ground Limestone ‡	→	
6.8	2.4	3.2	2.7	2.3	1.5
6.7	4.1	5.3	4.7	3.8	2.9
6.6	5.3	7.6	6.5	5.3	4.0
6.5	7.0	10.1	8.5	7.0	5.3
6.4	9.0	12.3	10.5	8.5	6.5
6.3	10.5	14.6	12.3	10.1	7.8
6.2	12.1	16.8	14.3	11.6	9.0
6.1	13.4	19.2	16.1	13.2	10.3
6.0	15.2	21.5	18.1	14.8	11.4
5.9	17.2	23.8	20.1	16.3	12.8
5.8	18.6	26.2	21.9	17.9	13.9
5.7	20.1	28.5	23.9	19.5	15.0
5.6	21.8	30.6	26.0	21.0	16.3
5.5	23.3	33.2	28.0	22.8	17.5
5.4	25.3	35.4	30.0	24.4	18.8
5.3	26.7	37.8	31.8	26.0	19.9
5.2	28.5	40.1	33.8	27.6	21.0
5.1	30.2	42.5	35.8	29.1	22.4
5.0	31.8	44.8	37.8	30.6	23.5
4.9	33.6	47.2	39.9	32.3	24.7
4.8	34.9	49.5	41.6	33.8	26.0

‡ Limestone with a neutralising value of more than 90%

2.6 Gaps in Knowledge

There is a lot of speculation in the South African agricultural industry as to which of the methods currently used to determine LR are most accurate. This speculation is further intensified due to the circumstance that no published evaluations of these methods have been performed. Further, very little information is provided on the accuracy of the methods themselves, as these methods have not been thoroughly investigated in most cases. Indirect methods, which are normally multi-variate models, are mostly used by analytical laboratories and consultants in South Africa. This should warrant caution, as the principles on which these methods are based might not be applicable to soils different from the initial soils used to develop these models. Further, the use of such empirical methods increases the room for error, as these methods do not take the inherent lime potential and/or buffering capacity of a given soil into consideration. Worryingly, there has also been no effort made in developing direct methods that would take these points into consideration, such as buffer or titration methods, to determine LR for common South African agricultural soils. This route would seem to show more potential than the current one taken, as the promise of rapidity, accuracy, and simplicity associated with direct methods outweighs any argument for the current indirect methods used. It would, therefore, be greatly beneficial for the South African agricultural industry to have an evaluation performed on some regularly used LR methods, along with investigating the potential applicability of some buffer methods on South African soils.

Chapter 3

Soil Description and Properties

3.1 Introduction

Sub-Saharan Africa is a region that faces severe problems related to food security, caused by a decreasing per-capita food production (Fageria & Baligar, 2003). To address this problem, it is crucial to minimize any restraints on crop production related to acidic soil. Soil acidification is regarded by some soil scientists to be one of the greatest threats concerning commercial agriculture in South Africa (du Plessis, 1986). Du Plessis (1986) reported that in 1980, 5.04 million hectares of top soil was shown to have been severely acidic ($\text{pH}_{\text{KCl}} < 4.5$), where a further 10.94 million hectares of top soil exhibited moderate acidity ($\text{pH}_{\text{KCl}} 4.5 - 5.5$). Venter *et al.* (2001) estimated that a total of approximately 16 million ha of South Africa's soil is acidic, which constitutes about 13% of the total land surface area.

Soil reactions, essentially controlled by soil pH, result in the transformation of many soil chemical elements (Plaster, 2009). These include important reactions within soil systems such as ion exchange, dissolution and precipitation of minerals, redox, adsorption and complexation reactions (Mcbride, 1994; Menzies, 2003), and therefore determine the availability of plant nutrients. Acidic soil, particularly at pH_w levels below 5.5, impairs plant growth in various ways. Deficiency of essential plant nutrients such as phosphorous, molybdenum, and calcium/magnesium are induced. First mentioned due to complexation with increased soluble aluminium concentrations; and secondly, calcium/magnesium deficiency on account of increased leaching. A further consequence of soil acidity is that the solubility of aluminium and manganese increases to the point where it becomes toxic. The latter consequence is recognised to be the main limitation to plant growth on acid soils (Menzies, 2003), particularly in relation to poor root and shoot growth. Subsoil acidity further inhibits the penetration of roots deeper into the soil, resulting in a shallower root system, thereby lowering utilisation of soil moisture and mineral nutrient reserves (Menzies, 2003).

It is estimated that the surface area of acid soil with a pH_{KCl} below 4.5 in the Eastern Free State (EFS) approximates about 365 000 ha (Bosch & Otto, 1995). According to van Zyl (2001), a third of all soil samples analysed by the ARC Small Grain Institute in Bethlehem during 1997 had a pH_{KCl} of 4.5 or less and an acid saturation of 8% or higher. In Kwa-Zulu Natal (KZN), most agricultural soils have a pH_{KCl} in the range of 3.9 – 5.0, causing soil acidity to be a major constraint to crop yields in the province, especially in the high-rainfall regions (Manson, 2000). According to Meyer *et al.* (1998), soil samples analysed by the Fertiliser Advisory Service of the South African sugar industry that had pH_w values below 5.0 increased from 18% to 43% between the 1980 and 1997. This increase in acidification was observed along with increased evidence of Ca and Mg deficiencies. In the winter rainfall region of the Western Cape (WCP), most of the soils, especially the subsoil, are acidic. According to Saayman and van Huyssteen (1981), 78% of soils samples analysed by the Oenological and Viticultural Research

Institute from 1978 to 1981 had pH_{KCl} values below 5.5. Bosch and Otto (1995) estimated that the surface area of acid soil under wheat cultivation for this region to be at least 65 000 ha. Further, according to Conradie (1983), 70% (*ca.* 30 000 ha) of vineyards in the region are cultivated on soils with pH_{KCl} values below 5.0. The North West Province (NWP) of South Africa is generally not associated with acidic soils, however recent reports from industry have pointed out that acidification of soils from this province is on the rise due to liberal use of NH_4 – based fertilisers.

Therefore, considering that soil acidity evidently remains to be an ongoing problem within various regions in South Africa, a study was conducted where the A and B horizons of 20 soils were sampled from the EFS, KZN, WCP, and NWPs of South Africa. The aim of this chapter is to give an overview of the sampling sites and the properties of the selected acid soils used throughout the study.

3.2 Materials and Methods

The A (0 – 300 mm) and B (300 – 600 mm) horizons of 20 acid soils were sampled from the EFS, KZN, WCP, and NWP. Composite samples were taken from each profile within the designated depth of the diagnostic horizon (See Tables 3 – 2 through 3 – 5). A list of soils sampled, along with their GPS – locations and classification is given in Table 3 – 1. Most of the soils sampled were from cultivated fields, except profile 3 (grass field), 22 (natural fynbos), 23 (natural fynbos), 29 (Eucalyptus plantation), and 30 (grass field). The soils were oven-dried at 40°C for a period of 24 hours. After the soils were dried, they were passed through a 2 mm sieve.

Soil pH was determined in a 1:2.5 soil to liquid ratio in distilled water and 1 M KCl suspension using a standard glass electrode. Exchangeable acidity was determined through a 30 minute extraction with 1 M KCl and titration of the filtrate with 0.05 M NaOH using phenolphthalein as indicator (Thomas, 1982). Exchangeable Al was estimated through addition of 1 M KF, and titrated with 0.05 M HCl until the pink colour of the indicator disappeared (Thomas, 1982). Titratable acidity was determined through extraction with a 0.5 M K_2SO_4 solution which was weakly buffered at pH 7 with K acetate, followed by titration with 0.1 M NaOH using phenolphthalein as indicator (Eksteen, 1969). Total acidity was determined using a BaCl_2 solution buffered at pH 8.2 with triethanolamine, and through titration to end point with 0.2 M HCl using methyl red and methylene blue as indicators. Basic cations were determined using a 1 M NH_4OAc solution adjusted to pH 7.0 (Thomas, 1982). The summation of the basic cations was denoted as the S – value. CEC was determined using 1 M NH_4OAc solution adjusted to pH 7.0 of which the analyte was analysed on an auto analyser.

Organic carbon was determined through the oxidative titration method of Walkley and Black (WB), as specified by Piper (1950). Total carbon was determined through dry combustion using a Leco instrument. Clay and fine silt content was determined through the pipette method (Gee & Bauder, 1986). For the conventional pipette method used to determine soil texture, organic matter was removed

with hydrogen peroxide, along with the removal of oxides using CBD, following dispersion with Calgon. Fe and Al oxides were determined through extraction with a CBD solution, of which the analyte was analysed on an atomic adsorption spectrophotometer (Mehra & Jackson, 1960).

3.3 Results and Discussion

3.3.1 Soil Classification

The soils sampled from each respective province were classified according to guidelines set out by the South African Taxonomic System (Soil Classification Working Group, 1991). A list of soils sampled along with their respective classifications can be found in Table 3 – 1.

Soils sampled from the EFS were predominantly yellow-brown apedal soils. Samples 11, 12, and 16 showed signs of plinthic horizons occurring deeper down in the soil profile. The morphology of these soils thus indicates regular wetting cycles, along with fluctuating water tables. These findings therefore serve to explain the low base cation contents of these soils in general, due to the high leaching potential that these soils are subjected to.

Soils sampled from KZN were predominantly red apedal soils. Sample 18 was the only yellow-brown apedal soil sampled. This soil also showed signs of wetness lower down in the profile. Samples 3 and 19 had notable amounts of C in the topsoils, and as such were classified as humic topsoils. The predominant red apedal characteristics of soils from KZN indicate that these soils are highly weathered. In addition, the morphology of these soils indicate that little to no limitations to drainage exists. This would serve to explain the low total base cation content of samples 2 and 3. However, the other soil samples had considerably higher amounts of basic cations, which is primarily attributed to previous fertiliser regimes and base rich parent materials.

Soils sampled from the WCP were predominantly red and yellow-brown apedal soils. However, samples 30 and 31 were neocutanic soils. Sample 22 was the only sample that had a humic topsoil. This is attributed to the dense fynbos vegetation under which this soil was sampled. In addition, the low base cation content of this soil is indicative of intense leaching, primarily caused by regular wetting cycles along with organic acids associated with the fynbos vegetation that may serve to increase the leaching of these cations. For the other soils, however, their morphology is indicative of intense weathering, along with extremely long periods of soil weathering.

Soils sampled from the NWP were predominantly red apedal soils. Sample 27 was the only one that was classified as yellow-brown apedal. This is attributed to the circumstance that this soil was sampled under an area that receives regular periods of irrigation. However, the majority of the soils sampled were well drained soils, yet contained substantial amounts of base cations. This is indicative of very little leaching that have taken place, and may also be attributed to previous fertiliser regimes and base rich parent materials.

Table 3 – 1. Classification of experimental soils

Province	Profile	Classification	GPS -
		S.A. Taxonomy	Coordinates
Eastern Free State	10	Clovelly 3100	S 27° 53' 52.7" E 28° 55' 29.5"
	11	Avalon 3100	S 27° 54' 37.8" E 28° 53' 47.5"
	12	Glencoe 3200	S 27° 54' 25.8" E 28° 54' 18.8"
	16	Avalon 3100	S 28° 09' 03.7" E 28° 55' 08.7"
	17	Clovelly 3100	S 28° 05' 21.2" E 29° 03' 10.6"
Kwa-Zulu Natal	2	Hutton 3100	S 30° 33' 11.4" E 29° 16' 07.8"
	3	Magwa 1100	S 29° 30' 59.3" E 29° 57' 13.7"
	7	Hutton 2200	S 27° 49' 17.1" E 30° 30' 12.4"
	18	Pinedene 3100	S 29° 10' 56.2" E 31° 27' 36.9"
	19	Inanda 1200	S 28° 51' 18.1" E 31° 17' 37.1"
Western Cape	22	Inanda 1100	S 33° 35' 46.3" E 18° 55' 11.7"
	23	Clovelly 1100	S 34° 03' 05.8" E 18° 56' 14.2"
	29	Hutton 1100	S 33° 55' 13.3" E 18° 54' 53.0"
	30	Oakleaf 2120	S 33° 57' 04.9" E 18° 52' 17.1"
	31	Oakleaf 2120	S 33° 56' 56.9" E 18° 52' 24.8"
North West	24	Hutton 3100	S 25° 58' 50.4" E 27° 01' 16.3"
	25	Hutton 2100	S 25° 58' 41.3" E 27° 00' 26.3"
	26	Hutton 3100	S 25° 58' 29.7" E 26° 59' 36.6"
	27	Clovelly 3100	S 25° 59' 04.2" E 27° 00' 15.8"
	28	Hutton 2100	S 25° 59' 27.1" E 27° 01' 03.2"

3.3.2 Soil Properties

3.3.2.1 Eastern Free State

Properties of the selected soils sampled from the EFS sites can be found in Table 3 – 2. The pH_s values of the soil population from the EFS used in this study were in a relatively narrow range of 3.6 – 4.3, with a mean value of 4.0. Similarly, the pH_w values of these experimental soils were also in a narrow range of 4.3 – 5.0, with a mean value of 4.8. An average difference of 0.7 pH units were observed between pH_s and pH_w . The $CEC_{pH\ 7}$ values of these soils were comparatively low on average (3.78 $cmol_c/kg$), which could be attributed to the low average carbon (WB - C – 0.75%; total C – 0.57%) and clay (10.36%) contents respectively. According to L.F Joseph (2016, Glen Agriculture Institute, Personal Communication), the low C values are typical for soils in the sampling area. The clay contents are lower than expected however, as typical clay content values range from between 19 – 25% for the area. The soils were mostly sampled from fields under potato cultivation, where very sandy soils are strongly preferred. The low CECs observed may consequently result in a significant leaching potential for cations. It should be noted however, that both samples 17 A and B are exceptions to the general population of experimental soils from the EFS, as they both respectively contain significantly higher amounts of C and clay. The $CEC_{pH\ 7}$ values of these two soils are therefore significantly higher compared to the rest of the experimental soils. The difference in average WB - C and total C (dry combustion) for the population of soils observed in Table 3 - 2 may be attributed to over-titration errors which may easily occur due to the inherent low C contents of these soils.

The extractable Ca and Mg values are generally relatively low for the population of soils, which can be attributed to the low CEC values. Once again, samples 17 A and B are exceptions to the general observation, as these soils contain significantly higher amounts of Ca and Mg. The neutral salt exchangeable acidity ranged between 0.35 – 1.75 $cmol_c/kg$ for the entire population of experimental soils sampled in the EFS. On average, the exchangeable acidity was in the order of 0.72 $cmol_c/kg$, which is relatively moderate. On average, the exchangeable Al content of the soil population was relatively low (0.48 $cmol_c/kg$), which does not pose a direct threat for crop production. In contrast to the exchangeable acidity values obtained, the population of soils showed a rather wide range of values for titratable acidity that were comparatively higher than exchangeable acidity values. It should be noted that sample 16 A was shown to be an exception to the norm, as the exchangeable acidity value was markedly higher than the titratable acidity value. This may be due to the duration of time to which this soil has been subjected to acidic conditions, which could result in intense dissolution of aluminosilicate minerals that further serves to explain the high exchangeable Al value (1.00 $cmol_c/kg$). The lowest titratable acidity value obtained (0.67 $cmol_c/kg$) was extracted for soil sample 11 B, which was shown to have the lowest total C (0.26%). In contrast, sample 17 A had the highest value (1.59 $cmol_c/kg$), along with the highest total C value (1.24%). The $BaCl_2$ total extractable acidity values

Table 3 – 2. Properties of experimental soils from the Eastern Free State

Sample No	pH _s	pH _w	Exch. Acidity	Exch. Al	Titrateable Acidity (pH 7.0)	BaCl ₂ Total Acidity	Ca	Mg	S - Value	Buffered CEC (pH 7.0)	WB C	Total C	Clay	Al Oxides	Fe Oxides
			←————— cmol/kg —————→									←————— % —————→			
10 A	3.9	4.4	0.85	0.60	1.04	3.4	0.40	0.20	0.77	2.18	0.58	0.47	2.45	0.06	0.27
10 B	4.1	4.9	0.60	0.40	0.76	2.4	0.34	0.18	0.63	1.68	0.43	0.23	2.48	0.05	0.26
11 A	4.1	4.7	0.55	0.35	0.80	2.8	0.52	0.34	1.05	1.90	0.61	0.42	5.05	0.07	0.33
11 B	4.2	4.9	0.35	0.25	0.67	2.0	0.50	0.23	0.89	1.83	0.67	0.26	5.28	0.08	0.32
12 A	3.9	4.6	0.95	0.75	1.53	5.0	1.10	0.40	1.69	3.21	1.09	0.93	5.47	0.07	0.17
12 B	4.3	5.0	0.45	0.25	0.93	3.2	1.46	0.53	2.20	3.25	0.67	0.41	14.02	0.09	0.44
16 A	3.6	4.3	1.75	1.00	1.23	3.4	0.68	0.22	1.08	2.75	0.49	0.38	3.38	0.06	0.25
16 B	3.8	4.4	0.85	0.70	1.10	2.4	0.89	0.35	1.43	2.75	0.39	0.31	6.43	0.07	0.27
17 A	4.1	5.0	0.45	0.30	1.59	8.0	3.62	1.67	6.06	8.47	1.38	1.24	28.92	0.20	1.08
17 B	4.3	5.4	0.35	0.15	1.35	7.8	3.71	2.57	7.33	9.73	1.17	1.05	30.12	0.24	1.19
Mean	4.0	4.8	0.72	0.48	1.10	4.0	1.32	0.67	2.31	3.78	0.75	0.57	10.36	0.10	0.46
Std. Error	0.07	0.10	0.13	0.08	0.10	0.66	0.38	0.24	0.71	0.86	0.10	0.11	3.19	0.02	0.11

were extremely low for the population of EFS soils. Total extractable acidity values ranged from 2.0 – 8.0 cmol_c/kg, with an average value of 4.0 cmol_c/kg. Once again, sample 11 B had the lowest total acidity value, whereas sample 17 A had the highest value, corresponding with the total C and clay content in these respective soils. This indicates that these soils have very low levels of reserve acidity, which can be attributed to the low average CEC_{pH 7}, total C, and clay content values. The Al oxide content of the experimental soils were in a relatively narrow range of 0.05 – 0.24%, with an average value of 0.10%. Sample 17 A and B was shown to be markedly different than the rest of the soil population, as these soils had the highest Al oxide contents of 0.20 and 0.24% respectively. The third highest value was determined as only being 0.09% for sample 12 B. The Fe oxide content of the soil population ranged between 0.17 – 1.19%, with an average value of 0.46%. Once again, sample 17 A and B were shown to contain the highest amounts of Fe oxides for the population of soils. Sample 17 A and B would resultantly contain more pH dependant charge compared to the rest of the soil population, which would result in higher extractable acidities for methods that have an extracting solution pH value that is significantly higher than the soil pH. This phenomenon can be seen from the total BaCl₂ acidity values obtained for these samples.

3.3.2.2 Kwa-Zulu Natal

Soil properties of experimental soils sampled from KZN can be found in Table 3 – 3. The pH_s values of the soil population from KZN used in this study were in a relatively narrow range of 3.6 – 4.3, with a mean value of 4.1. The pH_w values of these experimental soils were found to be in a relatively wider range of 4.3 – 5.5, with a mean value of 4.8. An average difference of 0.6 pH units were observed between pH_s and pH_w. The CEC_{pH 7} values of these soils were relatively high on average (8.73 cmol_c/kg), which could be attributed to the markedly high average carbon (WB - C – 2.34%; total C – 3.26%) and clay (34.38%) contents respectively. The high average C contents for the population of soils can be attributed to historically dense vegetation that could result from high average annual precipitation and relatively low temperatures.

The extractable Ca and Mg values ranged from 0.34 – 3.53 cmol_c/kg and 0.25 – 3.42 cmol_c/kg respectively. On average, the Ca and Mg contents (2.22 cmol_c/kg and 1.27 cmol_c/kg respectively) were shown to be of moderate content. According to Manson (2000), Ca deficiencies are extremely rare in KZN, whereas Mg deficiencies are routinely considered. From Table 3 – 3 it can be seen that the general Ca content of the soil population is at least approximately twice as large as that of Mg, except in the case of sample 7 B. The neutral salt exchangeable acidity values ranged from 0.10 – 4.75 cmol_c/kg, resulting in an average value of 1.92 cmol_c/kg. These significant exchangeable acidity values can be attributed to the generally high CEC_{pH 7} values observed for the population of soils, as the capacity to retain acidic cations are quite large. Similarly, exchangeable Al values were found to be in

Table 3 – 3. Properties of experimental soils from Kwa-Zulu Natal

Sample No	pH _s	pH _w	Exch. Acidity	Exch. Al	Titrateable Acidity (pH 7.0)	BaCl ₂ Total Acidity	Ca	Mg	S - Value	Buffered CEC (pH 7.0)	WB C	Total C	Clay	Al Oxides	Fe Oxides
							←————— cmol _c /kg —————→						←————— % —————→		
2 A	3.8	4.4	1.50	1.15	2.61	11.0	1.84	0.54	2.81	6.61	1.58	1.68	23.50	0.19	1.37
2 B	4.6	5.3	0.15	0.05	1.04	6.2	3.53	0.99	4.86	5.78	1.13	0.98	26.18	0.17	1.90
3 A	3.9	4.3	4.65	4.10	6.84	48.8	1.43	0.40	2.29	12.17	5.03	9.50	41.01	1.53	2.89
3 B	4.2	4.3	2.15	1.80	3.49	30.8	0.34	0.25	1.13	9.18	3.08	4.04	44.91	1.24	2.51
7 A	3.8	4.6	1.20	1.00	2.47	22.8	3.10	1.92	5.53	8.07	1.89	1.80	44.26	0.28	3.08
7 B	5.0	5.5	0.10	0.10	0.91	19.2	3.21	3.42	6.88	7.25	1.12	0.88	65.04	0.25	3.09
18 A	3.6	4.4	2.15	1.80	3.10	26.4	2.14	1.56	4.06	7.40	1.63	1.68	16.52	0.17	1.08
18 B	4.3	5.0	0.35	0.20	1.74	18.8	3.33	1.78	5.34	6.73	1.34	1.33	14.69	0.16	1.14
19 A	3.9	4.7	4.75	4.25	6.01	43.2	1.18	0.90	2.40	14.12	3.83	6.24	29.88	1.20	3.99
19 B	4.3	5.0	2.15	2.00	3.80	34.0	2.10	0.92	3.18	10.03	2.78	4.48	37.83	1.70	4.77
Mean	4.1	4.8	1.92	1.65	3.20	26.1	2.22	1.27	3.85	8.73	2.34	3.26	34.38	0.69	2.58
Std. Error	0.13	0.13	0.50	0.45	0.59	4.03	0.32	0.28	0.54	0.80	0.39	0.85	4.60	0.19	0.37

a rather wide range of 0.05 – 4.25 cmol_c/kg. Remarkably high exchangeable Al values were observed for samples 3 A and B, 18 A, and 19 A and B, which could be detrimental for crop production. The average exchangeable Al value of 1.65 cmol_c/kg determined for the population of soils is significantly high. In contrast to the exchangeable acidity values obtained, titratable acidity values were found to be in an extremely wide range of 0.91 – 6.84 cmol_c/kg. The highest of these values can be seen to correspond with high C contents in these soils. The average titratable acidity value (3.20 cmol_c/kg) can be seen to almost exceed the combined value of exchangeable Ca and Mg (3.49 cmol_c/kg), indicating high levels of acid saturation. This can be attributed to the high average rainfall prevalent in the region that would allow for significant quantities of base cations to be leached. Further, the high average carbon values for KZN can explain the high acid saturation levels that are indicated, as organic matter forms soluble complexes with base cations, which facilitates the loss of these cations through leaching (Brady & Weil, 2008). Total extractable acidity ranged widely from 6.2 – 48.8 cmol_c/kg, resulting in an average value of 26.1 cmol_c/kg. The highest of these values once again corresponded to high levels of C, along with notable Fe oxide values exceeding 2%. This is an indication of high levels of reserve acidity present in these soils, resulting from the geological age of these soils along with the period of time to which they were subjected to acidic conditions. Thus, it is expected that these soils will show to have substantial potential lime requirements. However, these high values associated with C and oxide contents, can also be attributed to significant amounts of pH dependant acidity being determined, due to the high extracting solution pH of 8.2.

Fe oxide values ranged from 1.08 – 4.77%, with an average value of 2.58% for the population of soils. In contrast to values obtained for Fe oxides, Al oxides ranged from 0.16 – 1.70%, with an average value of 0.69%. These significant CBD extractable oxide contents, along with high C levels in these soils, may explain the notable difference between exchangeable and titratable acidity values (Table 3 – 3). This can be attributed to the high pH value of the extracting solution used to determine titratable acidity, resulting in a significant amount of pH dependant acidity being determined as well.

3.3.2.3 Western Cape

Soil properties of experimental soils sampled from the WCP can be found in Table 3 – 4. The pH_s values of the soil population from the WCP used in this study were in a relatively wide range of 3.9 – 5.5, with a mean value of 4.2. The pH_w values of these experimental soils were found to be in a similarly wide range of 4.2 – 5.8, with a mean value of 4.8. An average difference of 0.6 pH units were observed between pH_s and pH_w. The CEC_{pH 7} values of these soils were relatively low on average (3.56 cmol_c/kg), ranging from 1.84 – 7.14 cmol_c/kg. The highest CEC_{pH 7} values were observed for soils that concomitantly contained significant total C, which in turn would allow for a significant capacity to generate exchange sites. WB - C values ranged from 0.58 – 3.51%, resulting in an average value of

1.24%. Values obtained for total C ranged from 0.39 – 5.72%, with an average value of 1.30%. The clay content of the population of soils ranged from 13.27 – 43.45%, with an average value of 24.57%. The exchangeable Ca and Mg levels in the population of soils ranged from 0.15 – 2.31 cmol_c/kg and 0.12 – 0.81 cmol_c/kg respectively. On average, the respective values of Ca and Mg were in the order of 0.78 cmol_c/kg and 0.47 cmol_c/kg. These extremely low average values, along with a very low S – value, are indicative of intense weathering and consequent leaching of soils that is prevalent in the WCP. These low average values can further be explained by taking into consideration the intense weathering that the parent materials present in the region have undergone over a period of 600 Ma (Oberholzer & Schloms, 2010). Resultantly, soils formed from these weathered materials would be depleted from primary minerals that could serve to supply nutrient elements, along with 2:1 clay minerals that would buffer nutrients against leaching (Oberholzer & Schloms, 2010). These soils would consequently show significantly low levels of base saturation. The neutral salt exchangeable acidity values ranged from 0.05 – 1.75 cmol_c/kg, with an average value of 1.02 cmol_c/kg. The exchangeable Al values ranged from 0.00 – 1.60 cmol_c/kg, with an average value of 1.02 cmol_c/kg. The difference between exchangeable acidity and exchangeable Al is relatively small. In contrast, the titratable acidity values ranged from 0.40 – 3.38 cmol_c/kg, resulting in an average value of 1.63 cmol_c/kg. The highest of these values once again corresponded with the highest WB - and total C value.

It should also be noted that the difference between exchangeable and titratable acidity for the population of soils is not as pronounced as was observed for the population of soils sampled from KZN (Table 3 – 3). This is attributed to lower levels of WB - and total C, along with lower levels of Fe and Al oxides, resulting in lower levels of pH dependant acidity being extracted. Total extractable acidity values ranged from 9.2 – 30.0 cmol_c/kg, with an average value of 13.5 cmol_c/kg. Sample 22 A was the only sample that had significantly higher quantities of total acidity relative to the remaining population of soils. It should be noted however, that this specific sample also contained the highest amount of C in comparison to the other soils of the population. The total acidity values of the majority of other soils ranged between approximately 10 – 20 cmol_c/kg, resulting in the low average value. Thus, the population of soils from the WCP can be expected to show lower levels of reserve acidity, which can further be attributed to the intense weathering that these soils have undergone, along with low C and resultantly low CEC_{pH 7} values. Fe oxide values ranged from 0.91 – 2.78%, with an average value of 1.58%. Al oxide values ranged from 0.21 – 1.17%, with an average value of 0.46%.

3.3.2.4 North West Province

Soil properties of experimental soils sampled from the NWP can be found in Table 3 – 5. The pH_s values of the soil population from the NWP used in this study were in a relatively wide range of 4.2 – 5.7, with a mean value of 4.9. The pH_w values of these experimental soils were found to be in a similarly wide range of 4.8 – 6.5, with a mean value of 5.7. An average difference of 0.7 pH units were observed

between pH_s and pH_w . The $CEC_{pH 7}$ values were in a relatively narrow range of 3.37 – 5.79 $cmol_c/kg$, resulting in an average value of 4.32 $cmol_c/kg$. On average, the WB - C (0.63 %) and total C (0.66%) values were low, ranging between 0.21 – 0.90% and 0.41 – 0.93% respectively. The clay content of the population of soils ranged from 13.70 – 26.00%, resulting in an average value 19.39%. These low C and clay content values may explain the relatively low $CEC_{pH 7}$ values observed in Table 3 – 5. Exchangeable Ca and Mg values ranged between 1.46 – 3.80 $cmol_c/kg$ and 0.62 – 1.38 $cmol_c/kg$ respectively, resulting in respective average values of 2.60 $cmol_c/kg$ and 0.95 $cmol_c/kg$. A high average S – value can be seen from Table 3 – 5 which closely resembles the average $CEC_{pH 7}$ value for the population of soils, indicating that these soils have a relatively high base saturation on average. The exchangeable acidity values fall within a low and narrow range of 0.00 – 0.45 $cmol_c/kg$, resulting in an average value of 0.10 $cmol_c/kg$. Considering the relatively high pH values for the population of soils, a high level of exchangeable acidity is not to be expected. Sample 25 A is the only sample that was shown to contain some exchangeable Al. In contrast to exchangeable acidity, more notable levels of titratable acidity can be observed from Table 3 – 5. Titratable acidity values ranged from 0.25 – 1.12 $cmol_c/kg$, with an average value of 0.52 $cmol_c/kg$. These values should warrant caution, as using this form of extractable acidity on these soils may lead to the eventual over liming of these particular soils. Total extractable acidity fell into a narrow range of 8.0 – 11.0 $cmol_c/kg$, with an average value of 9.2 $cmol_c/kg$. Notably, this average value is higher than that obtained from the EFS population of soils (Table 3 – 2), considering that those soils showed significantly higher levels of acidity. This significant difference in total acidity is attributed to higher average total C and Fe oxide contents observed for the NWP population of soils compared to that of the EFS. The Fe oxide content of the population of soils ranged from 1.12 – 1.90%, with an average value of 1.48%. The Al oxide content were found to be within a narrow range of 0.13 – 0.19%, resulting in an average value of 0.15%.

3.4 Conclusions

The population of soils from the EFS were shown to contain the lowest amounts of C, clay, Fe and Al oxides, along with very low levels of $CEC_{pH 7}$. This in turn shows that these soils can be expected to be weakly buffered in general, which warrants caution when considering lime recommendations. Soils from KZN on the other hand, generally contain high amounts of C and CBD-extractable Fe and Al oxides, along with an accompanying high $CEC_{pH 7}$. Accordingly, these soils may be expected to be strongly buffered as well as contain large amounts of reserve acidity. Lime recommendations should therefore be established whilst taking cognisance of this phenomenon in order to avoid under liming of these soils, especially when exchangeable acidity is used as a calculating parameter to determine lime requirement. Soils from the WCP are intermediary in terms of soils properties when compared to soils from the EFS and KZN. These soils contain relatively low amounts of C, along with low exchangeable Ca and Mg and $CEC_{pH 7}$ values. Yet exchangeable acidity values that are notably higher than those for soils from the EFS. Thus, these soils would possibly require higher amounts of lime in comparison to

soils from the EFS, but may not be as strongly buffered as the soils from KZN. Lastly, it was found that soils from the NWP are only moderately acidic at best in comparison to soils from other provinces, and would therefore not require significant quantities of lime.

Chapter 4

Evaluation of Lime Requirement Methods

4.1 Introduction

The lime requirement (LR) of a soil can generally be regarded as the amount of limestone (CaCO_3) needed by a certain depth of soil to improve the current acid condition to a state that is deemed desirable for optimal crop performance. The contribution of pH dependent acidity to the LR of a soil gradually tends to increase as soil pH is increased (van Lierop, 1990). Thus, the potential LR increases as a target pH increases. According to Reeve and Sumner (1970), exchangeable Al can serve as a reliable indicator of LR on highly weathered soils, such as those that generally occur in South Africa. Exchangeable Al is generally precipitated out a pH_w of about 5.5 to 6.0, resulting in little or no exchangeable Al to be found at higher soil pH values (Sanchez, 1974). Most laboratories in the Western Cape determine soil pH in 1 M KCl, and as such aims to calculate a LR in order to achieve a pH_{KCl} of 5.5. When the pH_{KCl} is below 5.5 (pH_w 6.5), the amount of active H^+ is considered too high, which causes an increase in Al^{3+} solubility and a resultant negative effect on root growth. In such cases, liming material should be applied in order to ameliorate the acidic soil to a more crop suitable condition.

In South Africa, indirect multi-variate models are generally used in order to determine the amount of liming material necessary to appropriately ameliorate soil acidity. These indirect methods are usually based on specific soil parameters that are routinely determined in soil laboratories. However, the accuracy of such methods tend to be doubted in most cases, especially in cases where there is aimed to achieve a desired target pH. The primary cause for doubt on the use of such methods, is that the parameters obtained through soil analysis are usually determined with some degree of error. In addition, calculating for LR based on these methods results in a general accumulation of error, with a resultant decrease in accuracy. A second cause for doubt is that the principles on which these methods rest may not be applicable to all soil forms, yet only to a narrow range of soils within a given geographic region. Thus, the use of such methods significantly reduces the applicability of these methods to the diverse range of soils commonly found in South Africa. However, no direct approaches to LR determination for South African soils have been employed.

The LR determined by most direct chemical methods, on the other hand, is an estimate of the amount of liming material needed by a given soil volume to achieve a target pH (Tran & van Lierop, 1981). The advantage of such methods therefore, is that they directly aim to determine the amount of acidity that need be neutralised in order to achieve a selected soil pH. Thus, the applicability of such methods are not as limited as is the case for indirect methods. LR methods that commonly consist of buffered solutions simply determine the proportion of exchangeable acidity of a soil that needs be neutralised. The amount of CaCO_3 needed to achieve a given soil pH is then obtained by calibrating the pH of the

soil-buffer mixtures against the LR established by an accepted reference method (Tran & van Lierop, 1981). The reference methods, which are generally time consuming, are assumed to give an accurate indication of the total amount of CaCO_3 needed to achieve a given soil pH. Due to the accuracy, rapidity, and simplicity associated with buffered LR tests, compared with the titration or incubation of soils, several methods have been proposed.

In this study, a commonly used soil- CaCO_3 incubation reference method was used to evaluate the ability of some commonly used South African indirect methods, along with two popular American rapid buffer tests, to predict a LR sufficient enough to reach a target pH_{KCl} of 5.5. The South African methods selected for the study include the widely-used Eksteen, Cedara, and ARC Small Grain Institute (Bethlehem) methods. It should be noted that the Cedara method is not based on achieving a target pH, however, but rather a target/missible acid saturation (PAS). However, due to the wide spread use of this method in Kwa-Zulu Natal, the method was nevertheless included in the study and evaluated in a suited manner. The American methods include the Shoemaker-McLean-Pratt single buffer (SMP-SB) and the Adams and Evans single buffer (AE-SB) methods. The principal way in which the suitability of a LR method is evaluated for a group of soils is through laboratory correlation studies. In such studies, various LR methods evaluated are compared to a reference method, such as titration of soils with $\text{Ca}(\text{OH})_2$ or by incubation of these soils with various amounts of CaCO_3 . Thus, this study had the following objectives:

- i) To evaluate the accuracy and precision of some South African lime requirement methods along with two American rapid buffer methods, on a wide range of soils, using a CaCO_3 -incubation study as a reference method;
- ii) To determine the effective range of these methods in order to suggest the most accurate lime requirement method for soil type per province.
- iii) To increase the accuracy of each method, where possible, by improving their calibrations.

4.2 Materials and Methods

Considering that the same soil samples were used throughout the study, standard methods used to determine soil chemical and physical properties of these soils can be found in Chapter 3, section 3.2. See Chapter 3, section 3.3.2 for a detailed description relating to soil chemical and physical properties for each respective soil. Tables 3 – 2 through 3 – 5 depicts all soil chemical and physical information obtained through procedures described in section 3.2.

The oven-dried, sieved experimental soils were incubated in duplicate with carefully weighed amounts of laboratory grade CaCO_3 as determined per selected LR method, for a period of 8 weeks at field water capacity (FWC). Lime requirement was calculated according the Shoemaker-McLean-Pratt single buffer (SMP-SB) method as described by Sims (1996); the Adams and Evans single buffer (AE-SB)

method as described by Sims (1996); the ARC method used by the Small Grain Institute in Bethlehem as described by van Zyl (2001); the Cedara method as described by Manson (2000), where a PAS of 10% was selected; the Eksteen method as described by Eksteen (1969) with some minor exceptions. For the Eksteen method, the Organic Matter Correction Factor (OMCF) was implemented where necessary as described by Smuts (2001). Another modification to the method was evaluated, which was based on calculating LR using 1 M KCl exchangeable acidity in the formula of Eksteen. In addition, for the calculation of LR using the method of Eksteen, instead of using Ca and Mg values determined through extraction with 0.1 M HCl as originally described by Eksteen (1969), 1 M NH₄OAc exchangeable Ca and Mg values were used. Further, in instances where the ratio of Ca to Mg was below 1.5, Mg was excluded from the LR calculation and Ca was multiplied by a factor of 1.25 as described by Smuts (2001).

In order to evaluate if the range and applicability of the Eksteen method may be expanded for a wider range of soils than it was originally developed for, a modification to the method was investigated. For this purpose, titratable acidity was corrected for by subtracting potential pH dependent acidity that might arise between pH_{KCl} 5.5 and 7.0. This was done by determining the average pH dependent acidity (ΔH) associated with each soil, along with expressing it on a unit pH basis according to the following formula:

$$\Delta H = \frac{(\text{Total extractable acidity at pH 7}) - (\text{Total neutral salt extractable acidity})}{7.0 - \text{field pH as measured in 1M KCl}}$$

Thus, in order to determine corrected acidity at a specific target pH for use in the modified Eksteen method, the following formula is used:

$$H_{\text{Corrected}} = H - \{(7.0 - \text{target pH}_{\text{KCl}}) \times \Delta H\}$$

FWC for each soil sample was determined in triplicate by the method of Alef and Nannipieri (1995). The field water capacity was further verified by adding increments of distilled water to 60 g of untreated soil placed in 100 mL plastic cups. Addition of water was ceased as soon as the water fully distributed throughout the soil in the cup, or when the average value of FWC water as predicted by the method of Alef and Nannipieri (1995) was neared, and the resultant mass was recorded. This exercise was also carried out in triplicate, after which the average mass value of distilled water added for this verification exercise was taken as mass (g) water content needed to achieve FWC. Soil sample density was determined through use of a 50 mL scoop. Soil was scooped up and was gently tapped 3 times from a height of 5 cm on a flat table top. The soil was levelled off using a metal ruler. The soil in the scoop was weighed on a calibrated analytical scale, and the mass was recorded. This exercise was repeated 3 times, and the average values were recorded. LR recommendations were corrected on a volume basis using these sample density values, in order to determine the equivalent mass of CaCO₃ in mg that needed to be added to 400 g of oven-dried soil. The cups containing the treated soil were placed on a calibrated

weighing scale, after which the scale was zero-ed. Distilled water was carefully added drop wise with a 25 mL syringe to the cups containing the treated soil until the added mass of distilled water was adequate to achieve FWC.

For the incubation trial, 400 g of soil was placed in a glass mason jar to which a predetermined amount of laboratory grade CaCO_3 , as predicted by each method evaluated in the study, was added. Carefully weighed CaCO_3 additions were made to a glass mason jar with a volume of 1.5 L to which 400 g of oven-dried soil was added. The jar was shaken for 5 minutes and rolled on a table counter for a further 1 minute to ensure homogenous mixing between the added CaCO_3 and soil. After mixing, 60 g of soil was scooped into 100 mL plastic cups, of which the exercise was carried out in duplicate. A control was included for each soil which underwent the same procedure as described above, yet to which no lime was added. The plastic cups containing the wetted soil were sealed with accommodating plastic lids, to which a 5 mm hole was punched that was plugged with cotton wool. This was done to ensure that appreciable gas exchange was still allowed for, whilst loss of moisture was aimed to be kept at a minimum. This exercise was repeated for each soil used in the study. The cups containing the soil were placed in carton boxes which were closed with an accompanying carton lid, and placed in a temperature controlled room at a constant temperature of 25°C.

After a period of 4 and 8 weeks, the soils were oven-dried at 40°C to complete dryness. Soil pH was determined in a 1:2.5 soil to liquid ratio in distilled water and 1 M KCl suspension using a standard glass electrode. Titratable acidity and exchangeable base cations were also determined as per procedure mentioned in section 3.2, however this was only done after the 4 and 8 week incubation period. Some cups were periodically weighed over the 8 week incubation period and a minimal moisture loss of 0.3 mL on average per sample was confirmed.

Results obtained from the incubation procedure were used to construct lime-response curves. This was done by plotting the resultant pH due to the addition of a predetermined amount of liming material to 400 g of soil. The regression equations that were calculated from these lime-response curves were used to determine the amount of CaCO_3 needed to achieve a pH_{KCl} of 5.5 for 400 g of soil. This was done by taking the inverse of the slopes of the regression equations used to construct the lime-response curves. Soil pH as determined in 1 M KCl was selected in order to overcome the potential accumulation of salts, that may serve to give inaccurate pH measurements if distilled water were used (McLean, 1973). The amount of $\text{CaCO}_3/400$ g soil was converted to tons CaCO_3/ha by using sample bulk density. Statistical analysis was performed on Dell's Statistica 13 and Microsoft Excel 2013. LRs as predicted by each method was related to incubation LR through linear regression analysis. The significance of the results were evaluated by performing a p-test. In order to evaluate the accuracy of predictions made with the regression equations presented in the Results and Discussion section, the standard error of estimation was determined. The lime response-curve regression equations for three sub-soils were

omitted (Samples 24 B, 26 B, and 27 B) due to their pH_{KCl} values exceeding 5.5. The use of their lime-response curves to calculate LR resulted in negative values.

4.3 Results and Discussion

4.3.1 Lime Response Graphs

Thirty-five samples experienced an increase in pH_{KCl} of control samples that received no lime during incubation. The average increase in pH_{KCl} for the population of soils was 0.11 pH units. Evaluation of the pH_{KCl} values for the untreated soils showed very little deviation from the original pH_{KCl} values. The average pH_{KCl} for the population of soils was 4.3 prior to incubation and 4.4 after incubation. Table 4 – 1 represents the lime response curves obtained for each soil through the soil-lime incubation procedure that were used to determine potential LR to pH_{KCl} 5.5, or a target acid saturation of 10% in the case of the Cedara method. Figures representing the lime response curves can be found in Appendix B. The lime responses graphs were analysed for both linearity and curvilinearity, yet linear relationships were selected as the correlation obtained between pH and CaCO_3 additions did not significantly increase when a curvilinear relationship was employed. Linear increases in pH to CaCO_3 additions have been reported by several researchers. Van Lierop (1983) reported linear increases in pH_w with additions of CaCO_3 to organic soils. Brown and Cisco (1984) reported that for 14 soils, all but one showed linear increases in pH_w up to pH 7.0 to CaCO_3 additions in a greenhouse pot trial. Dierolf (1986) also reported linear increases in pH_{KCl} with incremental increases in CaCO_3 . The linear equations in Table 4 - 1 were calculated from resultant pH_{KCl} after addition of a predetermined amount of CaCO_3 in mg per 400 g of soil. To facilitate the practical application of the following results, potential LR will be represented in tons of CaCO_3 per hectares of soil for 30 cm soil depth in the following sections, and not mg/400 g soil.

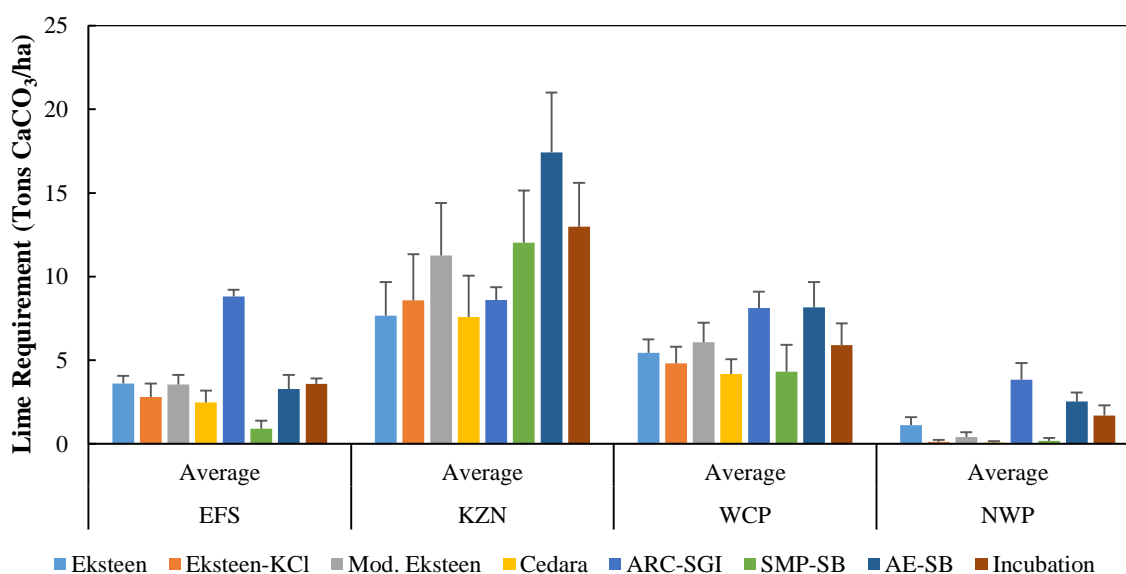


Figure 4 – 1. Average lime requirements, with standard error bars, as predicted each method evaluated for respective provinces included in the study

4.3.2 Evaluation of Methods

The average LR_s predicted by each method for the respective provinces are illustrated in Figure 4 – 1. LR recommendations in tons of ag-lime for each method were converted to tons of pure CaCO₃, assuming a neutralising value of 100%, for 30 cm soil depth. The predicted LR_s were further corrected for bulk density as was determined for each soil. LR values are thus reported on soil volume basis in tons/ha for a depth of 30 cm.

Table 4 – 1. Regression equations of final pH (KCl) (\bar{Y}) versus mg of CaCO₃/400 g soil added (X), used to calculate potential LR

Sample No.	Linear Equation	R ²
10 A	$\bar{Y} = 0.0039X + 4.00$	0.9413
10 B	$\bar{Y} = 0.0049X + 4.25$	0.9990
11 A	$\bar{Y} = 0.0045X + 4.10$	0.9614
11 B	$\bar{Y} = 0.0053X + 4.35$	0.9629
12 A	$\bar{Y} = 0.0028X + 4.15$	0.9992
12 B	$\bar{Y} = 0.0040X + 4.35$	0.9864
16 A	$\bar{Y} = 0.0040X + 3.80$	0.9035
16 B	$\bar{Y} = 0.0043X + 4.00$	0.8171
17 A	$\bar{Y} = 0.0018X + 4.35$	0.9911
17 B	$\bar{Y} = 0.0017X + 4.60$	0.9891
2 A	$\bar{Y} = 0.0014X + 3.80$	0.9972
2 B	$\bar{Y} = 0.0021X + 4.65$	0.9989
3 A	$\bar{Y} = 0.0003X + 4.00$	0.9962
3 B	$\bar{Y} = 0.0005X + 4.30$	0.9808
7 A	$\bar{Y} = 0.0013X + 3.85$	0.9960
7 B	$\bar{Y} = 0.0011X + 5.10$	0.9949
18 A	$\bar{Y} = 0.0014X + 3.70$	0.9923
18 B	$\bar{Y} = 0.0020X + 4.30$	0.9950
19 A	$\bar{Y} = 0.0004X + 4.00$	0.9793
19 B	$\bar{Y} = 0.0005X + 4.30$	0.9719
22 A	$\bar{Y} = 0.0005X + 4.35$	0.9974
22 B	$\bar{Y} = 0.0010X + 4.40$	0.9902
23 A	$\bar{Y} = 0.0016X + 4.15$	0.9929
23 B	$\bar{Y} = 0.0030X + 4.25$	0.9799
29 A	$\bar{Y} = 0.0022X + 4.10$	0.9920
29 B	$\bar{Y} = 0.0026X + 4.20$	0.9697
30 A	$\bar{Y} = 0.0026X + 4.15$	0.9951
30 B	$\bar{Y} = 0.0025X + 4.00$	0.9869
31 A	$\bar{Y} = 0.0031X + 4.50$	0.9985
31 B	$\bar{Y} = 0.0024X + 5.70$	0.9900
24 A	$\bar{Y} = 0.0022X + 5.25$	0.9884
25 A	$\bar{Y} = 0.0029X + 3.95$	0.9939
25 B	$\bar{Y} = 0.0047X + 4.55$	0.9715
26 A	$\bar{Y} = 0.0032X + 4.40$	0.9814
27 A	$\bar{Y} = 0.0029X + 5.10$	0.9701
28 A	$\bar{Y} = 0.0029X + 4.40$	0.9259
28 B	$\bar{Y} = 0.0032X + 4.75$	0.9201

The average predicted LR values for the Eastern Free State (EFS) as determined by use of each respective method ranged between 0.9 to 8.8 tons/ha for 30 cm soil depth. Generally, each LR method predicted less than 4 tons CaCO₃/ha on average. Predicted LR values for soils from the EFS ranged between 0.0 and 11.3 tons CaCO₃/ha for 30 cm soil depth between LR methods. LR values for each respective LR method, including the soil-lime incubation procedure, can be found in Appendix A, Table A – 1. Even though the Eksteen and modified Eksteen methods predicted average LRs that closely approximated the average LR predicted by incubation, no general trend was observed. The methods tended to either grossly over- or underestimate LR. This was essentially attributed to corrections applied to these respective LR methods. It seems as if these LR methods are considerably inaccurate in general on sandy, weakly buffered soils. The ARC Small Grain Institute method, however, was an exception to the general trend, as the average LR was well above 8 tons CaCO₃/ha for the provincial population of soils. All of the LR methods, except the ARC Small Grain Institute method, predicted less lime on average than what was predicted by the soil-lime incubation procedure. Nevertheless, the low average LR values (below 4 tons CaCO₃/ha) are in accordance with the general soil properties of these experimental soils. These soils had low exchangeable and total acidity values on average, along with a low buffering capacity potential due to low C and clay contents (Table 3 – 2). Therefore, high LRs would not generally be expected for these soils.

The LR values for Kwa-Zulu Natal (KZN) were the highest on average compared to the rest of the provincial groups of soils studied. The average predicted LR values as determined by use of each respective method ranged between 7.6 to 17.4 tons CaCO₃/ha for 30 cm soil depth. Predicted LR values for soils from KZN were in a wide range of between 0.0 and 39.9 tons CaCO₃/ha for 30 cm soil depth (Appendix A, Table A – 1). The LR values were generally below 13 tons CaCO₃/ha on average, with half of the LR methods predicting less than 9 tons CaCO₃/ha. The AE-SB LR method was an exception to the general trend, as the average LR as predicted by this method was well above 13 tons CaCO₃/ha. All of the LR methods, except the AE-SB method, predicted less lime on average than was predicted by the soil-lime incubation procedure. The relatively high average LRs for this province compared to the average LR for other provinces are in accordance with the general soil properties of these experimental soils. These soils had the highest exchangeable and total acidity values on average, along with a high buffering potential due to the notably high average C and clay contents (Table 3 – 3). Therefore, high LRs would be expected for these soils.

The LR values for the Western Cape Province (WCP) were intermediate on average compared to the rest of the provincial groups of soils studied. The average predicted LR values as determined by use of each respective method ranged between 4.2 to 8.2 tons CaCO₃/ha for 30 cm soil depth. The LR values were generally below 6.1 tons CaCO₃/ha on average, with three of the LR methods predicting less than 5 tons CaCO₃/ha for these experimental soils. Predicted LR values for soils from the WCP ranged between 0.0 and 17.8 tons CaCO₃/ha for 30 cm soil depth (Appendix A, Table A – 1). The ARC Small

Grain Institute and AE-SB methods were exceptions to the general trend. These respective methods had average predicted LR values in the range of 8 tons CaCO₃/ha. All of the LR methods, except the ARC Small Grain Institute and AE-SB methods, predicted less lime on average than was predicted by the soil-lime incubation

Table 4 – 2. Regression equations, correlation coefficients, and standard error of estimate (S_{x,y}) between the measured (X) and the incubation lime requirements (Y) in tons CaCO₃/ha for each respective province^a

Method	Regression Equation	r ^b	S _{x,y}
Eastern Free State			
Eksteen	$\hat{Y} = -0.2800X + 4.5932$	-0,40	1.03
Eksteen-KCl	$\hat{Y} = -0.0328X + 3.6782$	-0,08	1.11
Modified Eksteen	$\hat{Y} = 0.0427X + 3.4349$	0,07	1.11
Cedara	$\hat{Y} = -0.0297X + 3.6595$	-0,06	1.11
ARC-SGI	$\hat{Y} = 0.3404X + 0.5884$	0,41	1.02
SMP-SB	$\hat{Y} = 0.5809X + 3.0545$	0,83	0.62
AE-SB	$\hat{Y} = 0.3577X + 2.4130$	0,90	0.49
Kwa-Zulu Natal			
Eksteen	$\hat{Y} = 1.2794X + 3.1730$	0,98	1.59
Eksteen-KCl	$\hat{Y} = 0.9291X + 5.0064$	0,98	1.92
Modified Eksteen	$\hat{Y} = 0.8243X + 3.7065$	0,99	1.16
Cedara	$\hat{Y} = 1.0305X + 5.1737$	0,98	1.93
ARC-SGI	$\hat{Y} = 1.3790X + 1.1335$	0,41	7.99
SMP-SB	$\hat{Y} = 0.8206X + 3.1130$	0,98	1.78
AE-SB	$\hat{Y} = 0.6995X + 0.8049$	0,96	2.37
Western Cape Province			
Eksteen	$\hat{Y} = 0.9753X + 0.5943$	0,60	3.47
Eksteen-KCl	$\hat{Y} = 0.9772X + 1.2118$	0,75	2.85
Modified Eksteen	$\hat{Y} = 1.0050X - 0.1954$	0,90	1.85
Cedara	$\hat{Y} = 1.1053X + 1.2881$	0,75	2.85
ARC-SGI	$\hat{Y} = 0.4152X + 2.5349$	0,31	4.12
SMP-SB	$\hat{Y} = 0.7532X + 2.6599$	0,95	1.41
AE-SB	$\hat{Y} = 0.8079X - 0.6880$	0,95	1.37
North West Province			
Eksteen	$\hat{Y} = 1.1353X + 0.4338$	0,93	0.75
Eksteen-KCl	$\hat{Y} = 3.4252X + 1.2817$	0,68	1.49
Modified Eksteen	$\hat{Y} = 1.8244X + 0.9390$	0,85	1.08
Cedara	$\hat{Y} = 5.2441X + 1.2817$	0,68	1.49
ARC-SGI	$\hat{Y} = 0.5242X - 0.3161$	0,87	1.02
SMP-SB	$\hat{Y} = 2.2766X + 1.2817$	0,68	1.49
AE-SB	$\hat{Y} = 1.0186X - 0.8967$	0,88	0.97

^a To obtain approximate rates in tons ag-lime/ha divide by 0.75.

^b r values in bold are significant at p < 0.005.

procedure. The average LR values predicted are in accordance with the general soil properties of these experimental soils. These soils had a relatively high amount of exchangeable and total acidity, however, showed a low to moderate buffering capacity potential due to the low C contents on average (Table 3 – 4). It would therefore be expected that LR values would be less than those predicted for soils from KZN, yet more than those for soils from the EFS.

Table 4 – 3. Regression equations, correlation coefficients, and standard error of estimate ($S_{x,y}$) between the measured (X) and the incubation lime requirements (\hat{Y}) in tons CaCO_3/ha for both all and grouped soils^a

Method	Regression Equation	r^b	$S_{x,y}$
Soils requiring from 0.0 to 26.7 tons CaCO_3/ha soil to achieve $\text{pH}_{\text{KCl}} 5.5$			
Eksteen	$\hat{Y} = 1.3366X + 0.0877$	0,90	2.81
Eksteen-KCl	$\hat{Y} = 1.0242X + 1.8635$	0,91	2.69
Modified Eksteen	$\hat{Y} = 0.9163X + 1.1676$	0,96	1.86
Cedara	$\hat{Y} = 1.1422X + 1.9554$	0,90	2.71
ARC-SGI	$\hat{Y} = 0.8893X - 0.4824$	0,46	5.65
SMP-SB	$\hat{Y} = 0.8498X + 2.3382$	0,97	1.48
AE-SB	$\hat{Y} = 0.7107X + 0.4641$	0,97	1.56
Soils requiring from < 4.0 tons CaCO_3/ha soil to achieve $\text{pH}_{\text{KCl}} 5.5$			
Eksteen	$\hat{Y} = 0.4998X + 1.1528$	0,71	1.08
Eksteen-KCl	$\hat{Y} = 0.3580X + 1.7246$	0,54	1.29
Modified Eksteen	$\hat{Y} = 0.4578X + 1.4458$	0,65	1.16
Cedara	$\hat{Y} = 0.3968X + 1.7337$	0,54	1.29
ARC-SGI	$\hat{Y} = 0.3720X + 0.1039$	0,88	0.72
SMP-SB	$\hat{Y} = 0.8551X + 2.0559$	0,28	1.47
AE-SB	$\hat{Y} = 0.4637X + 1.0225$	0,54	1.29
Soils requiring from ≥ 4.0 tons CaCO_3/ha soil to achieve $\text{pH}_{\text{KCl}} 5.5$			
Eksteen	$\hat{Y} = 1.3406X + 0.8471$	0,88	3.36
Eksteen-KCl	$\hat{Y} = 0.9494X + 3.5543$	0,91	2.92
Modified Eksteen	$\hat{Y} = 0.8789X + 2.0601$	0,96	2.09
Cedara	$\hat{Y} = 1.0531X + 3.7506$	0,91	2.89
ARC-SGI	$\hat{Y} = 0.2319X + 12.398$	-0,05	7.05
SMP-SB	$\hat{Y} = 0.8080X + 3.0238$	0,98	1.46
AE-SB	$\hat{Y} = 0.7088X + 0.5750$	0,97	1.83

^a To obtain approximate rates in tons ag-lime/ha divide by 0.75.

^b r values in bold are significant at $p < 0.005$.

The LR values for the North West Province (NWP) were by far the lowest on average. The average predicted LR values as determined by use of each respective method ranged between 0.1 to 3.8 tons CaCO_3/ha for 30 cm soil depth. Most of the LR methods predicted well below 3 tons CaCO_3/ha on average. Predicted LR values for soils from the NWP ranged between 0.0 and 8.1 tons CaCO_3/ha for 30 cm soil depth. The ARC Small Grain Institute method was an exception to the general trend, as this method had a predicted LR of close to 4 tons CaCO_3/ha on average. All of the LR methods, except the

ARC Small Grain Institute and AE-SB methods, predicted less lime on average than was predicted by the soil-lime incubation procedure. However, the generally low average predicted LR values are to be expected of this province, as these experimental soils had low levels of exchangeable and total acidity and relatively high pH values on average (Table 3 – 5). Thus, a low lime potential lime requirement would be expected for these soils, yet the potential for further acidification should not be ignored.

Analysis from LR data in Table A – 1, reveals that 80% of the soil population had potential LRs below 10 tons CaCO₃/ha. In addition, 52.5% of all experimental soils had potential LRs below 4 tons CaCO₃/ha. Due to this observation, soils were grouped in those needing less or more than 4 tons CaCO₃/ha in order to facilitate a more in depth analysis of LRs as predicted by each method. The LRs predicted by each respective method are discussed and described in more detail in the following sections. The discussion will include a general analysis of the LR method performance in each province, followed by an analysis on the performance of each method on all soils.

4.3.2.1 Eksteen Method

Predicted LR values as determined by use of the Eksteen method ranged between 1.3 to 5.8 tons CaCO₃/ha for 30 cm soil depth for soils from the EFS. The average LR predicted by the Eksteen method was 100.3% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from the EFS (Figure 4 – 1). Despite this observation, the LR predictions made by this method on the EFS soils were quite imprecise. This was indicated by the poor correlation coefficient obtained between the predicted and incubation LRs (Table 4 – 2). No general trend was observed between LR as predicted by the method and LR by incubation. The method overestimated the LR in the majority of cases than was necessary to achieve the target pH_{KCl} of 5.5, as was predicted by incubation. The Eksteen method considerably overestimated the LR on samples 10 to 16, which had LRs of less than 4 tons CaCO₃/ha. These soils were low in C (less than 1% total C) and clay, along with relatively low quantities of exchangeable acidity (Table 3 – 2). Samples 12 A, and 17 A and B were exceptions to the general trend, as the Eksteen method underestimated the LR necessary to achieve the target pH_{KCl}. These two experimental soils had the highest C and clay contents relative to rest of the population of soils from the EFS (Table 3 – 2).

Predicted LR values as determined by use of the Eksteen method ranged between 0.2 to 17.9 tons CaCO₃/ha for 30 cm soil depth for soils from KZN. The average LR predicted by the Eksteen method was 59% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from KZN. Despite this discrepancy, the LRs predictions made by this method was as precise as most other methods evaluated. This was indicated by the similar correlation coefficients obtained for all other methods, except the ARC-SGI method (Table 4 – 2). The method substantially underestimated the LRs for these experimental soils to achieve the target pH_{KCl}. On average, the method's predicted LR was approximately 5 tons CaCO₃/ha less than was predicted by the soil-lime incubation procedure. Further,

none of the experimental soils had C contents of less than 1%, which would therefore require the implementation of the OMCF as described by Smuts (2001), in order to calculate LR. It is clear that such a correction for pH dependant acidity is unnecessary in this case, as these soils had substantial amounts of total acidity that would serve to replenish any acidity neutralised by the addition of lime (Table 3 – 3). These soils would therefore be expected to have high LRs, and would necessarily need large amounts of lime due to their high levels of reserve acidity and resultant strong buffering capabilities. Therefore, the primary problem associated with the Eksteen method is the implementation of the OMCF that causes the method to underestimate the potential LR on soils with more than 1% C.

Predicted LR values as determined by use of the Eksteen method ranged between 0.5 to 8.0 tons CaCO_3/ha for 30 cm soil depth for soils from the WCP. The average LR predicted by the Eksteen method was 91.5% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for soils from the WCP. Although the average LR predictions made by this method closely approximated that of the average LR obtained by incubation, the method was considerably less precise than some other methods studied. This was indicated by the relatively poor correlation coefficient and notable standard error of estimate obtained between the predicted and incubation LRs (Table 4 – 2). The LR as predicted by the Eksteen method closely approximated that predicted by the soil-lime incubation procedure for sample 30 B. However, the method underestimated the LR for samples 22 A and B, 23 A, and 31 A, which may once again be attributed to their C content being larger than 1% (Table 3 – 4), and thus a large correction for acidity due to the implemented OMCF. The method further substantially overestimated the LR for all other soils from the WCP. It should be noted that the experimental population of soils had notable amounts of acidity, yet had relatively low C contents (Table 3 – 4). These soils are resultantly acidic, yet have moderate to weak buffering capabilities. The standard error for this method was also low (0.75), which indicates the LRs predicted by this method in the WCP did not vary much.

Predicted LR values as determined by use of the Eksteen method ranged between 0.0 to 4.6 tons CaCO_3/ha for 30 cm soil depth for soils from the NWP. The average LR predicted by the Eksteen method was 64.7% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for soils from the NWP. Considering the average LR underestimation observed for this method, it was found that the Eksteen method was generally the most precise of the methods evaluated on soils from the NWP. This was indicated by the significant correlation coefficient and the relatively small error of estimation (Table 4 – 2). Nevertheless, the method underestimated the LR needed to achieve the target pH for all soils, except sample 28 B. This experimental soil sample had no LR, even though the soil pH_{KCl} was 4.8. The soil also had a very low level of exchangeable acidity, further indicating no need for a lime application. Soils from the NWP had substantial amounts of Ca and Mg in most cases, which outweighed the titratable acidity values (Table 3 – 5). Thus, the Eksteen method would in practice

underestimate the LR in such scenarios, as the ratio between exchangeable bases and acidity is quite large.

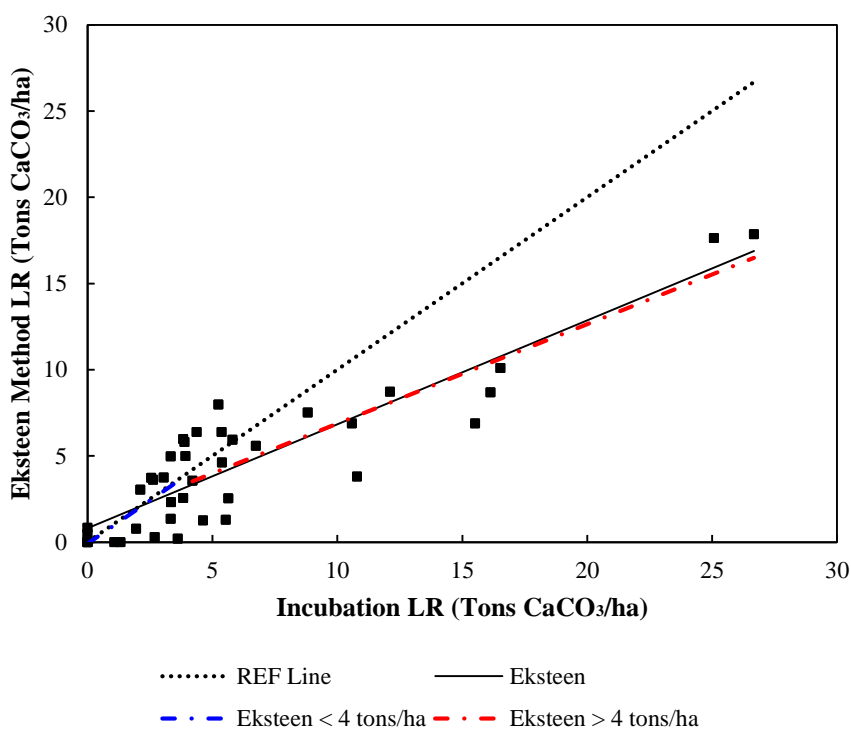


Figure 4 – 2. Relationship between the lime requirements of soils determined by incubation and the Eksteen method

Predicted LR values as determined by use of the Eksteen method ranged between 0.0 to 17.9 tons CaCO_3/ha for 30 cm soil depth for all soils selected for the study. The average LR predicted by the Eksteen method was 75.0% of the amount required to achieve pH_{KCl} 5.5 by incubation for the entire soil population. The method was less precise in general than the most other methods tested in this study, except for the ARC-SGI method. This was indicated by the lower correlation coefficient relative to other methods obtained for this method on all soils (Table 4 – 3). However, comparable correlation coefficients were obtained for the Eksteen-KCl and Cedara methods on all soils (Table 4 – 3). From Figure 4 - 2 it is evident that the Eksteen method tended, on the average, to underestimate the incubation LR, as indicated by the regression line fitted to the data. The average predicted LR was 2.1 and 7.0 tons CaCO_3/ha , or 95.5 and 68.0% of the incubation LR for soils requiring less and more than 4 tons CaCO_3/ha , respectively. From Table 4 – 3, it can be seen that the Eksteen method is less precise on soils that require less than 4 tons CaCO_3/ha than on soils that require more than that amount, as indicated by the correlation coefficients obtained, however a smaller standard error of estimate is obtained for soils with a LR of less than 4 tons CaCO_3/ha . This observation may be attributed to the OMCF applied to the Eksteen method for soils with a C content of more than 1%. For soils that needed more than 4 tons CaCO_3/ha to achieve target pH, 73.7% of them had C contents above 1%. Thus, it is evident that the OMCF applied to the method results in notable error for the determination of LR. The Eksteen

method only overestimated the LR of 30.0% of the experimental population of soils, which were only from the EFS and WCP.

These soils had WB-C values in the range of 0.39 to 0.94%, CBD extractable Al contents of 0.05 to 0.35%, and CEC_{pH7} in the range of 1.68 to 3.47 $cmol_c/kg$. Further, in 83.3% of the instances where the Eksteen method overestimated the LR, soils had clay contents of less than 20%. This reinforces the observation that the Eksteen method has the potential to overestimate LR on weakly buffered, sandy soils (Smuts, 2001). In addition, the method substantially underestimated the LR for 60.0% of the experimental population of soils. In 70.8% of the instances where the Eksteen method underestimated the LR, soils had WB-C values above 1%. Thus, the underestimation of LR observed for this method may be ascribed to the OMCF implemented in the method on soils with more than 1% C. It can therefore be argued that too much of the titratable acidity was corrected for based on the C content of these soils.

The accuracy of the LR predictions made with the Eksteen method can be improved, however, by using the appropriate regression equations provided in Table 4 - 3 for soils requiring more than 4 tons $CaCO_3/ha$, or for soils that have a potential LR of between 0.0 and 26.7 tons $CaCO_3/ha$. However, applying the latter correction would cause the Eksteen method to generally overestimate LR on soils with a potential LR of less than 2 tons $CaCO_3/ha$, whilst progressively underestimating the LR on soils with a potential LR more than that (Figure 4 – 2).

4.3.2.2 Eksteen-KCl Method

Predicted LR values as determined by use of the Eksteen method, modified through implementation of 1M KCl exchangeable acidity for LR calculation, ranged between 0.0 to 8.5 tons $CaCO_3/ha$ for 30 cm soil depth for soils from the EFS. The average LR predicted by the Eksteen-KCl method was 77.8% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from the EFS (Figure 4 – 1). The LR predictions made by this method on the EFS soils was found to be quite imprecise. This was indicated by the very poor correlation coefficient obtained between the predicted and incubation LR's (Table 4 – 2). LR's as predicted by the Eksteen-KCl method closely approximated that predicted by incubation for samples 10 A and B, 12 A, and 16 B. These samples had exchangeable acidity values in the range of 0.60 to 0.95 $cmol_c/kg$ (Table 3 – 2). However, the Eksteen-KCl method underestimated the LR needed to achieve target pH_{KCl} on samples 11 A and B, 12 B, and 17 A and B. These samples had exchangeable acidity values below 0.55 $cmol_c/kg$ (Table 3 – 2). In addition, the Eksteen-KCl method predicted more than twice the needed LR to achieve the target pH_{KCl} , as predicted by the soil-lime incubation procedure for sample 16 A. This sample had an exchangeable acidity value of 1.75 $cmol_c/kg$ (Table 3 – 2).

Predicted LR values as determined by use of the Eksteen-KCl method ranged between 0.0 to 23.4 tons $CaCO_3/ha$ for 30 cm soil depth for soils from KZN. The average LR predicted by the Eksteen method was 66.2% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from KZN. Despite this

discrepancy, the LR's predictions made by this method was as precise as most other methods evaluated. This was indicated by the similar correlation coefficients obtained for all other methods (Table 4 – 2).

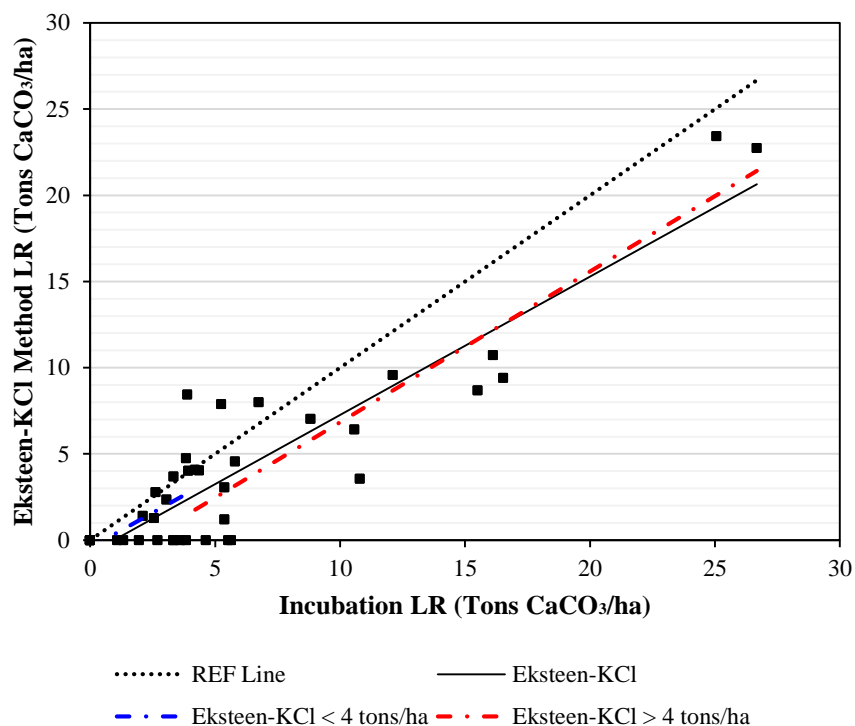


Figure 4 – 3. Relationship between the lime requirements of soils determined by incubation and the Eksteen-KCl method

The method underestimated the LR's for all of the experimental soils, yet predicted LR values were closer to the actual incubation LR than the Eksteen method on soils that had substantial amounts of C (Samples 3 A and B, 18 A, and 19 A; Table 3 – 3). Further, the method did not have a predicted LR for samples 2 B and 7 B, due to the very low exchangeable acidity values (Table 3 – 3). These soils actually did have LR's in excess of 2 tons CaCO₃/ha, as can be seen from the predicted incubation LR values in Table 4 – 4. Even though these soils had low levels of exchangeable acidity, it was still shown to contain substantial amounts of both titratable and total acidity (Table 3 – 3).

Predicted LR values as determined by use of the Eksteen-KCl method ranged between 0.0 to 8.7 tons CaCO₃/ha for 30 cm soil depth for soils from the WCP. The average LR predicted by the Eksteen-KCl method was 81.4% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from the WCP. Although the average LR predictions made by this method was slightly less than that of the average LR obtained with the soil-lime incubation procedure, the method was considerably more precise than the Eksteen method. This was indicated by the higher correlation coefficient and lower standard error obtained between the predicted and incubation LR's (Table 4 – 2). The LR as predicted by the modified Eksteen method closely approximated that predicted by the soil-lime incubation procedure for sample 29 B. The method overestimated the LR for samples 23 A and B, and 29 A. These samples had notable

amounts of exchangeable acidity, whilst having low Ca and Mg contents (Table 3 – 4). However, the method underestimated the LR for samples 22 A and B, 29 A, 30 A and B, and 31 A.

Predicted LR values as determined by use of the Eksteen-KCl method ranged between 0.0 to 1.2 tons CaCO₃/ha for 30 cm soil depth for soils from the NWP. The average LR predicted by the Eksteen-KCl method was 5.9% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from the NWP. Considering the notable underestimation of the average LR observed for this method, it was further found that the Eksteen-KCl method was relatively imprecise compared to other method evaluated on soils from the NWP. The method underestimated the LR for sample 25 A, which was the only experimental soil for which the method determined a LR. This soil had a higher lime potential than the other experimental soils in the population, due to the comparatively larger exchangeable, titratable, and total acidity values (Table 3 – 5). It is therefore quite evident that the Eksteen-KCl is notably insensitive to determine the LR of soils with low potential LRs.

Predicted LR values as determined by use of the Eksteen-KCl method ranged between 0.0 to 23.4 tons CaCO₃/ha for 30 cm soil depth for all soils selected for the study. The average LR predicted by the Eksteen-KCl method was 68.3% of the amount required to achieve pH_{KCl} 5.5 by incubation for the entire soil population. The method was less precise in general than the most other methods tested in this study, however, it was slightly more precise than the Eksteen method. This was indicated by the correlation coefficient relative to other methods obtained for this method on all soils (Table 4 – 3). However, a comparable correlation coefficient was obtained for the Cedara method on all soils (Table 4 - 3). From Figure 4 – 4 it is evident that the Eksteen method tended, on the average, to notably underestimate the incubation LR, as indicated by the regression line fitted to the data. The average predicted LR was 1.4 and 7.1 tons CaCO₃/ha, or 63.6 and 68.9% of the incubation LR for soils requiring less and more than 4 tons CaCO₃/ha, respectively. From Table 4 – 3, it can be seen that the Eksteen-KCl method is less precise on soils that require less than 4 tons CaCO₃/ha than on soils that require more than that amount, as indicated by the different correlation coefficients. The Eksteen-KCl method only overestimated the LR of 10.0% of the experimental population of soils. However, this method is expected to underestimate LR in general, as the use of 1 M KCl exchangeable acidity does not serve as a reliable indicator of all the acidity that needs to be neutralised in order to achieve a certain target pH. In 57.7% of the instances where the Eksteen-KCl method underestimated the LR, soils had WB-C values above 1%. This is attributed to the weaker capacity of K⁺ as a replacing cation to displace tightly bound Al³⁺ from exchange sites (Nõmmik, 1983; Hargrove & Thomas, 1984). It should be noted that Al³⁺ that has been adsorbed and polymerised, and that has not been displaced by a cation such as K⁺, can still affect the actual LRs of soils due to its acidic nature (McLean, 1976). Further, a neutral unbuffered salt solution such as 1 M KCl does not allow for a determination of reserve and pH dependant acidity, which could both substantially react with added liming material. The method substantially underestimated the LR for 65.0% of the experimental population of soils. However, in

76.9% of the instances where underestimation of LR occurred, soils had acid saturations values at soil pH of below 40%. Thus, this indicates that the Eksteen-KCl method would tend to underestimate LR where base cations dominate cation exchange sites.

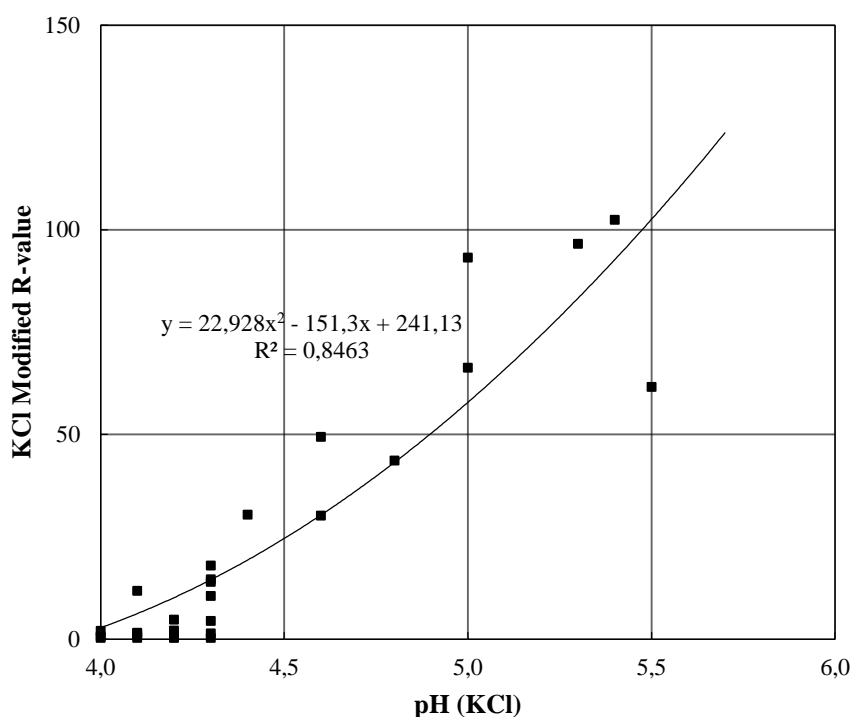


Figure 4 – 4. Relationship between the modified R-value, based on 1 M KCl exchangeable acidity, and pH_{KCl}

This is directly attributed to the ratio of base cations to exchangeable acidity (R-value) used in the calculation of LR with this method. In addition, the R-values used in the Eksteen method were originally calibrated with the inclusion of titratable acidity at pH 7. Thus, using a different form of determinable acidity, such as 1 M KCl exchangeable acidity, would in essence result in a change of R-values. It would therefore be necessary to evaluate the relation between R-values based on another form of acidity and soil pH in order to establish a relationship worth implementing in this method. Based on soil data from Chapter 3, new R-values were calculated based on 1 M KCl exchangeable acidity. The data were plotted against soil pH_{KCl} values, which indicated a significant difference in R-values based on exchangeable acidity in relation to soil pH_{KCl} (Figure 4 – 4). According to this modification, pH 5.0 and 5.5 corresponds to R-values of 58 and 103 respectively.

These values are an order greater than those initially proposed by Eksteen (1969) for similar pH values. Yet, applying these R-values to the calculation of LR with the Eksteen-KCl method did, accordingly result in a higher correlation coefficient (0.8651) when related to the LR by incubation, as can be seen from Figure 4 – 5. However, considering the slight improvement in accuracy, the method will still progressively tend to underestimate the LR of soils. Nevertheless, further work will be needed in order

to significantly increase the accuracy of the Eksteen-KCl method, yet this task was beyond the scope of this study.

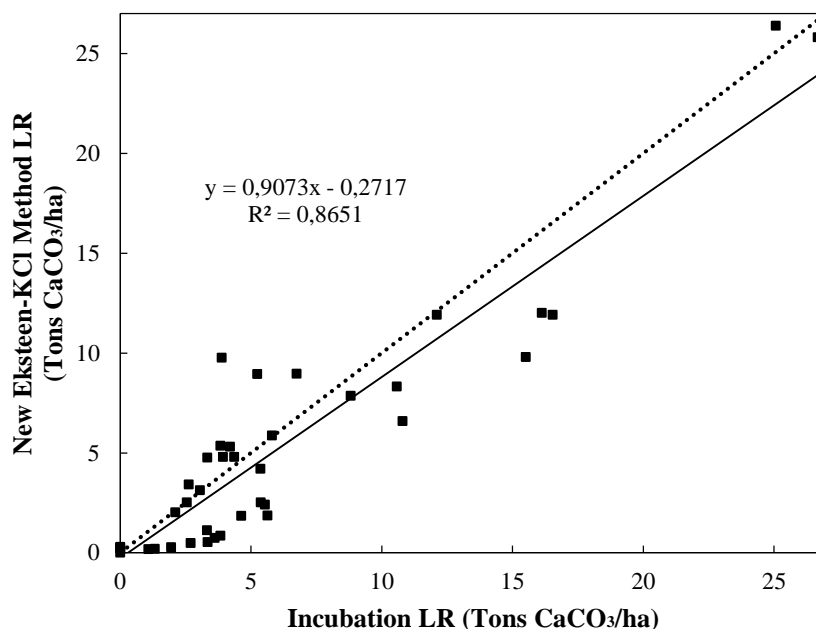


Figure 4 – 5. Relationship between the lime requirements of soils determined by incubation and the modified Eksteen-KCl method

4.3.2.3 Modified Eksteen Method

Predicted LR values as determined by use of the modified Eksteen method ranged between 0.8 to 7.0 tons/ha for 30 cm soil depth for soils from the EFS ranged between. The average LR predicted by the modified Eksteen method was 97.2% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from the EFS (Figure 4 – 1). Despite the close approximation to the average LR as determined through incubation, the LR predictions made by this method on the EFS soils was found to be significantly imprecise. This was indicated by the very poor correlation coefficient obtained between the predicted and incubation LRs (Table 4 – 2). LRs as predicted by the modified Eksteen method closely approximated those predicted by the soil-lime incubation procedure for samples 11 A and B, and 12 B. The method overestimated the LR of samples 10, 12 A, and 16 needed to achieve the target pH_{KCl} . Total acidity values for these soils were below 3.5 cmol_c/kg, thus indicating that these experimental soils did not require substantial amounts of lime to reach the target pH. Also, the total C values of these soils were very low (Table 3 – 2). It would therefore seem that the correction applied to the titratable acidity, did not correct enough of the titratable acidity based on an estimated pH dependent acidity in the calculation. This is due to a very small difference in exchangeable and titratable acidity. Thus, these experimental soils were taken as being more acidic than they were, resulting in the

overestimation of the LRs. Further, the method underestimated the LRs for samples 17 A and B, which were the only samples to have total C values above 1%. In this case, the exact opposite happened relative to the experimental soils that had been over limed. Due to the high total C contents of the under limed soils, the difference between exchangeable and titratable acidity was quite large (Table 3 – 2). Thus, the correction attributed too much pH dependant acidity to the soil, resulting in a larger correction of titratable acidity.

Predicted LR values as determined by use of the modified Eksteen method ranged between 0.2 to 28.5 tons/ha for 30 cm soil depth for soils from KZN. The average LR predicted by the modified Eksteen method was 86.9% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for soils from KZN (Figure 4 – 1). In addition, the LRs predictions made by this method was found to be the most precise out of all methods evaluated (Table 4 – 2). LR as predicted by the modified Eksteen method only closely approximated that predicted by the soil-lime incubation procedure for sample 18 A. The method further underestimated the LRs needed to achieve the target pH for samples 2 A and B, 3 B, 7 A and B, 18 B, and 19 B. In most cases, these soils had notable amounts of exchangeable Ca and Mg, along with total C values above 1% (Table 3 – 3). Thus, applying a correction to the titratable acidity based on an estimated pH dependent acidity, in addition to soils having such large quantities of exchangeable base cations, would cause the method to predict significantly less lime than needed to achieve a certain target pH value. The method did slightly overestimate the LR for samples 3 A and 19 A that required substantial amounts of lime to achieve the target pH. It should be noted that, even though the method

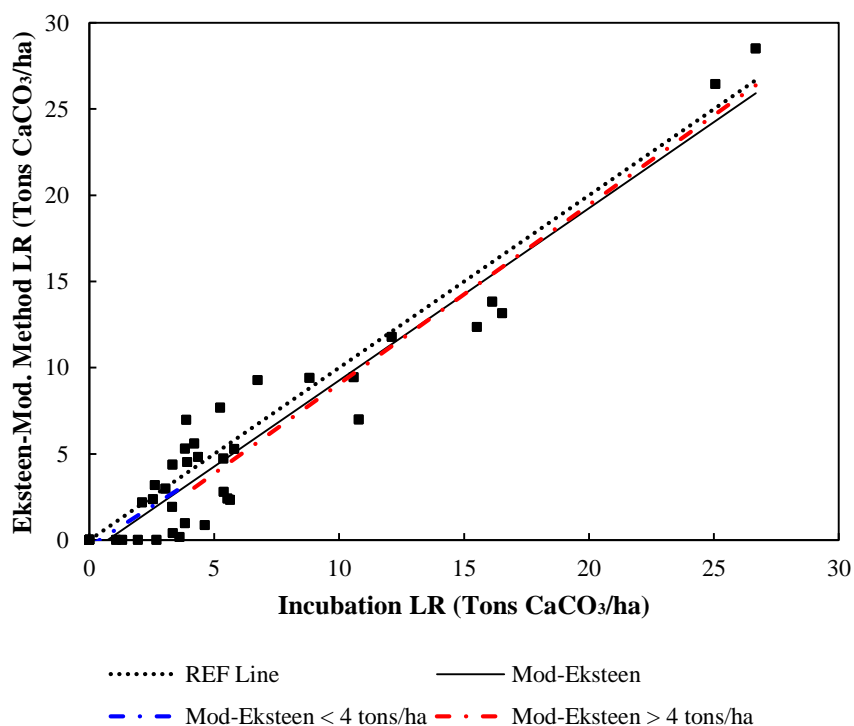


Figure 4 – 6. Relationship between the lime requirements of soils determined by incubation and the modified Eksteen method

shows potential to be used on these soils, applying empirical corrections to soil parameters may result in significant inaccuracies due to the accumulation of calculation error.

Predicted LR values as determined by use of the modified Eksteen method ranged between 0.0 to 12.3 tons/ha for 30 cm soil depth for soils from the WCP. The average LR predicted by the modified Eksteen method was 103.4% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for soils from the WCP (Figure 4 – 1). Although the average LR predictions made by this method slightly overestimated that of the average LR obtained by incubation, the method was considerably more precise than the other indirect LR methods studied (Table 4 – 2). This indicates that the modified Eksteen method is quite suitable for the soils on which it was originally developed. The LR as predicted by the modified Eksteen method closely approximated that predicted by the soil-lime incubation procedure for samples 29 B and 30 B. The method overestimated the LR for samples 22 B, 23 A and B, and 29 A. The method further underestimated the LR for samples 30 A and 31 A. However, the degree of inaccuracy on these soils were not as pronounced as those for the Eksteen method. Predicted LR values as determined by use of the modified Eksteen method ranged between 0.0 to 2.8 tons/ha for 30 cm soil depth for soils from the NWP. The average LR predicted by the Eksteen method was 23.5% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for soils from the NWP (Figure 4 – 1). Considering the average LR underestimation observed for this method, it was found that the modified Eksteen method was reasonably precise in relation to the other methods evaluated on soils from the NWP (Table 4 – 2). However, the method underestimated the LR all soil samples for which the method determined a LR. Thus, it is quite evident that the modified Eksteen method is not well suitable to determine the LR of soils that require small amounts of lime, or that have appreciable quantities of exchangeable base cations.

Predicted LR values as determined by use of the modified Eksteen method ranged between 0.0 to 28.5 tons CaCO_3/ha for 30 cm soil depth for all soils selected for the study. The average LR predicted by the modified Eksteen method was 88.3% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for the entire soil population. The method was found to be the most accurate of all other indirect LR methods tested in this study. This was indicated by the high correlation coefficient relative to other methods obtained for this method on all soils (Table 4 – 3). Interestingly, comparable correlation coefficients were obtained for the SMP-SB and AE-SB methods on all soils (Table 4 – 3).

From Figure 4 – 6 it is evident that the modified Eksteen method tended, on the average, to underestimate the incubation LR, as indicated by the regression line fitted to the data. The average predicted LR was 1.7 and 9.3 tons CaCO_3/ha , or 77.3 and 90.3% of the incubation LR for soils requiring less and more than 4 tons CaCO_3/ha , respectively. From Table 4 – 3, it can be seen that the modified Eksteen method is less precise on soils that require less than 4 tons CaCO_3/ha than on soils that require more than that amount, as indicated by the correlation coefficients. The Eksteen method overestimated

the LR of 40.0% of the experimental population of soils. In 70% of the instances in which the Eksteen method overestimated LR, the soils had exchangeable Ca and Mg contents below 0.9 cmol_c/kg, respectively. In all but one instance, the soils had titratable acidity values above 1.0 cmol_c/kg. This indicates that the modified Eksteen method would tend to overestimate the LR of soils that have undergone intense leaching of base cations, yet that have notable amounts of pH dependant acidity. In such cases, the R-value would be quite low, which would result in a notable LR prediction in order to achieve an R-value of 10 to reach the target pH_{KCl} of 5.5.

The method underestimated the LR for only 45.0% of the experimental population of soils. In 50.0% of the instances where the Eksteen method underestimated the LR, soils had total C values above 1%. In addition, in 83.3% of the instances where underestimation occurred, soils had exchangeable Ca + Mg contents above 2 cmol_c/kg. Thus, the underestimation of LR observed for this method may be ascribed to the correction of titratable acidity based on an estimated pH dependent acidity implemented in the method. It can therefore be argued that too much of the titratable acidity was corrected for in relation to the Ca and Mg contents of these soils. In such cases, the soil would seem to be less acid than it necessarily is due to the increased contribution of Ca and Mg in the calculation, which results in an underestimation of LR. The accuracy of the LR predictions made with the modified Eksteen method can be significantly improved, however, by using the appropriate regression equations provided in Table 4 – 3 for soils requiring more than 4 tons CaCO₃/ha, or for soils that have a potential LR of between 0.0 and 26.7 tons CaCO₃/ha. However, applying both corrections would cause the modified Eksteen method to generally underestimate LR on all soils (Figure 4 – 6).

4.3.2.4 Cedara Method

As has been mentioned previously, the Cedara method was not developed to attain a target pH, but rather a target PAS. As such, evaluation of the Cedara method will proceed to evaluate the method's accuracy pertaining to a target acid saturation/PAS of 10%. In addition, the Cedara method will also be evaluated in terms of the resultant pH_{KCl} that was achieved. Predicted LR values as determined by use of the Cedara method ranged between 0.0 to 7.6 tons/ha for 30 cm soil depth for soils from the EFS. The average LR predicted by the Cedara method was 69.4% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from the EFS (Figure 4 – 1). In addition to this general underestimation of LR, it was found that the LR predictions made by this method on the EFS soils were quite imprecise (Table 4 – 2). LRs as predicted by the Cedara method closely approximated that predicted by the soil-lime incubation procedure for samples 10 A and B. However, the method consistently underestimated the LR needed to achieve the target pH_{KCl} for all soils, except sample 16 A. The average LR predicted by the Cedara method was 178.57% of the amount required to achieve an acid saturation of 10%. Based on data in Appendix A (Table A – 2), acid saturation levels were well below the selected 10% for all EFS soils after a one month incubation period. LRs in order to obtain a PAS of 10% as predicted by

the Cedara method closely approximated that predicted by the soil-lime incubation procedure for samples 11 and 12. The method further did not predict any LR for sample 17 A and B, due to the low exchangeable acidity (Table 3 – 2), even though those soils had the largest LRs as was predicted by the soil-lime incubation procedure. It can be seen that the Cedara method is not a suitable method to indicate the potential LR for the population of EFS soils, especially for attaining a PAS of 10%.

Predicted LR values as determined by use of the Cedara method ranged between 0.0 to 21.0 tons/ha for 30 cm soil depth for soils from KZN. The average LR predicted by the Cedara method was 58.5% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for soils from KZN (Figure 4 – 1). Despite this discrepancy, the LRs predictions made by this method was as precise as most other methods evaluated. This was indicated by the similar correlation coefficients obtained for all other methods, except the ARC-SGI method (Tables 4 – 2). The method had predicted LRs substantially lower than was needed in all cases. It was additionally found that the average LR predicted to attain a PAS of 10% was 78.4% of the amount required as predicted by incubation for soils from KZN. Further, the method predicted the least amount of lime in most cases to achieve the target pH, with samples 3 A and B, and 19 A being exceptions to the general trend. Nevertheless, the method was sufficient in predicting a LR to achieve an acid saturation below the target of 10% in most cases, after a 1 month incubation period. However, the method slightly underestimated the LR for samples 2 A and 19 B, as these soils were shown to have final acid saturation values of 11.82 and 10.64% respectively (Appendix A; Table A – 2). Further, the method did not have a predicted LR for samples 2 B and 7 B, due to the low exchangeable acidity values and high S – values of these soils (Table 3 – 3). These soils therefore had acid saturation levels below that of the target acid saturation. Thus, the Cedara method is acceptably suitable for use in KZN based on the principals for which it was developed.

Predicted LR values as determined by use of the Cedara method ranged between 0.0 to 7.6 tons/ha for 30 cm soil depth for soils from the WCP. The average LR predicted by the Cedara method was 71.2% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for soils from the WCP. In addition to the underestimation of LR associated with this method, the method was considerably less precise than the modified Eksteen, SMP-SB, and AE-SB methods (Table 4 – 2). The average LR predicted by the Cedara method to attain a PAS of 10% was 87.5% of the amount required as predicted by incubation for soils from the WCP. Interestingly, similar correlation coefficients were obtained between the Cedara and Eksteen-KCl method. The LR as predicted by the Cedara method closely approximated that predicted by the soil-lime incubation procedure for sample 23 B. The method did however overestimate the LR compared to the incubation procedure for samples 23 A and 29 A. Further, the method substantially underestimated the LR for all other soils in the population. As has been noted before, the Cedara method is based on achieving a target PAS. The method estimated the correct amount of lime to bring most soils below 10% acid saturation (Appendix A; Table A – 2). However, the method did underestimate the LR needed to achieve such a PAS for samples 22 A and B, as these

soils had respective acid saturations of 17.41 and 13.63% after a one month incubation period (Appendix A; Table A – 2).

Predicted LR values as determined by use of the Cedara method ranged between 0.0 to 0.8 tons/ha for 30 cm soil depth for soils from the NWP. The average LR predicted by the Cedara method was 5.9% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for soils from the NWP. Considering the considerable average LR underestimation observed for this method, it was found that the Cedara method was moderately accurate soils from the NWP. However, the method underestimated the LR for sample 25 A, which was also the only experimental soil for which the method determined a lime requirement. The trend for the Cedara method is similar to that observed for the modified Eksteen method. In addition, the average LR predicted by the Cedara method in order to attain a target PAS of 10% was 25.0% of the amount required as determined by incubation. It is therefore quite clear, that exchangeable acidity does not adequately indicate the potential LR of a soil, especially in cases where the LR is low.

Predicted LR values as determined by use of the Cedara method ranged between 0.0 to 21.0 tons CaCO_3/ha for 30 cm soil depth for all soils selected for the study. The average LR predicted by the

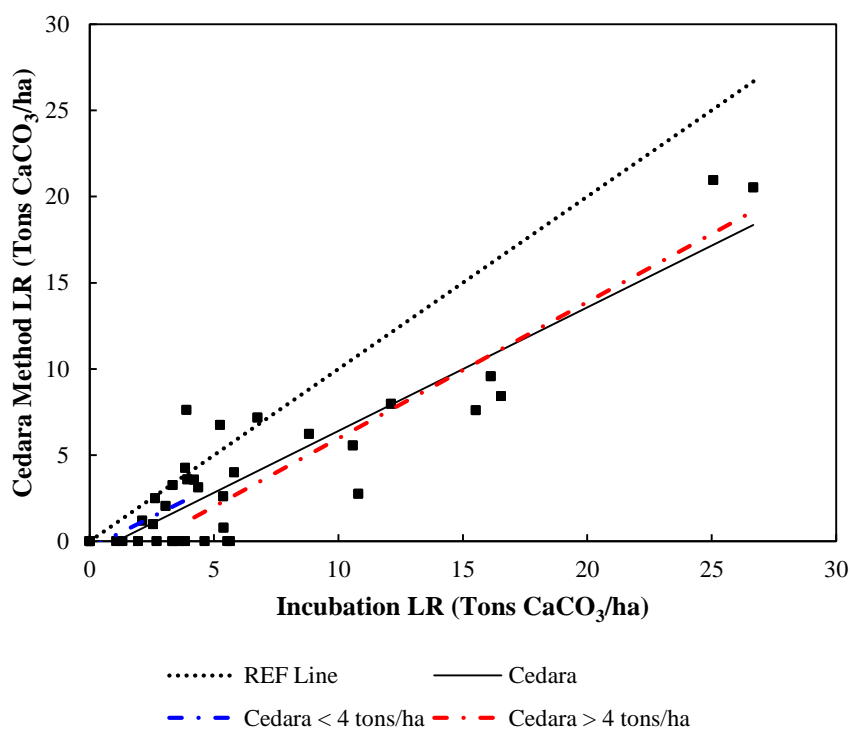


Figure 4 – 7. Relationship between the lime requirements of soils determined by incubation and the Cedara method to achieve a target pH_{KCl} of 5.5

Cedara method was 60.0% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for the entire soil population. The method was less precise in general than the most other methods tested in this study, except for the ARC-SGI method. This was indicated by the lower correlation coefficient relative to other methods obtained for this method on all soils (Table 4 – 3). In addition, the average predicted LR needed to obtain a target PAS of 10% was 87.80% of the amount required as determined by incubation

for all soils. From Figure 4 – 7 it is evident that the Cedara method tended, on the average, to underestimate the incubation LR, as indicated by the regression line fitted to the data. The underestimation observed for this method increased as the incubation LR increased. In the case of attaining a target PAS of 10%, the average predicted LR was 1.5 and 9.7 tons CaCO_3/ha , or 136.4 and 75.2% of the incubation LR for soils requiring less and more than 4 tons CaCO_3/ha , respectively. From Figure 4 – 8 it is clear that the Cedara method would tend to progressively underestimate LR needed to attain a target PAS of 10% for soils with a potential LR of more than 4 tons CaCO_3/ha . In addition, from Table 4 – 3 it can be seen that the Cedara method is considerably less precise on soils that require less than 4 tons CaCO_3/ha than on soils that require more than that amount, as indicated by the correlation coefficients.

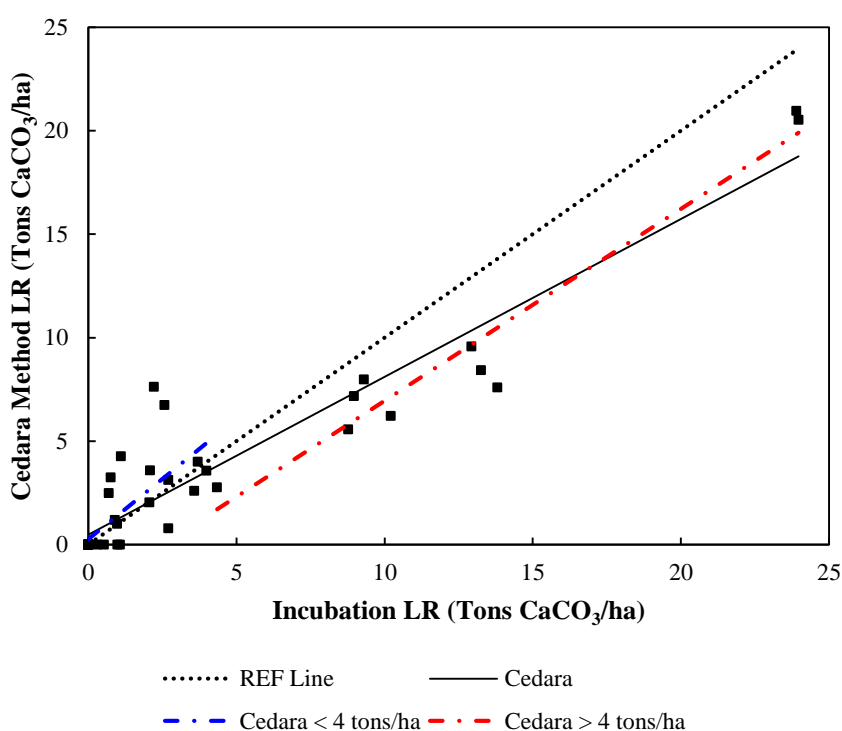


Figure 4 – 8. Relationship between the lime requirements of soils determined by incubation (target acid saturation of 10%) and the Cedara method

The Cedara method only overestimated the LR of 7.5% of the experimental population of soils, which were only from the EFS and WCP. These soils had acid saturation values above 50%, Ca + Mg values below $1.0\text{cmol}_c/\text{kg}$, and exchangeable acidity values larger than $0.95\text{cmol}_c/\text{kg}$. In such cases, calculation of LR by the Cedara method would result in a considerable LR, especially to a PAS of 10%. However, the problem arises when the soils are weakly buffered, as was the case in this this circumstance. These soils had total C levels below 0.6%. In addition, the method substantially underestimated the LR for 70.0% of the experimental population of soils. In 53.6% of the instances where the Cedara method underestimated the LR, soils had WB-C values above 1%. Thus, the underestimation of LR observed for this method may once again be ascribed to the weak displacing

potential of K^+ for Al^{3+} , which would result in an underestimation of exchangeable acidity in soils with substantial levels of OM. In addition, a method based on neutral salt exchangeable acidity will generally predict less lime than what is needed, as such a method does not take pH dependant acidity into consideration that may occupy exchange sites and contribute to acid saturation. This would serve to explain the general underestimation where it aimed to achieve a target PAS of 10%, as soil reserve acidity is not taken into consideration where acidity is determined through use of a neutral salt extraction. As such, non-exchangeable acidity would serve to replenish the neutralised exchangeable acidity, which would result in a higher acid saturation than was anticipated. The accuracy of the LR predictions made with the Cedara method can be improved, however, by using the regression equations provided in Table 4 – 3 for soils requiring more than 4 tons $CaCO_3$ /ha. Nevertheless, the method will continuously underestimate the LR of a soil to achieve a target pH of 5.5, yet the method is sufficient to use in order to obtain a certain target PAS.

4.3.2.5 ARC-SGI Method

Predicted LR values as determined by use of the ARC-SGI method ranged between 7.1 to 11.3 tons/ha for 30 cm soil depth for soils from the EFS. The average LR predicted by the ARC-SGI method was 244.4% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from the EFS. In addition to the considerable overestimation of LRs observed, the LR predictions made by this method on the EFS soils were quite imprecise. This was indicated by the poor correlation coefficient obtained between the predicted and incubation LRs (Table 4 – 2). The method predicted substantially more lime than was needed to achieve the target pH_{KCl} for every soil. This observation is explained through the use of soil pH, specifically the change in pH desired, to determine LR. The experimental soils from the EFS used in the study had low pH_{KCl} values in general (Table 3 – 2). This would result in a considerable change in pH when aiming for pH_{KCl} 5.5, which would need large amounts of lime to achieve when using this method. Also, this method does not take the buffering capacity of a soil into consideration at all, which allows one to conclude that such a method is quite insensitive to accurately reflect the potential LR of a soil.

Predicted LR values as determined by use of the ARC-SGI method ranged between 4.5 to 11.9 tons/ha for 30 cm soil depth for soils from KZN. The average LR predicted by the ARC-SGI method was 66.2% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from KZN. In addition to this discrepancy, the LRs predictions made by this method was significantly less precise compared the other methods evaluated. This was indicated by the very poor correlation coefficient obtained between the predicted and incubation LRs (Table 4 – 2). LRs as predicted by the ARC-SGI method closely approximated those predicted by the soil-lime incubation procedure for samples 2 A and 18 A. However, the method underestimated LRs for samples 3 A and B, and 19 A and B. These experimental soils were shown to have the largest LRs out of the entire soil population, due to their high C,

exchangeable, titratable, and total acidity contents. In addition, these soils also had the highest CEC_{pH7} values, which would indicate for a larger lime potential. Further, the method overestimated LRs for samples 2 B, 7 A and B, and 18 B, which had relatively lower LRs as was predicted by the soil-lime incubation procedure. The method also had the lowest standard error compared to other methods, indicating that there was not such a large difference between the predicted LRs for the experimental soil population. The method is therefore quite insensitive when determining the true LR of a soil, especially on soils with considerable LRs. It is also quite evident that an indirect method of LR determination based on desired change in pH, is not well suited for these soils with large lime potentials.

Predicted LR values as determined by use of the ARC-SGI method ranged between 0.0 to 10.6 tons/ha for 30 cm soil depth for soils from the WCP. The average LR predicted by the ARC-SGI method was 137.3% of the amount required to achieve $pH_{KCl} 5.5$ by incubation for soils from the WCP. The LR predictions made by this method on the WCP soils was found to be significantly imprecise. This was indicated by the very poor correlation coefficient obtained between the predicted and incubation LRs (Table 4 – 2). The ARC-SGI method underestimated the LR of samples 22 A and B. The pH_{KCl} of these soils were slightly higher than the other experimental soils in the population, thus the desired change in pH would not have been as comparatively large. Nevertheless, these soils had substantial amounts of acidity (Table 3 – 4). The method further overestimated the LR of all other soils, as the pH_{KCl} values were below 4.1 in most cases (Table 3 – 4).

Predicted LR values as determined by use of the ARC-SGI method ranged between 0.0 to 8.1 tons/ha for 30 cm soil depth for soils from the NWP. The average LR predicted by the ARC-SGI method was 223.5% of the amount required to achieve $pH_{KCl} 5.5$ by incubation for soils from the NWP. Considering the average LR overestimation observed for this method, it was found that the ARC-SGI method was generally the most precise on soils from the NWP. This was indicated by the high correlation coefficient obtained between the predicted and incubation LRs (Table 4 – 2). The LR as predicted by the ARC-SGI method closely approximated that predicted by the soil-lime incubation procedure for sample 24 A, yet was slightly below. The method further substantially overestimated the LR for the remainder of soils, except samples 24 B and 26 B, where the method correctly had no LR estimation. These soils had pH_{KCl} values of 5.7 and 5.6 respectively (Table 3 – 5).

Predicted LR values as determined by use of the ARC-SGI method ranged between 0.0 to 11.5 tons $CaCO_3$ /ha for 30 cm soil depth for all soils selected for the study. The average LR predicted by the ARC-SGI method was 121.7% of the amount required to achieve $pH_{KCl} 5.5$ by incubation for the entire soil population. The method was notably the most imprecise in general than the most other methods tested in this study. This was indicated by the lowest correlation coefficient relative to other methods obtained for this method on all soils (Table 4 – 3). From Figure 4 – 9 it is evident that the ARC-SGI method tended, on the average, to overestimate the incubation LR for soils with potential LRs below

7.7 tons CaCO_3 , as indicated by the regression line fitted to the data. The average predicted LR was 5.7 and 9.2 tons CaCO_3/ha , or 259.1 and 89.3% of the incubation LR for soils requiring less and more than 4 tons CaCO_3/ha , respectively. From Table 4 – 3, it can be seen that the ARC-SGI method is less precise on soils that require more than 4 tons CaCO_3/ha than on soils that require less than that amount, as indicated by the coefficients of determination. The ARC-SGI method overestimated the LR of 70.0% of the experimental population of soils.

When using the ARC-SGI method, the maximum attainable LR for this method is 15.2 tons CaCO_3/ha ,

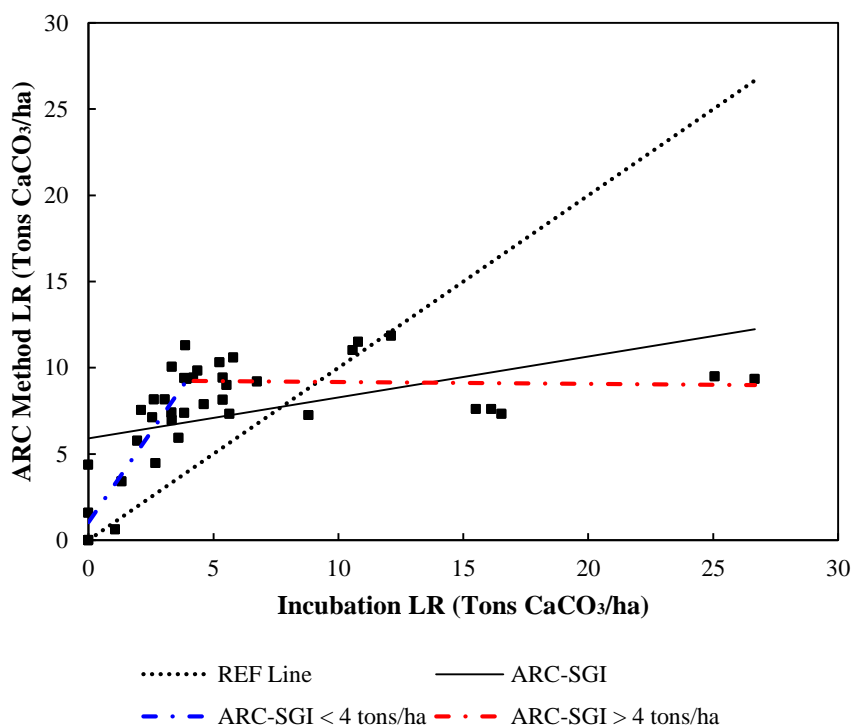


Figure 4 – 9. Relationship between the lime requirements of soils determined by incubation and the ARC-SGI method

assuming a pH_{KCl} of 3.5 and a clay content of 100% with a target pH of 5.5. It is therefore evident that the ARC-SGI is extremely limited in range, and is considerably insensitive to determine the amount of acidity that needs to be neutralised in order to obtain a target pH. However, it is possible to improve the accuracy of the method, by limiting the application thereof on soils with a potential LR of less than 4 tons CaCO_3/ha . Using the regression equation for soils with a LR of less than 4 tons CaCO_3/ha in Table 4 – 3 will make the method considerably more accurate than in its contemporary state.

4.3.2.6 SMP-SB Method

Predicted LR values as determined by use of the SMP-SB method ranged between 0.0 to 3.8 tons/ha for 30 cm soil depth for soils from the EFS. The average LR predicted by the SMP-SB method was 25.0% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from the EFS (Figure 4 – 1). Despite this discrepancy, the LR predictions made by this method on the EFS soils were somewhat

precise. This was indicated by the significant correlation coefficient obtained between the predicted and incubation LR_s (Table 4 – 2). Inaccuracies observed for the method was primarily attributed to the fact that the method has not been calibrated on such soils. The method was only able to predict the LR of three experimental soils, sample 12 A, and 17 A and B. Nevertheless, the method still predicted less lime than was needed to obtain the target pH as was predicted by the soil-lime incubation procedure. These experimental soils were the only ones that had WB-C contents above 1%. In addition, samples 17 A and B had CEC_{pH 7} values well above 8.0 cmol_c/kg. This observation therefore reinforces statements made on the inaccuracy of this method on soils with low CEC's and potential LR_s. In addition, the population of experimental soils from the EFS was shown to not have appreciable quantities of exchangeable Al (Table 3 – 2). It is therefore quite evident that the SMP single buffer method is not well suited for use on soils in the EFS, possibly due to the way it was calibrated. Nevertheless, the method has not been developed for soils such as those that have been selected from the EFS, due to the low CEC's and potential LR_s of these soils.

Predicted LR values as determined by use of the SMP-SB method ranged between 1.1 to 28.2 tons/ha for 30 cm soil depth for soils from KZN. The average LR predicted by the SMP-SB method was 92.3% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from KZN. Despite the underestimation of average LR, the LR_s predictions made by this method were as precise as most other methods evaluated on KZN soils. This was indicated by the similar correlation coefficients obtained for all other methods, except the ARC-SGI method (Table 4 – 2). LR_s as predicted by the SMP method closely approximated those predicted by the soil-lime incubation procedure for sample 3 B. The method slightly overestimated the predicted LR_s for samples 3 A and 19 A and B, which had the highest C contents (Table 3 – 3). The method is expected to underestimate the LR of organic soils, due to the decreased reactivity of H⁺ with the buffer (Sims, 1996). However, this was not observed to be the case for these soils. Further, the method tended to underestimate the predicted LR for samples 2 A and B, 7 A and B, and 18 A and B. These soils had C contents well below 2% and CBD extractable Al contents of less than 0.30% (Table 3 – 3). Considering the above mentioned observations, there is an indication that the SMP was less accurate than expected due to the initial calibration of the method. Nevertheless, the method holds the possibility of being considerably accurate if calibrated properly to the soils prevalent in KZN.

Predicted LR values as determined by use of the SMP-SB method ranged between 0.0 to 15.8 tons/ha for 30 cm soil depth for soils from the WCP. The average LR predicted by the SMP-SB method was 72.9% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from the WCP. Although the average LR predictions made by this method underestimated that of the average LR obtained by incubation, the method was one of the most precise methods evaluated on soils from the WCP. This was indicated by the similar correlation coefficient obtained between the predicted LR_s for the AE-SB method and incubation LR_s (Table 4 – 2). The LR as predicted by the SMP-SB method closely

approximated that predicted by the soil-lime incubation procedure for sample 22 A. This soil had the highest amount of exchangeable Al, WB and total C, along with the highest CEC_{pH7} (Table 3 – 4). The method did however slightly overestimate the LR needed to achieve the target pH for samples 22 B and 23 A. These soils had large quantities of exchangeable Al, yet had lower total acidities compared to sample 22 A. The method further underestimated the LR for all other soils, possibly due to their low CEC_{pH7} values (Table 3 – 4).

Predicted LR values as determined by use of the SMP-SB method ranged between 0.0 to 1.8 tons/ha for 30 cm soil depth for soils from the NWP. The average LR predicted by the SMP-SB method was 11.8% of the amount required to achieve $pH_{KCl} 5.5$ by incubation for soils from the NWP. Considering the average LR underestimation observed for this method, it was found that the SMP-SB method was generally imprecise on soils from the NWP. The method underestimated the LR needed to achieve the target pH for sample 25 A. The method failed to determine the LR needed on all other soils that was shown to indeed have a LR. This was to be expected however, as the SMP method was not developed for soils with LRs below 4.5 tons/ha and that do not have substantial amounts of exchangeable Al. Predicted LR values as determined by use of the SMP-SB method ranged between 0.0 to 28.2 tons $CaCO_3$ /ha for 30 cm soil depth for all soils selected for the study. The average LR predicted by the SMP-SB method was 73.3% of the amount required to achieve $pH_{KCl} 5.5$ by incubation for the entire soil population. Quite possibly because of the way it was calibrated, this method was found to on average be the most precise relative to other methods evaluated in this study (Table 4 – 3). Similar correlation coefficients, however, were obtained for the modified Eksteen and AE-SB methods (Table 4 – 3). However, similar results obtained in this experiment and those published by Shoemaker *et al.* (1961) and Tran and van Lierop (1981) demonstrate the accuracy and applicability of buffer calibrations for widely differing soils from different geographic regions. From Figure 4 – 10 it is evident that the SMP-SB method tended, on the average, to underestimate the incubation LR, as indicated by the regression line fitted to the data, for soils with a potential LR of less than 20.9 tons $CaCO_3$ /ha. The average predicted LR was 0.2 and 9.0 tons $CaCO_3$ /ha, or 9.1 and 87.4% of the incubation LR for soils requiring less and more than 4 tons $CaCO_3$ /ha, respectively.

From Table 4 – 3, it can be seen that the SMP-SB method is considerably less precise on soils that require less than 4 tons CaCO_3/ha than on soils that require more than that amount, as indicated by the correlation coefficients. The difference in proportions of predicted LR by use of this buffer from soils with a LR of less and more than 4 tons CaCO_3/ha , suggests that such a proportion is not linear, but rather curvilinear. In addition, according to van Lierop (1990), the relationship between soil-buffer pH and LR is not linear but curvilinear (Figure 4 – 11). Accordingly, the appropriate regression equation from Table 4 – 3 for all soils was used to adjust for predicted LR with use of the SMP-SB. A curvilinear regression equation was calculated for the relationship between the adjusted LR predicted by this method (\hat{Y}) and soil-buffer pH (X), as can be seen in Figure 4 – 11.

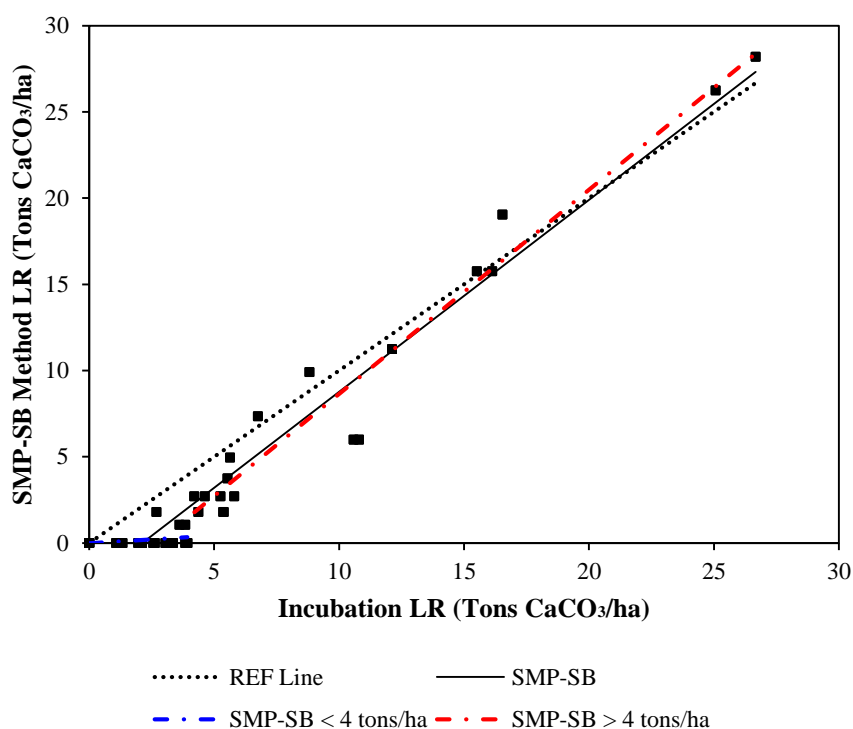


Figure 4 – 10. Relationship between the lime requirements of soils determined by incubation and the SMP-SB method

Resultantly, implementation of the curvilinear regression equation presented in Figure 4 – 11 resulted in a slightly higher correlation coefficient ($r = 0.977$) between the incubation and modified SMP-SB measured LR (Figure 4 – 12). The ideal slope of 1.0 (Figure 4 – 12) indicates that the newly calibrated SMP-SB soil-buffer pH, and the predicted LR that result from use thereof, closely approximates incubation LR along with the original calibration of Shoemaker *et al.* (1961). The improvement in

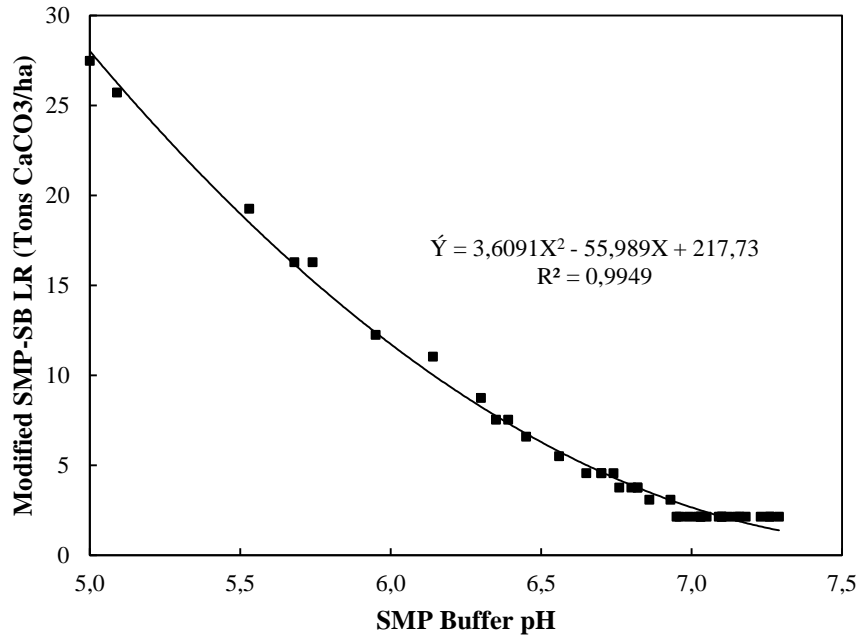


Figure 4 – 11. Relationship between the SMP-SB soil-buffer pH and corrected lime requirement prediction, based on incubation lime requirement

accuracy was attributed to a better approximation of the exponential relationship between the soil-buffer equilibrium pH and the estimated incubation LR by using two regression equations instead of one. However, the newly calibrated SMP-SB method shows immense potential to be accurately used on a notably wide range of soils, to which regional boundaries have a negligible impact.

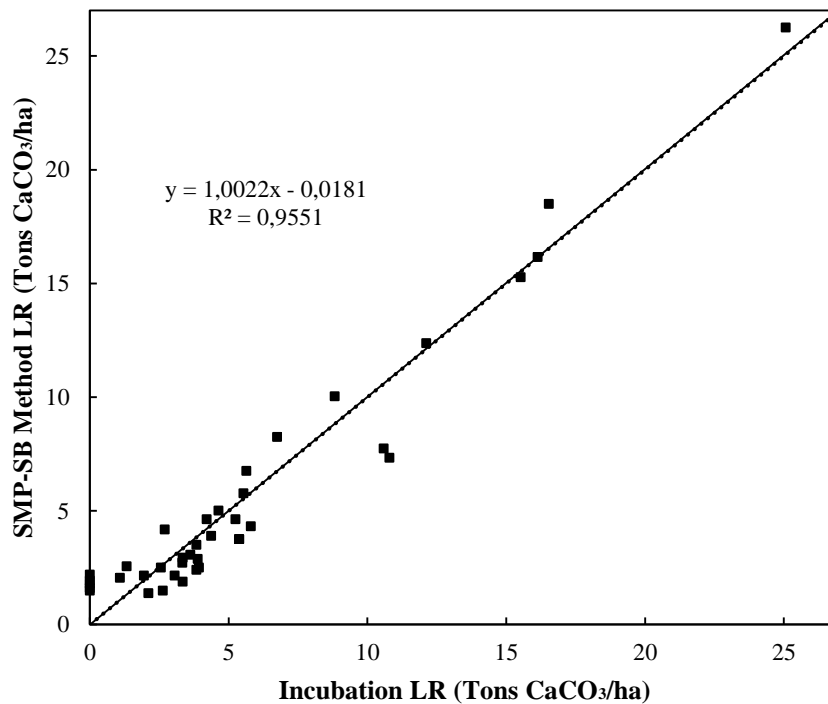


Figure 4 – 12. Relationship between the lime requirements of soils determined by incubation and the modified SMP-SB method

4.3.2.7 AE-SB Method

Predicted LR values as determined by use of the AE-SB method ranged between 0.2 to 8.7 tons/ha for 30 cm soil depth for soils from the EFS. The average LR predicted by the AE-SB was 91.7% of the amount required to achieve pH_{KCl} 5.5 by incubation for soils from the EFS. Despite this discrepancy, the LR predictions made by this method on the EFS soils was found to be the most precise. This was indicated by the significant correlation coefficient and the notably low standard error of estimate obtained between the predicted and incubation LRs (Table 4 – 2). LRs as predicted by the AE-SB method closely approximated that predicted by the soil-lime incubation procedure for samples 12 B and 16 A. However, the method underestimated the LR of a majority of experimental soil needed to achieve the target pH_{KCl} . The $\text{CEC}_{\text{pH}7}$ values of all of these soils were below $3.25 \text{ cmol}_c/\text{kg}$. Samples 17 A and B were exceptions to the general trend, as the AE-SB method predicted a notably higher LR than was needed to achieve the target pH. These soils had the highest C contents, along with substantial $\text{CEC}_{\text{pH}7}$ values, compared to the rest of the soil population. Some studies have shown that the AE-SB method has the tendency to overestimate LR, which is attributed to the initially high buffer pH (pH 8.0) which may include pH dependant acidity that need not be neutralised to achieve a certain target pH (Fox, 1980). Compared to the instances in which the SMP-SB method did indeed predict a LR for these experimental soils, the AE-SB method predicted substantially higher LRs than the SMP-SB method. This difference may be attributed to the lower buffer pH (pH 7.5) of the SMP-SB method. However, it can be seen that AE-SB method does indeed have the capacity to predict the LR of the EFS population

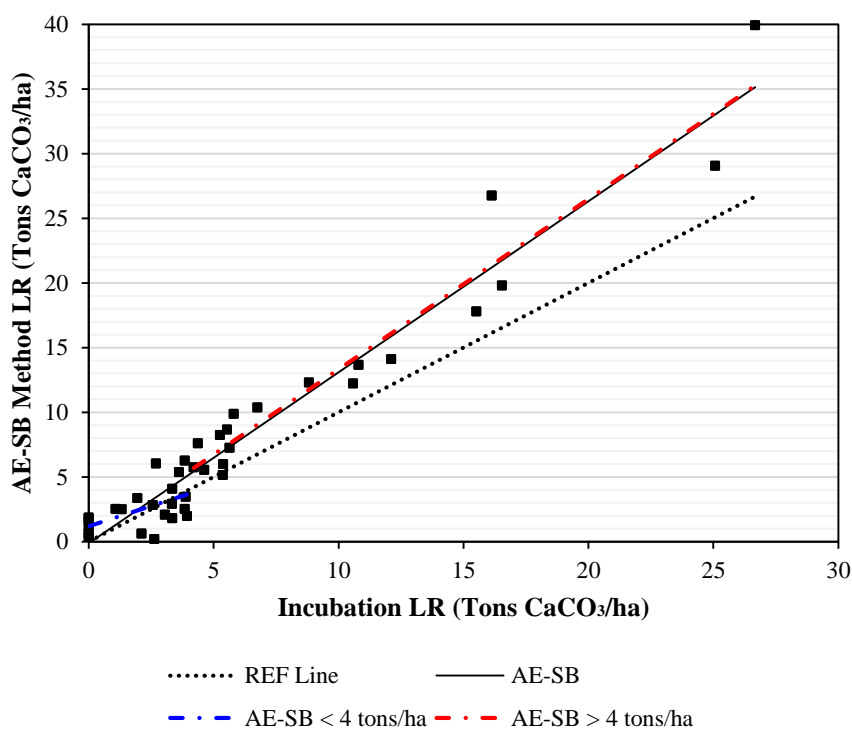


Figure 4 – 13. Relationship between the lime requirements of soils determined by incubation and the AE-SB method

soils, yet calibration of this method is needed. Nevertheless, the method seems to hold the most potential for determining the potential LR of soils from the EFS with reasonable accuracy.

Predicted LR values as determined by use of the AE-SB method ranged between 5.4 to 39.9 tons/ha for 30 cm soil depth for soils from KZN. The average LR predicted by the AE-SB method was 133.8% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for soils from KZN. Despite this discrepancy, the AE-SB method was sufficiently accurate, as indicated by the coefficient of correlation in Table 4 – 2. However, the method overestimated the LR needed to achieve the target pH in all cases. This was to be expected however, as the method was developed for soils with low $\text{CEC}_{\text{pH } 7.0}$ and low OM contents (Adams and Evans, 1962). The average LR as determined by incubation for soils from KZN was 13.0 tons CaCO_3/ha . If used as originally proposed, the AE-SB method is limited to predicting LRs in the range of about 0.0 to 6.0 tons CaCO_3/ha (Adams & Evans, 1962). In addition, the high initial buffer pH also contributed to the overestimation of LR, as can be seen when comparing predicted LRs obtained through the use of the SMP method.

Predicted LR values as determined by use of the AE-SB single buffer method ranged between 1.1 to 17.8 tons/ha for 30 cm soil depth for soils from the WCP. The average LR predicted by the AE-SB method was 139.0% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for soils from the WCP. Although the average LR predictions made by this method notably overestimated that of the average LR obtained by incubation, the method was considerably more precise than any other LR method studied. This was indicated by the relatively high correlation coefficient and lowest standard error of estimate obtained between the predicted and incubation LRs (Table 4 – 2). The LR as predicted by the AE-SB method closely approximated the amount of lime needed to achieve the target pH for samples 30 A and 31 A. These two soils had similar amounts of total C and CBD – Fe, yet no other soil properties were similar (Table 3 – 4). It cannot therefore be explained without making substantial assumptions as to why the method was more accurate on these soils. Nevertheless, the method overestimated the LR needed to achieve the target pH for all other soils. The predicted LRs by the AE-SB method was also substantially greater than those predicted by the SMP-SB method.

Predicted LR values as determined by use of the AE-SB method ranged between 0.4 to 6.0 tons/ha for 30 cm soil depth for soils from the NWP. The average LR predicted by the AE-SB was 147.1% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for soils from the NWP. Considering the average LR overestimation observed for this method, it was found that the AE-SB method was the second most precise of the methods evaluated on soils from the NWP after the Eksteen method. This was indicated by the significant correlation coefficient and the relatively small error of estimation (Table 4 – 2). However, the method overestimated the LR for all soils except sample 28 A. The method was shown to be more accurate in actually determining a LR for these experimental soils, yet consistently

overestimated the LR. This can be attributed to the fact that the method has not been calibrated on these soils, which would explain the slight overestimation in most cases.

Predicted LR values as determined by use of the AE-SB method ranged between 0.2 to 39.9 tons CaCO_3/ha for 30 cm soil depth for all soils selected for the study. The average LR predicted by the AE-SB method was 130.0% of the amount required to achieve $\text{pH}_{\text{KCl}} 5.5$ by incubation for the entire soil population. Despite this discrepancy, the method was found to be one of the most precise methods in general, after the SMP-SB method. This was indicated by the high significant correlation coefficient relative to other methods obtained for this method on all soils, along with the second lowest standard error of estimate (Table 4 – 3). However, comparable correlation coefficients were obtained for the modified Eksteen method on all soils (Table 4 – 3). From Figure 4 – 13 it is evident that the AE-SB method tended, on the average, to overestimate the incubation LR for soils with a LR above 1.6 tons CaCO_3/ha , as indicated by the regression line fitted to the data. However, this general trend was found to not hold true in all cases. The average predicted LR was 2.6 and 13.7 tons CaCO_3/ha , or 118.2 and 133.0% of the incubation LR for soils requiring less and more than 4 tons CaCO_3/ha , respectively.

From Table 4 – 3, it can be seen that the AE-SB method is less precise on soils that require less than 4

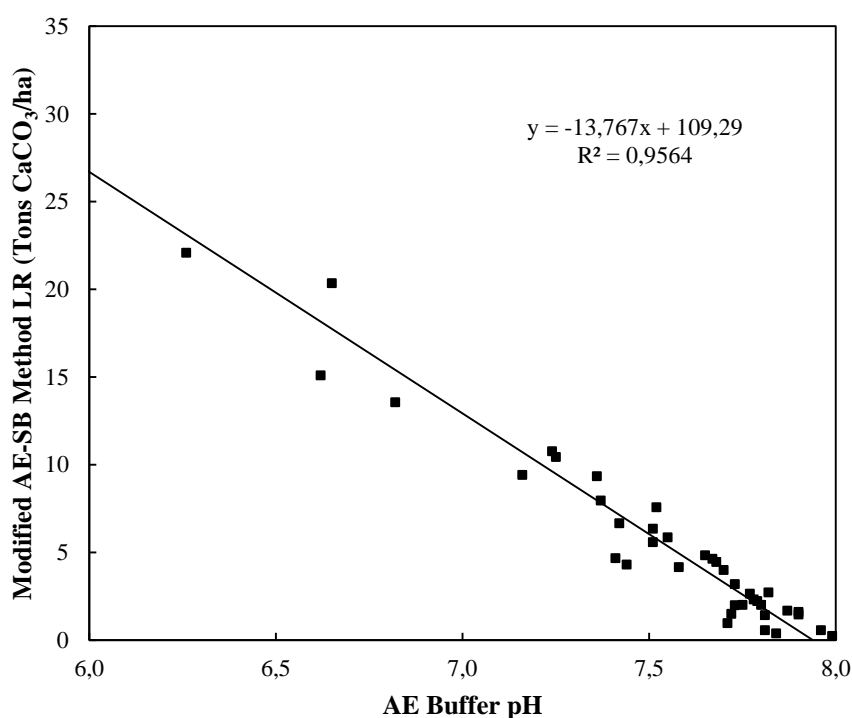


Figure 4 – 14. Relationship between the AE-SB soil-buffer pH and corrected lime requirement prediction, based on incubation lime requirement

tons CaCO_3/ha than on soils that require more than that amount, as indicated by the correlation coefficients obtained, however a smaller standard error of estimate is obtained for soils with a LR of less than 4 tons CaCO_3/ha . This may be attributed to the way the method was calibrated, along with

the capacity of the buffer to detect very small differences in acidity. Tran and van Lierop (1981) observed that the reason for the limited range of this buffer was that it reacted with approximately twice as much soil acidity as was neutralised by CaCO_3 to pH_w 6.5. Presumably, the high initial buffer pH of 8.0 used for the AE-SB method brought about superfluous ionisation of H^+ from soils (van Lierop, 1983). It seems as if Adams and Evans (1962) were aware that their buffer reacted with more acidity than would be neutralised by addition of CaCO_3 to reach a target pH_w of 6.6, due to their recommendation of using an “acid to be neutralised” formula. Application of this formula resulted in still excessive predicted LR, however its use did result in an increase in the precision of predictions. Considering that the “acid to be neutralised” formula was applied to the method during this experiment, it was observed that the method did in fact predict excessive LR.

The general overestimation of predicted LR associated with the AE-SB method can be corrected for by using the appropriate regression equations in Table 4 – 3, especially for soils that have a LR of more than 4 tons CaCO_3/ha . In order to attempt to improve the general accuracy of the method, however, a similar approach was followed as was discussed for the SMP-SB method in Section 4.3.4.6. Figure 4 – 14 represents the relationship between the modified AE-SB predicted LR and the soil-buffer pH. A linear regression was fitted, due to a relatively small difference between average LR for soils requiring less and more than 4 tons CaCO_3/ha , as this indicates that the soil-buffer pH and LR relationship is linear. However, implementation of the regression equation presented in Figure 4 – 14, did not result in a significant increase in correlation between the AE-SB method LR and incubation (Figure 4 – 15). Thus, this observation indicates that correction of the soil-buffer pH relationship to incubation LR is

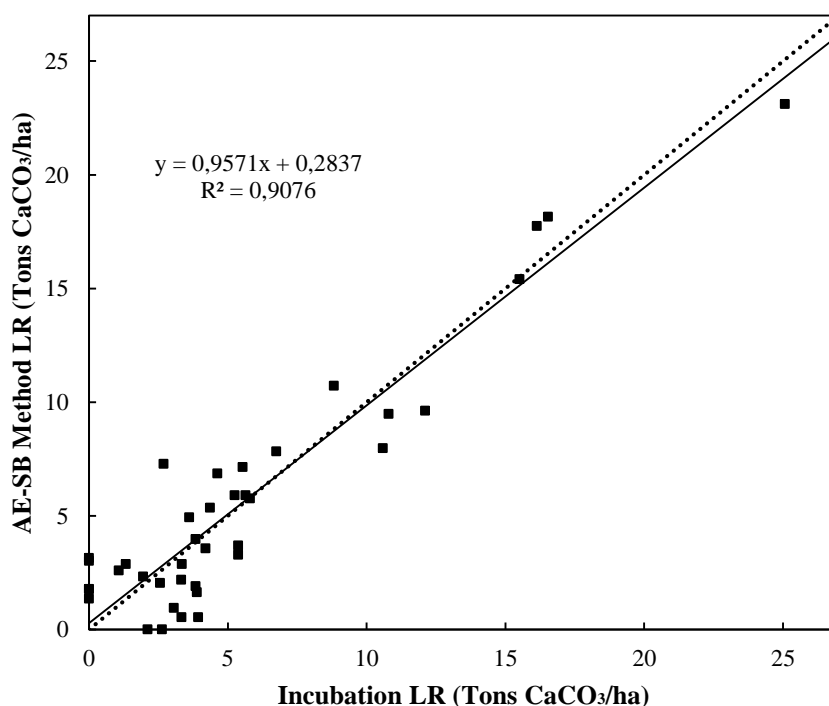


Figure 4 – 15. Relationship between the lime requirements of soils determined by incubation and the modified AE-SB method

not sufficient. Nevertheless, the accuracy of the method was slightly improved to 101.7% of the incubation LRs of the incubation requirements.

According to Tran and van Lierop (1981), the useful range and accuracy of the AE-SB method can be expanded by using a wider 1:4 soil:diluted-buffer ratio, instead of the 1:2 ratio originally recommended by Adams and Evans (1962). After use of a wider soil:buffer ratio, it was found that the LR of soils with incubation LRs between 0.0 and 15 tons CaCO_3/ha could be determined. In addition, an increase in correlation (0.85) was observed between the incubation and predicted LR by use of the method, compared to the original (0.78). Moreover, the accuracy of the method was also improved to 114% of the incubation requirements. Thus, such a modification to the method should be investigated in future research relating the applicability of the AE-SB method to soils from South Africa.

4.4 Conclusions

Results from this experiment indicate that the modified Eksteen, SMP-SB, and AE-SB methods have the widest range in applicability on soils from South Africa. Practically identical relationships were obtained between these methods and incubation LRs on all soils selected for this experiment. The modified Eksteen method was shown to have a large range of applicability and was generally quite accurate on all soils, except the weakly buffered sands from the Eastern Free State. However, the rapid buffer procedures that were evaluated were shown to hold the most potential on all soils due to their general accuracy. The AE-SB method tended to significantly overestimate the LR of most soils, however, after correction and recalibration, the method was slightly more accurate. Further, the SMP-SB method was shown to hold the most potential after re-calibration, allowing for use on soils with a potential LR of larger than 2.5 tons CaCO_3/ha .

The Eksteen method did not perform as well as was anticipated. This was attributed to conservative modifications proposed by Smuts (2001) that were not evaluated experimentally. The method was shown to significantly underestimate the LR of soils with C contents of larger than one. Thus, the OMCF implemented in the method was shown to be the most limiting factor associated with the method. The Eksteen-KCl method and Cedara methods performed similarly on all soils. This indicates that the principles behind both methods are quite similar. In addition, the Cedara method was sufficiently accurate to determine the LR needed to obtain a PAS of 10%, except on soils from the Eastern Free State. However, these methods consistently underestimated the LR of most soils, as especially the Cedara method was not developed to determine a LR to obtain a target pH. This underestimation of LR associated with these methods was further also attributed to limitations of using 1 M KCl exchangeable acidity as a means to determine LR. Further, even after correction by use of the most appropriate regression equation, both methods would on average consistently underestimate LR.

The ARC-SGI method was shown to be the most inaccurate method on all soils. This was attributed to the implementation of a relationship between change in pH_{KCl} and a resultant change in acid saturation. Such a principle cannot be applied to all soil forms, as the degree of acid saturation at a given pH is not similar for all soils. This is due to the differing abilities of various colloids to retain exchangeable cations, and as such, differing combinations of these colloids exists in soils. Thus, the applicability of the ARC-SGI method is not as broad as would be expected of a LR method. However, after correction of the method by use of the most appropriate regression equation, it was found that the method will exhibit reasonable accuracy on soils with a potential LR of less than 4 tons CaCO_3/ha .

It is recommended that the AE-SB buffer be used for routine LR recommendations on soils of the Eastern Free State due to its ability to detect extremely small differences in acidity. The ARC-SGI method may also be used for these soils, after correcting the estimated LR with the appropriate regression equation for soils that require less than 4 tons CaCO_3/ha ; however, this is not advised due to the general flaws associated with the method. For soils from Kwa-Zulu Natal, the modified Eksteen and SMP-SB methods hold the most potential for routine use. Both the AE-SB and SMP-SB methods hold the greatest potential for soils of the Western Cape. The recalibrated AE-SB and ARC-SGI methods may be successfully applied to soils from the North West Province. It should be noted that the rapid buffer procedures evaluated in the experiment contain extremely toxic chemicals such as K_2CrO_4 and p-nitrophenol. Therefore, modifications of these methods made by Sikora (2006) for the SMP-SB method, and that of Sikora and Moore (2008) for the AE-SB method should be investigated for potential implementation in routine LR determination. These methods will need to be recalibrated in order to be sufficiently accurate on soils from South Africa. In addition, it is recommended that more work be carried out on the development of a rapid buffer procedure that would be inherently suitable for use on the old, highly weathered and intensely leached soils from South Africa. The method would need to be able to accurately determine the LR of both highly and weakly buffered soils in order to remove any geographic limitations in use.

Chapter 5

Soil Properties in Relation to Lime Requirement and Lime Requirement Methods

5.1 Introduction

Soil acidity may chiefly be partitioned into exchangeable and non-exchangeable components. Exchangeable acidity, which is commonly extracted with 1M KCl, is primarily dominated by monomeric Al in highly leached soils (Kamprath, 1970), and generally approaches negligible levels when soil pH_w exceeds 5.5 (Sanchez, 1974). Non-exchangeable acidity, that which is titratable or pH dependent, primarily originates from the dissociation of acidic functional groups of soil organic matter (OM), deprotonation of hydroxy-Al polymers associated with the colloidal fraction of the soil, from amorphous aluminosilicates, and the broken edges of oxides and clay minerals (Curtin, *et al.*, 1984).

Lime requirement (LR) methods in South Africa mostly rely on determining LR based on the exchangeable fraction of soil acidity. The primary reason for this is that it is considered that exchangeable Al is a sufficient criterion for liming highly weathered soils that are commonly found throughout South Africa (Reeve & Sumner, 1970). In addition, the determination of LR based on exchangeable acidity alone allows for the elimination of the most primary factors associated with poor crop growth on acid soils, without accruing substantial costs. However, it may be argued that due to inadequate amounts of liming material that is resultantly applied to the soil, substantial amounts of reserve acidity may still exist in the soil. This results in re-acidification of the soil over time, which would require further applications of liming material not too far from the original application. This would especially be true in areas where legumes are commonly cultivated, and also in areas where liberal use of ammonium based fertilisers are the norm.

Agricultural production in South Africa faces substantial challenges on acidic soil. In some cases, such as in the province of Kwa-Zulu Natal, extensive areas are at least moderately acidic. As concern regarding soil acidity has been part of the discourse in most agricultural regions of South Africa, little to no information is available regarding the nature of soil acidity for most provinces in the country or on the quantities of liming material needed to optimally ameliorate soil acidity in various geographic regions. This has allowed for a lot of speculation to originate as to which ways are best to approach the problem of soil acidity and the amelioration thereof. Such is the extent of the problem, that there are instances to be found where soil principles that may very easily vary from soil to soil are implemented on all soils. Such principles include liming to achieve a specified base saturation, or basing lime requirement on a specific change in pH. Accordingly, the objectives of this work were to:

- i) examine the relationship between types of soil acidity and soil properties;

- ii) understand the relationship between lime requirement and lime requirement methods with types of acidity and soil properties;
- iii) select most critical soil properties affecting lime requirement.

5.2 Materials and Methods

Considering that the same soil samples were used throughout the study, standard methods used to determine soil chemical and physical properties of these soils can be found in Chapter 3, section 3.2. See Chapter 3, section 3.3.2 for a detailed description relating to soil chemical and physical properties for each respective soil. Tables 3 – 2 through 3 – 5 depicts all soil chemical and physical information obtained through procedures described in section 3.2.

In addition to soil properties discussed in section 3.3.2, four additional properties not discussed in the aforementioned section were included in this section. Firstly, the $\Delta\text{pH}(\text{KCl}) \times \% \text{WB-C}$ function, investigated by Keeny and Corey (1963), was calculated by multiplying the difference between target pH_{KCl} (5.5) and field pH_{KCl} of the original sample with the % WB-C. The $\Delta\text{pH}(\text{KCl}) \times \% \text{Clay}$ function (Keeney & Corey, 1963) was derived similarly, except for the substitution of % WB-C with % clay. Secondly, the variable charge of all soils were calculated by subtracting ECEC (Sum of exchangeable bases and exchangeable acidity) from $\text{CEC}_{\text{pH } 7}$ as specified by Sumner and Noble (2003). Thirdly, acid saturation was calculated through division of exchangeable acidity by the summation of the S – value and exchangeable acidity, which was further multiplied by 100 to yield a percentage value. Lastly, the clay + silt variable discussed in this section was calculated through addition of the clay and fine silt components of the textural analysis described in section 3.2. Complete information regarding all soil properties for each respective soil can be found in Appendix A.

LR was calculated according to each method, as was specified in Section 4.2. Incubation LR was similarly described in Section 4.2. Statistical analysis was performed on Dell's Statistica 13. LRs as predicted by each method, including the incubation procedure, was related to selected soil properties by use of linear regression analysis. The significance of the results were evaluated by performing a p-test. In the case where multiple regression analysis was performed, a p-test was performed at the 1% confidence level, along with the determination of a standard error of estimate ($S_{x,y}$).

5.3 Results and Discussion

5.3.1 Relationship between Lime Requirement and Selected Soil Properties

In Table 5 – 1, the results of simple correlations of several soil properties with LR are shown. The first point of interest is that pH, whether measured in water ($r = -0.51$) or 1 M KCl ($r = -0.49$) correlated significantly with LR. This is attributed to the fact that a relatively wide range in pH values were used. The pH values of the soils used in this study as determined in water and 1 M KCl, ranged between 4.2 to 6.5 and 3.6 to 5.7, respectively (Tables 3 – 2 through 3 – 5). In addition, a given soil will generally

have a larger LR at a very low pH value compared to when the pH value is somewhat higher, provided all other soil properties are similar. However, the application of the pH concept to a colloidal system such as an acid soil, results therein that the dissociated fraction of H^+ is less than unity and tends to vary from one type of clay or organic matter (OM) component to another (McLean, 1973). Thus, it is not possible to accurately determine total soil acidity from pH alone, which is pivotal to LR determination. This can be seen from Table 5 – 3, where no significant correlation was found between both pH_w ($r = -0.24$) and pH_{KCl} ($r = -0.18$) and total acidity. Nevertheless, soil pH can generally indicate the degree of acid saturation depending upon the predominant clay type (McLean, 1973). In addition, soil pH can also indicate the degree of dissociation of H^+ from cation exchange sites, or the extent of H^+ production through Al hydrolysis (McLean, 1973).

Evidence for the abovementioned two points can be seen in Table 5 – 2, where both pH_w and pH_{KCl} correlated significantly with acid saturation ($r = -0.73$; $r = -0.64$) and exchangeable Al ($r = -0.54$; $r = -0.49$). Thus, as pH decreases, a resultant increase in both acid saturation and exchangeable Al occurs. In addition, both acid saturation ($r = 0.61$) and exchangeable Al ($r = 0.95$) significantly correlated with LR. Exchangeable Al is generally considered the main acidity component in soils of low base saturation (McLean, 1973). Thus, the significant correlation obtained between acid saturation and LR is to be expected, as the neutralisation of H^+ or Al on exchange sites and the replacement of Ca and/or Mg is the principle reaction of liming. Also, exchangeable Al is generally precipitated out a pH_w of about 5.5 to 6.0, resulting in little or no exchangeable Al to be found at higher soil pH values (Sanchez, 1974). From Table 5 – 3 it is evident that neither pH_w ($r = -0.29$) nor pH_{KCl} ($r = -0.27$) significantly correlated with variable charge. Therefore, it is clear that soil pH has no potential to indicate the probable reversible charge associated with pH dependent acidity that might develop due to a change in pH, which will be able to react liming material added. Nevertheless, these findings illustrate that soil pH is both an indication of the soil's condition and a resultant cause of many soil reactions that occur. Soil pH is arguably the most widely used index for judging whether a soil is acid, as well as for acid intensity (Coleman & Thomas, 1967; McBride, 1994). However, it is clear from the abovementioned factors relating to the indicative ability of pH in terms of soil acidity, that soil pH as a parameter has difficulty to quantitatively determine any form of soil acidity, and the resultant LR, without significant assumption and variation. A conservative assumption would be that soil pH, although a useful index, should be regarded as more empirical than otherwise (Coleman & Thomas, 1967). Soil pH should therefore remain as a tool to indicate, instead of estimate, soil acidity. As such, soil pH is mainly useful for indicating the extent to which chemical or biological processes will occur in the soil, which in effect will determine nutrient availability and the solubility of certain elements.

Table 5 – 1. Simple correlation coefficients for lime requirement, as determined by incubation, and soil properties

Property	Incubation Lime Requirement
pH (H ₂ O)	-0.51
pH (KCl)	-0.49
Exchangeable Acidity	0.93
Titratable Acidity (pH 7)	0.99
Total Acidity	0.91
Exchangeable Al	0.95
CBD-extractable Al	0.84
Buffered CEC _{pH7}	0.77
Variable Charge	0.89
Acid Saturation	0.61
WB-C (%)	0.94
Total C (%)	0.93
Clay (%)	0.34
Silt (%)	0.38
Clay + Silt (%)	0.36
(Δ pH _{KCl}) x (WB-C %)	0.98
(Δ pH _{KCl}) x (Clay %)	0.65

r values in bold are significant at $p < 0.05$

A close linear relationship was found between exchangeable ($r = 0.93$), titratable ($r = 0.99$), and total acidity ($r = 0.91$) and LR (Table 5-1). This indicates that these forms of acidity are all valid parameters that strongly influence the LR of a soil. Exchangeable acidity significantly correlated with pH_w ($r = -0.59$), pH_{KCl} ($r = -0.54$), WB-C ($r = 0.83$), and total C ($r = 0.84$) (Table 5-2). The significant correlation between exchangeable acidity and soil pH can be attributed to the principle that the unbuffered, neutral 1 M KCl exchangeable acidity theoretically measures the acidity present at a given soil pH. In addition, according to Coleman and Thomas (1967), monomeric Al³⁺ almost entirely contributes to exchangeable acidity. This is due to the phenomenon that H⁺ does not accumulate without limit in a soil, as H⁺ ions become internally adsorbed due to reaction with clay colloids (McBride, 1994). Subsequently Al³⁺ is released into the soil solution and partially neutralised, due to the removal of H⁺ from the soil solution, to form Al(OH)²⁺ and Al(OH)₂⁺ which is subject to adsorption and complexation by OM (McLean,

1973). This is evidenced from Table 5 – 3, where it can be seen that exchangeable Al significantly correlated with WB-C ($r = 0.86$) and total C ($r = 0.87$). However, the OM not only adsorbs acidic cations that manifest in exchangeable form, but also complexes/chelates acidic cations into forms which are not readily displaced through ordinary exchange reactions (Clark & Nichol, 1966). Further, aside from complexation to OM, partially neutralised $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$ can also polymerize on clay surfaces as continuous layers of non exchangeable acidity (McLean, 1973). Due to the acidic nature of the non-exchangeable Al components, such forms can still affect the LR of a soil. From Table 5 – 3 it can be seen that neither exchangeable acidity nor Al significantly correlated with both % clay ($r = 0.23$; $r = 0.25$) and % silt ($r = 0.26$; $r = 0.29$), respectively. However, CBD-extractable Al significantly correlated with both % clay ($r = 0.42$) and % silt ($r = 0.54$), as well as WB-C ($r = 0.89$) and total C ($r = 0.88$). These results are indicative of CBD's ability to extract non-crystalline Al oxides and hydroxides that may have polymerised on humus and clay colloids. In addition, CBD-extractable Al significantly correlated with LR ($r = 0.84$). Thus, it is evident that exchangeable acidity determines electrostatically bound acidic cations, whereas CBD-extractable Al is able to determine some of the non-exchangeable Al. As such, it is evident that exchangeable acidity in itself is not sufficiently able to serve as a quantitative measurement of the potential LR for a given soil, but rather the immediate LR. Interestingly, the high correlation coefficient (0.99) obtained between titratable acidity and LR was not to be expected, due to the high pH (7.0) of the extracting solution used to determine this form of acidity and the fact that the LR is only the amount of liming material needed to achieve $\text{pH}_{\text{KCl}} 5.5$ ($\text{pH}_w 6.5$). It can be seen in Table 5 – 3 that a strong relationship exists between titratable acidity and both WB-C ($r = 0.92$) and total C ($r = 0.93$). Also, titratable acidity significantly correlated with both % clay ($r = 0.33$) and % silt ($r = 0.36$). This is of interest, as a strong relationship was also found to exist between LR and WB-C ($r = 0.94$) and total C ($r = 0.93$), and to a lesser extent between % clay ($r = 0.34$), and % silt ($r = 0.38$).

Table 5 – 2. Simple regression coefficients for commonly analysed soil properties and factors that influence lime requirement

Property	pH (H ₂ O)	pH (KCl)	WB-C (%)	Total C (%)	Clay (%)	Silt (%)	Clay + Silt (%)
Exchangeable Acidity	-0.59	-0.54	0.83	0.84	0.23	0.26	0.25
Titratable Acidity	-0.51	-0.48	0.94	0.93	0.33	0.36	0.35
Total Acidity	-0.24	-0.18	0.92	0.91	0.53	0.42	0.55
Exchangeable Al	-0.54	-0.49	0.86	0.87	0.25	0.29	0.27
CBD-extractable Al	-0.22	-0.14	0.89	0.88	0.42	0.54	0.46
Acid Saturation (%)	-0.73	-0.64	0.49	0.48	-0.08	0.08	-0.07
Buffered $\text{CEC}_{\text{pH } 7.0}$	-0.02	-0.05	0.82	0.78	0.57	0.51	0.59
Variable Charge	-0.29	-0.27	0.90	0.88	0.33	0.48	0.36

r values in bold are significant at $p < 0.05$

However, due to the abovementioned factors discussed previously, it is not surprising that the content of OM and LR are highly correlated in soils (Keeney & Corey, 1963). In addition, due to the potential for hydroxy-Al ions to accumulate on clay and silt surfaces, it would be expected that some degree of significant correlation would be found between texture and LR. Thus, from these observations, it is evident that titratable acidity is an excellent measure of the potential LR of a soil; as such a measurement of acidity seems to include most of the pivotal acidity that need be neutralised in order to obtain a target pH_{KCl} 5.5. This observation is sensible, as this form of acidity is expected to measure significant amounts of non-exchangeable residual H^+ associated with carboxyl groups and Fe and Al hydrated oxides, due to the deprotonation thereof at such a high pH value. According to Brady and Weil (2008), this residual acidity component may be 1000 times greater than the active acidity component in sandy soils, and even 50 000 to 100 000 time greater in a soil with high clay and organic matter contents when determined from total acidity at pH 8.2. This observation may serve to explain the lower correlation obtained between total acidity and LR, as a significant amount of this form of acidity need not be neutralised in order to achieve a target pH_{KCl} of 5.5. However, total acidity significantly correlated with WB-C ($r = 0.92$), total C ($r = 0.91$), and clay + silt ($r = 0.55$). These findings indicate that BaCl_2 -TEA total acidity is able to measure most acidity associated with the soil colloidal system, whether exchangeable or non-exchangeable. This is attributed to the strong H^+ displacing capacity of Ba^{2+} from acidic exchange sites, and the high initial buffer pH of 8.2 which would cause much of the pH dependent acidity to dissociate. It is therefore clear that total acidity is indicative of the potential LR of a soil, as it measures most of the potentially reactive acidity in a soil. However, titratable acidity is a better potential indicator for LR, as this form of acidity more realistically quantifies the amount of acidity that need be neutralised in order to obtain a target pH_{KCl} of 5.5.

Table 5 – 3. Simple correlation coefficients for pH dependent functions and soil properties

Property	Correlation Coefficient	
	$(\Delta\text{pH}_{\text{KCl}}) \times (\text{WB-C } \%)$	$(\Delta\text{pH}_{\text{KCl}}) \times (\text{Clay } \%)$
Exchangeable Acidity	0.91	0.58
Titratable Acidity	0.98	0.64
Total Acidity	0.88	0.62
Exchangeable Al	0.93	0.57
CBD-extractable Al	0.80	0.50
Acid Saturation (%)	0.59	0.34
Buffered $\text{CEC}_{\text{pH } 7}$	0.75	0.55
Variable Charge	0.86	0.51

r values in bold are significant at $p < 0.01$

Thus, as was seen for the modified Eksteen method evaluated in Section 4.3.4.3, use of titratable acidity in LR methods may produce desirable results. However, it is recommended that a correction of titratable acidity be applied in order to correct for any excess pH dependent acidity that need not be neutralised, as was the case for the modified Eksteen method (Correction described in Section 4.2).

Work done by Ross *et al.* (1964) found that soil properties other than soil pH, which are useful indicators of LR are, in order of decreasing importance: CEC > OM > exchangeable H⁺ > clay content. It should be noted that exchangeable H⁺ in this regard was determined by subtracting the total base content of soils from the CEC_{pH7}. This form of acidity primarily results from replacement of exchangeable Al or dissociation of organic acid groups between the soil pH and pH 7.0 (Ross, *et al.*, 1964). This is synonymous with variable charge, which is the difference between CEC_{pH7} and ECEC. This form of pH dependant acidity was chosen as a variable of interest for this study. Results from this experiment indicate similar findings as was obtained by Ross *et al.* (1964), as significant correlations were found between LR and WB-C ($r = 0.94$), variable charge ($r = 0.89$), CEC_{pH7} ($r = 0.77$), and clay + silt ($r = 0.36$). These findings indicate that variable charge components, such as organic acid groups associated with OM, Al- and Fe oxides and hydroxides, and the broken edges of silicate clays play a pivotal role in the LR of a soil. In order to determine the contribution of OM to the furnishing of H⁺ for a given change in soil pH, Keeny and Corey (1963) calculated a function which consisted of a target pH_w 6.5, minus the initial pH_w, multiplied by the OM content expressed in %. This function has been found to be a good predictor of LR, especially for soils with low exchangeable Al contents (Keeney & Corey, 1963; Ross, *et al.*, 1964). The (Δ pH) (OM %) function was found to be strongly correlated with LR ($r = 0.884$) in their study (Keeney & Corey, 1963). The potential for this function to serve as a predictor of LR is due to the Δ pH term that sets the limits of the lime response curve. In addition, the percentage OM is included as an approximation of soil buffering capacity, and is thus proportional to the slope of the lime response curve. However, some modifications were made to the original function in this study, such as the exclusion of OM, and rather the inclusion of C itself. Also, pH_{KCl} was used, as the incubation LR was determined from linear regression graphs where pH_{KCl} was the dependent variable. The reason for the inclusion of the (Δ pH) (C %) and (Δ pH) (Clay %) functions are to represent the pH dependent sites associated with C and clay, respectively (Pionke, *et al.*, 1968).

A strong linear relationship was found between both (Δ pH) (C %) ($r = 0.98$) and (Δ pH) (Clay %) ($r = 0.65$) functions and LR (Table 5 – 1). These findings illustrate the strong linear relationship between the pH dependent acidity associated with the colloidal system and LR. However, from these findings it is also clear that the C content plays a more prominent role as a factor to LR than the clay content. The highly significant correlations obtained between the (Δ pH) (C %) and (Δ pH) (Clay %) functions with all forms of acidity and Al evaluated in this study further affirm the predictive ability of these functions (Table 5 – 3). The significant correlation obtained between the (Δ pH) (C %) function and exchangeable Al ($r = 0.93$) and CBD-extractable Al ($r = 0.80$) indicates that much of the supposed pH

dependent acidity associated with C below $\text{pH}_{\text{KCl}} 5.5$, results from Al that has been bound with C. Indeed, hydroxy-Al ions adsorbed on both clay minerals and OM controls the major part of the buffering region involved in practical liming in many soils (Thomas, 1996). Interestingly, the highest significant correlation was obtained between titratable acidity and (ΔpH) (C %) ($r = 0.98$) and (ΔpH) (Clay %) ($r = 0.64$). This is indicative of the strong ability of titratable acidity to estimate most of the potentially reactive acidity that would react with the amount of liming material added to a given soil to achieve $\text{pH}_{\text{KCl}} 5.5$. The relatively lower significant correlation obtained between total acidity and (ΔpH) (C %) ($r = 0.88$) is attributed to the exclusion of potentially ionisable acidity associated with OM that might manifest above $\text{pH}_{\text{KCl}} 5.5$. Thus, the (ΔpH) (C %) function primarily estimates electrostatically bound acidic cations. However, the significant correlations obtained between variable charge and the (ΔpH) (C %) ($r = 0.86$) and (ΔpH) (Clay %) ($r = 0.51$) functions indicate the ability of these functions to estimate the pH dependent acidity component that necessarily results from an increase in pH.

From the evaluation of linear regression analysis between certain soil factors and LR, it is evident that certain relationships do exist. In order to develop a model to accurately predict incubation LR to achieve a target pH_{KCl} of 5.5, multiple regression analysis was performed. The equation ($p < 0.001$) that accounted for 96.76% ($S_{x,y} = 0.4806$) of the variation observed is as follows:

$$\hat{Y} = 0.2196(\text{CEC}_{\text{pH } 7} - \text{ECEC}) + 1.528(\text{TA}) - 0.7732$$

where \hat{Y} is LR in $\text{kg CaCO}_3/\text{kg}$ of soil, $(\text{CEC}_{\text{pH } 7} - \text{ECEC})$ is variable charge in cmol_c/kg , and TA is titratable acidity buffered at pH 7.0 in cmol_c/kg . LR values are reported in $\text{kg CaCO}_3/\text{kg}$ of soil in order to account for variation in bulk density. All b (co-efficients) values in the equation were significant at $p < 0.05$. From Figure 5 – 1 it can be seen that the regression equation is suitably able to predict the incubation LR with notable accuracy. The equation predicted 100.0% of the average LR for the entire population of soils needed to achieve a target pH_{KCl} of 5.5. On average, the method was able to accurately predict the LR needed to obtain a target pH_{KCl} of 5.5 in 97.86% of cases. The relative accuracy of the regression equation is attributed to the inclusion of the most pivotal soil factors revealed in this study to most strongly influence LR predicted by incubation. Titratable acidity was shown to strongly reflect the potential LR of a soil. However, variable charge is more indicative of the potential pH dependent acidity that may manifest due to an increase in pH within a pH range of between 3.6 and 7.0.

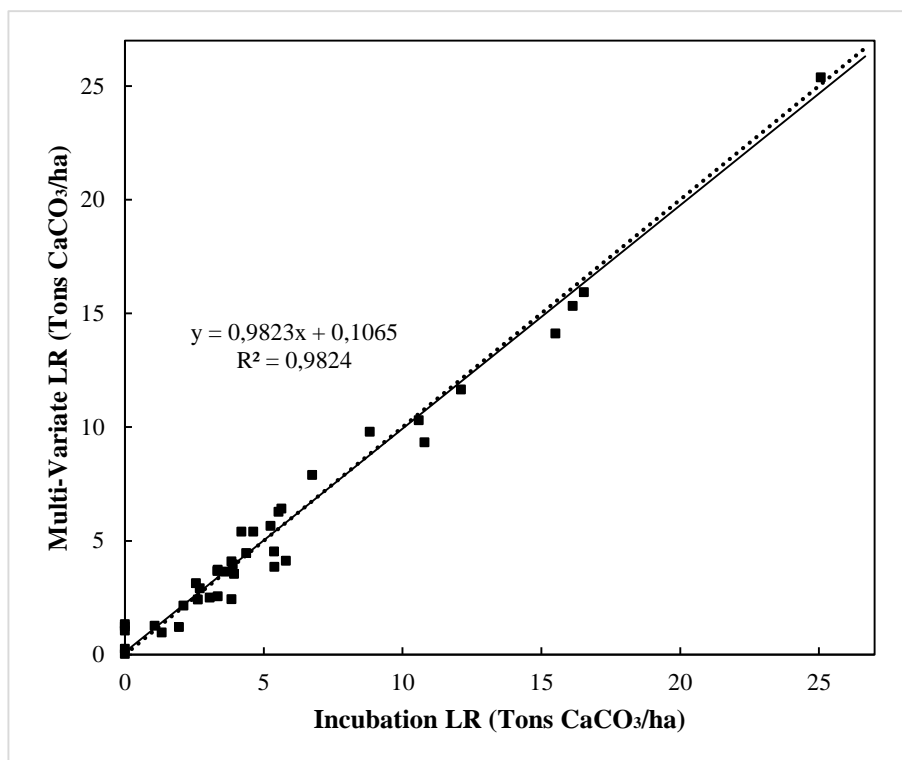


Figure 5 – 1. Predicted lime requirement versus incubation lime requirement to achieve pH (KCl) 5.5

As such, the regression equation may be suitably used in order to predict the potential LR of a soil, provided the soil properties fall within the parameters of those used in this study (Tables 3 – 2 through 3 – 5). Thus, the predictive ability of the abovementioned regression equation allows the use thereof as method to replace more time consuming reference methods used to determine LR, such as the incubation or titration procedures. Therefore, such an equation holds the potential to allow for sufficiently accurate evaluation of LR methods that are used by a particular entity. In addition, the regression equation presented in Figure 5 – 1 may also be used to correct for the predicted LR by use of the multiple regression equation proposed earlier. However, the use of the mentioned regression equation would lead to slight overestimation of LR on soils with a potential LR of more than 6.0 tons CaCO_3/ha .

5.3.2 Relationship between Lime Requirement Methods and Soil Properties

Table 5 – 4 shows simple correlation coefficients obtained between each respective LR method evaluated in Section 4.3.2 and selected soil properties. The relationship between each respective LR method and the soil properties listed in Table 5 – 4 is discussed in the following sub-sections.

Table 5 – 4. Simple correlation coefficients for lime requirement methods and soil properties

Property	Eksteen	Eksteen-KCl	Mod. Eksteen	Cedara	ARC-SGI	SMP-SB	AE-SB
pH (H ₂ O)	-0.68	-0.55	-0.57	-0.54	-0.92	-0.40	-0.50
pH (KCl)	-0.62	-0.49	-0.53	-0.48	-0.99	-0.37	-0.44
Exchangeable Acidity	0.96	0.99	0.99	0.99	0.50	0.93	0.92
Titrateable Acidity	0.91	0.94	0.98	0.94	0.47	0.98	0.97
Total Acidity	0.77	0.83	0.86	0.83	0.22	0.94	0.93
Exchangeable Al	0.95	0.99	0.99	0.99	0.47	0.95	0.93
CBD-extractable Al	0.73	0.77	0.80	0.78	0.13	0.90	0.86
Buffered CEC _{pH 7}	0.51	0.61	0.65	0.61	0.09	0.80	0.77
Variable Charge	0.73	0.79	0.83	0.80	0.25	0.91	0.88
Acid Saturation	0.80	0.78	0.77	0.78	0.59	0.63	0.64
WB-C (%)	0.76	0.84	0.89	0.85	0.26	0.96	0.95
Total C (%)	0.78	0.85	0.89	0.86	0.21	0.95	0.93
Clay (%)	0.20	0.25	0.25	0.24	-0.01	0.34	0.45
Silt (%)	0.24	0.22	0.26	0.23	0.10	0.42	0.33
Clay + Silt (%)	0.21	0.26	0.26	0.26	-0.00	0.37	0.47
(Δ pH _{KCl}) x (WB-C %)	0.86	0.90	0.95	0.90	0.48	0.95	0.96
(Δ pH _{KCl}) x (Clay %)	0.61	0.56	0.60	0.55	0.63	0.56	0.71

r values in bold are significant at $p < 0.01$

5.3.2.1 Eksteen Method

As discussed in Section 4.3.4.1, the Eksteen method was found to generally underestimate the LR of the population of experimental soils. The first point of interest is the correlation coefficient obtained between LR as predicted by the Eksteen method and titrateable acidity ($r = 0.91$). Relative to other methods evaluated, except the ARC-SGI method, the correlation coefficient was lower (Table 5 – 4). This is directly attributed to the organic matter correction factor (OMCF) that is implemented in the calculation of LR. As such, this finding is indicative of an error in the correction of titrateable acidity based on WB-C. Thus, the method would tend to underestimate LR due to this requirement, as titrateable acidity was shown to be a strong indicator of incubation LR ($r = 0.99$). In addition, a relatively lower correlation coefficient was obtained between Eksteen LR and WB-C ($r = 0.76$). This indicates that the Eksteen method is somewhat less sensitive to accounting for acidity that could originate from WB-C. Again, this is attributed to the OMCf implemented in the method, which would cause a weaker

relationship to occur between the method and WB-C. This was evidenced in Section 4.3.4.1, as the method was found to considerably underestimate LR on soils with more than 1% WB-C. As was shown previously, a strong relationship is found between WB-C and titratable acidity. Therefore, the correction of titratable acidity based on the parameter that strongly influences the quantity thereof, causes considerable error.

The Eksteen LR method most strongly correlated with exchangeable acidity ($r = 0.96$). This observation serves to explain the general underestimation of LR by use of this method, as exchangeable acidity does not serve to account for much, if any, pH dependent acidity. In addition, a significant correlation was obtained between the Eksteen method and exchangeable Al ($r = 0.95$). Thus, LRs predicted by this method is sufficient to neutralise the acidity present at soil pH, however, little to no pH dependent acidity is accounted for in the calculation of LR. This is evidenced by the relatively weaker relationships observed between total acidity ($r = 0.77$) and variable charge ($r = 0.73$). Also, no significant correlation was obtained between the Eksteen method LRs and % clay ($r = 0.20$), % silt ($r = 0.24$), and % clay + silt ($r = 0.21$). From Table 5 – 2 it can be seen that titratable acidity did correlate significantly with texture (% clay + silt; $r = 0.35$). Thus, titratable acidity is able to measure the pH dependent acidity associated with texture to some degree. Therefore, correcting titratable acidity based on a parameter that primarily influences the quantity thereof, allows for error to occur, which necessarily leads to the underestimation of LR. However, the LR method significantly correlated with acid saturation ($r = 0.80$), yet this is attributed to the strong relationship observed between exchangeable acidity and the Eksteen method LR. In addition, the method significantly correlated with pH_w ($r = -0.68$) and pH_{KCl} ($r = -0.62$). This is attributed to the relationship between the R-value and pH. However, as was discussed previously, pH is not a true predictor of LR, and a significant correlation between LR as predicted by the method and pH is not necessarily of practical value.

The relationships observed between the Eksteen method's predicted LRs and the abovementioned soil properties serve to explain the general underestimation of LR associated with the method. Thus, it is recommended that the LR method be used with some caution, especially on soils with more than 1% WB-C.

5.3.2.2 Eksteen-KCl Method

As discussed in Section 4.3.4.2, the Eksteen-KCl method was found to consistently underestimate the LR of the population of experimental soils. This observation was essentially attributed to the weaker capacity of K^+ as a replacing cation to displace tightly bound Al^{3+} from exchange sites. Thus, the use of 1 M KCl exchangeable acidity does not serve as a reliable indicator of all the acidity that needs to be neutralised in order to achieve a certain target pH, and in essence, a method based on such a form of acidity would tend to underestimate the potential LR. As can be seen from Table 5 – 4, the Eksteen-KCl method was shown to demonstrate a strong relationship between both exchangeable acidity ($r =$

0.99) and exchangeable Al ($r = 0.99$). This is to be expected, however, as the calculation of LR by use of this method is based on the amount of exchangeable acidity present in a given soil. Further, a significant correlation was observed between the method and CBD-extractable Al. However, this may be more apparent than real, and can be attributed to some exchangeable Al that would have been extracted with a CBD solution. The non-significant correlation coefficients obtained between % silt ($r = 0.22$) and % clay ($r = 0.25$) are indicative of this observation. It was previously shown in this Chapter that a significant relationship does exist between texture and CBD-extractable Al. Thus, from these observations, it is evident that the Eksteen-KCl method does not account for much of the pH dependent acidity that may manifest in a soil with a given increase in pH.

From Table 5 – 4 it can be seen that the Eksteen-KCl method significantly correlated with WB-C ($r = 0.84$) and total C ($r = 0.85$). However, this significant relationship is attributed to the association between exchangeable acidity, more specifically exchangeable Al, and C (Table 5 – 2). As such, a relationship that exists between the method and C may be misleading. This is explained by the concept that, due to the method being based on exchangeable acidity, the method does not account for the pH dependent acidity associated with C. Thus, a method primarily based on electrostatically bound acidic cations, would in essence result in the underestimation of LR in order to achieve a specific target pH. However, from Table 5 – 4 it can be seen that the method significantly correlated with the $(\Delta\text{pH}_{\text{KCl}}) \times (\text{WB-C } \%)$ function ($r = 0.90$). Yet, this relationship is attributed to the strong relationship that exists between exchangeable Al and the $(\Delta\text{pH}_{\text{KCl}}) \times (\text{WB-C } \%)$ function ($r = 0.93$). It should be noted that some of the exchangeable Al present in a soil, might only be partially neutralised into non-exchangeable $\text{Al}(\text{OH})_2^{2+}$ and $\text{Al}(\text{OH})_2^+$ which is subject to adsorption and complexation by OM. This would result in additional pH dependent acidity that might arise, and would explain why a LR based on exchangeable acidity is not sufficient to obtain a specific target pH. Indeed, high LR soils generally contain substantial amounts of acidic Al (van Lierop, 1990), especially soils that have larger amounts of OM. Yet, other factors may serve to reduce plant growth on acid soils, besides Al, such as excessive Mn, low quantities of exchangeable Ca and Mg, and reduced microbial activity. In such cases, a LR method that only predicts the amount of liming material required to neutralise exchangeable Al, results in a lower soil pH than would be achieved if other LR methods were used (van Lierop, 1990).

Considering the limitations of the method related to soil properties and achieving a target pH highlighted above, the method does indeed have potential in certain circumstances. Such an approach to a LR method, i.e. the use of exchangeable acidity, may be successfully adopted in areas where crop production is limited by highly acidic, aluminous soils, and inadequate availability or expensive limestone (van Lierop, 1990). Thus, such a method eliminates the primary limitation to plant growth, at a minimal and more economic cost.

5.3.2.3 Modified Eksteen Method

As discussed in Section 4.3.4.3, the modified Eksteen method was found to underestimate the LR of the population of experimental soils on average. However, the method was found to be considerably more accurate in general than the other variations of the Eksteen method. The method was found to significantly correlate with exchangeable acidity ($r = 0.99$), exchangeable Al ($r = 0.99$), titratable acidity ($r = 0.98$), and total acidity ($r = 0.86$). This indicates that the method may be suitably applied to eliminate the most limiting factors associated with acid soils. Thus, the method predicts a sufficient LR to neutralise excessive amounts of exchangeable Al, as well as adequate amounts of pH dependent acidity to achieve a given target pH_{KCl} of 5.5. This is indicated by the significant correlation obtained between CBD-extractable Al ($r = 0.80$), which may serve as a source of pH dependent acidity, as well as variable charge ($r = 0.83$). Thus, the method is able to account for the approximation of pH dependent acidity that might arise due to an increase in soil pH due to liming. A significant correlation was also obtained between WB-C ($r = 0.89$) and total C ($r = 0.89$). This observation is primarily attributed to the relationship observed in Table 5 – 2 between titratable acidity and WB-C ($r = 0.94$) and total C ($r = 0.93$).

No significant relationship was observed between % clay ($r = 0.25$) and % silt ($r = 0.26$). As such, this would indicate that the method is somewhat insensitive to account for the pH dependent acidity that might originate on clay colloids. Thus, such an observation may serve to explain the general underestimation of LR observed for this method in Section 4.3.4.3. The method was also found to show the strongest relationship with $(\Delta pH_{KCl}) \times (WB-C \%)$ function ($r = 0.95$), compared with the other indirect methods evaluated. This indicates that the method is reasonable sensitive to account for the pH dependent acidity and resultant buffering capacity associated with organic matter. Also, a significant correlation was obtained between the method and the $(\Delta pH_{KCl}) \times (Clay \%)$ function ($r = 0.60$), however, this is essentially attributed to the relationship observed between titratable acidity and the function ($r = 0.64$). Thus, even though the method in itself is quite insensitive to texture, titratable acidity accounts for the pH dependent acidity that might arise from texture. In addition, a significant correlation was also obtained between the method and variable charge ($r = 0.83$), which further indicates the sensitivity to pH dependent acidity.

5.3.2.4 Cedara Method

As was shown in Section 4.3.4.4, LRs as predicted by the Cedara method closely approximated that predicted by the Eksteen-KCl method. The method was generally found to be as accurate and precise as the Eksteen-KCl method. In addition, from Table 5 – 4 it can be seen that the relationship between the Cedara method and selected soil properties are practically identical to that observed for the Eksteen-KCl method. Thus, the Cedara method will not be discussed in as much detail as other methods.

5.3.2.5 ARC-SGI Method

As discussed in Section 4.3.4.5, the ARC-SGI method was found to substantially overestimate the LR of the population of experimental soils on average. This was essentially attributed to the notable influence that a desired change in pH has on the LRs predicted by the method. This influence can clearly be observed from Table 5 – 4, as the ARC-SGI method significantly correlated with both pH_w ($r = -0.92$) and pH_{KCl} ($r = -0.99$). However, due to the difficulties of using soil pH as a predictor of LR described in Section 5.3.1, such inaccuracies associated with the method are easily understood. In addition, the method did not significantly correlate with neither WB-C ($r = 0.26$) and total C ($r = 0.21$). As was shown previously, C plays a pivotal role in the determination of LR. Also, the method did not correlate with total acidity ($r = 0.22$), which indicates that the method is not suitable to determine the amount of acidity that need be neutralised to achieve a given target pH.

The method did however significantly correlate with exchangeable acidity ($r = 0.50$) and exchangeable Al ($r = 0.47$). This would explain the significant correlation obtained between the method and acid saturation ($r = 0.59$), as acid saturation was calculated from exchangeable acidity. However, the method was also developed, by use of regression analysis, based on the degree of change in acid saturation for a given change in pH_{KCl} . Thus, the principals on which the method was originally based holds true for the set of experimental soils used in this study. Yet, the non-existent relationships between soil parameter that most strongly influence the buffering capacity of a soil, and thus the LR thereof, explains the inaccuracies observed for this method. In addition, a significant correlation was obtained between the method and the $(\Delta\text{pH}_{\text{KCl}}) \times (\text{Clay } \%)$ function ($r = 0.64$). Thus, the method is somewhat sensitive to the pH dependent acidity that might arise from clay colloids for a given change in pH. However, a weaker, yet significant, relationship was obtained between the method and the $(\Delta\text{pH}_{\text{KCl}}) \times (\text{WB-C } \%)$ function ($r = 0.48$). This should warrant caution, as the contribution of OM to buffering capacity is greater than that of clay (Curtin & Rostad, 1997). It should also be noted that the contribution of organic matter to buffering capacities in highly weathered can also be significant, even at low quantities (Coleman & Thomas, 1967). Thus, these observations definitively explain the inaccuracies associated with the ARC-SGI method.

5.3.2.6 SMP-SB Method

As discussed in Section 4.3.4.6, the SMP-SB method was found to underestimate the LR of the population of experimental soils on average. However, the method was shown to be the most precise on average compared to other methods evaluated in the study. This was essentially attributed to the way in which the method was originally calibrated. From Table 5 – 4 it can be seen that the method significantly correlated with exchangeable acidity ($r = 0.93$), titratable acidity ($r = 0.98$), and total acidity ($r = 0.94$). This indicates that the buffer is suitable to react with most of the acidity that need be neutralised in order to achieve a target pH_{KCl} of 5.5. Interestingly, the method significantly correlated

with exchangeable Al ($r = 0.93$) and CBD-extractable Al ($r = 0.90$). This observation is attributed to the ability of the buffer to specifically react with Al in soils (Shoemaker, *et al.*, 1961). It is therefore specifically this observation that may serve to explain the general precision of the method. Also, the method was shown to be the method that most significantly correlated with variable charge ($r = 0.91$). Thus, the buffer is suitably designed to account for pH dependent acidity that may arise due to a change in pH due to liming. However, this strong relationship may also be ascribed to the significant correlation observed between LR as predicted by the method and $CEC_{pH 7}$ ($r = 0.80$). This is an observation of interest, since it has been reported that the CEC of OM is primarily pH dependent (Keeney & Corey, 1963).

The method significantly correlated with WB-C ($r = 0.96$) and total C ($r = 0.95$). This observation would therefore serve to explain the significant relationship between LR as predicted by the method and $CEC_{pH 7}$. The strong relationship that was observed between the method and C may also be attributed to the relationship between exchangeable and CBD-extractable Al and C. Regarding texture, the method was found to only significantly correlate with % silt ($r = 0.42$). This may be attributed to the inability of the method to detect small differences in acidity. Thus, the buffer is not able to react with some of the pH dependent acidity associated with clay. This is indicated by the relatively lower significant correlation coefficient observed between the method and the $(\Delta pH_{KCl}) \times (\text{Clay } \%)$ function ($r = 0.56$). This relationship is similar to that obtained between LR methods based on 1 M KCl exchangeable acidity and the $(\Delta pH_{KCl}) \times (\text{Clay } \%)$ function. However, a significant correlation was obtained between the method and the $(\Delta pH_{KCl}) \times (\text{WB-C } \%)$ function ($r = 0.95$). This indicates that LRs as predicted by the buffer is strongly influenced by the pH dependent acidity associated with OM. However, according to Sims (1996), in soils with very high amounts of OM contents the decreased reactivity of H^+ with the buffer causes inaccuracies associated with the underestimation of LR.

Considering the strong relationships observed between the SMP-SB method and the soil properties that most strongly influence the LR of a soil, the benefits of using a direct buffer method to estimate LR is clear. The ability of the buffer to react with primary factors that determine the LR of a soil allows for the increased accuracy observed for the method. As such, the method has few limitations regarding the areas and types of soils that it can be applied to. However, caution should still be exercised on soils with low LRs and that have very low amounts of exchangeable Al.

5.3.2.7 AE-SB Method

As discussed in Section 4.3.4.7, the AE-SB method was found to substantially overestimate the LR of the population of experimental soils on average. This was primarily attributed to the very high initial buffer pH of 8.0, along with the fact that the method was not calibrated on the soils used in this study. From Table 5 – 4 it can be seen that the method significantly correlated with exchangeable acidity ($r = 0.92$), titratable acidity ($r = 0.97$), and total acidity ($r = 0.93$). This indicates that the buffer sufficiently

reacts with most of the acidity that need be neutralised in order to achieve a target pH_{KCl} of 5.5. In addition, the AE-SB method also significantly correlates with both WB-C ($r = 0.95$) and total C ($r = 0.93$). Considering the strong relationships that exist between C and the abovementioned forms of soil acidity (Table 5 – 2), it is expected that a strong relationship would exist between the method and C.

An interesting observation is that of the significant relationships that exists between the AE-SB method and the $(\Delta\text{pH}_{\text{KCl}}) \times (\text{WB-C } \%)$ ($r = 0.96$) and $(\Delta\text{pH}_{\text{KCl}}) \times (\text{Clay } \%)$ ($r = 0.71$) functions. This is indicative of the buffer's ability to bring about superfluous deprotonation of H^+ from soils, due to the high initial buffer pH of 8.0. This is especially true of the clay content of soils, as a significant correlation was observed between the AE-SB method and % clay ($r = 0.45$). The AE-SB method was the only LR method that was shown to exhibit a relationship with texture. It is therefore evident that the buffer is able to react with most of the acidity associated with the colloidal system. The method was also found to significantly correlate with variable charge ($r = 0.88$), and as such, is able to account for variable charge that might arise due to an increase in pH.

It is evident that the AE-SB method is able to account for forms of acidity that are pivotal to accurate LR. However, the buffer's ability to determine excessive amounts of acidity, most evidently due to the high initial buffer pH, may cause overestimation in LR. The method should therefore be limited to soils of low LR, as overestimation of LR might easily occur on soils with high LRs that would have substantial amounts of reserve acidity.

5.4 Conclusions

The primary purpose of this study was to find the combination of soil properties that most strongly influence the LR of a soil as determined by incubation. It was found that soil pH has no direct effect on the LR of a soil, but rather an indirect effect due to the ability of soil pH to influence the chemical condition of a soil. Soil C was found to be a significant contributor to LR due to its association with soil acidity. However, it was the pH dependent acidity associated with C that was shown to be of substantial influence regarding the LR of a soil. Texture was found to have some significant influence over the LR of a soil, however, this influence was outweighed by C in most cases.

Titrateable acidity was found to be the soil property that most strongly influenced the LR of a soil. In addition, variable charge that would manifest due to an increase in pH was also shown to exhibit significant relationships with soil parameters that most strongly influence LR. Results from this study revealed that soil properties other than soil pH, which are strongly related to LR are, in order of decreasing importance $\text{WB-C} > \text{variable charge} > \text{CEC}_{\text{pH } 7} > \text{clay} + \text{silt}$. Considering that the degree to which variable charge manifests is strongly associated with the C content, CEC, and texture, it was decided that variable charge was most prominent. Therefore, a multiple regression equation was calculated that utilised only titrateable acidity and variable charge. The multiple regression equation was

able to account 96.76% of the variation observed for incubation LR, and was 97.86% accurate in predicting the LR for each specific soil to obtain a target pH_{KCl} of 5.5 on average.

The secondary purpose of this study was to find the combination of soil properties that most strongly influenced the LR of each method evaluated in the study. It was found that each of the indirect methods evaluated in this study was most strongly influenced by exchangeable acidity and Al. In addition, the methods were also shown to have significant relationships with C, however, this was primarily attributed to the association of soil acidity with C. The ARC-SGI method was an exception to the general trend, as the method most significantly correlated with soil pH. The strong influence of soil pH on the LRs predicted by use of this method was the main causal factor that resulted in the inaccuracies associated with this method. Further, it was shown that the ARC-SGI method was more strongly influenced by the pH dependent acidity associated with clay, than with that associated with C. It was found that the direct buffer methods evaluated in this study were most strongly influenced by essentially all of the soil properties studied. This is indicative of the ability of these methods to directly determine the amount of acidity that may originate from various sources in the soil, in order to make a sufficiently accurate LR. It is therefore recommended that the application of buffer methods be utilised in order to more accurately determine LR in South Africa. In addition, the wider application of such methods, should in principle result in the development of more refined and sophisticated methods that would be more suitable to South African soils.

The results from this study indicate that the most vital soil properties that need be determined in order to sufficiently estimate the LR of a soil are, in no particular order:

Walkley-Black C, titratable acidity at pH 7.0, exchangeable cations, buffered CEC at pH 7.0 and texture. Considering these findings, however, it is crucial that more research be carried out in order to evaluate the economic implications of basing LR on the abovementioned soil properties, in relation to crop performance and long term soil management.

Chapter 6

General Conclusions

Twenty acidic top and sub-soils were sampled from four provinces in South Africa. Laboratory studies were conducted with the sampled soils to evaluate seven commonly used methods used to determine soil lime requirement (LR). The first method evaluated was the original Eksteen method with organic matter correction factor (OMCF) derived by Smuts (2001), commonly used in the Western Cape province of South Africa. Two modifications of the Eksteen method were also evaluated, namely: (i) Eksteen-KCl method, where the use of 1 M KCl exchangeable acidity instead of the originally proposed titratable acidity at pH 7, and (ii) Modified-Eksteen method, where a correction factor was applied to titratable acidity that was derived from soil data obtained in this study. The fourth method evaluated was the Cedara method, most commonly used in the Kwa-Zulu Natal province of South Africa. The ARC-SGI method, developed primarily for Free State Soils by the Agricultural Research Centre at the Small Grain Institute in Bethlehem in the Free State province was also evaluated. In addition to these five local methods, two American rapid buffer methods were also evaluated. The first is the Shoemaker-McLean-Pratt single buffer (SMP-SB) method most commonly used in the North East and North Central regions of the United States. The second rapid buffer method is the Adams and Evans single buffer (AE-SB) method most commonly used in the South East and Mid-Atlantic regions of the United States.

Chapter 3 reported on the general chemical and physical characterisation of the soils sampled, that were used in this study. Results from this study revealed that soils from the Eastern Free State (EFS) were the most weakly buffered soils, and contained small amounts of C, clay, Fe and Al oxides, along with very low levels of $CEC_{pH\ 7}$. Soils from Kwa-Zulu Natal (KZN) were revealed to be strongly buffered with large amounts of reserve acidity. These soils generally contained high amounts of C and Fe and Al oxides, along with a resulting high $CEC_{pH\ 7}$. Soils from the Western Cape Province (WCP) were revealed to be intermediate in terms of soils properties when compared to soils from the EFS and KZN. These soils generally contained low amounts of C, along with low exchangeable Ca and Mg and $CEC_{pH\ 7}$ values. Lastly, soils from the North West Province (NWP) were revealed to be only moderately acidic at best in comparison to soils from other provinces, and would therefore not require significant quantities of lime.

Chapter 4 reported on a laboratory study where a widely accepted reference method, $CaCO_3$ -soil incubation, was used to evaluate the seven methods of interest used to determine LR. Results from this study revealed that that the modified Eksteen, SMP-SB, and AE-SB methods have the widest range in applicability on soils from South Africa. The original Eksteen method was shown to significantly underestimate the LR of soils with C contents of larger than 1%. Thus, the organic matter correction

factor (OMCF) implemented in the method was shown to be the most limiting factor associated with the method. The Eksteen-KCl method and Cedara methods performed similarly and consistently underestimated the LR of most soils. This was attributed to limitations of using 1 M KCl exchangeable acidity as a means to determine LR in order to achieve a target pH_{KCl} that is notably higher than the initial field pH. Further, even after correction by use of the most appropriate regression equation, both methods would on average consistently underestimate LR. The ARC-SGI method was shown to be the most inaccurate method on all soils. This was attributed to the implementation of a relationship between change in pH_{KCl} and a resultant change in acid saturation. However, after correction of the method by use of the most appropriate regression equation, it was found that the method will exhibit reasonable accuracy on soils with a potential LR of less than 4 tons CaCO_3/ha , yet the use of this method is not recommended in general. The rapid buffer procedures that were evaluated was shown to hold the most potential on all soils due to their general accuracy. The AE-SB method tended to significantly overestimate the LR of most soils, however, after correction and recalibration, the method was slightly more accurate. Further, the SMP-SB method was shown to hold the most potential after re-calibration, allowing for use on soils with a potential LR of larger than 2.5 tons CaCO_3/ha .

Chapter 5 reported on a correlation study to investigate the relationship between soil properties and both LR and LR tests. It was revealed that soil properties other than soil pH, which are useful indicators of LR are, in order of decreasing importance $\text{WB-C} > \text{variable charge} > \text{CEC}_{\text{pH } 7} > \text{clay} + \text{silt}$. It was also found that soil pH was not directly related to the LR of a soil, but rather had an indirect effect due to the ability of soil pH to influence the condition of a soil. Further, soil C was found to be a significant contributor to LR due to its association with soil acidity. However, the pH dependent acidity associated with C was also shown to be of substantial influence regarding the LR of a soil. In addition, texture was found to have some significant influence over the LR of a soil, however, this influence was outweighed by C in most cases. Titratable acidity was found to be the soil property that most strongly related to the LR of a soil. In addition, variable charge was also shown to exhibit significant relationships with soil parameters that most strongly influence LR. For these reasons, a multiple regression equation was calculated that utilised only titratable acidity and variable charge, and is presented as follows:

$$\hat{Y} = 0.2196(\text{CEC}_{\text{pH } 7} - \text{ECEC}) + 1.528(\text{TA}) - 0.7732$$

where \hat{Y} is LR in $\text{kg CaCO}_3/\text{kg}$ of soil, $(\text{CEC}_{\text{pH } 7} - \text{ECEC})$ is variable charge in cmol_c/kg , and TA is titratable acidity buffered at pH 7.0 in cmol_c/kg . LR values are reported in $\text{kg CaCO}_3/\text{kg}$ of soil in order to account for variation in bulk density. The multiple regression equation was able to account for 96.76% of the variation observed for incubation LR, and was 97.86% accurate in predicting the LR for each specific soil to obtain a target pH_{KCl} of 5.5 on average. Regarding the relationship between soil properties and LR methods, it was revealed that each of the indirect methods evaluated in this study

was most strongly influenced by exchangeable acidity and Al. In addition, the methods were also shown to have significant relationships with C; however, this was primarily attributed to the association of soil acidity with C. The ARC-SGI method was an exception to the general trend, as the method most significantly correlated with soil pH. It was also revealed that the direct buffer methods evaluated in this study were most strongly influenced by essentially all of the soil properties studied. This is indicative of the ability of these methods to directly determine the amount of acidity that may originate from various sources in the soil, in order to make a sufficiently accurate LR. It is therefore recommended that the application of buffer methods be utilised in order to more accurately determine LR in South Africa.

Evidence from the various chapters indicated the effectiveness of using direct means to determine LR through the application of buffer methods. A limitation to the completed work was a lack of calibrating LR with crop LRs. This is an aspect which has largely been ignored in South Africa, and should be a priority for future research. Considering the general applicability of these rapid buffer methods, it is recommended that further work be carried out in order to develop a rapid buffer procedure more suited for the highly weathered soils of South Africa. In addition to this, more work should be done on calibrating such a method on agricultural soils in order to account for a decrease in the reactivity of liming materials on agricultural soils, along with problems associated with the mixing efficiency thereof. The modified Eksteen method was shown to be the most accurate indirect method evaluated. As such, it may be used with reasonable confidence on a wide variety of soils. However, caution should be exercised on weakly buffered, lightly textured soils, as overestimation of LR may occur on such soils with use of this method.

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Appendix A

Table A – 1. Predicted lime requirement by use of each respective method

Sample No	Lime Requirement Method							
	Eksteen	Eksteen (KCl)	Eksteen (Mod.)	Cedara	ARC-SGI	SMP Single Buffer	AE Single Buffer	Incubation LR
	← Tons/ha CaCO ₃ →							
10 A	5.0	4.0	4.5	3.6	9.4	0.0	2.0	3.9
10 B	3.6	2.8	3.2	2.5	8.2	0.0	0.2	2.6
11 A	3.7	2.4	3.0	2.0	8.2	0.0	2.1	3.1
11 B	3.0	1.4	2.2	1.2	7.5	0.0	0.6	2.1
12 A	3.6	4.1	5.6	3.6	9.4	2.7	5.7	4.2
12 B	3.7	1.3	2.4	1.0	7.1	0.0	2.8	2.6
16 A	5.8	8.5	7.0	7.6	11.3	0.0	3.5	3.9
16 B	5.0	3.7	4.4	3.2	10.1	0.0	1.8	3.3
17 A	1.3	0.0	2.4	0.0	9.0	3.8	8.7	5.5
17 B	1.3	0.0	0.8	0.0	7.9	2.7	5.5	4.6
2 A	6.9	6.4	9.4	5.6	11.0	6.0	12.2	10.6
2 B	0.2	0.0	0.2	0.0	5.9	1.1	5.4	3.6
3 A	17.9	22.7	28.5	20.5	9.4	28.2	39.9	26.7
3 B	8.7	10.7	13.8	9.6	7.6	15.8	26.8	16.1
7 A	3.8	3.6	7.0	2.8	11.5	6.0	13.7	10.8
7 B	0.3	0.0	0.0	0.0	4.5	1.8	6.0	2.7
18 A	8.7	9.6	11.8	8.0	11.9	11.3	14.1	12.1
18 B	2.5	0.0	2.3	0.0	7.3	5.0	7.2	5.6
19 A	17.6	23.4	26.4	21.0	9.5	26.3	29.0	25.1
19 B	10.1	9.4	13.1	8.4	7.3	19.1	19.8	16.5
22 A	6.9	8.7	12.3	7.6	7.6	15.8	17.8	15.5
22 B	7.5	7.0	9.4	6.2	7.3	9.9	12.3	8.8
23 A	5.6	8.0	9.3	7.2	9.2	7.4	10.4	6.7
23 B	6.0	4.7	5.3	4.3	9.4	1.1	6.3	3.8
29 A	8.0	7.9	7.7	6.7	10.3	2.7	8.2	5.2
29 B	6.4	4.0	4.8	3.1	9.8	1.8	7.6	4.4
30 A	6.4	3.1	4.7	2.6	9.4	1.8	5.1	5.4
30 B	5.9	4.6	5.3	4.0	10.6	2.7	9.9	5.8
31 A	1.4	0.0	1.9	0.0	7.4	0.0	2.9	3.3
31 B	0.5	0.0	0.0	0.0	0.0	0.0	1.1	0.0
24 A	0.0	0.0	0.0	0.0	0.6	0.0	2.5	1.1
24 B	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0
25 A	4.6	1.2	2.8	0.8	8.1	1.8	6.0	5.4
25 B	0.8	0.0	0.0	0.0	5.8	0.0	3.4	2.0
26 A	2.3	0.0	0.4	0.0	7.0	0.0	4.1	3.3
26 B	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0
27 A	0.0	0.0	0.0	0.0	3.4	0.0	2.5	1.3
27 B	0.0	0.0	0.0	0.0	1.6	0.0	1.8	0.0
28 A	2.5	0.0	1.0	0.0	7.4	0.0	2.5	3.8
28 B	0.8	0.0	0.0	0.0	4.4	0.0	1.7	0.0

Table A – 2. Acid saturation (%) for each respective lime requirement method^a

Sample No.	Lime Requirement Method						
	Eksteen	Eksteen (KCl)	Eksteen (Mod.)	Cedara	ARC-SGI	SMP Single Buffer	AE Single Buffer
10 A	0.00	0.00	0.00	0.00	0.00		11.44
10 B	0.00	0.00	0.00	0.00	0.00		29.14
11 A	0.00	2.98	1.76	5.26	0.00		3.60
11 B	0.00	1.25	0.00	2.71	0.00		10.87
12 A	5.87	4.29	2.61	5.72	0.00	9.14	0.26
12 B	0.00	5.89	1.03	7.01	0.00		0.99
16 A	0.00	0.00	0.00	0.00	0.00		1.62
16 B	0.00	0.00	0.00	0.00	0.00		2.12
17 A	6.74		4.85	0.00	0.00	2.96	0.00
17 B	4.92		4.14	0.00	0.00	3.05	0.97
2 A	7.10	7.81	8.30	11.82	1.43	9.19	1.00
2 B	7.23		6.53		0.00	2.06	2.30
3 A	8.33	4.47	23.07	4.92	21.66	1.47	0.00
3 B	10.49	8.37	18.59	8.45	14.26	2.93	0.00
7 A	8.92	9.96	5.18	9.55	0.69	5.81	0.00
7 B	3.58		3.45		0.00	1.66	0.00
18 A	5.70	4.01	4.40	5.93	2.67	2.52	1.41
18 B	5.67		4.44		0.92	1.76	0.53
19 A	14.41	3.11	11.41	4.82	18.19	2.58	2.02
19 B	8.80	9.48	13.28	10.64	13.41	1.27	2.53
22 A	22.97	14.56	41.99	17.41	17.76	4.22	1.87
22 B	11.17	11.70	8.60	13.63	10.53	5.97	2.70
23 A	11.55	3.64	6.98	4.57	1.89	5.56	0.00
23 B	0.00	0.00	0.00	0.00	0.00	12.02	0.00
29 A	0.00	0.00	0.00	0.00	0.00	8.85	0.00
29 B	0.00	1.76	0.00	3.55	0.00	10.34	0.00
30 A	0.85	9.26	5.48	10.20	0.00	4.80	2.08
30 B	0.83	2.95	1.88	2.60	0.00	7.04	0.00
31 A	7.28		3.32		0.00		2.38
31 B	0.61				0.00		0.00
24 A					2.90		0.14
24 B							0.83
25 A	2.68	11.50	7.42	14.93	0.00	9.42	1.57
25 B	3.48				0.00		0.00
26 A	3.32		10.28		0.00		0.60
26 B							0.30
27 A					0.00		0.19
27 B					1.29		0.43
28 A	4.09		6.92		0.00		2.48
28 B	3.15				0.00		0.61

^a Values are omitted in instances where a specific lime requirement method did not predict a LR

Appendix B (Lime Response Graphs)

