

**DETERMINATION OF THE LIME REQUIREMENT OF SANDY, ORGANIC-RICH,
AND STRUCTURED, HIGH Mg:Ca RATIO SOILS BY THE EKSTEEN METHOD**

by

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DECLARATION

I, the undersigned, hereby declare that work contained in this thesis consists in entirety of my own original research.

It has not, in whole or in part, been submitted to any other University for the purpose of obtaining a further degree.

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ABSTRACT

The Eksteen method of lime requirement determination, based on the ratio of Ca+Mg:H (R-value), is widely used in the Western Cape and has proven to be extremely accurate for most soils. However, the Eksteen method is known to give erroneous predictions of lime requirement for certain soil groups. These include sandy soils (notably pale coloured sandy soils), organic-rich topsoils and strongly structured, Mg-rich subsoils. The objective of this study was to examine the nature of the Eksteen R:pH relationship for these problem soils, and to develop appropriate modifications to the Eksteen method, where possible.

A population of both normal and problem soils was selected and analysed, the R:pH relationships of the soils were determined, and various relationships were examined. The principal findings with regard to the nature of the Eksteen R:pH relationship were as follows:

1. The lime requirements of pale coloured sandy soils can be most accurately determined on an equivalent basis relative to the total extractable acidity, after the total extractable acidity has been corrected for residual lime.
2. The previously observed and acknowledged inaccuracy of the Eksteen method on organic-rich soils stems from the pH-dependant acidity component of the organic matter. The accuracy with which the lime requirement of these soils is predicted by the Eksteen method can be greatly improved by the application of an organic matter correction factor (OMCF) to the total extractable acidity, which is the parameter on which the lime requirement is then based.
3. In structured, Mg-rich subsoils the pH-neutralising capacity of Mg is considerably lower than that of Ca, a factor which is not taken into account by the Eksteen method. The Eksteen method can nevertheless be corrected to overcome this discrepancy. The high levels of Mg in the structured, Mg-rich subsoils cannot be attributed to minerals in these subsoils containing brucite interlayers.
4. Toxic levels of Al may only be expected at soil pH values below approximately 4.7 as determined in 1M KCl. Soil organic matter and CEC have marked affects on Al extractability.

In accordance with the objective that appropriate modifications to the Eksteen method should be developed if possible, theoretically-based correction factors were developed which will permit the use of the Eksteen method to be confidently extended to those soil groups (pale coloured sandy soils, organic-rich topsoils and strongly structured, Mg-rich subsoils) for which it was formerly considered unreliable.

UITTREKSEL

Die Eksteen metode van kalkbehoeftebepaling, gebaseer op die verhouding van $Ca+Mg:H$ (R-waarde), word oor die algemeen wyd in die Wes-Kaap gebruik en is baie akkuraat vir meeste gronde bewys. Dit is egter bekend dat die Eksteen metode verkeerde kalkbehoefte vir sekere grondgroepe voorspel. Hierdie sluit sanderige gronde (veral lig gekleurde sandgronde), organiesryke bogronde en sterk gestrukteerde, Mg-ryke ondergronde in. Die doel van hierdie studie was om die aard van die Eksteen R:pH verwantskap vir hierdie probleemgronde te bepaal, waar moontlik.

'n Populasie van beide normaal en probleemgronde is geselekteer en geanaliseer, die R:pH verwantskap van die gronde is bepaal en verskeie verwantskappe is ondersoek. Die hoof bevindinge ten opsigte van die aard van die Eksteen R:pH verwantskap was as volg:

1. Die kalkbehoefte van lig gekleurde sandgronde kan akkuraat bepaal word op 'n ekwivalente basis, relatief tot die totale ekstraheerbare suurheid, nadat die totale ekstraheerbare suurheid gekorrigeer is vir residuele kalk.
2. Die voorheen bekende onakkuraatheid van die Eksteen metode op organiesryke gronde het sy oorsprong by die pH-afhanklike suurheid komponent van organiese materiaal. Die akkuraatheid waarmee die kalkbehoefte van hierdie gronde met behulp van die Eksteen metode voorspel kan word, kan noemenswaardig verbeter word deur die totale ekstraheerbare suurheid te korrigeer met behulp van 'n organiese materiaal korreksie faktor (OMKF). Die aangepaste totale ekstraheerbare suurheid is dan die parameter waarop die kalkbehoefte gebaseer word.
3. In gestrukteerde, Mg-ryke ondergronde is die pH-neutraliseringsvermoë van Mg aansienlik laer as die van Ca, 'n faktor wat selde in berekening gebring word by die Eksteen metode. Die Eksteen metode kan tog gekorrigeer word om hierdie tekortkoming te oorkom. Die hoë vlakke van Mg in gestrukteerde, Mg-ryke ondergronde kan nie aan die teenwoordigheid van minerale in die ondergrond, wat brusiet tussenlae bevat, toegeskryf word nie.
4. Toksiese Al vlakke sal alleenlik by grond pH waardes laer as ongeveer 4.7, soos bepaal in 1M KCl, verag word. Grond organiese materiaal en KUK het 'n noemenswaardige effek op ekstraheerbare Al.

In ooreenstemming met die doelwitte om toepaslike wysigings aan die Eksteen metode aan te bring, is teoreties gebaseerde korreksiefaktore ontwikkel, wat die gebruik van die Eksteen metode verder verbreed om daardie grondgroepe (lig gekleurde sanderige gronde, organies-ryke bogronde en sterk gestrukteerde, Mg-ryke ondergronde) in te sluit waarvoor dit vantevore as onbetroubaar beskou is.

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1. OVERVIEW

1.1 Introduction

According to Conradie (1983), analysis of soil samples show that more than 70% of vines in the Western Cape are grown in soils with a pH_{KCl} of less than 5.0. This situation has apparently not changed over the past 17 years (W.J. Conradie, 1999, ARC Infruitec-Nietvoorbij, personal communication). Soil acidity decreases plant growth, either by inducing deficiencies of such elements as phosphorus, molybdenum and calcium, or through the direct toxic effects of aluminium, manganese or hydrogen ions (Marschner, 1995). Such toxicities are probably the most common causes of reduced yields (Ritchie, 1989). The toxic effects of aluminium are primarily root-related. With increasing soil acidification, root penetration into the subsoil is inhibited, leading to a shallower root system, with a correspondingly lower utilization of mineral nutrients and water from the subsoil (Marschner, 1995). High soil acidity levels, coupled with a low calcium status, constitute a serious soil problem for the cultivation of deciduous fruit and potatoes in some areas in the Western and Southern Cape. Such conditions lead to the development of bitterpit in apples (Steenkamp, 1983) and internal brown spot in potatoes (Bester, 1993).

Over-liming of sandy soils promotes potato scab through the creation of a high soil pH. Lambert & Manzer (1991) found that, in soils that were inoculated with *Streptomyces scabies*, at a $\text{pH}_{\text{H}_2\text{O}}$ of 5.5, up to 80% of the total harvest were infected with potato scab. This would not have been the case had a method of lime requirement determination been employed which more accurately reflected the levels of carbonate reserves. Over-liming on any soil type has further ramifications: it may lead to decreased plant-available phosphorus, and to trace element deficiencies. Further, it is becoming increasingly clear that soils with a long history of maintenance liming contain large reserves of unreacted lime (J.J.N. Lambrechts, 1995, University of Stellenbosch, personal communication); an aspect that is very rarely taken into consideration during lime requirement determinations.

Most advisory institutions in the Western Cape currently use the Eksteen method (Eksteen, 1969) to calculate the amount of lime required to raise the soil pH to a specific level. This method is based on the relationship between the R-value $\{(\text{Ca}+\text{Mg})^1 \div \text{H}^2\}$ and pH, and was developed for topsoils with a Mg:Ca ratio of approximately 1:5 and a low organic matter content ($\leq 1,0\%$ C).

Although the Eksteen method is used with great success for wheat and pasture crops, serious problems are experienced where soils are encountered which are rich in organic material, are sandy, or have abnormally high ratios of extractable magnesium to calcium, as are frequently found in structured subsoils. Use of the Eksteen method for lime requirement determinations in these soils results in the organic-rich and sandy soils being over-limed, and the structured, high Mg:Ca ratio subsoils being under limed. Over-liming of organic-rich soils has no negative effects in terms of nutrition, as is the case with sandy soils, but leads to unnecessary costs being incurred.

¹ HCl extraction

² K_2SO_4 at pH 7 extraction

The Eksteen method results in predictions of lime requirement exceeding those of the Cedara (KCl extraction) method (Manson *et al.*, 1990). The difference can be as much as 1 - 6 ton ha⁻¹ for a soil depth of 15 cm for soils with more than 1% organic carbon. In contrast, the loss of crop quality and production from structured, high Mg:Ca ratio soils which are under-limed following the Eksteen method could exceed any savings which may stem from the lower lime requirement specified by this method.

The examples cited above indicate that the problems which are inherent in the Eksteen method when used for soils which are sandy, high in organic material or which have high exchangeable magnesium contents, are in urgent need of investigation, clarification and correction. These are the objectives of the work described in this thesis.

1.2 Literature Review

According to Woodruff (1967) the first chemical test for soil acidity was litmus paper. However, litmus paper was found to be of no practical value for determining the lime requirement of soils.

Veitch (1902) proposed treating the soil with enough lime water [Ca(OH)₂] to make the soil solution alkaline to phenolphthalein, but noted that the quantities of lime suggested by this method far exceeded the amount of lime necessary for good crop performance in the field. Nonetheless, many researchers in the field of soil acidity have since used the basic concept embodied in Veitch's method, and a number of modifications have been developed (Easton, 1980). With the development of better apparatus for determining soil pH, titration methods similar to that used by Veitch became the principle means by which lime requirements were determined. Prior to 1923, the method which was in vogue in South Africa for estimating lime requirement was one which was based on the total lime content of the soil as determined by acid (HCl) extraction (Hall, 1923). As subsequently became apparent, this procedure overestimated the actual lime requirement of most of the soils tested.

In order to overcome the perceived disadvantages of acid dissolution techniques, Mehlich (1938) utilised a buffer solution (pH 8.2) consisting of triethanolamine acetate (TEA-OAc) and Ba(OH)₂ to estimate the lime requirement of acid soils. Later, Woodruff (1948) developed a refined buffer method. This involved mixing the soil with a solution which was buffered at pH 7 by paranitrophenol and Ca(OAc)₂. The lowering of the pH of the buffer solution by the added soil was considered to be an indication of the lime requirement (Easton, 1980). The methods of Mehlich (1938) and Woodruff (1948) were the predecessors of many other buffered methods, based on the same principles. These included the SMP single buffer (Shoemaker *et al.*, 1962), SMP double buffer (McLean *et al.*, 1978), Adams-Evans buffer (Adams & Evans, 1962) and the Yuan double buffer (Yuan, 1974). The Woodruff, SMP single buffer, Adams-Evans and Mehlich methods are still in general the most widely used methods of lime requirement determination in the United States of America.

Kamprath (1970) developed a new approach. He appreciated that aluminium is the most harmful factor in acid soil. He, therefore, used the amount of aluminium extracted by a neutral salt solution, such as KCl, as a criterion of extractable acidity. The same approach was embodied in the Cedara method used in

South Africa (Manson *et al.*, 1990). The Fruit and Fruit Technology Research Institute (FFTRI) in South Africa developed a refinement of the Cedara method in 1979. This refined method was also based on exchangeable Al, but embodied a regression model based on the relationship between exchangeable Al and the amount of lime that is required to achieve a soil pH_{KCl} of 5.5. The FFTRI method was, in consequence, considerably more accurate than the Cedara method (Kotzé & Joubert, 1979).

The objective of all of the methods, which were based on Kamprath's approach, was that of eliminating the negative effects of aluminium. However, those methods did not aim to establish the specific, optimum pH levels required by individual crops.

The method of lime requirement determination developed by Eksteen (1969) was specifically adapted for use with the topsoils in the winter rainfall region of South Africa. These soils are characterised by low levels of organic material. The Eksteen method is capable of determining the lime requirement of soils where a pH_{KCl} value in excess of 5.0 is required. Liming for a pH higher than 5 increases the effective cation exchange capacity (ECEC). It also increases the amount of exchangeable calcium in the soil. Wider application of the Eksteen method exposed certain shortcomings. Although no publications have appeared in literature concerning the problem areas, it was nevertheless clearly apparent to soil acidity researchers that the Eksteen method failed to give good results for organic-rich soils, sandy soils and medium to strongly structured subsoils with relative high magnesium to calcium ratios.

A number of authors (Keeney & Corey, 1963; Ross *et al.*, 1964; Evans & Kamprath, 1970; Van Lierop, 1983) have noted that organic material has a substantial influence on the lime requirement of soils. Organic material results in significant increases in estimated lime requirement. This is of particular concern in view of the fact that Van Lierop & Mackenzie (1975) have found that maximum crop production on organic-rich soils is achieved at a lower pH that is usually required for peak production from mineral soils. An explanation for this anomaly became apparent when Evans & Kamprath (1970) showed that organic material decreases the availability of aluminium in soil. Aluminium forms soluble and insoluble complexes with organic compounds, as well as being non-specifically adsorbed on exchange sites. According to Ross *et al.* (1964) soil factors, other than pH, which are useful as indicators of lime requirement are, in order of decreasing importance: cation exchange capacity > organic matter content > exchangeable hydrogen > clay content.

During an evaluation of the different pH buffer methods used for determining lime requirement, Tran & Van Lierop (1981) found that all the methods tested tended to overestimate the lime requirements of soils which were characterised by inherently low lime requirements. Most notable amongst these were sandy soils containing little silt or clay.

1.3 The Eksteen method for the determination of lime requirement

1.3.1 Principles

As previously stated, the Eksteen method was originally developed for topsoils in the winter rainfall region of South Africa. This method is based on the principle that, for every plant or crop, there exists an optimum balance between base cations (Ca & Mg) and soil acidity (H). This balance is expressed as the R-value $\{(Ca+Mg) \div H\}$. The method was fully described by Eksteen (1969). Calcium and Mg are determined in a 0.1M HCl extraction. The purpose of the acid extractant is to account for any residual lime that may be present in the soil. The soil acidity (H) is determined in a leachate obtained using a 0.5M K_2SO_4 extracting solution, that is weakly buffered at pH 7 with potassium acetate, by titration with 0.1M NaOH. Trials in which soils were incubated with lime revealed that the relationship between the R-value and the soil pH_{KCl} is as shown in Figure 1.1. According to this relationship, R-values of 5 and 10 relate to soil pH (KCl) values of, respectively, 5.0 and 5.5. The formula which is used to determine the lime requirement (x) was derived from the following principles:

$$\text{If } R = \frac{\text{base cations}}{H} \quad (\text{where } H \text{ is soil acidity at pH 7})$$

and if lime (x) (base cations) is applied to the soil it will change the R-value as follows:

$$R = \frac{\text{base cations} + x}{H - x}$$

Therefore, to determine the amount of lime, or bases, to be applied to achieve a specific R-value that will denote the optimum balance between base cations and soil acidity for a specific crop, x must be solved:

$$R = \frac{\text{base cations} + x}{H - x}$$

$$RH - Rx = \text{base cations} + x$$

$$Rx + x = RH - \text{base cations}$$

$$x(R + 1) = RH - \text{base cations}$$

$$x = \frac{RH - \text{base cations}}{R + 1}$$

When the 'base cations' expression is replaced with (Ca+Mg), and a field calibration factor (F) is added, the formula used to determine the lime requirement (x) becomes:

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

with H, Ca and Mg in $\text{cmol}_c \text{ kg}^{-1}$ and x the amount of lime required, in t ha^{-1} for a soil depth of 15 cm (based on the assumption that a hectare of soil, 15 cm deep, weighs 2000 ton). The R-value is the value, selected by the user, which corresponds to the desired soil pH in accordance with Figure 1.1.

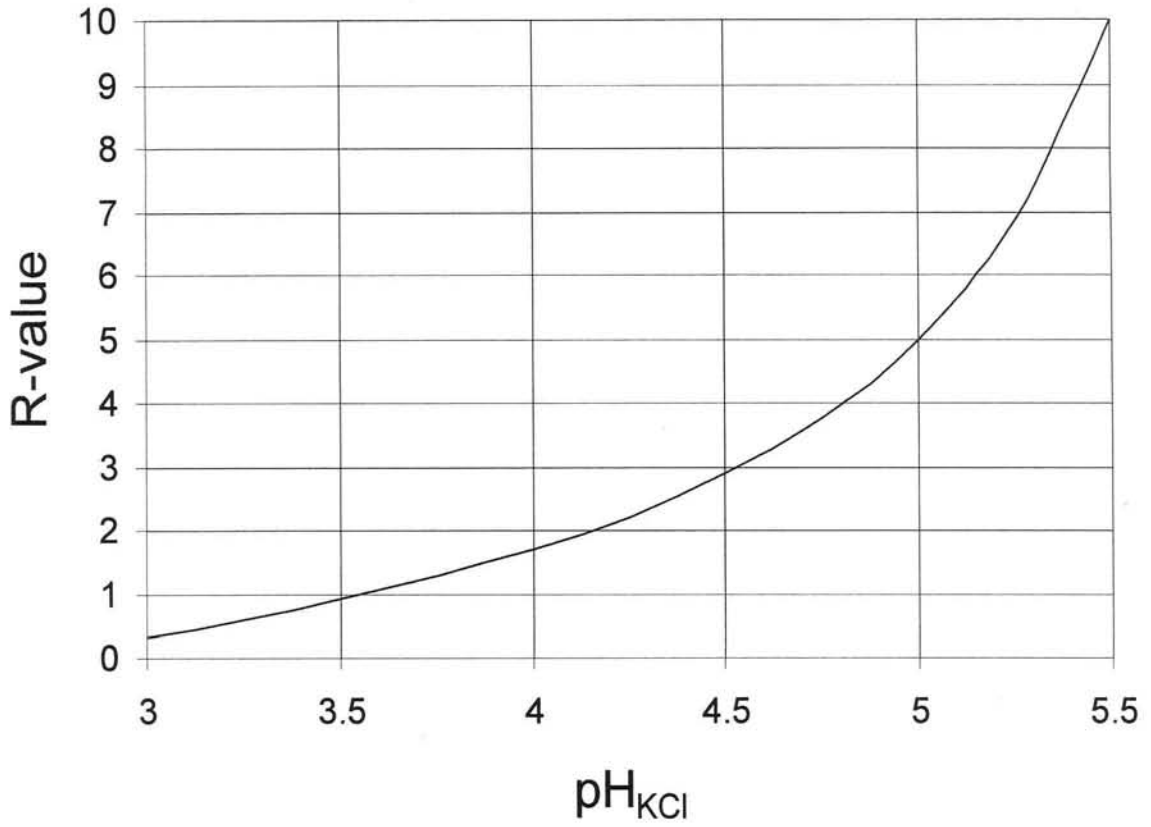


Figure 1.1 Relationship between R-value $[(\text{Ca}+\text{Mg})/\text{H}]$ and the soil pH_{KCl} (Adapted from Eksteen, 1969).

The field calibration factor (F) has a value of 4 for soils that are low in organic matter and have a CEC of less than 7.0 cmol_c kg⁻¹.

According to Lambrechts & Smuts (1998) the field calibration factor (F) encompasses the following assumptions:

- Neutralisation at a soil pH of less than 5.0 is 100%. At soil pH values between pH 5.0 and 5.5 only about 50% of the liming material is neutralised by soil acidity.
- The purity of calcitic lime, according to law, must be at least 70 % (Government Notice R. 799, Government Gazette 5552, 20 May 1977)³.
- The soil bulk density is 1500 kg m⁻³ and not the popularly used 1333 kg m⁻³.
- The lime is seldom uniformly mixed into the soil. A 75% mixing efficiency is assumed.

1.3.2 Acknowledged adaptations to the Eksteen method

As noted in Section 1.2, practical application of the Eksteen method in the agricultural industry led to the realisation that this method seriously overestimated the amount of lime required to neutralise organic-rich soils. Conradie (1994) proposed a set of correction factors, that increase in proportion to the organic carbon content of the soil (Table 1.1), that should be applied to the lime requirement predicted by the Eksteen method.

Table 1.1 Correction factors to adapt the Eksteen determined lime requirement of soils with different levels of organic carbon (Conradie, 1994).

Organic carbon (%)	Fraction of the calculated lime requirement that should be applied (%)
0 – 1	100
1 – 2	80
2 – 3	60
3 – 4	40

In contrast to the overestimation of lime requirement in organic soils, researchers noted that the Eksteen method tended to underestimate the lime requirement in subsoils which were characterised by pedo- and prismatic structures (Soil Classification Working Group, 1991), and by relatively high ratios of Mg to Ca (1:1 and larger). This led to the supposition that the Mg in such soils does not actively react to neutralize soil acidity. In order to overcome this shortcoming J.J.N. Lambrechts (1998, University of Stellenbosch, personal communication) adapted the Eksteen formula as follows:

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

³ Regulations regarding fertilizers: Fertilizers, farm feeds, agricultural remedies and stock remedies act, 1947 (act 36 of 1947)

This formula assumes an 'ideal' Mg:Ca ratio of 1:4.

When put into practice, these adaptations were found to be highly effective in extending the applicability of the Eksteen method to organic soils and to magnesium-rich subsoils. However, the adaptations remained empirical in nature, reflecting pragmatic solutions to the practical problem of estimating lime requirement in situations for which the Eksteen method was not originally developed.

1.4 Objectives

As already stated, the Eksteen method of lime requirement is inaccurate on organic rich soils, sandy soils and magnesium rich subsoils. The purpose of this study was to determine:

- ❑ The effect of organic material on the relative concentration of acidic ions.
- ❑ The alkalinity of magnesium relative to calcium in magnesium rich clayey subsoils.

In addition to the above objectives, the information derived from this study was to be used to determine:

- ❑ the R:pH relationship for the different problem soils, and / or
- ❑ to develop new procedures and adaptations of the Eksteen method of lime requirement calculation.

If the above objectives are met, the prediction of lime requirement will improve significantly. Accurate prediction of lime requirement will ensure that soils are accurately limed, thereby minimising the internal fruit quality defects which are associated with under-liming and the trace element problems which often occur following over-liming.

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2. SOIL SELECTION CRITERIA AND GENERAL CHEMICAL AND PHYSICAL CHARACTERISATION

2.1 Soil selection criteria and field sampling

This research was carried out on a population of Western Cape soils. Prior to the implementation of the soil sampling program, locations were identified having soils which possessed those specific characteristics which the sample population was required to represent. The criteria used during soil selection and sampling were as follows:

1. "Normal" soils: loamy soils with a normal Mg:Ca ratio (approximately 1:5), a CEC less than 7.0 $\text{cmol}_c \text{ kg}^{-1}$ and a low organic material content (< 1% organic carbon). Prediction of the lime requirement of these soils should fall within the scope of the Eksteen method.
2. Topsoils with a wide range of organic carbon contents.
3. Pedo- and prismatic structured subsoils with a high Mg:Ca ratio (ratio of 1:1 and higher).
4. Sandy soils: <5% clay, with a variable amount of organic carbon.

Lime status

From each of the soils represented in categories 1 to 4 above, two samples were taken, one from an orchard or other cultivated area which had a history of liming, and the other from an area of land which, although closely adjacent to the cultivated soil, had no apparent history of previous cultivation or lime addition. The latter samples were assumed to have received no lime. A total of 78 samples were collected. Not all the collected samples clearly adhered to the above criteria but, in order to maximise the range and scope of this work, all of the soils were included in the experimental soil population.

The soil samples were taken from different locations in the Ceres district (approximately 33°22' S, 19°19' E), and from a location near Villiersdorp (approximately 33°59' S, 19°18' E). The organic topsoils were collected on the farm Dennekruijn in the Witzenberg Valley in the Ceres district. Although soil forms were identified, soil sampling did not take place in accordance with the identified soil horizons, but according to the relative organic material content as visually identified in the field on the basis of colour. Other samples were taken in the vicinity of the Gydo pass on a farm owned by Du Toit Boerdery. These samples were all from very acid, well-structured subsoil horizons. The sandy topsoil samples were taken on the farms Dankbaar and Fairfield, close to the town of Ceres in the Warm Bokkeveld.

All the other structured subsoil samples were taken on the farm Queen Anne near Villiersdorp. Deep soil cultivation and partial mixing obscured the identity of the horizons and their original depths in the profile, making measurement of horizon depths impossible. In all the profiles a gravelly E horizon was present. Only samples from the A horizons, and from the subsoil B horizons, were used for further study.

The location, soil form (where identified), sample depth (where measured), sample number and gravel content of each sample are listed in Table 2.1. The numbering system used is detailed below:

- The first digit indicates the location where the soil sample was taken eg:
 1. Dennekruin in the Witzenberg Valley
 2. Dankbaar & Fairfield (Warm Bokkeveld)
 3. Queen Anne (Villiersdorp)
 4. Du Toit Farm at the top of the Gydo Pass.

- The second digit indicates whether the sample was taken on unlimed or cultivated area (limed):
 1. Unlimed
 2. Limed

- The third and fourth digits indicate the number of limed or unlimed samples which were taken at that specific location. For example at Dennekruin (Witzenberg Valley) 14 unlimed soil layers were sampled and the numbering of the samples ranges from 1101 for the first sample to 1114 for the last.

2.2 Determination of physical and chemical soil characteristics

The objective of this exercise was to characterise each soil, both chemically and physically, to the maximum extent possible using standard tests that are routinely used for research and advisory purposes.

2.2.1 Pretreatment

Prior to analysis, the soil samples were air dried to constant mass on newspaper-lined shallow wooden trays at ambient room temperature, then passed through a 2mm round-hole sieve. The $\leq 2\text{mm}$ samples were stored in brown paper bags on open shelves in a well ventilated room. Only where the $> 2\text{mm}$ fraction of the soil exceeded 5%, was the gravel content of the sample recorded. Gravel content was determined on a mass basis after dry sieving.

2.2.2 Physical analysis

Particle size analysis was carried out using the hydrometer method for the clay ($<0.002\text{ mm}$) and silt ($0.02\text{-}0.002\text{ mm}$) fractions, while the coarse ($0.5\text{-}2\text{ mm}$) and medium ($0.5\text{-}0.2\text{ mm}$) sand fractions were determined by dry sieving. Fine sand ($0.2\text{-}0.02\text{ mm}$) fractions were calculated by subtracting the four determined sand fractions from 100 percent. The methods employed were the standard methods employed at ARC Infruitec-Nietvoorbij as developed by De Kock (undated). The results of the particle size analysis are presented in Appendix I.

2.2.3 Chemical Analysis

2.2.3.1 pH: pH was determined in both water and 1M KCl solution, with a 1:2.5 soil:solution ratio, after a one-hour equilibration period. pH was measured electrometrically using a combined (glass/calomel) electrode in a constantly stirred suspension. Temperature compensation was automatically applied.

Table 2.1 Location, number of profiles sampled, soil form, lime status, sample depth, sample number and gravel content of the soil sample population.

Location	Profile number	Soil form* (where identified)	Lime Status	Sampling Depth (cm)	Sample number	Gravel content (%) (mass basis)
1. Dennekrui Witzenberg Valley	1	Inanda (Ia)	unlimed	0-60	1101	<5
			unlimed	60-120	1102	<5
			unlimed	120-180	1103	<5
	2	Sweetwater (Sr)	unlimed	+180	1104	<5
			unlimed	0-20	1105	<5
			unlimed	20-75	1106	<5
	3	Sweetwater (Sr)	unlimed	+75	1107	<5
			unlimed	0-20	1108/1109	<5
			unlimed	20-50	1110	<5
	4	Sweetwater (Sr)	unlimed	+50	1111	<5
			unlimed	0-30	1112	<5
			unlimed	30-60	1113	<5
	5	Inanda (Ia)	unlimed	+60	1114	<5
			limed	0-30	1201	<5
			limed	30-60	1202	<5
	6	Magwa (Ma)	limed	+60	1203	<5
			limed	0-25	1204	<5
			limed	25-50	1205	<5
	7	Sweetwater (Sr)	limed	50-80	1206	<5
			limed	+80	1207	<5
limed			0-50	1208	<5	
8	Sweetwater (Sr)	limed	50-120	1209	<5	
		limed	+120	1210	<5	
		limed	0-30	1211	<5	
9	Sweetwater (Sr)	limed	30-55	1212	<5	
		limed	+55	1213	<5	
		limed	0-25	1214	<5	
10	Sweetwater (Sr)	limed	25-45	1215	<5	
		limed	+45	1216	<5	
		limed	0-40	1217	<5	
			limed	40-110	1218	<5
			limed	+110	1219	<5
2. Dankbaar Ceres (Warm Bokkeveld)	1	**	unlimed	0-30	2101	<5
	2	**	unlimed	0-30	2102	<5
	3	**	unlimed	0-30	2103	<5
	4	**	unlimed	0-30	2104	<5
	5	**	unlimed	0-30	2105	<5
	6	**	limed	0-30	2201	<5
	7	**	limed	0-30	2202	<5
	8	**	limed	0-30	2203	<5
	9	**	limed	0-30	2204	<5
2. Fairfield Ceres (Warm Bokkeveld)	1	**	unlimed	0-30	2106	<5
	2	**	unlimed	0-30	2107	<5
	3	**	unlimed	0-30	2108	<5
	4	**	limed	0-30	2205	<5
	5	**	limed	0-30	2206	<5
	6	**	limed	0-30	2207	<5
	7	**	limed	0-30	2208	<5
	8	**	limed	0-30	2209	<5
3. Queen Anne Villiersdorp	1	Estcourt (Es)	unlimed	0-15	3101	9
			unlimed	+25	3102	11
	2	Estcourt (Es)	unlimed	0-15	3103	43
			unlimed	+30	3104	35
	3	Estcourt/Klapmuts (Es/Km)	unlimed	0-20	3105	22
			unlimed	+40	3106	<5
	4	Klapmuts (Km)	unlimed	0-20	3107	15
			unlimed	+40	3108	8
	5	Klapmuts (Km)	unlimed	0-25	3109	19
			unlimed	+45	3110	5
	6	Klapmuts (Km)	unlimed	0-25	3111	29
			unlimed	+45	3112	<5
7	Estcourt (Es)	limed	***	3201	47	
		limed	***	3202	44	
8	Estcourt (Es)	limed	***	3203	33	
		limed	***	3204	50	
9	Estcourt/Klapmuts (Es/Km)	limed	***	3205	32	
		limed	***	3206	17	
10	Klapmuts (Km)	limed	***	3207	34	
		limed	***	3208	7	
11	Klapmuts (Km)	limed	***	3209	28	
		limed	***	3210	23	
12	Klapmuts (Km)	limed	***	3211	12	
		limed	***	3212	11	
4. Du Toit Farm, Gydo Pass	1	**	unlimed	30-55	4101	<5
			unlimed	55-80	4103	<5
	2	**	unlimed	30-50	4102	<5
			unlimed	50-80	4104	<5

*Soil Classification Working Group (1991)

**No soil forms were identified

***Deep soil cultivation and partial mixing made it impossible to determine horizon depths.

2.2.3.2 **Soil resistance** (ohms): The resistance of a saturated soil/deionised water paste was determined in a standard USDA soil cup after a one-hour equilibrium period at 20 °C.

2.2.3.3 **Organic carbon**: Determined by the Walkley-Black method (Soil Classification Working Group, 1991).

2.2.3.4 **Total extractable acidity (pH 7)³**: Determined in a 0.5M K₂SO₄ leachate, that was weakly buffered at pH 7 with CH₃COOK, by titration with 0.1M NaOH as described by Eksteen (1969). For this procedure 20g of soil was leached to a total volume of 200 cm³. The only difference between the method employed in this study and that originally used by Eksteen was that the soil sample/extraction solution mixtures used here were agitated for one hour before leaching, rather than being allowed to stand overnight. A refinement of the original method was that the pH of the extracting solution was verified with a pH-meter before use.

2.2.3.5 **Cation Exchange Capacity (CEC) and exchangeable⁴ Ca, Mg, K and Na**: Determined with the so called leaching and occluded solution procedure, by leaching 20g of soil with 0.2M NH₄OAc buffered at pH 7 under reduced pressure followed by leaching with 0.2M K₂SO₄. Ammonium was determined in the K₂SO₄ leachate by direct distillation as described by the Soil Classification Working Group (1991). Exchangeable cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) were determined in the ammonium acetate (NH₄OAc) leachate by atomic absorption spectrophotometry.

2.2.3.6 **T-value**: The T-values were calculated as equivalent to the sum of the exchangeable Ca²⁺, Mg²⁺, K⁺ and Na⁺, plus the total extractable acidity at pH 7.

2.2.3.7 **Extractable acidity at soil pH**: Determined in an extract obtained by shaking 10g of soil in 70 cm³ of 1M KCl for 60 minutes. The supernatant solution was separated from the soil by filtration and the soil washed with an additional 30 cm³ of 1M KCl to a total volume of 100 cm³. Extractable acidity was determined by titration with 0.05M NaOH. The aluminium content was determined by means of a 0.05M HCl titration following the addition of NaF to free the Al from its hydroxides, as described by The Non-affiliated Soil Analysis Work Committee (1990).

2.2.3.8 **Neutral salt (KCl) exchangeable aluminium**: 50 cm³ of 1M KCl was added to 20g of soil and allowed to equilibrate, at rest, for one hour, after which the mixture was transferred to a sintered filter and leached with KCl until a final volume of 200 cm³ was reached. The Al in the leachate was determined by inductively coupled plasma-emission spectroscopy (ICP).

³ Also known as Eksteen acidity.

⁴ More correctly defined as extractable cations since the soluble salt component is included. If the soil resistance is very high ($\geq 600 \Omega$) the soluble salt component is negligible and the extractable cations should closely approximate the exchangeable cations. This was the case here, with the exception of samples 1204 (500 Ω), 3108 (590 Ω) and 3110 (420 Ω). For this dissertation the term exchangeable cations will be used.

The results for pH, resistance, organic carbon, total extractable acidity, exchangeable bases, CEC and T-value are presented in Appendix II. The results for extractable acidity, exchangeable aluminium, together with additional calculations and manipulations that will be explained in later sections, are presented in Appendix III.

2.3 Regrouping of soil samples

On the basis of the physical (Appendix I) and chemical (Appendix II) analyses the samples were regrouped into the four predetermined soil groups according to the following slightly revised criteria:

- Normal:** Loamy soils with a normal Mg:Ca ratio (approximately 1:5), a low organic material content (< 1% organic carbon) and a CEC of less than 7 cmol_c kg⁻¹ soil.
- Organic:** Soils containing more than 1.2 % organic carbon but do not qualify as a sandy soil.
- Structured:** Pedo- or prismatic sub-soils with an Mg:Ca ratio of 1:1 or greater.
- Sandy:** Soils with less than 5% clay but with varying amounts of organic carbon.

The soils were grouped as listed in Table 2.2. Two samples: numbers 3107 and 3109, were grouped with normal soils even though they contained >1% organic carbon. These soils were initially sampled as normal soils because of their very pale colours. On analysis, they were found to contain a disproportionately large amount of organic material. The organic material consisted of finely divided but largely undecomposed plant residue that did not in the dry state show the characteristic dark colour of organic-rich soils. Undecomposed organic residues lack the exchange characteristics of humified organic material. Sample number 1203 was also an exception. It was grouped as an organic soil because of its dark soil colour. However, it only contained 0.91% organic carbon. Samples 1104, 1216 and 1219 were regrouped as structured soils because of their high Mg:Ca ratios, even though they were sampled from subsoil horizons with a weak to moderately developed blocky structure.

Table 2.2 Grouping of soils samples following revised criteria.

Soil sample no.	Soil group	Soil sample no.	Soil group	Soil sample no.	Soil group
1101	organic	1213	organic	3103	normal
1102	organic	1214	organic	3104	structured
1103	organic	1215	organic	3105	normal
1104	structured	1216	structured	3106	structured
1105	organic	1217	organic	3107	normal
1106	organic	1218	organic	3108	structured
1107	organic	1219	structured	3109	normal
1108	organic	2101	sandy	3110	structured
1109	organic	2102	sandy	3111	normal
1110	organic	2103	sandy	3112	structured
1111	organic	2104	sandy	3201	normal
1112	organic	2105	sandy	3202	structured
1113	organic	2106	sandy	3203	normal
1114	organic	2107	sandy	3204	structured
1201	organic	2108	sandy	3205	normal
1202	organic	2201	sandy	3206	structured
1203	organic	2202	sandy	3207	normal
1204	organic	2203	sandy	3208	structured
1205	organic	2204	sandy	3209	normal
1206	organic	2205	sandy	3210	structured
1207	organic	2206	sandy	3211	normal
1208	organic	2207	sandy	3212	structured
1209	organic	2208	sandy	4101	structured
1210	organic	2209	sandy	4102	structured
1211	organic	3101	normal	4103	structured
1212	organic	3102	structured	4104	structured

Normal: Loamy soils with a normal Mg:Ca ratio (approximately 1:5), a low organic material content (< 1% organic carbon) and a CEC of less than 7 cmol_c kg⁻¹ soil.

Organic: Contain more than 1.2 % organic carbon but do not qualify as a sandy soil.

Structured: Pedo- or prismatic sub-soils with an Mg:Ca ratio of 1:1 or greater.

Sandy: Soils with less than 5% clay but with varying amounts of organic carbon.

2.4 References

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3. RELATIONSHIPS BETWEEN SOIL PARAMETERS

Examination of the physical (Appendix I) and chemical properties (Appendix II) of the soils revealed the existence of several relationships. These are individually described below.

3.1 Relationship between CEC and T-value

Since the T-value is the sum of the exchangeable bases (Ca, Mg, K and Na) plus the total acidity as determined for the Eksteen method at pH 7, the T-value should closely approximate the determined CEC. However, the determined CEC was, on average, 33.6% higher than the T-value. A positive correlation ($r = 0.94$) exists between the determined CEC and the T-value as shown in Figure 3.1. This relationship, which has excellent fit ($R^2 = 0.89$), is described by the linear regression equation:

$$\text{T-value} = -0.0348 + 0.7525(\text{CEC})$$

The high CEC as compared with the T-value appears to be an artefact of the technique employed. Gillman *et al.* (1983) used the method for CEC described by the Soil Survey Staff (1972), which is very similar to the method used in the present study. They found that the CEC values were higher than those given by other methods. Gillman *et al.* (1982) found that by using centrifugation, rather than leaching as in the method described by the Soil Survey Staff (1972), lower CEC values were obtained. Apparently not all of the free ammonium was removed. This led to the anomalously high CEC values being observed. Gillman *et al.* (1982) also postulated that, particularly with oxidic soils, chemisorption of acetate onto oxide surfaces could increase the negative charge. The determination of CEC is thus a very precise procedure. The above relationship can be used to calculate the CEC from the T-value.

3.2 Relationships between CEC, clay content and organic matter

The CEC of soil arises mainly from negatively charged sites on soil organic matter and clay minerals (Parfitt *et al.*, 1995). The CEC of organic matter is caused by the dissociation of phenolic, hydroxyl and, mainly, carboxyl functional groups (Talibudeen, 1981; Parfitt *et al.*, 1995). In Figure 3.2 the relationship between the CEC and the clay content is illustrated. By using the boundary line concept of Webb (1972), a definite positive trend can be illustrated. The boundary line defines the minimum relationship between the CEC and the clay content. Although the vertical shift from the boundary line could be due to differences in clay mineralogy, it is more likely to be due to variation in the organic matter content of the soil (Kapland & Estes, 1985).

If organic material is the cause for the upward shift in Figure 3.2, it is unclear why samples 4103 and 4104 should be so far above the boundary line since they contain virtually no organic material. Since the method of CEC determination relies on the ability of the soil to retain NH_4^+ , and since silt may also contribute to cation exchange, it is possible that the silt content of a soil may also influence its CEC. Figure 3.3 suggests that this may be the case for samples 4103 and 4104. From Figure 3.4, in which the organic carbon content of the samples is shown, it is apparent that samples containing more organic matter tend to have higher CEC values than those which contain less organic material at any given level

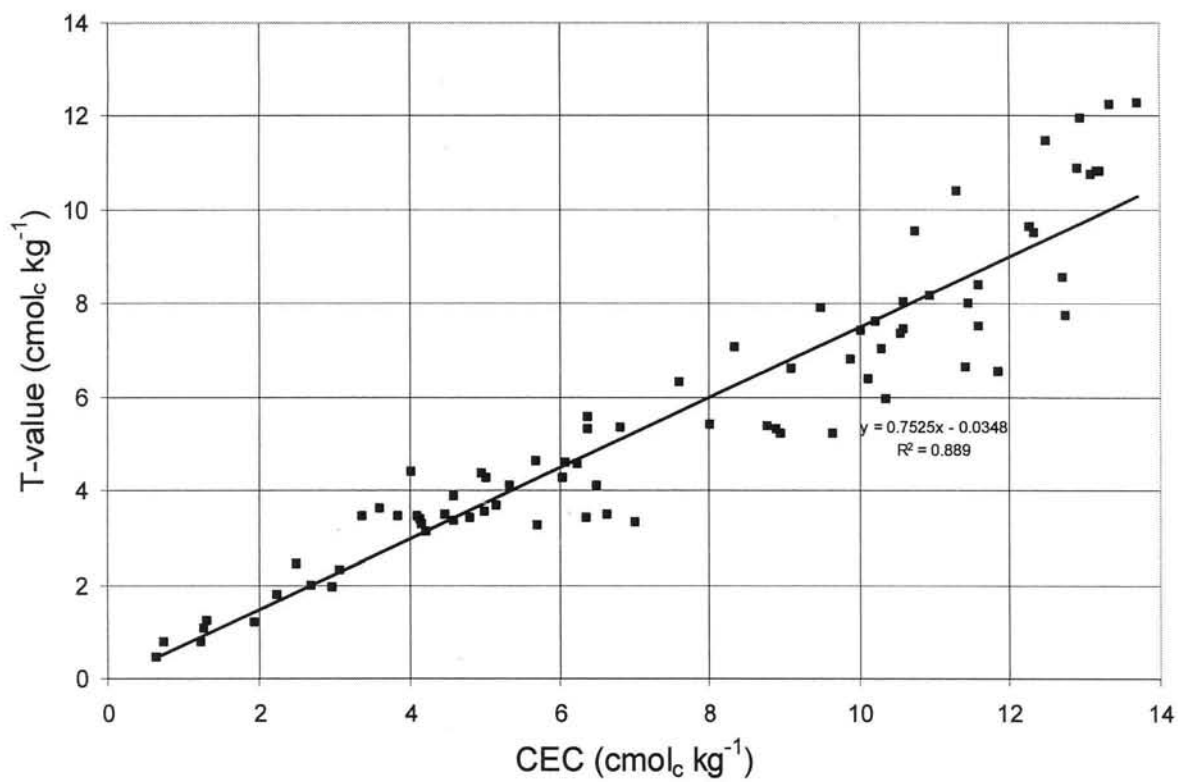


Figure 3.1 Relationship between the T-value (sum of Ca, Mg, K, Na and H) and cation exchange capacity (CEC at pH 7) of selected Western Cape soils.

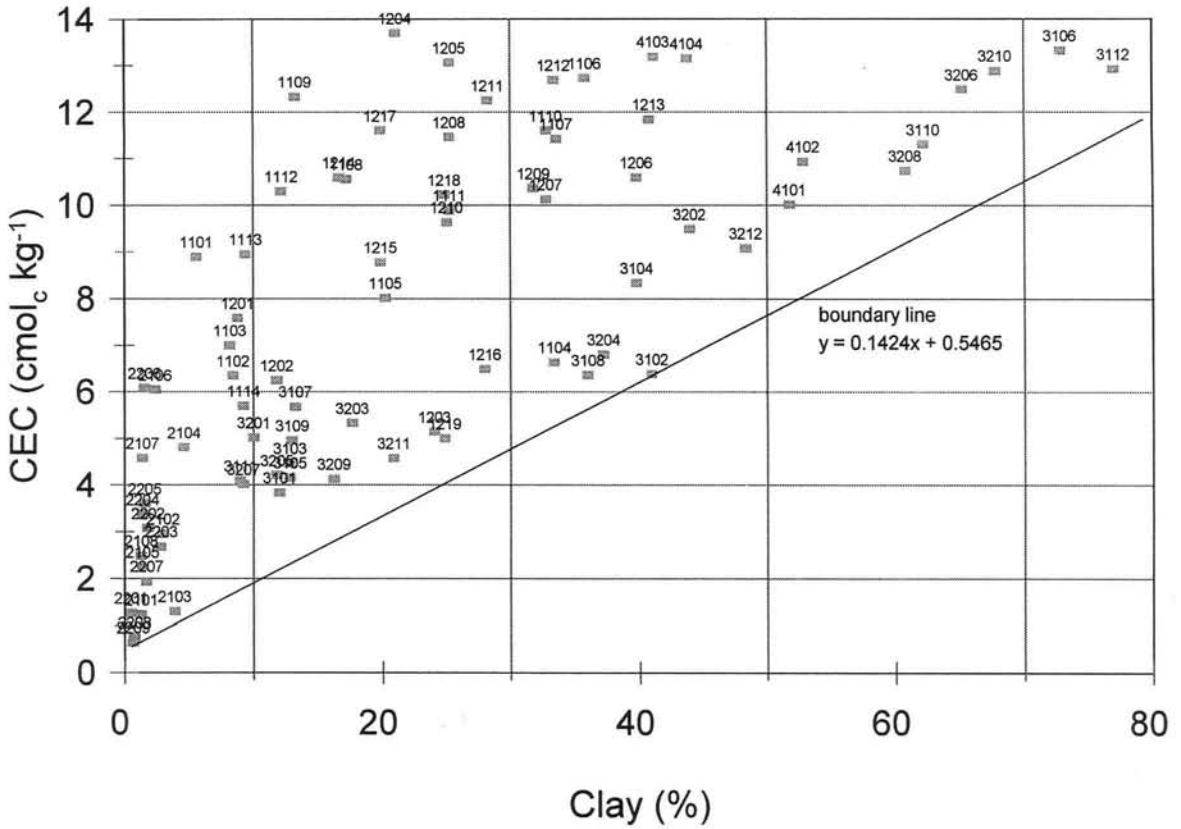


Figure 3.2 Relationship between cation exchange capacity (CEC at pH 7) and clay content of selected Western Cape soils. The boundary line defines the minimum relationship between the CEC and the clay content.

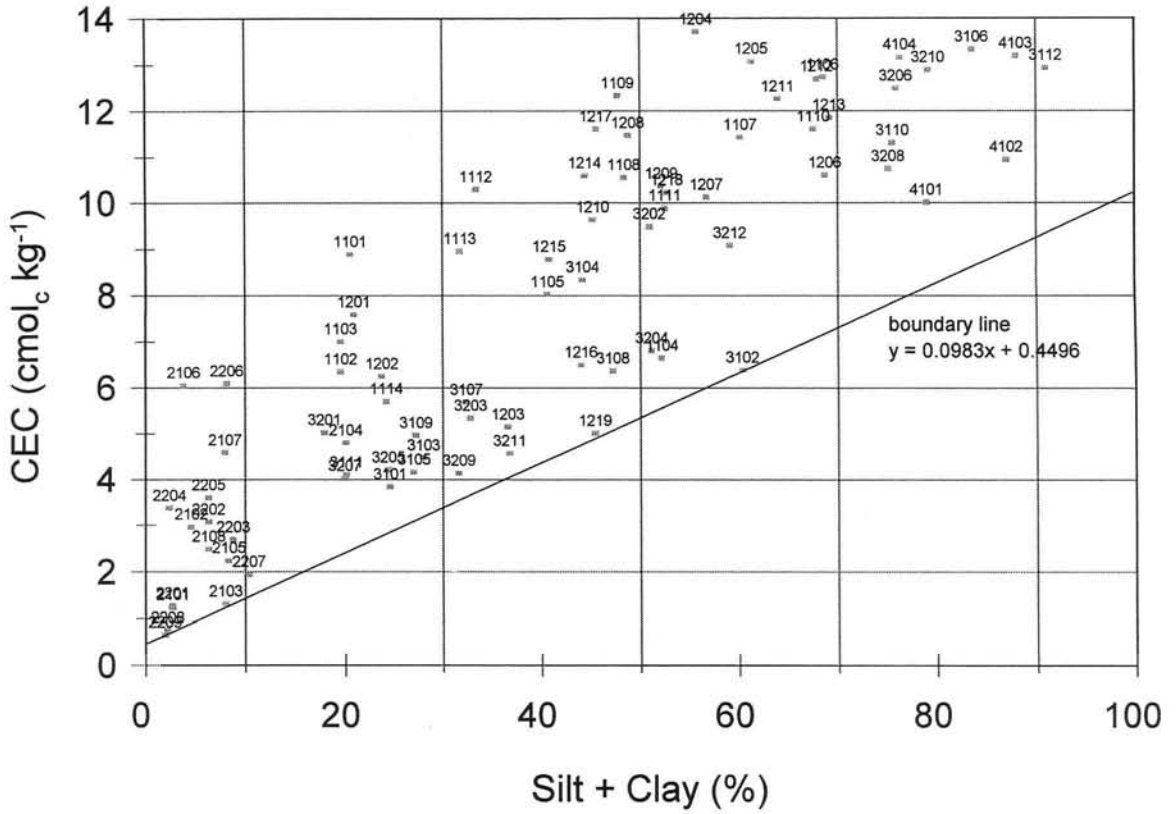


Figure 3.3 Relationship between cation exchange capacity (CEC at pH 7) and silt+clay content of selected Western Cape soils. The boundary line defines the minimum relationship between the CEC and the silt+clay content.

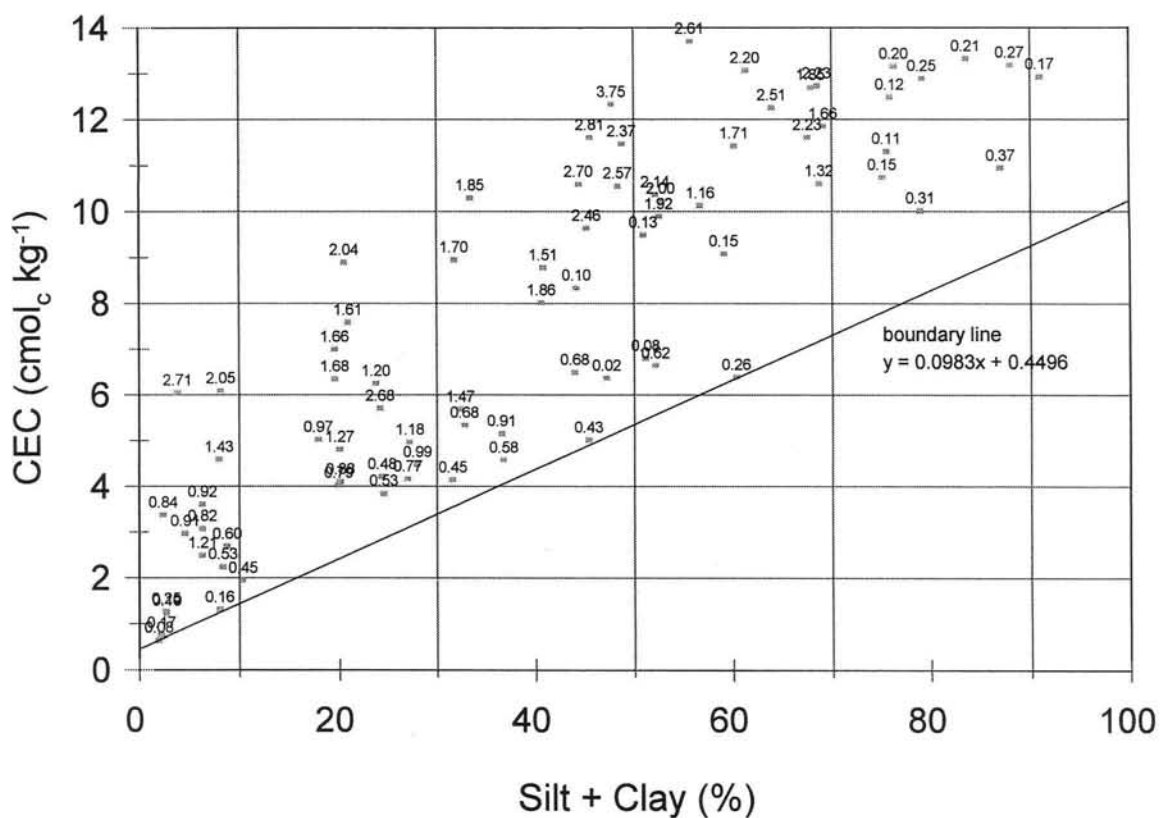


Figure 3.4 Relationship between cation exchange capacity (CEC at pH 7) and silt+clay content of selected Western Cape soils. Each point is annotated with its organic carbon content (in %). The boundary line defines the minimum relationship between the CEC and the silt+clay content.

of silt + clay. In Figure 3.5 the effect of organic matter content on the CEC can clearly be seen. The samples above line A consist of those soils that were sampled as structured and which were, indeed, later grouped as structured. Those samples contain very little organic matter but have a very high clay + silt content. The three samples (1104, 1216 & 1219) between lines A and B are samples that were included in the structured soil group because of their high Mg:Ca ratios that resemble those of the structured soil group, even though they were not as strongly structured as was generally the case for the structured soils.

Because of the obvious relationship between CEC and organic matter, as well as that between CEC and clay + silt, a stepwise regression analysis was carried out using Statgraphics (version 7.11) to predict the CEC for the entire soil sample population, as well as for the different soil groups. In view of the relationship between T-value and CEC, a similar analysis was carried out to predict the T-value for the entire sample population from these parameters. The three parameters were introduced into the equation at a 95% probability level. For both CEC and T-value, all three parameters were significant for the entire soil sample population, and were therefore included in the model. The prediction models for CEC and T-value (only for the entire sample population) are as follows:

Entire soil sample population

$$\text{CEC} = 0.3593 + 0.1488 (\text{Clay}\%) + 0.0896 (\text{Silt}\%) + 1.9892 (\text{C}\%)$$

$$R^2 = 0.914$$

$$\text{T-value} = 0.5867 + 0.1258 (\text{Clay}\%) + 0.0530 (\text{Silt}\%) + 1.1300 (\text{C}\%)$$

$$R^2 = 0.809$$

Normal soils

$$\text{CEC} = 2.1028 + 0.0877 (\text{Clay}\%) + 1.5785 (\text{C}\%)$$

$$R^2 = 0.642$$

Organic soils

$$\text{CEC} = 2.0597 + 0.1037 [(\text{Silt}+\text{Clay})\%] + 1.5604 (\text{C}\%)$$

$$R^2 = 0.760$$

Sandy soils

$$\text{CEC} = 0.6263 + 0.0893 (\text{Silt}\%) + 2.1554 (\text{C}\%)$$

$$R^2 = 0.910$$

Structured soils

$$\text{CEC} = -0.2695 + 0.1654 (\text{Clay}\%) + 0.1104 (\text{Silt}\%)$$

$$R^2 = 0.783$$

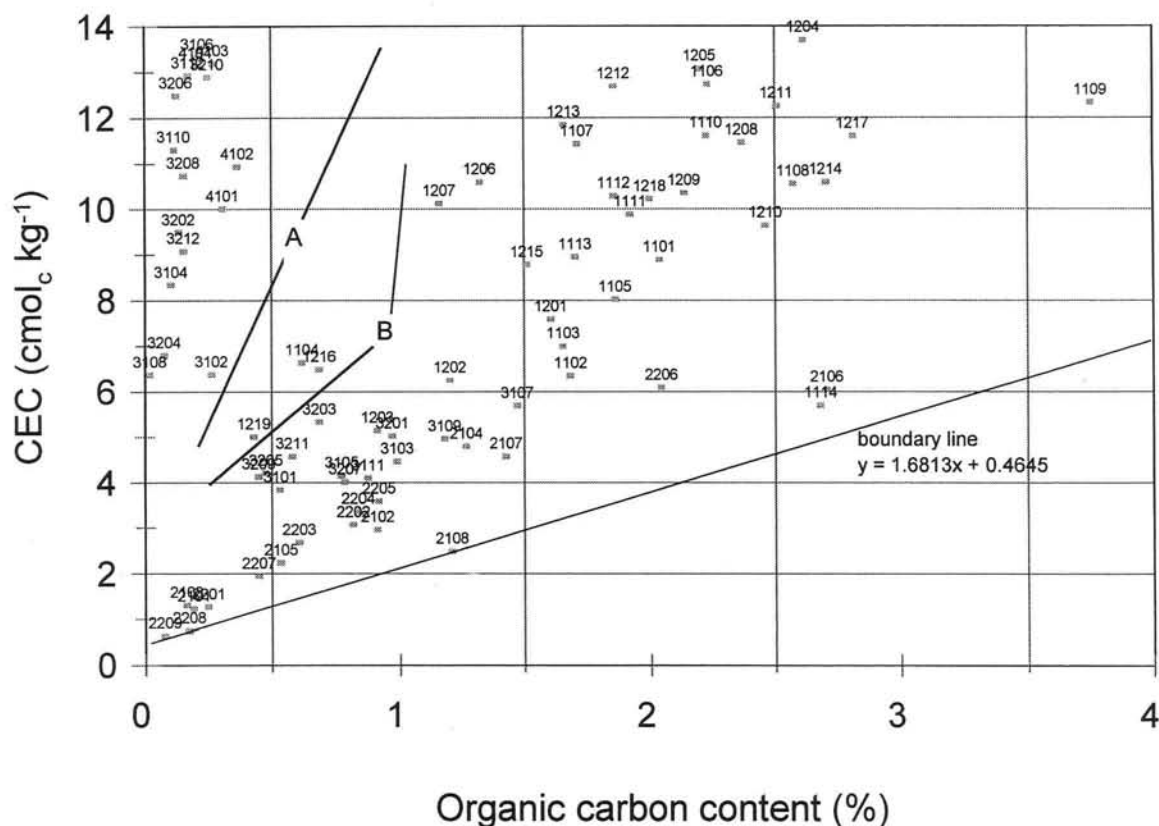


Figure 3.5 Relationship between cation exchange capacity (CEC at pH 7) and organic carbon content of selected Western Cape soils. Samples to the left of line A are structured soils with a very high clay + silt content. Samples between lines A and B were included in the structured soil group but have only weak to moderately developed blocky structure. The boundary line defines the minimum relationship between CEC and organic carbon content.

According to these prediction models, both the CEC and T-value can be accurately predicted for the entire sample population using texture data and organic carbon content. According to the CEC prediction model, the CEC of clay is $14.8 \text{ cmol}_c \text{ kg}^{-1}$, the CEC of silt is $8.9 \text{ cmol}_c \text{ kg}^{-1}$ and the CEC for organic carbon is $198.9 \text{ cmol}_c \text{ kg}^{-1}$. A CEC of $8.9 \text{ cmol}_c \text{ kg}^{-1}$ is very high for silt. The non-significance of clay in the case of organic soils could be due to difficulty in separating clay from organic material during analysis. Satyavathi *et al.* (1994) similarly related CEC to the clay, silt and organic carbon contents of soils during multiple regression analysis. They noted that the accuracy with which CEC could be predicted from developed models was limited to the specific geographic and climatic zone for which the model was developed, and within which it was assumed that the composition of the clay and soil organic matter was essentially homogeneous. When comparing the CEC and T-value prediction models for the entire soil sample population the most noticeable difference is in terms of the organic carbon (C%) coefficient. This could probably be the basis for the large difference between CEC and T-value. Gillman *et al.* (1982) found marked differences between CEC determination methods for soils that have variable charge characteristics, but effects on exchangeable base cations were much smaller. Plots for the observed vs. the predicted CEC, and observed vs. predicted T-values, are given in Figures 3.6 and 3.7, respectively. From Figure 3.6 it can be seen that there are no outliers. The greater scatter observed in Figure 3.7 is indicative of a lower degree of accuracy in predicting T-value relative to the accuracy with which CEC can be predicted.

3.3 Relationship between pH-dependant acidity and organic matter content

The pH-dependant charge in mineral soils arises from protonation and deprotonation of functional groups located on inorganic soil minerals such as kaolinite, amorphous materials, metal oxides, oxihydroxides and hydroxides, and layer silicates coated with metal oxides and soil organic matter (Sparks, 1995). Organic matter is a variable charge soil component and makes a major contribution to the CEC even where the soil organic content is low (Stevenson, 1982). The major acidic functional groups are carboxyls, quinones, phenolic OH-groups and enols. Carboxyl and phenolic groups can deprotonate at pH levels which commonly occur in soils, and contribute significantly to the negative charge (Sparks, 1995).

Because the soils used in this work differed markedly in terms of pH, the effect of organic matter on pH-dependant acidity could not be readily determined. Neither, in consequence, could meaningful comparisons be drawn between soils or soil groups. According to Bache (1979) an unbuffered salt can be used to determine the CEC at the natural pH of the soil. Gillman *et al.* (1982) found, in a comparison between different methods of CEC determination, that the CEC of the soil increased as the buffer pH of the extracting solution increased. There was no difference in the amount of basic cations extracted between the different extracting solutions. These differences are therefore due to acidic cations. As the pH of the extracting solution increases, pH-dependant components progressively deprotonate to generate more acidic cations. Therefore the pH-dependant acidity for a specific soil sample can be defined in terms of the difference between total acidity as determined by the Eksteen method, which is weakly buffered to pH 7, and that determined in 1M KCl (assumed to be at field pH).

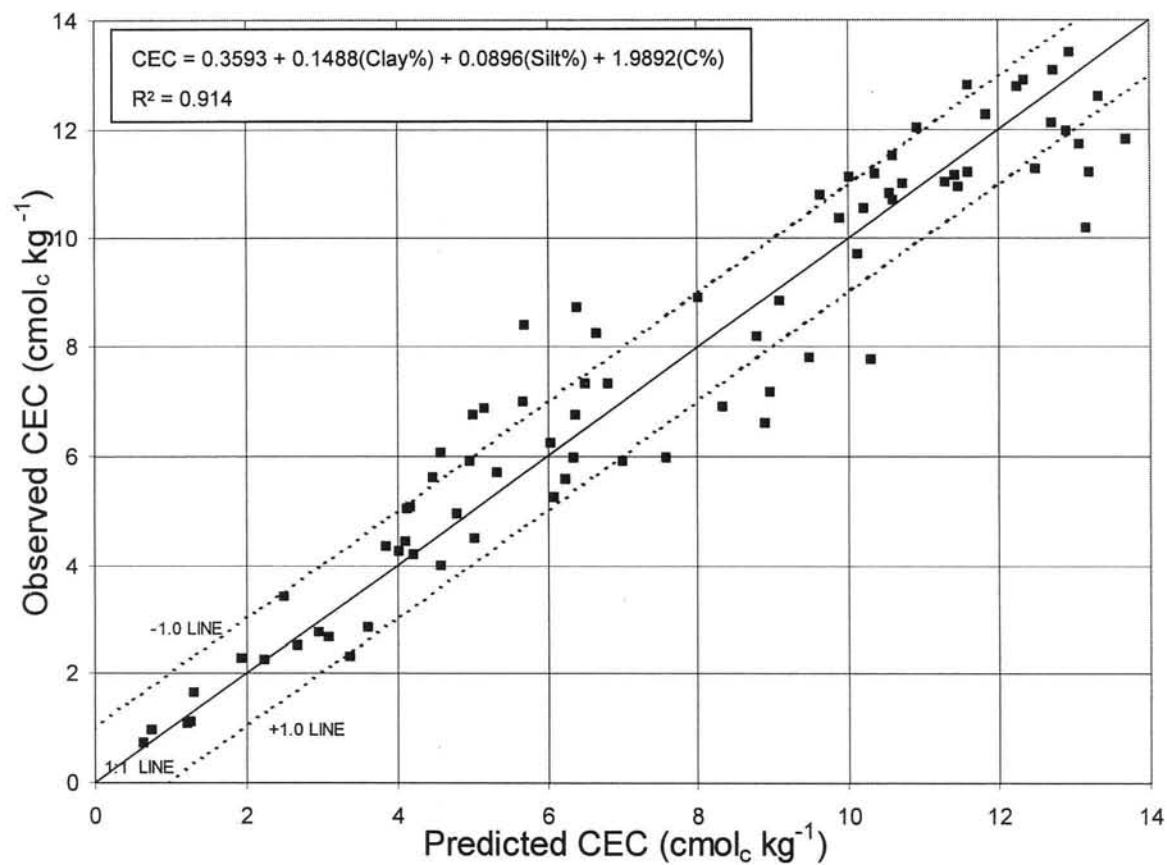


Figure 3.6 Comparison between the observed cation exchange capacity (CEC determined at pH 7) of selected Western Cape soils, and the CEC predicted by the regression model based on clay, silt and organic carbon content. According to the regression model the CEC of clay, silt and organic carbon is 14.8, 8.9 and 198.9 $\text{cmol}_c \text{kg}^{-1}$ respectively.

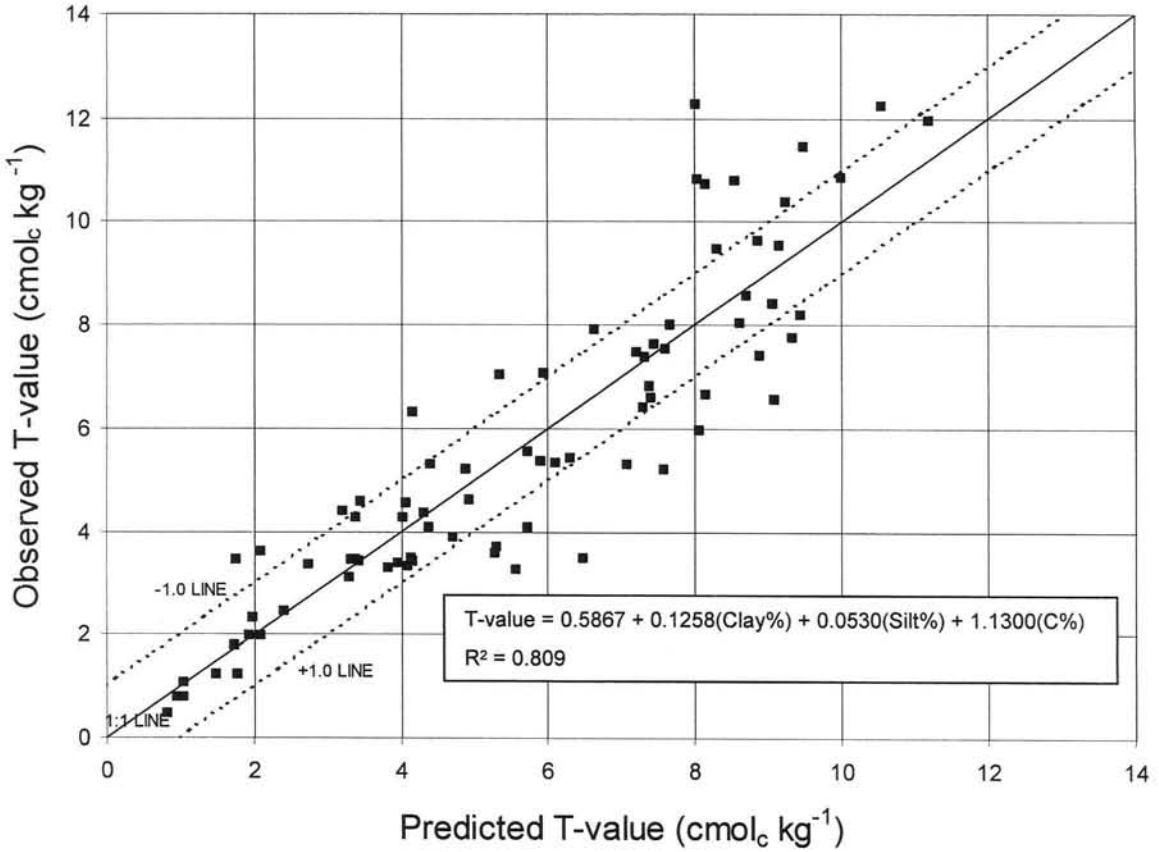


Figure 3.7 Comparison between the calculated T-value and the T-value predicted by the regression model based on the clay, silt and organic carbon content of selected Western Cape soils. According to the regression model the contribution of clay, silt and organic carbon to the T-value is 12.6, 5.3 and 113.0 $\text{cmol}_c \text{kg}^{-1}$ respectively.

It is suggested that mean pH-dependant acidity (ΔH) may be expressed on a unit pH basis by dividing this soil-specific pH-dependant acidity by the pH difference that exists between the Eksteen extractant (pH 7) and the field pH. This manipulation can be shown by the following relationship:

$$\Delta H = \frac{(\text{Total extractable acidity at pH 7}) - (\text{Total neutral salt extractable acidity at field pH})}{7.0 - \text{field pH}_{\text{KCl}}}$$

where ΔH = mean pH-dependant acidity in $\text{cmol}_c \text{ kg}^{-1} \text{ pH unit}^{-1}$

In Appendix III the ΔH values calculated using the above equation, as well as other acidity parameters, are listed for all soils. Since ΔH is expressed in terms of $\text{cmol}_c \text{ kg}^{-1} \text{ pH unit}^{-1}$ the values calculated for each soil can be compared directly.

Only five soils have negative ΔH values (Appendix III). Sample 2205 is negative because the field pH (as determined in 1M KCl) was higher than pH 7. The four structured samples, 4101, 4102, 4103 and 4104, which were sampled at the same location but at different depths, also had negative ΔH values. These four samples were characterised by large 1M KCl exchangeable Al values but very low levels of organic matter. It was expected that during the pH 7 acid extraction procedure that the monomeric Al could hydrolyse and generate an equivalent quantity of hydrogen ions (Bertsch, 1989). However, this did not appear to take place. A possible reason for this decrease in Al acidity is polymerisation of the Al at the neutral pH of the extracting solution. According to Stol *et al.* (1976) the OH/Al ratio of the Al-polymers formed by this process depends on the stage of polymerisation and can be as low as 1.33. This is far removed from the OH/Al ratio of 3 which results when monomeric Al hydrolyses fully to produce $\text{Al}(\text{OH})_3$ precipitate. This suggests that, if polymerisation did occur during hydrolysis at the neutral pH of the Eksteen extraction then it did not generate the full complement of H^+ . In consequence the Eksteen total acidity remained low relative to the 1M KCl total acidity, resulting in negative values for ΔH .

From Figure 3.8 it is clear that mean pH-dependant acidity (ΔH) bears little relationship to the soil clay content. This implies that most of the mean pH-dependant acidity is likely to be derived from the organic matter. The relationship between ΔH and organic carbon content is more clearly defined, as shown in Figure 3.9. Stepwise regression was carried out using Statgraphics (version 7.11) to predict the mean pH-dependant acidity (ΔH) from organic carbon and clay content. Both the parameters were significant at 95% probability and were therefore introduced into the model. The prediction model for ΔH is as follows:

$$\Delta H = 0.0844 + 0.2587 (\text{C}\%) + 0.0043 (\text{Clay}\%)$$

$$\Delta H \text{ expressed as } \text{cmol}_c \text{ kg}^{-1} \text{ pH unit}^{-1}$$

$$R^2 = 0.646$$

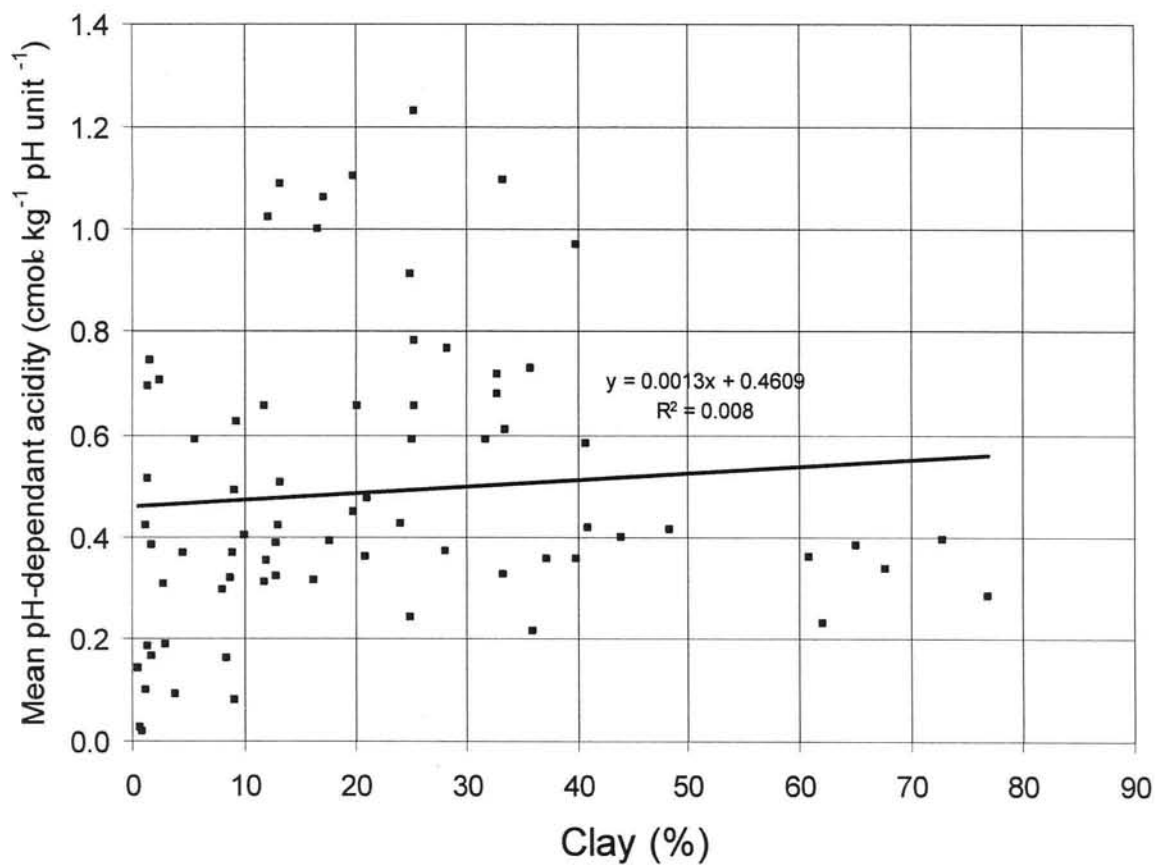


Figure 3.8 Relationship between the mean pH-dependant acidity (ΔH) and the clay content for a selected Western Cape soil sample population, excluding samples 2205, 4101, 4102, 4103 and 4104.

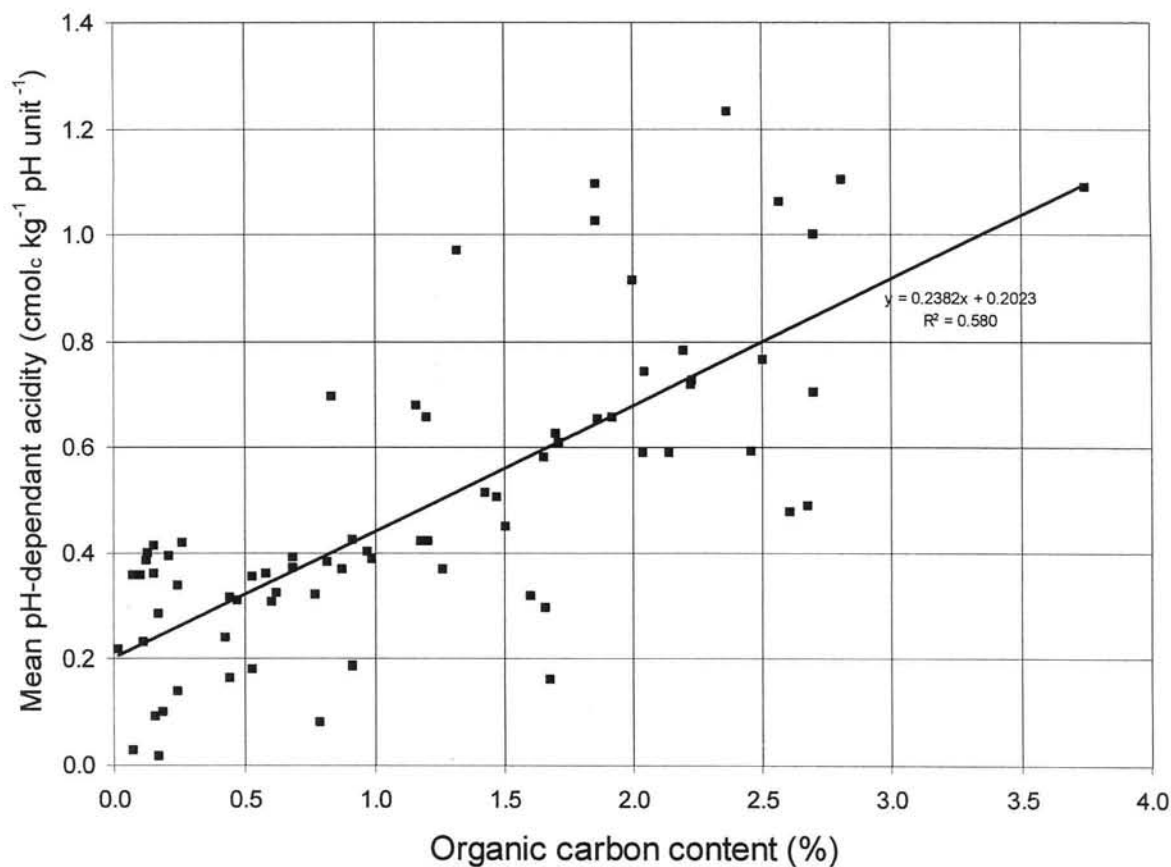


Figure 3.9 Relationship between the mean pH-dependant acidity (ΔH) and the organic carbon content for selected Western Cape soil sample population, excluding samples 2205, 4101, 4102, 4103 and 4104.

According to this prediction model the mean pH-dependant acidity can be reasonably accurately predicted using organic carbon and clay content. From the coefficients of the independent variables it is clear that organic material is by far the main contributor to mean pH-dependant acidity. The contribution from clay minerals appears to be minimal. This effect of organic material can clearly be seen in Table 3.1 where the mean pH-dependant acidity for the different soil groups is given. The organic soils have ΔH values which are, on average, at least twice as high as in normal, structured and sandy soil groups. The high mean pH-dependant acidity levels in the organic-rich soils effects the lime requirement of these soils. This will be discussed later.

Table 3.1 Effect of organic carbon content on mean pH-dependant acidity (ΔH) in different soil groups (excluding samples 2205, 4101, 4102, 410 and 4104).

Soil Group	Mean organic carbon content (%)	Mean pH-dependant acidity (ΔH) ($\text{cmol}_c \text{ kg}^{-1} \cdot \text{pH unit}^{-1}$)
Normal	0.814	0.351
Organic	2.031	0.711
Sandy	0.853	0.316
Structured	0.233	0.340

3.4 Conclusions

Clay, silt and organic material contributed to the CEC of the soil and can be used in prediction models to accurately predict CEC and T-value. Organic material contributed most of the pH-dependant acidity. The contribution made to pH-dependant acidity by the mineral component of the soil appeared to be minimal.

3.5 References

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4. EFFECT OF EXTRACTANT, EXTRACTION METHOD, SOIL GROUP AND LIME STATUS ON EXTRACTABLE CATIONS

This trial was carried out to determine the effect of different extractants and extraction methods on the extractability of Ca, Mg, K and Na from the experimental soils, notably with regard to the effect of liming history and soil group.

4.1 Materials and methods

Three extractants and methods were tested. These were:

- 1 0.2M ammonium acetate (NH_4OAc), buffered at pH 7, as used in this study for the determination of CEC and exchangeable cations.
- 2 A 0.1M hydrochloric acid (HCl) extraction with a total extraction volume of 200 cm^3 as routinely performed by the Eksteen method to determine extractable bases (Eksteen, 1969).
- 3 A 0.2M sodium chloride (NaCl) extraction was carried out to evaluate the effect of a weak (weaker than NH_4^+) exchanging cation. The extraction procedure was identical to that of the ammonium acetate extraction.

The extractable cations in the NH_4OAc and NaCl leachates were determined by atomic absorption spectrophotometry and, in the HCl leachate, by inductively coupled plasma emission spectroscopy (ICP). In the NaCl leachate only the Ca and Mg were determined. The results of these analyses are presented in Appendix IV. The results from these extractions were subjected to an analysis of variance using SAS (Appendix V). Student's LSD was calculated at the 5% level of probability to facilitate comparison between treatment means.

4.2 Results and discussion

The comparative means are listed in Table 4.1. Soil group had a significant ($P=0.0001$) effect on the extractable Ca, Mg, K and Na (Appendix V). This was anticipated in view of the diversity of the soils that made up the sample population. As expected, on average more Ca was extracted from the limed, than from the unlimed soil groups, although this effect was not significant for the structured and normal soil groups. Mg and Na were extracted in greater quantities from the unlimed and limed structured soil group than were extracted from the other soil groups. According to Curtin *et al.* (1994) soils have a stronger tendency to accumulate exchangeable Na when Mg, rather than Ca, is the complementary cation. This was directly related to a preference by exchange sites for Ca over Mg, which makes Na more competitive against Mg than against Ca. Lime status did not affect the extraction of K or Na, but significantly affected extractable Ca (Table 4.1). The difference between the extracted Mg for the limed and unlimed, structured soils could probably be attributed to differences between sample locations. This could also be true for the sandy soils, as could liming with dolomite. These results were much as expected in terms of the selection criteria which guided the soil sampling process. From Table 4.1 it is apparent that the extractants were equally effective in extracting Mg, K and Na. However, 0.1M HCl extracted appreciable more Ca than did 0.2M NH_4OAc or 0.2M NaCl.

The relatively large amount of Ca that was extracted by HCl, compared to NH_4OAc and NaCl, reflected the solubilising effect of this acid extractant on unreacted or residual lime, particularly in the limed soils. Calcium may also have been extracted from such Ca-bearing minerals as calcic plagioclase by acid dissolution, although this was not significant when comparing unlimed soils.

Table 4.1 Effect of soil group, liming status and extraction method on extractable Ca, Mg, K and Na.

Effect of soil group and liming status (mean of three extraction methods)

Soil group	Lime status	Ca	Mg	K	Na
Organic	Limed	3.951a	1.246c	0.269a	0.133b
	Unlimed	1.603bc	0.585c	0.237a	0.046bc
Normal	Limed	2.444b	1.024c	0.117bc	0.133b
	Unlimed	1.961b	1.017c	0.220ab	0.105bc
Structured	Limed	0.954cd	4.431a	0.066c	0.461a
	Unlimed	0.515d	3.528b	0.053c	0.358a
Sand	Limed	1.862b	0.620c	0.066c	0.022c
	Unlimed	0.400d	0.164d	0.025c	0.069bc
LSD (5%)		0.863	0.843	0.117	0.104

Effect of extraction method and liming status (mean of soil groups)

Extraction method	Lime status	Ca	Mg	K	Na
0.1M HCl	Limed	3.765a	1.849	0.151	0.182
	Unlimed	1.482bc	1.328	0.127	0.162
0.2M NH_4OAc	Limed	1.928b	1.620	0.170	0.165
	Unlimed	0.807c	1.436	0.146	0.139
0.2M NaCl	Limed	2.274b	1.658	-	-
	Unlimed	0.984c	1.485	-	-
LSD (5%)		0.705	nsd	nsd	nsd

Means within columns followed by the same letter are not significantly different (Student's LSD).

nsd = no significant difference

The NaCl extraction process was as effective as NH_4OAc in extracting Ca and Mg. Since NH_4^+ is regarded as a powerful displacing/exchanging agent this result was unexpected. A possible reason for the similar levels of Ca and Mg removal by NaCl and by NH_4OAc was the fact that although the NH_4OAc exchange reaction was buffered close to neutral pH the NaCl extraction (because NaCl is an extremely poor pH buffering medium) could have been carried out at close to soil pH. Soil pH was, in most cases, far below $\text{pH}_{\text{KCl}} 7$. This lower extraction pH would have helped to dissolve salts, minerals and residual lime, thereby offsetting the higher exchange capabilities of NH_4OAc . An alternative reason could have

been that at the high levels of sodium saturation that prevailed during the NaCl-extraction, clay and organic material might progressively disperse. Physical dispersion of the clay and silt particles would enhance breakdown of clay- and organic-, or clay-organic-aggregates, thereby improving access to normally difficult-accessible exchange sites by exchanging Na^+ . A factor which would limit dispersion is the concentration of the NaCl extracting solution. Quirk & Schofield (1955) saturated soils with Na and then leached the soils with various concentrations of NaCl-solution. The threshold concentration was determined at 0.25M, which is somewhat greater than the 0.2M which was used in the present extraction trial. It is therefore highly probable that some dispersion did occur in the present trial, although soils could have varied in terms of the extent to which dispersion occurred.

4.3 Conclusions

Significantly more Ca was extracted from limed than from unlimed soils. Lime status generally did not affect extractable Mg, K and Na. HCl, NH_4OAc and NaCl were equally effective in extracting Mg, K and Na. HCl extracted significantly more Ca than did NH_4OAc and NaCl. The relatively greater ability of HCl to extract Ca, was attributed to the solubilising effect of the acidic solution on residual lime and Ca-bearing minerals.

4.4 References

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5 R:pH RELATIONSHIPS AND LIME REQUIREMENT

5.1 Introduction

The focus of this study was the Eksteen method of lime requirement determination (Eksteen, 1969), with particular reference to sandy, organic-rich and structured soils with high Mg:Ca ratios. These are soil types for which the Eksteen method is generally acknowledged to yield inaccurate predictions of lime requirement. Fundamental to the Eksteen method is the ratio of extractable (Ca + Mg) to extractable acidity, which is termed the R-value. The R-value, which corresponds to the desired soil pH (which may vary from crop to crop), might be determined from Figure 1.1 and substituted in the Eksteen formula. The amount of lime required to achieve that specific pH can then be calculated. The R:pH relationship shown in Figure 1.1 is assumed to apply to all soil types. However, this assumption could be erroneous. If so, then the R-values could themselves introduce errors in the calculation of lime requirements for those soils for which the R:pH relationship shown in Figure 1.1 does not accurately apply. In these cases recalibration of the R:pH curve for soils characterised by specific characteristics could lead to improved lime requirement predictions. The work described in this section was carried out to test this hypothesis.

5.2 Procedure

A best fit model for R-value vs. pH_{KCl} was sought for the entire soil sample population, as well as for the sandy, organic-rich and structured, high Mg:Ca ratio soils. All the samples with a sum of Ca + Mg, as determined in the 0.1 M HCl extraction, exceeding the CEC, were excluded. This was carried out to ensure that samples which contain residual lime were excluded, since these samples would result in excessively high calculated R-values. The analytical data used in this work are presented in Appendix VI. CurveExpert 1.3, a freeware software program (<http://www.ebicom.net/~dhyams/cvxpt.htm>) that fits more than 30 possible models, was used for this exercise. Each model was compared with the Eksteen standard curve (Figure 1.1) in terms of those R-values which corresponded to pH_{KCl} 5.0 and pH_{KCl} 5.5. On the Eksteen standard R:pH curve, these pH values correspond to R values of 5 and 10, respectively.

5.3 R:pH relationships

5.3.1 Entire soil sample population

The R:pH relationship for the sample population is shown in Figure 5.1. Twelve samples were excluded because the sum of Ca + Mg exceeded the CEC. The model that best describes the R:pH relationship of the sample population is a power function and is formulated as follows:

$$R = a \cdot \text{pH}^b$$

where: $R^2 = 0.894$

$$a = 2.672 \times 10^{-7}$$

Standard error of estimate (S.E.E.) = 1.358

$$b = 10.2870$$

This describes the data set very well, mainly because the cluster of R-values which correspond to pH values below 5.0 is very tight for all soil groups, and the R-values which correspond to higher pH values follow a reasonably consistent trend. The model gives R-values of 4.1 and 11.0 at pH 5.0 and pH 5.5,

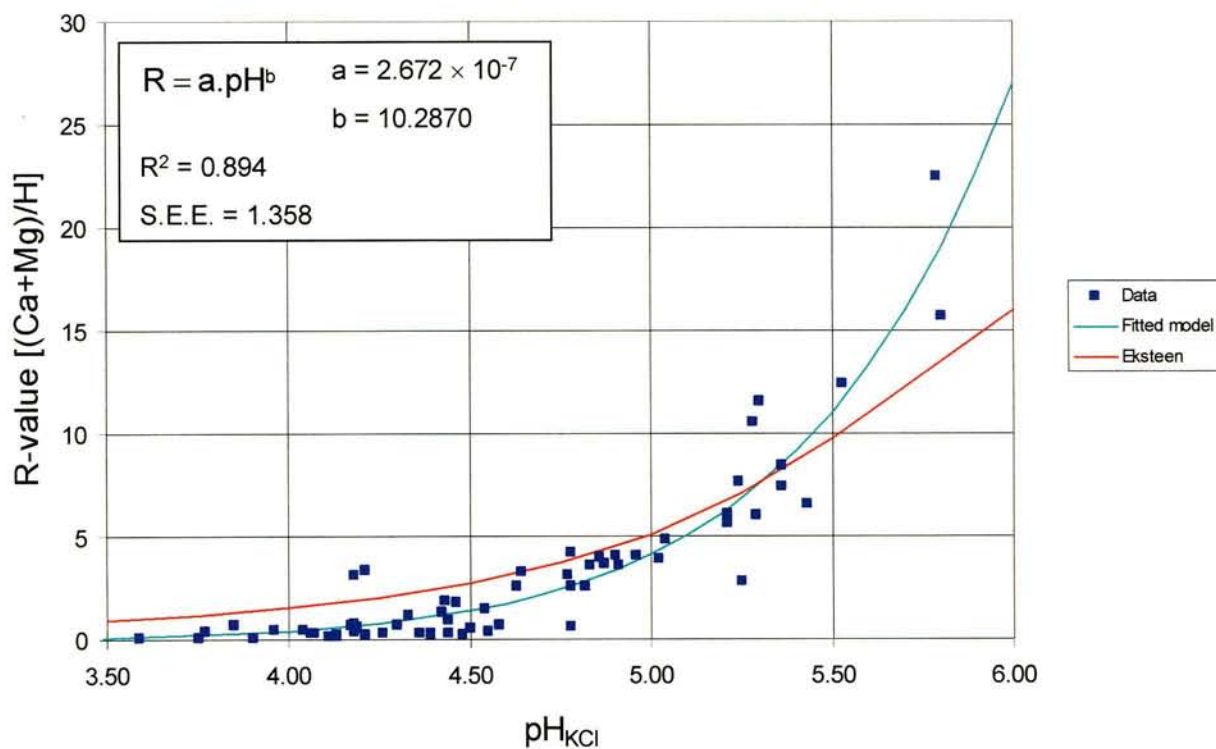


Figure 5.1 Best-fit model representing the R:pH relationship for the entire sample population of selected Western Cape soils, excluding samples that contain residual lime (HCl extractable Ca+Mg>CEC). The Eksteen standard curve is included for comparison.

respectively. These R-values correspond fairly closely to respectively 5 and 10 of the Eksteen standard curve. It is clear from Figure 5.1 that at low pH values the fitted model corresponds to lower R-values than the Eksteen standard curve, up to about pH 5.3 where the two lines intersect. However, above pH 5.3 the model diverges appreciably from the Eksteen standard curve, giving much higher R-values.

5.3.2 Normal soils

The best-fit R:pH model for normal soils is given in Figure 5.2, together with the Eksteen standard curve. One sample (3207) was excluded from this soil group because it contained residual lime. The fitted model for the normal soils is a modified exponential function:

$$R = a \cdot e^{b/\text{pH}}$$

where: $R^2 = 0.923$

$a = 1284.5117$

S.E.E = 0.417

$b = -28.5037$

In theory, the fitted model should coincide with the Eksteen standard curve. However, it is apparent from Figure 5.2 that the fitted model differs from the Eksteen standard curve. The R-values which correspond to pH 5.0 and pH 5.5, respectively, are 4.3 and 7.2 for the model, as compared with 5.0 and 10.0 for the Eksteen standard curve. These differences could make a substantial difference to the lime requirement. The differences will be greatest for soils with low lime requirements. For example, sample 3109 had a lower lime requirement than sample 3101. The calculated lime requirement for sample 3101, using R-values 7.2 and 10 (to achieve a soil $\text{pH}_{\text{KCl}} 5.5$), was 2.36 and 2.82 t ha⁻¹, respectively, for a soil depth of 15 cm. When similarly calculated for sample 3109, the lime requirement was 0.63 and 1.32 t ha⁻¹, respectively, for a soil depth of 15 cm. The difference in lime requirement due to the difference in R-values is more than 100 % for sample 3109.

In the following sections the R:pH relationships of the organic, sandy and structured, high Mg:Ca soils will be compared with that of the normal soil group, rather than with the standard Eksteen relationship.

5.3.3 Organic soils

The distribution of data points as well as the best-fit model for the organic soils is presented in Figure 5.3. Samples 1201, 1204, 1205 and 1211 were excluded from the model because the sum of Ca + Mg exceeded the CEC. Sample 1202 is indicated in Figure 5.3 because it affected the curve fitting calculations so that the curve for the organic soil did not follow the typical Eksteen standard curve (Figure 1.1). The fitted model is a rational function and is as follows:

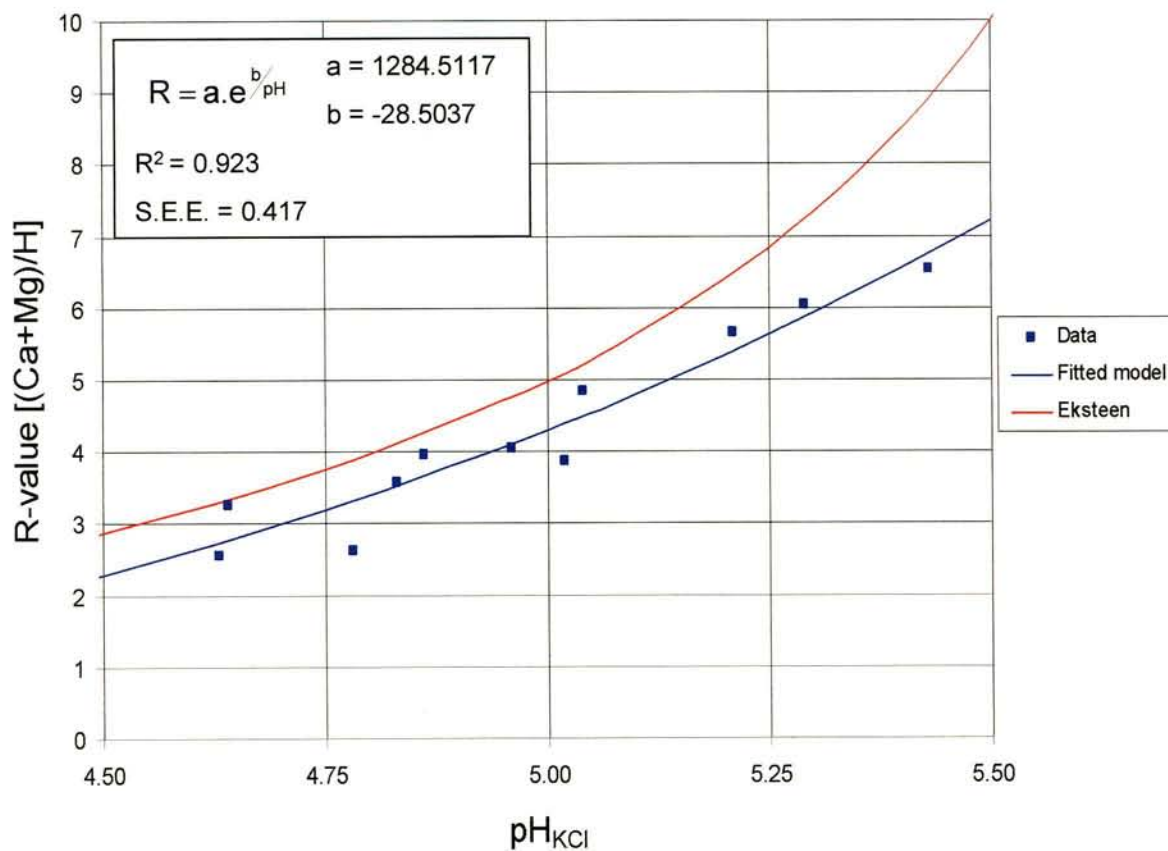


Figure 5.2 Best-fit model representing the R:pH relationship for selected Western Cape normal soils, excluding sample 3207 because it contained residual lime (HCl extractable Ca+Mg>CEC). The Eksteen standard curve is included for comparison.

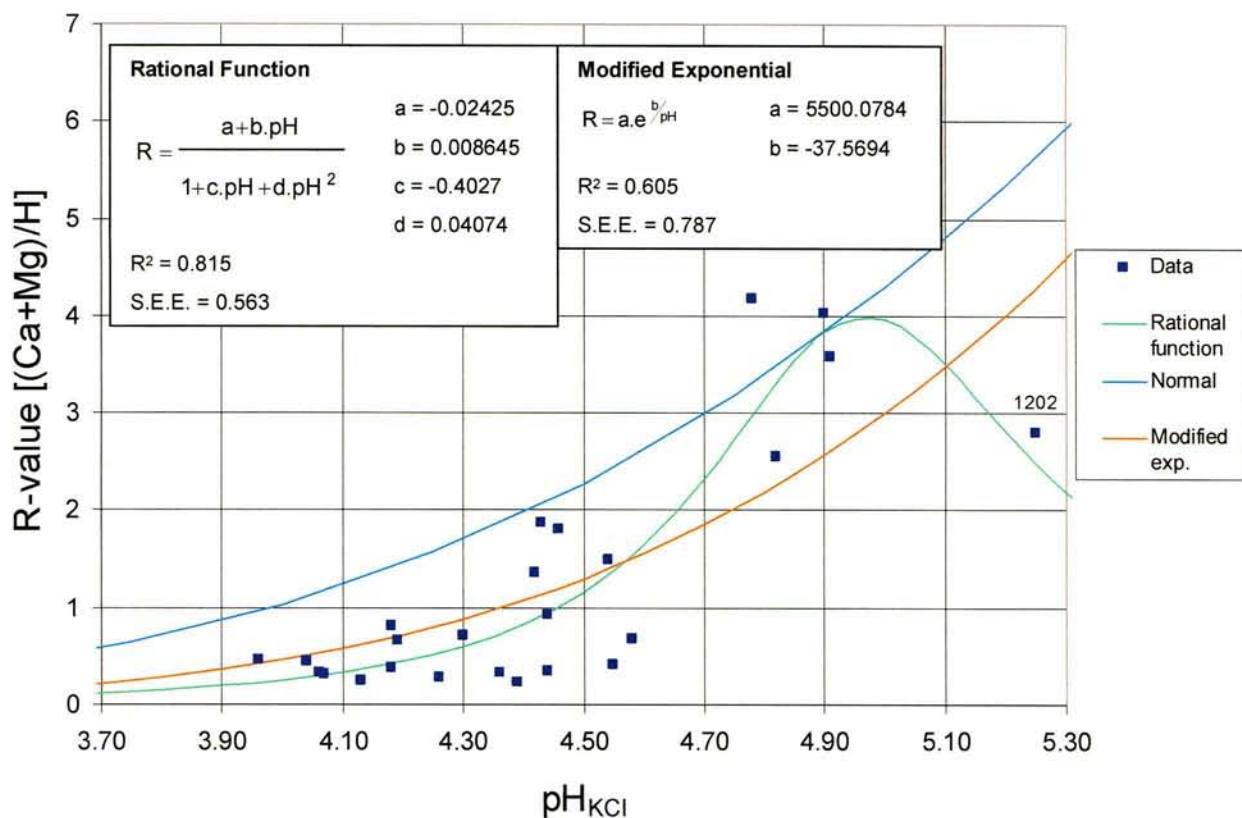


Figure 5.3 Best-fit rational function representing the R:pH relationship for selected Western Cape organic soils. A modified exponential curve was also fitted to make comparisons possible. Four samples were excluded because they contained residual lime (HCl extractable Ca+Mg>CEC). The model for normal soil is included for comparison.

$$R = \frac{a + b \cdot \text{pH}}{1 + c \cdot \text{pH} + d \cdot \text{pH}^2}$$

where: $R^2 = 0.815$

S.E.E = 0.563

$a = -0.02425$

$b = 0.008645$

$c = -0.4027$

$d = 0.04074$

Since the rational function above makes comparison difficult, the following modified exponential curve was also fitted:

$$R = a \cdot e^{b/\text{pH}}$$

where: $R^2 = 0.605$

S.E.E. = 0.787

$a = 5500.0784$

$b = -37.5694$

From Figure 5.3 it is evident that the fitted rational function cannot be compared to the normal soils at a pH above about 4.9, but a comparison can still be made at pH below 4.9. Both the rational function curve (if compared at $\text{pH} < 4.9$) and the modified exponential curve fitted to the organic samples, is lower than that for the normal soil group. The very low R-values can probably be ascribed to the pH-dependant acidity component which is associated with soil organic matter. As discussed in Section 3.3, the total acidity as determined by the Eksteen method is very high. At pH 7.0, acidic organic functional groups may be expected to dissociate, thereby increasing the extractable acidity and lowering the R-value, whereas at low soil pH levels the pH-dependant acidity components (dissociated protons) are associated with the functional groups and are not active in the soil solution. This means, in effect, that if two similar soils at the same field pH, but with different organic material contents are considered, more acidity would be extracted from the soil with the higher organic material content. This situation would only be applicable below a specific pH level below which some protons are still associated with organic functional groups. This pH-dependant acidity component of organic soils increases the extractable acidity levels and is the cause of over-liming on soils with high organic material contents. As shown by Lambrechts & Smuts (1998), the acidity determined at pH 7 (the H-value in the Eksteen formula) is the factor which has the most profound effect on the calculated lime requirement. The pH-dependant acidity increase with an increase in the organic matter content. It also increases as the soil pH decrease.

Recalibration of the R:pH relationship to correct the lime requirement is unlikely to prove a satisfactory, practical solution, largely because it would be necessary to compile different R:pH relationships for soils with different levels of organic carbon. The approach that has been used to date (Conradie, 1994) merely entails adjustment of the Eksteen-predicted lime requirement with factors as listed in Table 1.1, in accordance with the organic carbon content of the soil, and appears to be reasonably accurate and easy

to apply. The main disadvantage of this approach is that the correction factor is totally empirical, and that the organic content classes are very broad, suggesting that a new approach is necessary.

5.3.3.1 Derivation and application of an Organic Matter Correction Factor (OMCF)

This approach assumes that the mean pH-dependant acidity (ΔH) of the soils in the sample population that contain less than 1% organic carbon, is similar to the mean pH-dependant acidity for mineral soils as a whole. The mean pH-dependant acidity for the population of soils with less than 1% organic carbon ($\Delta H_{<1\%C}$) was determined as $0.300 \text{ cmol}_c \text{ kg}^{-1} \text{ pH unit}^{-1}$. The mean pH-dependant acidity of organic soils ($\Delta H_{\text{organic}}$) was corrected by subtracting this mean value for mineral soils ($\Delta H_{\text{organic}} - \Delta H_{<1\%C}$), to give a value of $0.411 \text{ cmol}_c \text{ kg}^{-1} \text{ pH unit}^{-1}$. Dividing this value (0.411) by the mean organic carbon content of the organic soils (2.031 %C) gave a value of 0.202, which indicates the mean pH-dependant acidity contribution of organic matter for every percentage of soil organic carbon at any specific soil pH. This value, which will henceforth be referred to as the **Organic Matter Correction Factor (OMCF)**, can be used to correct the total acidity as determined at pH 7.0 (H) before calculating the lime requirement.

Calculation of the OMCF is carried out in the following manner:

$$\begin{aligned} \text{OMCF} &= \frac{\Delta H_{\text{organic}} - \Delta H_{<1\%C}}{\text{mean \%C of organic soils}} \\ &= \frac{(0.711 - 0.300) \text{ cmol}_c \text{ kg}^{-1} \text{ pH unit}^{-1}}{2.031\%C} \\ &= 0.202 \text{ cmol}_c \text{ kg}^{-1} \text{ pH unit}^{-1} \%C^{-1} \end{aligned}$$

Figure 5.4 (data presented in Appendix VII) illustrates the application of the OMCF in the determination of the overestimated or excess lime requirement inherent in the Eksteen method over a range of soil pH values and organic carbon contents. Excess lime may be defined as lime which is specified by the Eksteen method but which serves only to neutralise the pH-dependant acidity derived from organic material. The excess lime requirement indicated in Figure 5.4 is the equivalent amount of lime required to neutralise the excess hydrogen derived from the organic material and is calculated from the OMCF. The only factors that were taken into account were soil bulk density, which was taken as 1500 kg m^{-3} , and lime purity, which was assumed to be 70% as required by law. Correction factors for neutralisation efficiency and uniformity of mixing as discussed in Section 1.3.1, were ignored.

The OMCF is a conservative value. Although the mineral soils were assumed to contain < 1% C, they still contain some organic carbon. This carbon is capable of contributing to pH-dependant acidity and was not allowed for when dividing by the average percent organic carbon of the organic soils. The reason for this non-correction was that Table 3.1 suggests that the mean pH-dependant acidity of mineral soils represents a minimum value which is applicable to most low organic matter-content soils.

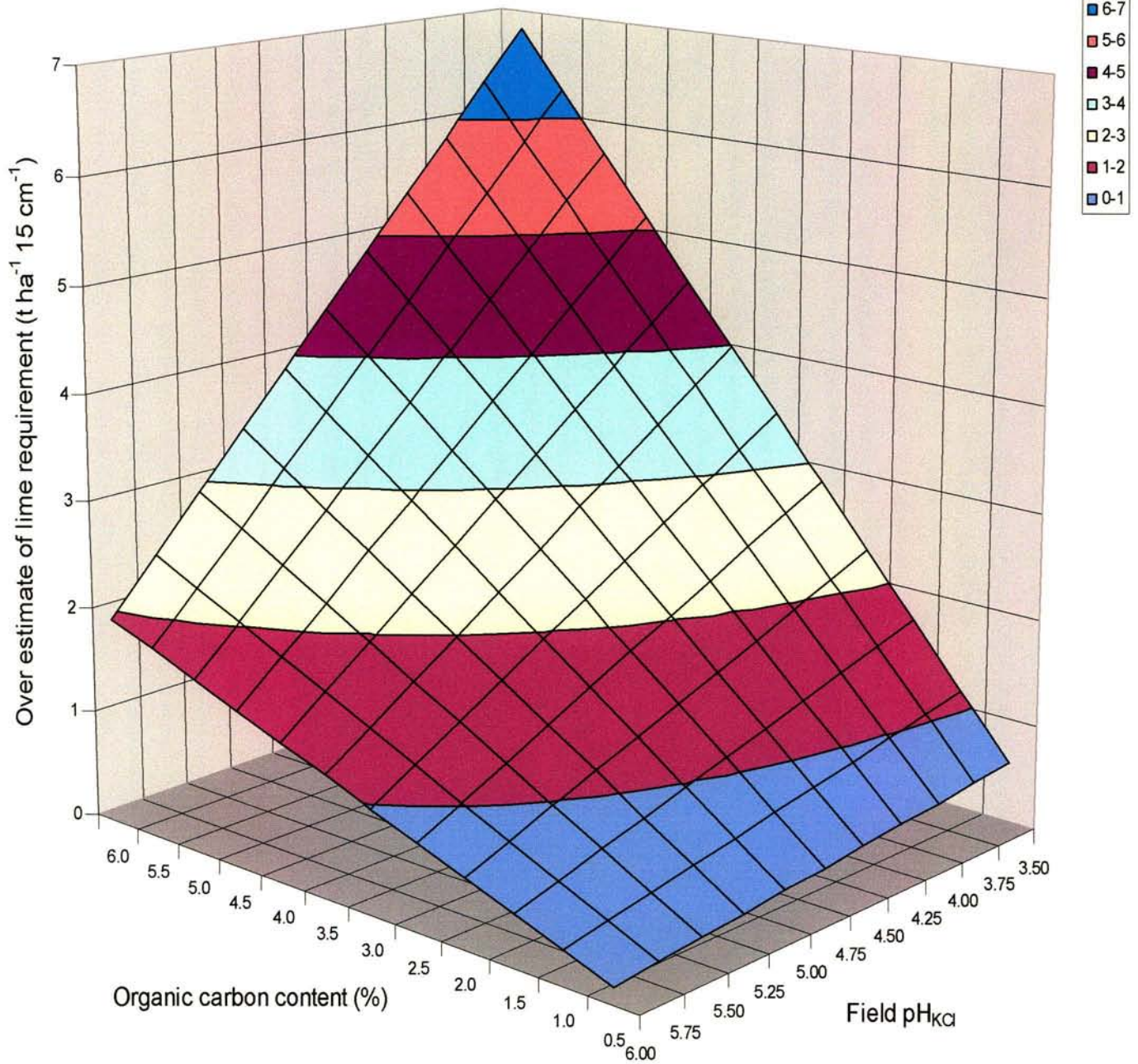
Range: $t\ ha^{-1}\ 15\ cm^{-1}$ 

Figure 5.4 Over-estimation of lime requirement of selected Western Cape soils over a range of organic carbon contents and pH values, calculated from the organic matter correction factor (OMCF) on an equivalent basis assuming a soil bulk density of $1500\ kg\ m^{-3}$ and a lime purity of 70%.

The OMCF should be used to correct the total extracted acidity (H) determined at pH 7. The corrected H-value should then be used in the standard Eksteen formula as used for the normal soil group. The H-value should be adapted as follows:

$$H_{\text{OMCF}} = H - \{(7 - \text{field pH}_{\text{KCl}}) \times \%C \times \text{OMCF}\} \quad (\text{Only for soils with } \%C > 1)$$

5.3.3.2 Comparison between Eksteen-predicted lime requirements after correction by the method of Conradie (1994) and by the H_{OMCF} approach

A comparison was drawn between the lime requirements predicted by the Eksteen method using the correction factor for organic carbon as proposed by Conradie (1994) and the modified Eksteen calculation using H_{OMCF} . An R-value of 7.2, as determined for normal soils and relating to a soil pH of 5.5, was used. For ease of comparison, all the organic soil samples with a pH of less than 5 and their relevant parameters are presented in order of increasing soil pH in Table 5.1. It appears from Figure 5.5 that in the case of soils which have a high lime requirement, the predicted lime requirement is lower where the method of Conradie (1994) is applied, whereas the opposite is true for soils with low lime requirements.

It is important to note that the method of Conradie (1994), which corrects the Eksteen-predicted lime requirement after the calculation, may on occasion, give a lime requirement where there is none. For this reason, correction of the acidity value before calculation of the lime requirement, as when using the H_{OMCF} concept is therefore preferable. It should also be remembered that organic matter contributes to the CEC as stated in Section 3.2, and that, according to Ross *et al.* (1964), CEC is the second most important soil factor after pH in determining lime requirement. Therefore, the CEC originating from organic material is another factor that may affect the lime requirement in soils with a high organic material content.

Table 5.1 Comparison between the lime requirements of selected Western Cape organic soils, as predicted by the Eksteen method after correction for organic matter as proposed by Conradie (1994) (A), and as predicted by the corrected acidity (H_{OMCF}) method (B). The R-value of 7.2 for normal soils was used for this determination.

Sample no.*	Lime status	pH _{KCl}	%C	H	H_{OMCF}^{**} ($\text{cmol}_c \text{ kg}^{-1}$)	Ca + Mg	Lime requirement ($\text{t ha}^{-1} 15 \text{ cm}^{-1}$)	
							A	B
1106	unlimed	3.96	2.23	5.81	4.44	2.71	11.45	14.27
1110	unlimed	4.04	2.23	5.29	3.96	2.37	10.46	12.74
1107	unlimed	4.06	1.71	5.19	4.17	1.73	13.91	13.81
1111	unlimed	4.07	1.92	4.77	3.63	1.50	12.82	12.03
1209	limed	4.13	2.14	5.09	3.85	1.30	10.34	12.88
1213	limed	4.18	1.66	5.19	4.25	1.97	13.82	13.95
1215	limed	4.18	1.51	4.05	3.19	1.57	10.77	10.44
1207	limed	4.18	1.16	3.84	3.18	3.14	9.57	9.63
1105	unlimed	4.19	1.86	3.63	2.57	2.40	9.26	7.87
1210	limed	4.26	2.46	4.57	3.21	1.27	9.26	10.64
1112	unlimed	4.30	1.85	4.67	3.66	3.34	11.82	11.22
1113	unlimed	4.36	1.70	4.05	3.14	1.31	10.87	10.40
1102	unlimed	4.39	1.68	3.22	2.33	0.74	8.76	7.84
1214	limed	4.42	2.70	3.63	2.22	4.95	6.20	5.39
1218	limed	4.43	2.00	3.32	2.28	6.24	5.17	4.97
1103	unlimed	4.44	1.66	3.11	2.25	1.09	8.31	7.37
1101	unlimed	4.44	2.04	3.11	2.06	2.88	5.71	5.81
1206	limed	4.46	1.32	3.11	2.43	5.62	6.54	5.80
1108	unlimed	4.54	2.57	3.11	1.83	4.65	5.19	4.16
1114	unlimed	4.55	2.68	2.70	1.37	1.13	5.36	4.28
1203	limed	4.58	0.91	2.28	1.83	1.54	7.26	5.69
1217	limed	4.78	2.81	2.70	1.44	11.29	2.38	0.00
1208	limed	4.82	2.37	2.91	1.87	7.43	3.96	2.93
1109	unlimed	4.90	3.75	2.49	0.90	10.03	1.54	0.00
1212	limed	4.91	1.85	2.49	1.71	8.90	3.52	1.65

*Samples included if pH_{KCl} < 5.0

** $H_{OMCF} = H - \{(7 - \text{field pH}_{KCl}) \times \%C \times OMCF\}$; $OMCF = 0.202 \text{ cmol}_c \text{ kg}^{-1} \text{ pH unit}^{-1} \%C^{-1}$

$$A = \frac{7.2H - (Ca + Mg)}{7.2 + 1} \times 4 \times \text{Correction factor of Conradie (1994)}; \quad B = \frac{7.2H_{OMCF} - (Ca + Mg)}{7.2 + 1} \times 4$$

Correction factor of Conradie (1994):

Organic carbon (%)	Fraction of the calculated lime requirement that should be applied (%)
0 – 1	100
1 – 2	80
2 – 3	60
3 – 4	40

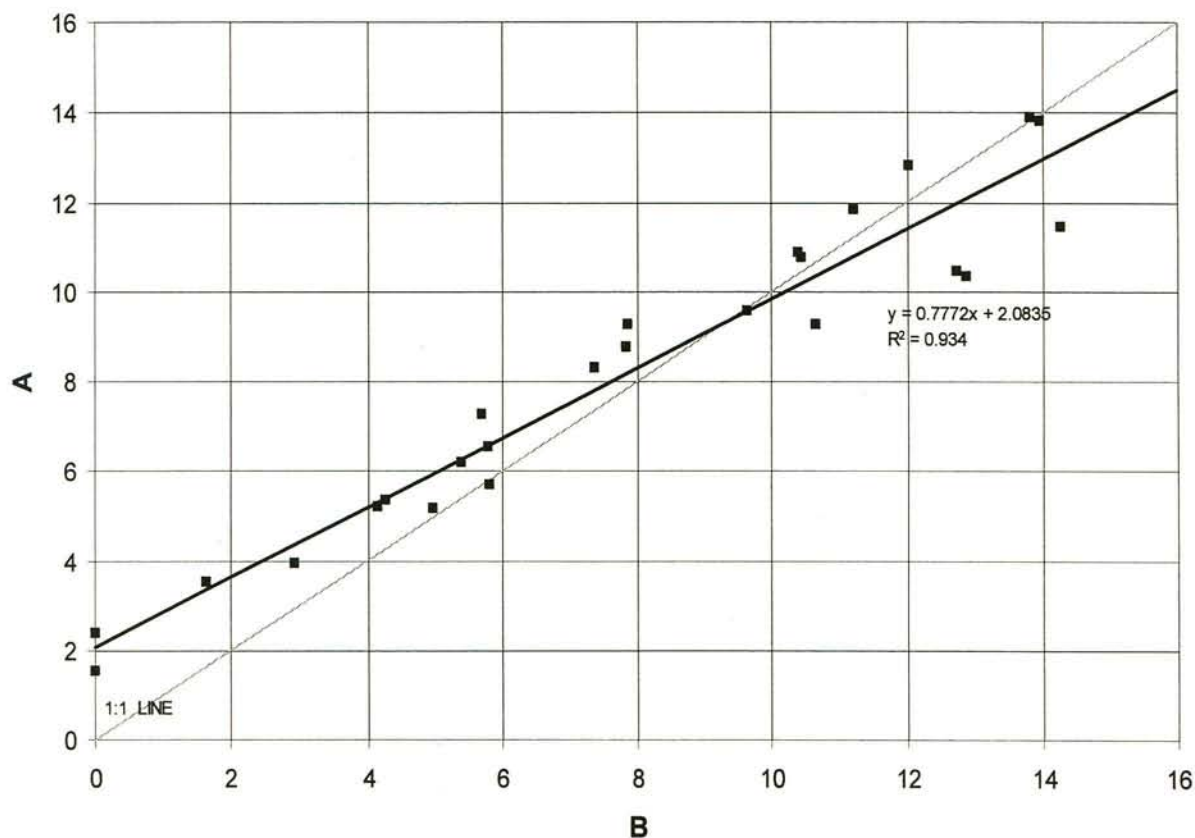


Figure 5.5 Comparison between the lime requirement of selected organic-rich Western Cape soils as predicted by the Eksteen method after correction for organic matter as proposed by Conradie (1994) (A), and the lime requirement determined using the corrected acidity (H_{OMCF}) (B). The R-value for normal soil (7.2) was used for calculation. H_{OMCF} can be calculated as follows: $H_{OMCF} = H - \{(7 - \text{field } pH_{KCl}) \times \%C \times OMCF\}$; where H is the total extractable acidity at pH 7, field pH_{KCl} is the soil pH_{KCl} , %C is the organic carbon content of the soil and OMCF is the organic matter correction factor of value $0.202 \text{ cmol}_c \text{ kg}^{-1} \text{ pH unit}^{-1} \%C^{-1}$.

5.3.4 Sandy soils

Eight samples were excluded from the group for the line fitting procedure, due to the presence of residual lime ($\text{Ca} + \text{Mg} > \text{CEC}$). A reciprocal model best fitted the R:pH data for the sandy soils. Figure 5.6 presents the distribution of data points for the group of sandy soils and the curve representing the best-fit model. The best-fit reciprocal model was the following:

$$R = \frac{1}{a \cdot \text{pH} + b}$$

where: $R^2 = 0.381$

$a = -2.7728$

S.E.E. = 0.743

$b = 13.8002$

The fitted model did not describe the data particularly well. Data points are widely scattered over a very limited pH range, which makes it difficult to make any valid conclusions. The model is only valid for the applied pH range and gives negative R-values at higher pH values. Extrapolation to pH values > 4.9 is therefore not feasible.

The low content of materials which might buffer the effects of excessive liming and high acidity (clay and organic matter) in most of the soils in this group, suggests that the recalibrated R:pH relationship would not be a practical tool for solving the over liming problem associated with the Eksteen method of lime determination for pale coloured sandy soils. Pale coloured sandy soils react excessively to any form of chemical manipulation.

Lambrechts & Smuts (1998) speculated that neutralisation of acidity after liming is likely to approximate 100% on sandy soils because the rapid hydraulic conductivity of these soils facilitates rapid movement of calcium so that unreacted lime does not remain in the reaction zone and pH levels do not increase excessively. It was therefore assumed that the field correction factor (F) in the Eksteen formula would be two (2) or less. Because of the danger of over-liming, an optimum pH of 5.0, that relates to an R-value of five, was also assumed, as shown in Figure 1.1. Aluminium toxicity is not a problem in sandy soils because of the predominantly quartzitic soil materials that do not contain appreciable aluminium. To avoid over-liming in sandy soils, the approach of Lambrechts & Smuts (1998), which uses a field correction factor (F) of two and an R-value of five instead of 10, is based on highly conservative assumptions. From the viewpoint of soil chemistry it is a sound practice to lime pale coloured sandy soils equivalent to the existing level of soil acidity. If the neutralisation efficiency is 100%, then the equivalent lime requirement will only need to be corrected for lime purity, soil bulk density and soil depth. The only factor not taken into consideration is the possible presence of residual lime. Residual lime can be allowed for in a manner similar to that used in the Eksteen method, as follows:

- The CEC of pale coloured sandy soils should not exceed $1.5 \text{ cmol}_c \text{ kg}^{-1}$ (Lambrechts & Smuts, 1998). If the sum of $\text{Ca} + \text{Mg}$ in the HCl acid extraction exceeds $1.5 \text{ cmol}_c \text{ kg}^{-1}$, the amount of

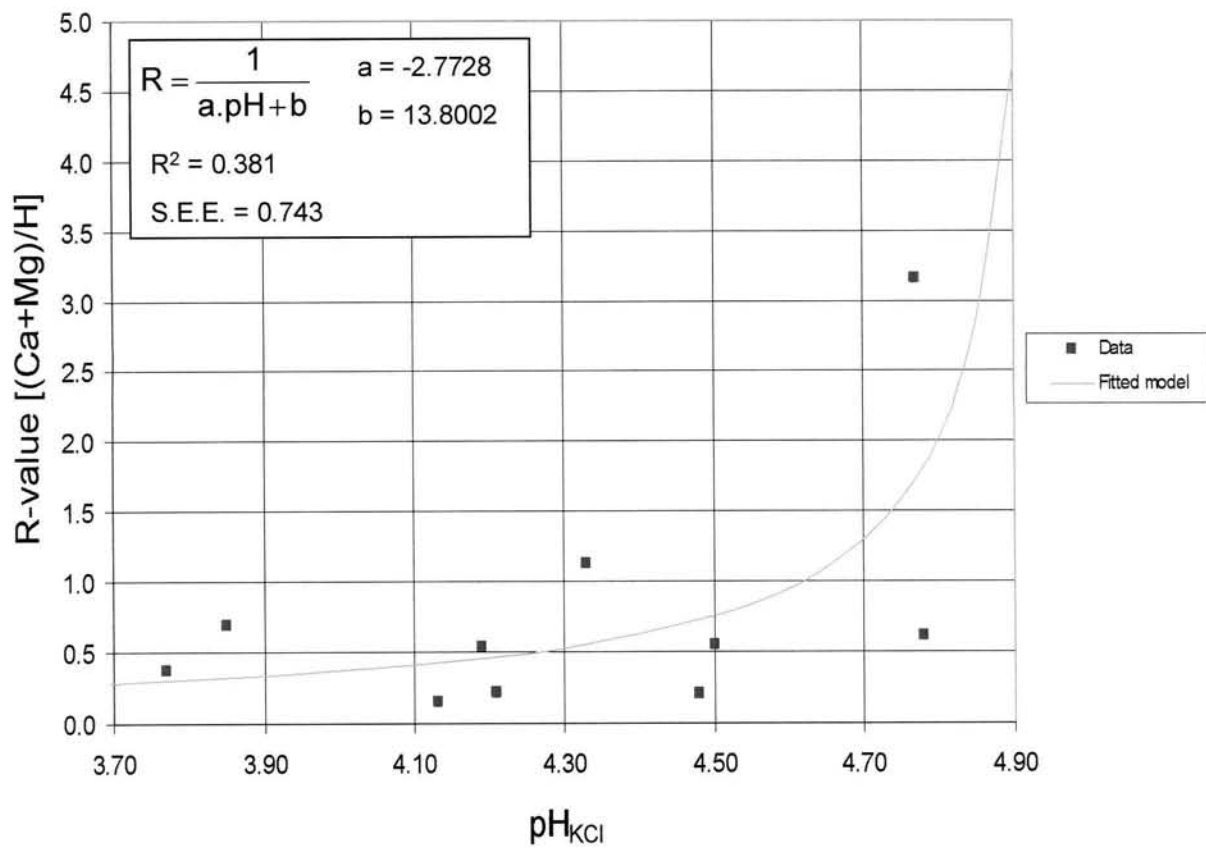


Figure 5.6 Best-fit model representing the R:pH relationship for selected Western Cape sandy soils. Seven samples that contained residual lime (HCl extractable Ca+Mg>CEC) were excluded.

Ca + Mg that exceeds 1.5 cmol_c kg⁻¹ (representing residual lime) should be deducted from the total extracted acidity (H) before the lime requirement is determined on an equivalent basis. Correction for residual lime is calculated as follows:

$$H_{\text{corrected}} = H - \{(Ca+Mg)-1.5\} \quad (\text{Only for soils with } Ca+Mg > 1.5)$$

H, Ca and Mg all expressed as cmol_c kg⁻¹

- After the soil acidity (H) has been corrected for residual lime (where necessary) the H or H_{corrected} value can be used to determine the lime requirement on an equivalent basis. This is a simple calculation and can be illustrated as follows:

$$\begin{aligned} 1 \text{ cmol H or } H_{\text{corrected}} \text{ kg}^{-1} &= 0.5 \text{ cmol Ca}^{2+} \text{ kg}^{-1} \\ &= 500 \text{ mg CaCO}_3 \text{ kg}^{-1} \\ &= 1.125 \text{ t CaCO}_3 \text{ for the 2.25 million kg of a hectare soil layer with a bulk} \\ &\text{density of } 1500 \text{ kg m}^{-3} \text{ and depth of } 15 \text{ cm} \end{aligned}$$

- This value must be corrected for the purity of calcitic lime which, according to law, should be at least 70%. The corrected lime requirement would then be:

$$\begin{aligned} &= (100/70) \times 1.125 \\ &= 1.61 \text{ t calcitic lime ha}^{-1} \text{ } 15 \text{ cm}^{-1} \text{ soil depth} \end{aligned}$$

A comparison between the lime requirements of sandy soils as determined by the method outlined above and that of Lambrechts & Smuts (1998) is presented in Table 5.2. In the latter case an R-value of five, and a field correction factor (F) of two, were assumed. All the samples from the sand soil group were used, except for those which had pH values in excess of 5.0. Organic matter content was ignored in this comparison, despite the fact that some of the samples contained sufficient amounts of organic carbon to disqualify them from the pale coloured sandy soil category. From Table 5.2 it is apparent that the requirements predicted by the two methods did not differ appreciably. However, the number of samples used in this comparison was too small for a full evaluation to be made.

Table 5.2 Comparison between the lime requirements of selected Western Cape sandy soils as calculated by the method of Lambrechts & Smuts (1998) (A) (R=5; F=2), and calculated on an equivalent basis using the soil acidity (H), or when soil Ca + Mg > 1.5, the H_{corrected} value (B).

Sample no.*	Lime status	pH _{KCl}	H	H _{corrected} ** (cmol _c kg ⁻¹)	Ca + Mg	Lime requirement (t ha ⁻¹ 15 cm ⁻¹)	
						A	B
2107	unlimed	3.77	2.91	not calculated	1.07	4.49	4.68
2101	unlimed	3.85	0.62	not calculated	0.43	0.89	1.00
2104	unlimed	4.13	2.91	not calculated	0.46	4.70	4.68
2203	limed	4.19	1.56	not calculated	0.84	2.32	2.51
2105	unlimed	4.21	1.66	not calculated	0.36	2.65	2.67
2108	unlimed	4.33	1.45	1.30	1.65	1.87	2.09
2102	unlimed	4.48	1.87	not calculated	0.39	2.99	3.01
2106	unlimed	4.50	3.11	2.90	1.71	4.61	4.67
2207	limed	4.77	0.52	0.38	1.64	0.32	0.61
2103	unlimed	4.78	0.73	not calculated	0.45	1.07	1.17

*Samples included if pH_{KCl} < 5.0

** H_{corrected} = H - {(Ca+Mg)-1.5}; only when soil Ca+Mg > 1.5

$$A = \frac{5H - (Ca + Mg)}{5 + 1} \times 2$$

$$B = H \text{ or } H_{\text{corrected}} \times 1.61$$

5.3.5 Structured, high Mg:Ca ratio soils

From Figure 5.7 it is clear that the samples in the structured, high Mg:Ca ratio soil group fall into two subgroups in terms of their R:pH relationships. One subgroup falls below line A. The second subgroup conforms to the general R:pH trend as illustrated in Figure 1.1. The curve in Figure 5.7 was fitted only to the samples which plot above line A. Samples 1104, 1216, 1219, 4101, 4102, 4103 and 4104 were excluded. The fitted line is a saturation growth-rate model and is defined as follows:

$$R = \frac{a \cdot \text{pH}}{b + \text{pH}}$$

where: R² = 0.858

a = -1.5855

S.E.E. = 2.238

b = -6.2757

In Figure 5.8 each R:pH data point was annotated with its Mg:Ca ratio. From these points it is apparent that for any given soil pH the R-values increase with increasing Mg:Ca ratios. The soil samples below line A were characterised by R-values and Mg:Ca ratios which were in most cases disproportionately small, despite the fact that most of them qualified as structured soils.

It is, perhaps, pertinent that the three samples 1104, 1216 and 1219 that were not initially sampled as structured soils but were later grouped with the structured soil group, fell into the subgroup which was excluded from the R:pH model, as were the very strongly structured, highly acid samples 4101, 4102, 4103 and 4104.

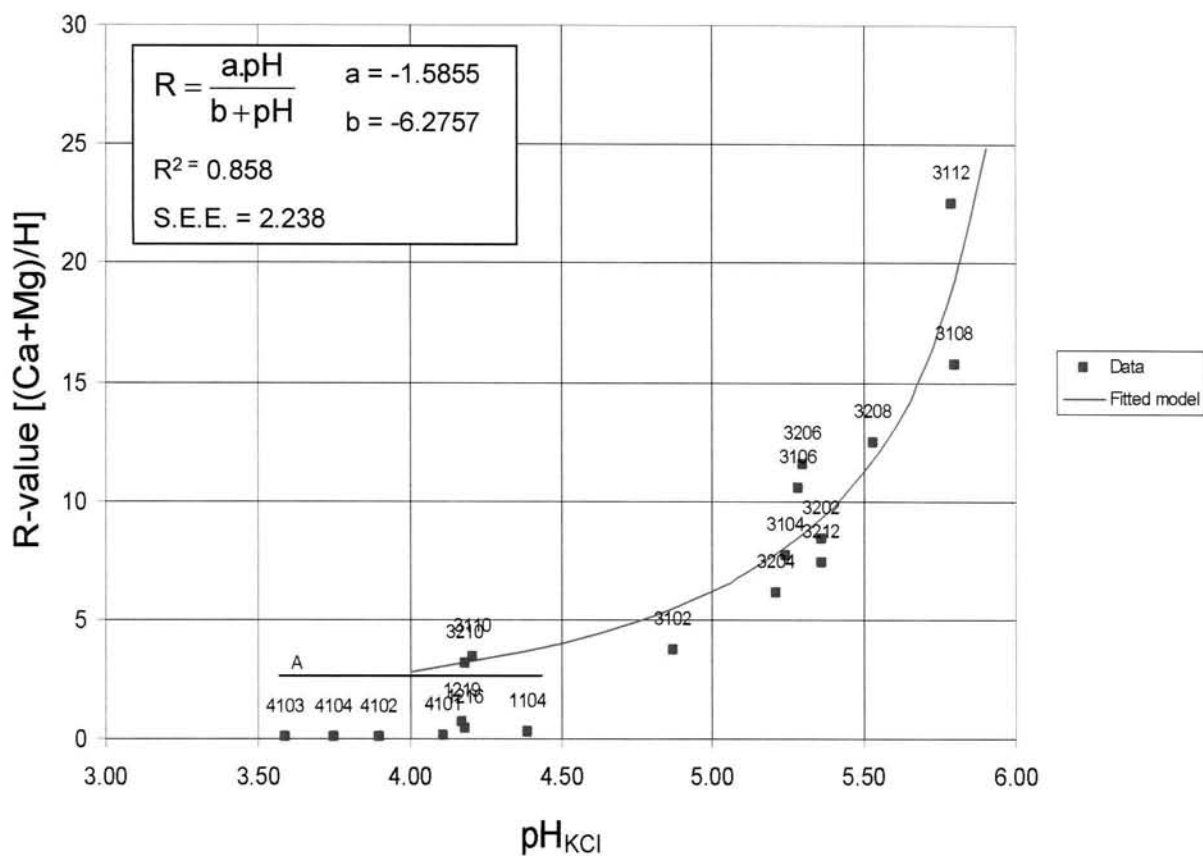


Figure 5.7 Best-fit model representing the R:pH relationship for selected Western Cape structured soils with high Mg:Ca ratios. Samples falling below line A were excluded from the model.

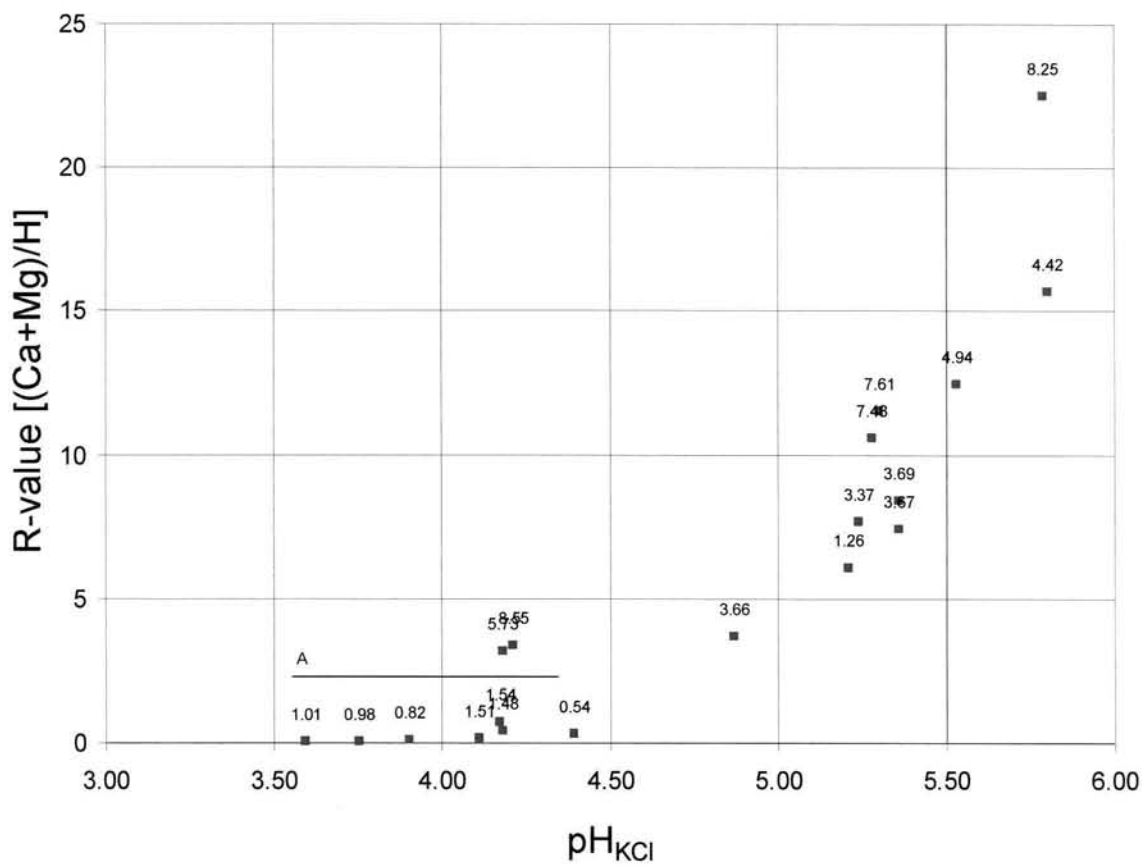


Figure 5.8 Distribution of data points representing the structured, high Mg:Ca ratio soil group. Each point is annotated with its Mg:Ca ratio.

The method employed by J.J.N. Lambrechts (University of Stellenbosch, personal communication, 1998) to adapt the Eksteen method for strongly structured subsoils containing high levels of extractable Mg, was based on the assumption that Mg is less effective in neutralising acidity than is Ca.

Figure 5.8 indicates a link between the R-value and Mg:Ca ratio. However, total extractable Mg also appears to be important, as was suggested by the fact that, whereas the highest extractable Mg level for the subgroup of excluded samples was $0.96 \text{ cmol}_c \text{ kg}^{-1}$ (sample 1219), the lowest Mg value for the included sample subgroup was $2.48 \text{ cmol}_c \text{ kg}^{-1}$ (sample 3204).

For the structured soil group the fitted model gives R-values of 6.2 and 11.2 at pH values of 5.0 and 5.5 respectively. These R-values are appreciably higher than those for normal soils. The high R-values are due to the high levels of extractable Mg in the structured soils which is pertinent in terms of the interpretation that the acidity neutralising capacity of Mg in structured soils is limited (Conradie, 1994). From Figures 5.7 and 5.8 it would appear that the Eksteen lime requirement depends on the Mg:Ca ratio in soils which contain a relative abundance of Mg. Wild & Keay (1964) and Peterson *et al.* (1965) found, with vermiculite, that when the Mg-saturation is above a certain level (30% to 40%), a strong adsorption preference for Mg occurs, apparently because of a structural affinity for hydrated Mg ions. However, in soils which contain little Mg the Mg:Ca ratio seems to have little effect on the Eksteen lime requirement. It is thus possible that the absolute levels of extractable Mg in the excluded soil subgroup were not high enough to affect the R-value. The low R-values of these soils were the main reason for exclusion from the fitted model.

Since the low total Mg soils do not conform to the R:pH calibration model they should be treated as normal soils from a lime determination viewpoint. The lower limit for total extractable Mg at which the Eksteen lime requirement will be affected by the Mg:Ca ratio appears to lie between $0.96 \text{ cmol}_c \text{ kg}^{-1}$ and $2.48 \text{ cmol}_c \text{ kg}^{-1}$.

From the available data it is not possible to quantify the neutralising capacity of the Mg in the structured soils. Without this information, alternative approaches to the Eksteen method cannot be formulated. Because the Mg and Ca levels for the sample soils in the structured, high Mg:Ca group differ widely, the fitted R:pH model represents no more than an average for the subgroup of structured samples which were included. Likewise the R-values which were derived from the model will probably only be applicable to that specific soil subgroup. The practical approach to lime requirement determination in structured soils as formulated by J.J.N. Lambrechts (University of Stellenbosch, personal communication, 1998) entails ignoring the extractable Mg and replacing the Ca + Mg component of the Eksteen formula with the expression: $1.25 \times \text{Ca}$, thereby assuming a Mg:Ca ratio of 1:4, relative to the soil Ca content, as explained in Section 1.3.2. Though effective in practice, this approach means that the neutralising capacity of the measured soil Mg is ignored.

Table 5.3 presents a comparison between lime requirements as predicted by the method of J.J.N. Lambrechts (University of Stellenbosch, personal communication, 1998), using the normal soil R-value of 7.2, with those of the Eksteen method using the R-value (11.2) derived from the fitted model for that soil population as well as the standard Eksteen calculation, using an R-value of 10 to achieve a soil pH of 5.5. Only samples with a pH below 5.5 were used for this comparison and the samples are arranged in sequence of increasing pH. Very few of the samples had pH values below 5, and this limited the pH range over which a comparison could be made. Nevertheless, it is evident from Table 5.3 that the standard Eksteen lime requirement (C), using an R-value of 10, consistently underestimated the lime requirement relative to the other two methods of calculation (A & B). Furthermore, it is clear that the method of J.J.N. Lambrechts (University of Stellenbosch, personal communication, 1998) consistently overestimates the lime requirement relative to the Eksteen method, using the calibration-derived R-value of 11.2. Since the R-value used in the Eksteen method was specifically derived for that sample population, rather than being an assumed value, it may be argued that the Eksteen/calibrated R-value method was likely to have been the most accurate of the two methods. This could not be verified under field conditions. However, the fact that calibration of the R-values resulted in lower lime predictions than the $(1.25 \times \text{Ca})$ modification of the approach of the Eksteen formula as proposed by J.J.N. Lambrechts (University of Stellenbosch, personal communication, 1998) implies that this latter method of lime requirement determination should be further refined.

Table 5.3 Comparison between lime requirement to obtain a pH_{KCl} of 5.5 in selected Western Cape, structured, high Mg:Ca ratio soils as predicted by the Eksteen method using a model fitted R-value of 11.2 (A), and the Eksteen method as adapted for structured, high Mg:Ca ratio subsoils by J.J.N. Lambrechts (University of Stellenbosch, personal communication, 1998) (B), using an R-value of 7.2 as for normal soils. The lime requirement as calculated by the Eksteen method using the standard R-value of 10, is also given for comparison (C).

Sample no.*	Lime status	pH_{KCl}	H	Ca ($\text{cmol}_e \text{ kg}^{-1}$)	Mg	Lime requirement ($\text{t ha}^{-1} 15 \text{ cm}^{-1}$)		
						A	B	C
3210	limed	4.18	2.28	1.07	6.13	6.01	7.36	5.67
3110	unlimed	4.21	1.97	0.70	5.98	5.05	6.49	4.74
3102	unlimed	4.87	1.04	0.83	3.02	2.56	3.15	2.38
3204	limed	5.21	0.73	1.97	2.48	1.22	1.36	1.03
3104	unlimed	5.24	0.73	1.29	4.33	0.84	1.78	0.61
3106	unlimed	5.28	0.83	1.04	7.75	0.17	2.28	0.00
3206	limed	5.30	0.73	0.98	7.44	0.00	1.97	0.00
3202	limed	5.36	0.73	1.31	4.84	0.66	1.76	0.42
3212	limed	5.36	0.73	1.16	4.25	0.91	1.86	0.69

*Samples included if $\text{pH}_{\text{KCl}} < 5.5$

$$A = \frac{11.2H - (\text{Ca} + \text{Mg})}{11.2 + 1} \times 4$$

$$B = \frac{7.2H - 1.25\text{Ca}}{7.2 + 1} \times 4$$

$$C = \frac{10H - (\text{Ca} + \text{Mg})}{10 + 1} \times 4$$

5.3.5.1 Estimation of Mg neutralising capacity

The R:pH relationship for the structured high Mg:Ca ratio subsoils is illustrated in Figure 5.7. By using these soil-specific R-values, the lime requirement of these soils to obtain a pH of 5.5 could be calculated, as was done in Table 5.3. The normal soils, which were the topsoils of the structured soils, had an R-value of 7.2 at pH 5.5. In the previous section the high R-values of the structured soil group were attributed to the limited neutralising capacity of Mg, where an R-value of 11.2 corresponded to a soil pH of 5.5. The soil Mg content that is effective in neutralising soil acidity could then be calculated, using the R-value of normal soils (7.2) in the Eksteen formula, then solving for Mg, on the basis that the lime requirement (x), Ca and H are known. The method for solving Mg was as follows:

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

$$\frac{x}{F} = \frac{RH}{R + 1} - \frac{Ca}{R + 1} - \frac{Mg}{R + 1}$$

$$\frac{Mg}{R + 1} = \frac{RH}{R + 1} - \frac{Ca}{R + 1} - \frac{x}{F}$$

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

By calculating the effective Mg content for all twelve of the soils that were used to determine the R:pH relationship for structured soils, the average ratio of effective Mg content to soil Mg content could be determined. Even those that had no lime requirement (negative values), could be used. This ratio of effective Mg to soil Mg can be used to adapt the Eksteen formula for the structured high Mg:Ca ratio soils. In Appendix VIII the effective Mg content of the twelve soil samples are listed, together with an example of the calculation procedure. The ratio of effective Mg to soil Mg is also given in Appendix VIII. The average ratio was calculated at 0.53 implying that only about half of the soil Mg is effective in neutralising soil acidity. Therefore, for high Mg:Ca ratio soils the Eksteen formula can be adapted as follows:

$$x = \frac{RH - (Ca + 0.5Mg)}{R + 1} \times F$$

The contribution of Mg is significantly greater in this formula than in the adapted formula of J.J.N. Lambrechts (University of Stellenbosch, personal communication, 1998). It must be kept in mind that the above formula could well be applicable only to the soil populations used in this study. Testing will be needed to determine whether this formula can effectively be applied to a wider population of structured Mg-rich soils.

5.4 Conclusions

The R:pH relationship of the population of normal soils in this research differed from that of the standard Eksteen relationship. Over-liming of organic-rich soils is a consequence of the pH-dependant acidity associated with organic matter. Therefore, the total extracted acidity (H) should be corrected with the organic matter correction factor (OMCF) before the lime requirement is calculated with the Eksteen formula. Due to the lack of buffer capacity of pale coloured sandy soils, it was suggested that these soils be limed, on an equivalent basis, to their total extractable acidity. If $Ca + Mg > 1.5$, the extractable acidity must be corrected for residual lime before the lime requirement is calculated. The neutralising capacity of Mg in the structured, high Mg:Ca ratio subsoils was not equivalent to that of Ca. Magnesium was only half as effective as Ca in neutralising soil acidity. This difference must be taken into account during the calculation of the lime requirement.

5.5 References

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6. EXCHANGEABLE ALUMINIUM

6.1 Introduction

The presence of soluble aluminium (Al) has been shown to be a major limiting factor with regard to sustained plant production on acid soils (Noble & Harding, 1989). For this reason Kamprath (1970) and Reeve & Sumner (1970) individually suggested that the calculation of lime requirement should be based on the exchangeable Al content, the principal function of the lime being to eliminate Al toxicity. The Cedara method of lime requirement determination used in South Africa is based on this principle. Methods of lime requirement determination based on Al-neutralisation have been found to be highly effective on highly weathered soils. The objective of this section was to determine the relationship between soil pH and exchangeable Al.

6.2 Materials and methods

Exchangeable Al was determined on each sample in the soil population by the methods described in Sections 2.2.3.7 and 2.2.3.8. Both methods entailed extractions with 1M KCl. In Method 2.2.3.7, the soil sample was shaken with KCl for one hour after which the Al in the KCl leachate was freed from its hydroxides by the addition of NaF and determined by titration with HCl. In the case of Method 2.2.3.8, the Al in the KCl leachate after a one-hour standing period, was determined by inductively coupled plasma emission spectroscopy (ICP).

6.3 Comparison between methods

From Figure 6.1 it is clear that there is a strong linear relationship ($R^2 = 0.997$) between the two methods of determining exchangeable Al. It is of interest that Method 2.2.3.8, which entailed leaching the soil with 1M KCl, extracted 13.9% more Al on average than did Method 2.2.3.7, which entailed active shaking. The equilibration time in both methods was one hour. Lin & Coleman (1960) used different 1M neutral salt solutions to extract exchangeable Al and found that the solutions extracted similar amounts of Al, provided that the leaching process was sufficiently exhaustive. In this trial the fact that the method which merely entailed allowing the soil to stand in contact with the KCl, apparently extracted more Al than where the soil/KCl suspension was actively shaken, appears contradictory on the principle that active shaking might be expected to extract more Al than merely allowing the suspension to remain stationary. However, there are two mechanisms which could have given rise to this anomaly:

- During the equilibration period, K^+ in the KCl extracting solution may exchange for Al^{3+} on the exchange sites. This exchange is driven by the concentration gradient that is created between the soil solution and the exchange complex during extraction. When exchange equilibrium is reached, the exchanged Al in the soil solution would be in equilibrium with Al on the exchange complex. Therefore, provided that Al is present in the equilibrium solution, some Al will always remain adsorbed onto the exchange complex. The extraction method, that entails leaching, will reinstate the Al concentration gradient by continually replacing the soil solution and should therefore extract more Al.

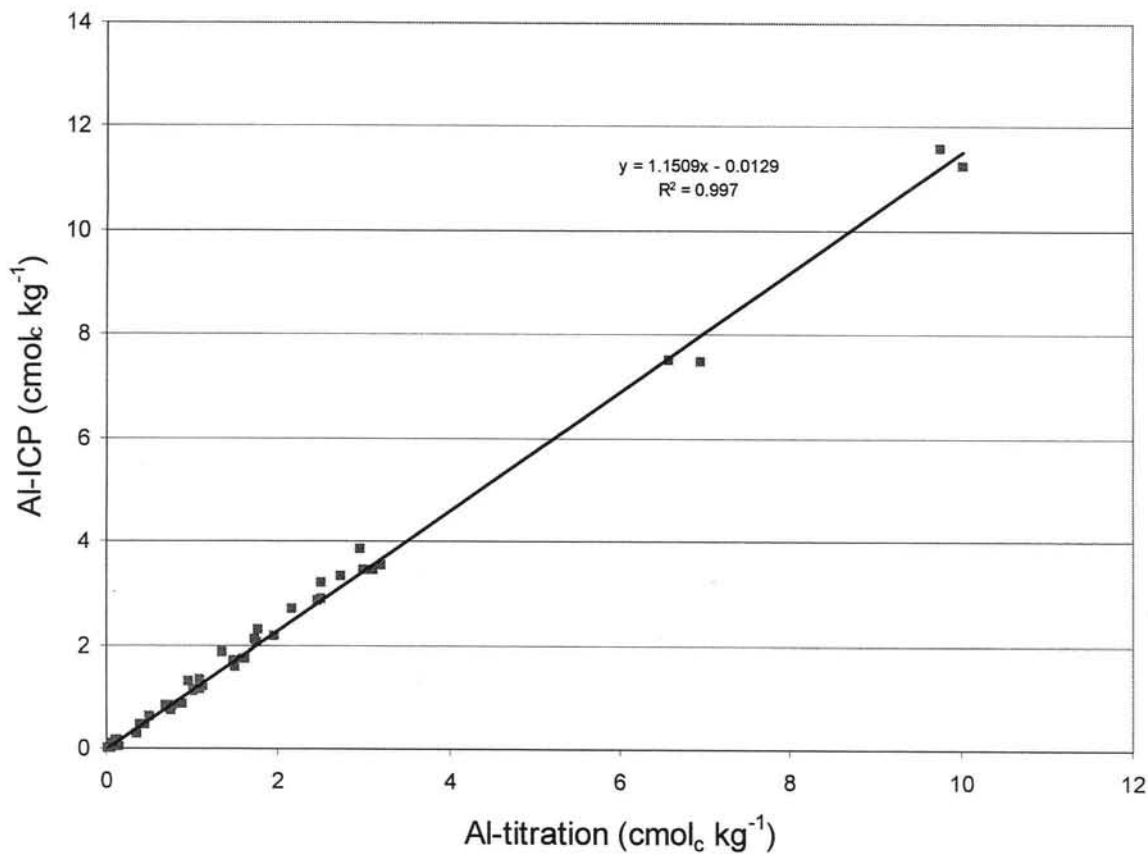


Figure 6.1 Relationship between exchangeable Al as determined by ICP in a 1M KCl leachate after a one hour equilibration period at rest, and Al as determined by HCl titration in a 1M KCl extract following a one hour period of shaking and the addition of NaF to free the Al from its hydroxides.

- If it is accepted that the ICP method of Al determination, which involves ionisation and breakdown of compounds at a temperature of 11 000 °C, is a more exhaustive method of Al determination than is the ambient-temperature titration method, despite the addition of NaF. The formation of Al polymers may be expected to cause fewer hydroxides to be freed by the addition of NaF. This polymer formation would reduce the amount of Al determined by titration. Such polymers would, in contrast, break down during ICP analysis.

6.4 Relationships between exchangeable Al and soil pH

Pionke & Corey (1967) observed that exchangeable Al concentrations were primarily related to soil pH. In this present study it is clear from Figure 6.2 that pH, as determined electrometrically in a soil / 1M KCl suspension (Method 2.2.3.1), has a major effect on exchangeable Al (ICP-determined). A boundary line was visually inserted in Figure 6.2 at pH_{KCl} 4.64. According to the boundary line, concentrations of exchangeable Al at pH_{KCl} levels of approximately 4.7 and greater was negligible. Therefore Al toxicity would appear to be worthy of consideration only at pH_{KCl} values lower than approximately 4.7.

6.5 Relationships between exchangeable Al, CEC and organic matter

According to Kotzé (1974) exchangeable Al is a function of pH, CEC and organic matter. Exchangeable Al is affected by these three factors in the following manner:

1. A decrease in pH increases exchangeable Al.
2. An increase in CEC increases exchangeable Al.
3. An increase in organic matter content decreases exchangeable Al (Poinke & Corey, 1967; Thomas, 1975; Hoyt, 1977).

Since the sample population used in this study varied widely in terms of pH, CEC and organic matter content, it was not possible to critically examine the effect of these factors independently from one another. Kotzé (1974) found that, below pH 5.0, the relationship between exchangeable Al and pH is parabolic. Such a parabolic relationship was found for the present soil population studied (Figure 6.2). A stepwise regression analysis using Statgraphics (version 7.11) was applied to those soils from the sample population which had pH values of less than 5.0, to determine the effect of pH, CEC and organic matter on exchangeable Al (determined with ICP). Soils with pH levels above 5.0 contained negligible amounts of exchangeable Al and were therefore excluded. All three variables [exponent pH, CEC and organic matter content (expressed as % carbon)] were introduced into the model at a 95% probability. The prediction model was not very strong, with an R^2 value of 0.524. The prediction model was as follows:

$$\text{Exchangeable Al} = 1.5912 - 0.000043 (\text{exp.pH}) + 0.3961 (\text{CEC}) - 1.0912 (\%C)$$

This relationship accords with the findings of Kotzé (1974). The negative coefficient introduced by the % organic carbon confirms that an increase in organic matter causes a decrease in exchangeable Al. It is pertinent in Section 3.2, that increasing organic matter contents were associated with increasing CEC

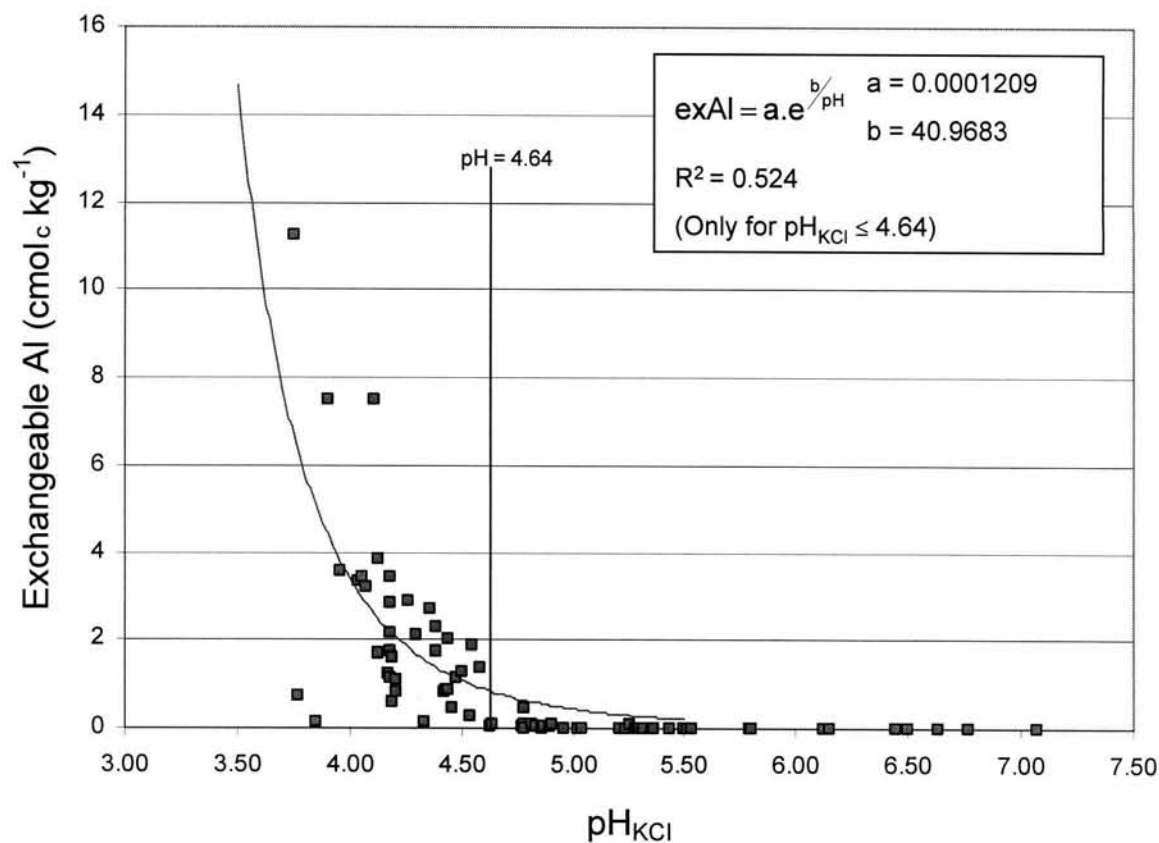


Figure 6.2 Relationship between exchangeable Al as determined by ICP in a 1M KCl leachate after a one hour equilibration period at rest, and soil pH determined electrometrically in a continuously stirred 1M KCl suspension. The boundary line was visually inserted to indicate the pH_{KCl} value above which exchangeable Al concentrations is negligible.

values. However, high CEC values due to the presence of relatively abundant organic matter are associated with lower levels of exchangeable Al than where the high CEC value due to inorganic material. This is consistent with the limited occurrence of Al in organic material, in contrast to the presence of Al as a structural and potentially releasable component of many soil minerals.

6.6 Conclusions

Toxic concentrations of exchangeable Al are unlikely to occur at soil pH_{KCl} levels of approximately 4.7 and above. Soil organic matter reduces exchangeable Al.

6.7 References

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7. SEQUENTIAL FRACTIONAL EXTRACTION OF Ca AND Mg

7.1 Introduction

As noted in Sections 1.3.2, 5.3.5 and 5.3.5.1, Mg has a very limited ability to neutralise soil acidity under certain conditions, which may lead to underestimation of the lime requirement predicted for high Mg soils by the Eksteen method. The hypothesis, which is tested in this section, is that Mg is present in the soil in a semi-crystalline form, e.g. brucite type interlayers, and that these interlayers slowly dissolve during extraction procedures. Such release would inevitably be slower under normal soil conditions than during chemical extraction. Fractional extractions were carried out to determine whether release of Mg from brucite type minerals was causing the high extractable Mg levels in the structured, high Mg:Ca ratio subsoil samples.

7.2 Materials and methods

7.2.1 Soils: Soils were selected from the organic, normal and structured, high Mg:Ca ratio soil groups. The normal samples consisted of the topsoils overlying the structured, Mg-rich subsoils. The selected soil samples, and certain of their characteristics, are listed in Table 7.1.

7.2.2 Clay mineral analysis: A sample of each of the soils used in this work was analysed by the Institute for Soil, Climate and Water (Agricultural Research Council, Pretoria) for clay minerals on the $<2.0 \mu\text{m}$ fraction by X-ray diffraction. Results of these analyses are presented in Table 7.2.

7.2.3 Sequential fractional extractions: The fractional extractions were carried out under reduced pressure in Buchner funnels, using 0.2M NH_4OAc buffered at pH 7 as a displacing agent. After placing a filter paper into the funnel and seating it firmly under vacuum, the vacuum was disconnected and 20.0 g of soil was spread evenly across the filter. Fifteen cm^3 of 0.2M NH_4OAc was added to the soil, care being taken to ensure that the even spread of the soil was not disturbed. After the elapse of a 60-second interval the vacuum was reconnected. Reduced pressure was maintained for 5 minutes after the last visible traces of extractant solution had disappeared. The filtrate in the collecting tube was then removed and the process repeated. A total of 10 consecutive extraction cycles were performed on each sample at ambient room temperature. The concentration of Ca and Mg was determined in each filtrate by means of an atomic absorption spectrophotometer. The results of these extractions for the selected organic, normal and structured, high Mg:Ca ratio soils, are presented in Appendix IX A.

7.3 Discussion

Figures 7.1, 7.2 and 7.3, respectively, illustrate the patterns of Ca and Mg release during fractional extraction from respectively the organic, normal and structured, high Ca:Mg ratio soils as presented in Table 7.3. The Ca and Mg release is expressed as a cumulative percentage of the total amount that was extracted by the 10 consecutive extractions. The organic and the normal soil samples had similar extraction curves except that Ca and Mg were initially extracted with greater ease from the normal soils. This was probably a reflection of the greater CEC values of the organic soils.

Table 7.1 Summary of soil characteristics of selected Western Cape soil samples for fractional extraction of Ca and Mg.

Sample no.	Soil group	pH _{KCl}	Clay (%)	C (%)	CEC (cmol _c kg ⁻¹)	Exchangeable cations (cmol _c kg ⁻¹)			
						Ca	Mg	K	Na
1105	organic	4.19	20.2	1.86	8.02	0.99	0.43	0.32	0.04
1204	organic	6.12	21.0	2.61	13.71	7.42	2.26	1.90	0.17
1211	organic	5.50	28.2	2.51	12.26	6.03	1.69	0.41	0.27
3105	normal	5.04	12.8	0.77	4.16	1.73	0.60	0.18	0.05
3111	normal	5.02	9.0	0.88	4.10	1.60	0.62	0.26	0.13
3209	normal	4.64	16.2	0.45	4.13	1.27	0.96	0.08	0.16
3106	structured	5.28	72.8	0.21	13.33	0.90	9.66	0.12	0.74
3110	structured	4.21	62.2	0.11	11.31	0.36	7.07	0.09	0.88
3112	structured	5.79	77.0	0.17	12.93	0.81	9.89	0.11	0.73
3202	structured	5.36	44.0	0.13	9.49	1.19	5.52	0.18	0.28
3206	structured	5.30	65.2	0.12	12.49	0.89	8.80	0.10	0.95

Table 7.2 Mineralogy of the clay fractions of selected Western Cape soil samples for fractional extraction of Ca and Mg.

Sample no.	Quartz (%)	Mica (%)	Smectite (%)	Kaolinite (%)	Goethite (%)	Interstratified clay minerals (%)	Vermiculite (%)	Serpentine (%)
1105	14	24	12	34	5	11		
1204	12	28		36	6	8	10	
1211	14	26		32	5	10	13	
3105	14	57	5	22	2			
3106		32		58	10			
3110	6	34	8	46	6			
3111	25	46	7	18	1			
3112		30		58	12			
3202		28		53	11	8		
3206		39		54	7			
3209	12	53		14	2		6	13

It is also noteworthy that, for the organic and normal soils, Mg was predominantly extracted with greater ease than Ca. This was anticipated because, according to Edmeades (1980), most soil minerals and soils show a preference for Ca relative to Mg. However, in the case of the structured, high Mg:Ca ratio soils, Ca was extracted with greater ease than was Mg. In contrast to the organic and normal soils, extractable Ca from the structured, high Mg:Ca ratio soils became undetectably small after four to seven extractions (Appendix IX A). From Figures 7.1, 7.2 and 7.3 it would appear that the release of Ca and Mg over the first two extractions was greater from the structured soils than from the normal and organic soils. Nearly 90% of the Ca and Mg in the structured soils were removed in the first two extractions. This slower rate of release from, especially, the organic soils is more clearly apparent from the tabulated data (Table 7.3). It is apparent from the values shown in Table 7.3 that the ease of Ca and Mg extraction from the samples decreased in the sequence: structured, high Mg:Ca ratio samples > normal samples > organic samples. Since the organic carbon content was relatively low in the structured, high Mg:Ca ratio samples, and intermediate in the normal samples, it appears probable that organic content is the factor which most effectively controls rate of release (buffering) of Ca and Mg with regard to sequential

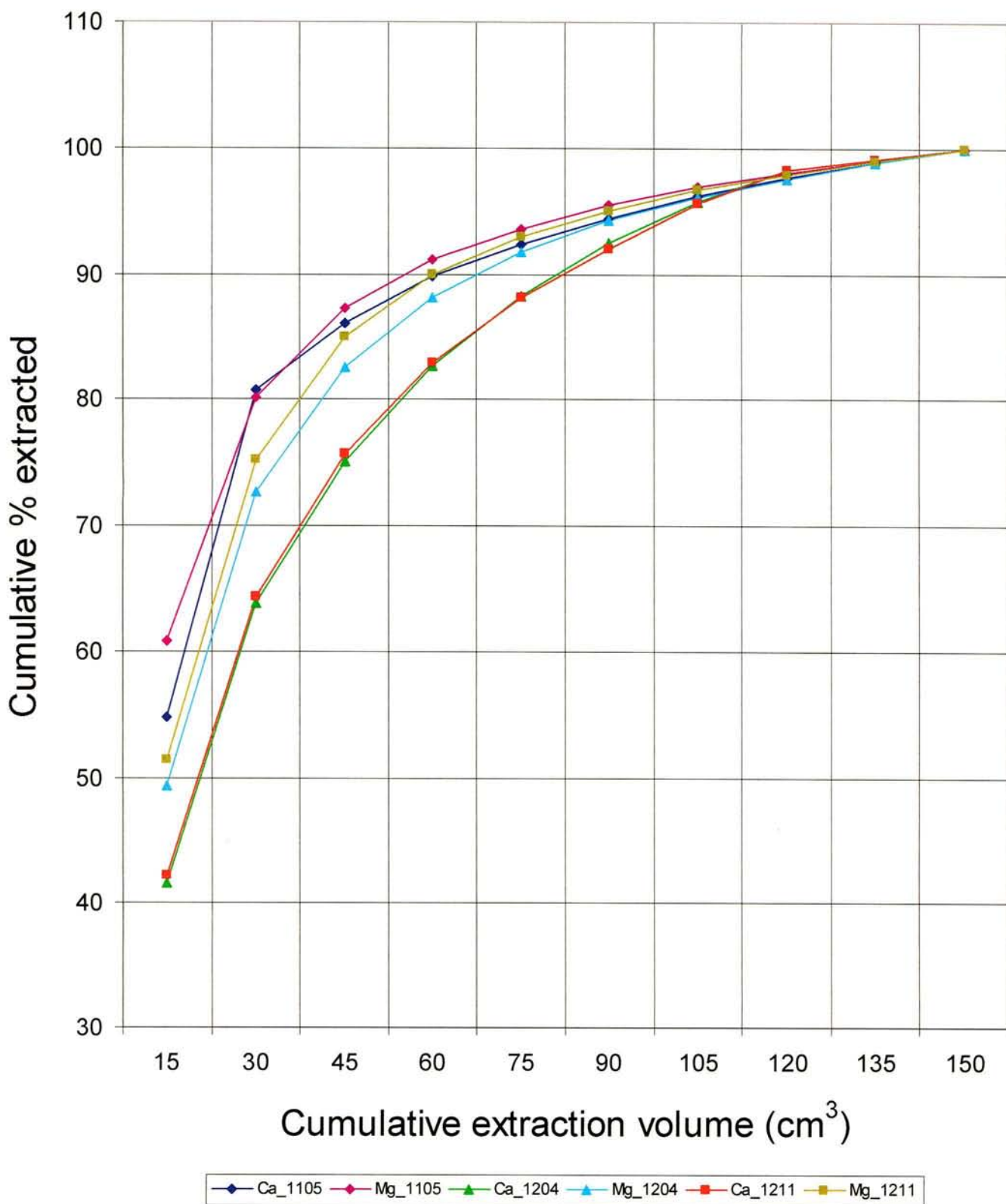


Figure 7.1 Fractional extraction of Ca and Mg with 0.2M NH₄OAc, buffered at pH 7, from selected Western Cape organic soil samples.

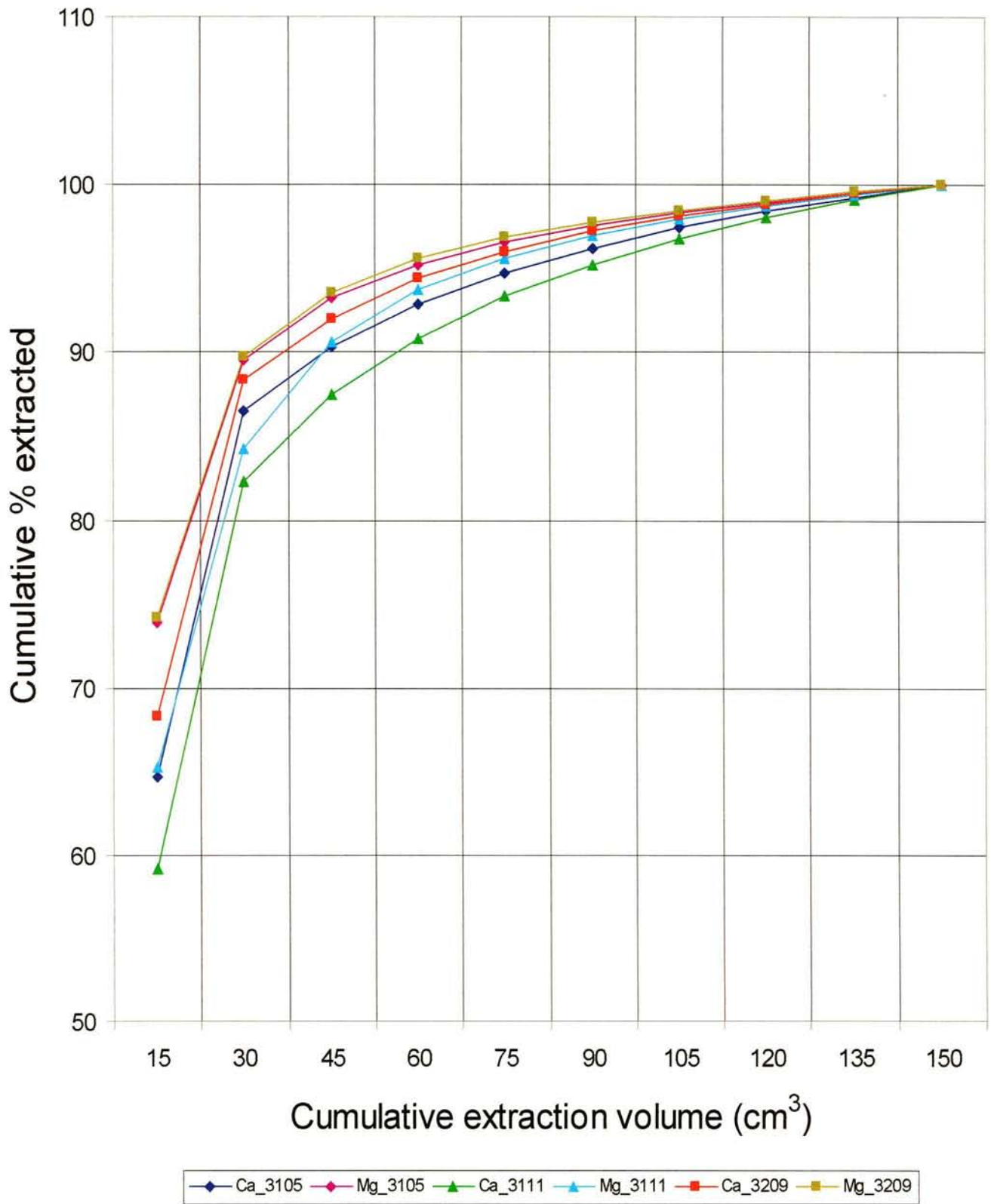


Figure 7.2 Fractional extraction of Ca and Mg with 0.2M NH_4OAc , buffered at pH 7, from selected Western Cape normal soil samples.

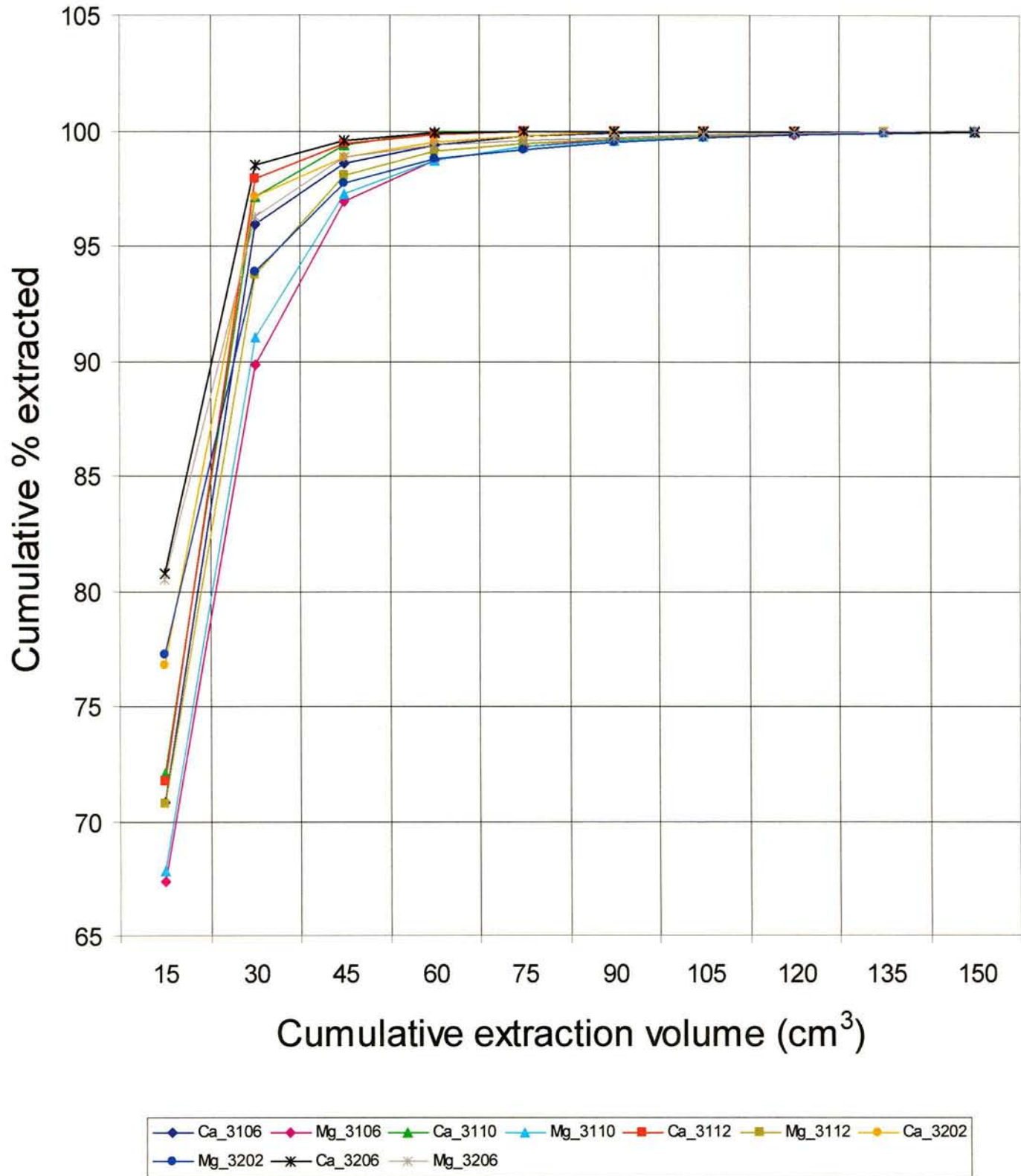


Figure 7.3 Fractional extraction of Ca and Mg with 0.2M NH₄OAc, buffered at pH 7, from selected Western Cape structured, high Mg:Ca ratio soil samples.

Table 7.3 Fractional extractions of Ca and Mg using 0.2M NH₄OAc extracting solution, buffered at pH 7, of three Western Cape soil groups.

Organic soil samples

Cumulative extraction volume (cm ³)	Ca (Cumulative extraction %)			Mg (Cumulative extraction %)		
	Sample no.					
	1105	1204	1211	1105	1204	1211
15	54.7	41.6	42.3	60.9	49.4	51.4
30	80.8	63.8	64.3	80.2	72.7	75.2
45	86.1	75.1	75.7	87.2	82.5	84.9
60	89.8	82.7	83.0	91.2	88.1	89.9
75	92.3	88.3	88.1	93.6	91.7	92.9
90	94.5	92.4	92.0	95.5	94.3	95.1
105	96.2	95.7	95.7	97.0	96.1	96.7
120	97.6	98.3	98.2	98.1	97.5	97.9
135	98.8	99.2	99.2	99.1	98.8	99.0
150	100.0	100.0	100.0	100.0	100.0	100.0

Total amount extracted (mg kg ⁻¹)					
100.3	788.7	686.1	27.7	133.1	117.0

Normal soil samples

Cumulative extraction volume (cm ³)	Ca (Cumulative extraction %)			Mg (Cumulative extraction %)		
	Sample no.					
	3105	3111	3209	3105	3111	3209
15	64.7	59.2	68.3	73.8	65.3	74.2
30	86.6	82.3	88.3	89.5	84.3	89.8
45	90.3	87.4	92.0	93.2	90.6	93.6
60	92.9	90.9	94.5	95.2	93.7	95.6
75	94.8	93.3	96.0	96.6	95.6	96.9
90	96.2	95.2	97.2	97.6	96.9	97.8
105	97.4	96.8	98.1	98.3	98.0	98.5
120	98.4	98.0	98.9	99.0	98.8	99.1
135	99.3	99.1	99.5	99.5	99.4	99.6
150	100.0	100.0	100.0	100.0	100.0	100.0

Total amount extracted (mg kg ⁻¹)					
175.4	152.6	129.8	37.4	32.6	57.0

Structured soil samples

Cumulative extraction volume (cm ³)	Ca (Cumulative extraction %)					Mg (Cumulative extraction %)				
	Sample no.									
	3106	3110	3112	3202	3206	3106	3110	3112	3202	3206
15	70.8	72.1	71.8	76.8	80.8	67.4	67.8	70.8	77.2	80.5
30	95.9	97.1	97.9	97.1	98.5	89.8	91.0	93.7	93.9	96.3
45	98.6	99.4	99.4	98.8	99.6	96.9	97.3	98.0	97.7	98.8
60	99.4	100.0	99.9	99.5	99.9	98.7	98.7	99.1	98.8	99.4
75	99.7	100.0	100.0	99.8	100.0	99.3	99.3	99.5	99.2	99.6
90	99.9	100.0	100.0	99.9	100.0	99.6	99.6	99.7	99.5	99.7
105	100.0	100.0	100.0	100.0	100.0	99.8	99.8	99.8	99.7	99.8
120	100.0	100.0	100.0	100.0	100.0	99.9	99.9	99.9	99.8	99.9
135	100.0	100.0	100.0	100.0	100.0	99.9	99.9	99.9	99.9	100.0
150	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Total amount extracted (mg kg ⁻¹)										
100.8	35.0	92.2	120.5	94.7	673.1	468.8	700.6	377.3	613.3	

extraction procedures. According to Tate & Theng (1980) organic materials in soils are able to hold Ca and Mg as carboxylate salts and as chelates. The slight preference shown for Mg over Ca by the structured soils is difficult to explain. Vermiculite and soils containing vermiculite are known to exhibit a preference for Mg (Wild & Keay, 1964; Peterson *et al.*, 1965; Dolcater *et al.*, 1968). Vermiculite preferably adsorbs Mg when the percentage of Mg^{2+} ions in the equilibration solution exceeds 30 to 40, or when Mg^{2+} is the dominant adsorbed cation (Peterson *et al.*, 1965). However, according to the clay mineral analysis (Table 7.2), the structured soils do not contain vermiculite.

The supposition that Mg would be released from minerals present in the structured, high Mg:Ca ratio subsoils could not be proved. The steeply inclined cumulative extraction curves from these soils (Figure 7.3) implied that Mg was not being released from Mg-rich minerals such as brucite in sufficient quantities to maintain a constant level of extractable Mg in the face of successive extractions. Furthermore, it appears from Table 7.3 that most of the Mg was extracted during the first few extractions. The largest component of the Mg, therefore, appears to be in a readily exchangeable form. There is, therefore, no evidence for the existence in the structured, high Mg:Ca ratio soils of a Mg-yielding, brucite-type mineral. On the other hand, the slight preference that was shown for Mg over Ca could be related to the presence of such minerals. It is possible that the severity of the 0.2M NH_4OAc extraction process was not sufficient to facilitate the release of Mg from structural sites on soil minerals. In order to investigate this possibility, two structured and one normal sample were selected for further study. These soils were extracted using the same technique as previously but using 0.1M HCl as the extracting solution. The results of the 0.1M HCl and extractions are presented in Appendix IX B, with the cumulative extraction percentages given in Table 7.4. The results of these extractions are presented graphically in Figure 7.4, with the comparative NH_4OAc extraction presented in Figure 7.5.

Table 7.4 Fractional extraction of two selected Western Cape structured soil samples (3106, 3202) and one normal soil sample (3105) using 0.1M HCl as extracting solution.

Cumulative extraction volume (cm ³)	Ca (Cumulative extraction %)			Mg (Cumulative extraction %)		
	Soil group/Sample no.			Soil group/Sample no.		
	Normal 3105	Structured 3106	Structured 3202	Normal 3105	Structured 3106	Structured 3202
15	77.7	39.0	40.9	78.3	41.4	42.3
30	93.9	64.9	69.1	92.2	67.3	70.4
45	96.8	78.8	82.8	94.8	79.9	83.4
60	97.8	85.5	88.9	96.2	86.8	89.8
75	98.5	90.3	93.0	97.2	91.4	93.7
90	98.9	93.7	95.7	97.9	94.4	96.2
105	99.3	96.3	97.5	98.5	96.5	97.7
120	99.7	98.1	98.7	99.1	98.1	98.8
135	99.9	99.2	99.5	99.6	99.2	99.5
150	100.0	100.0	100.0	100.0	100.0	100.0

Total amount extracted (mg kg ⁻¹)						
234.0	84.0	111.3	37.1	593.7	324.6	

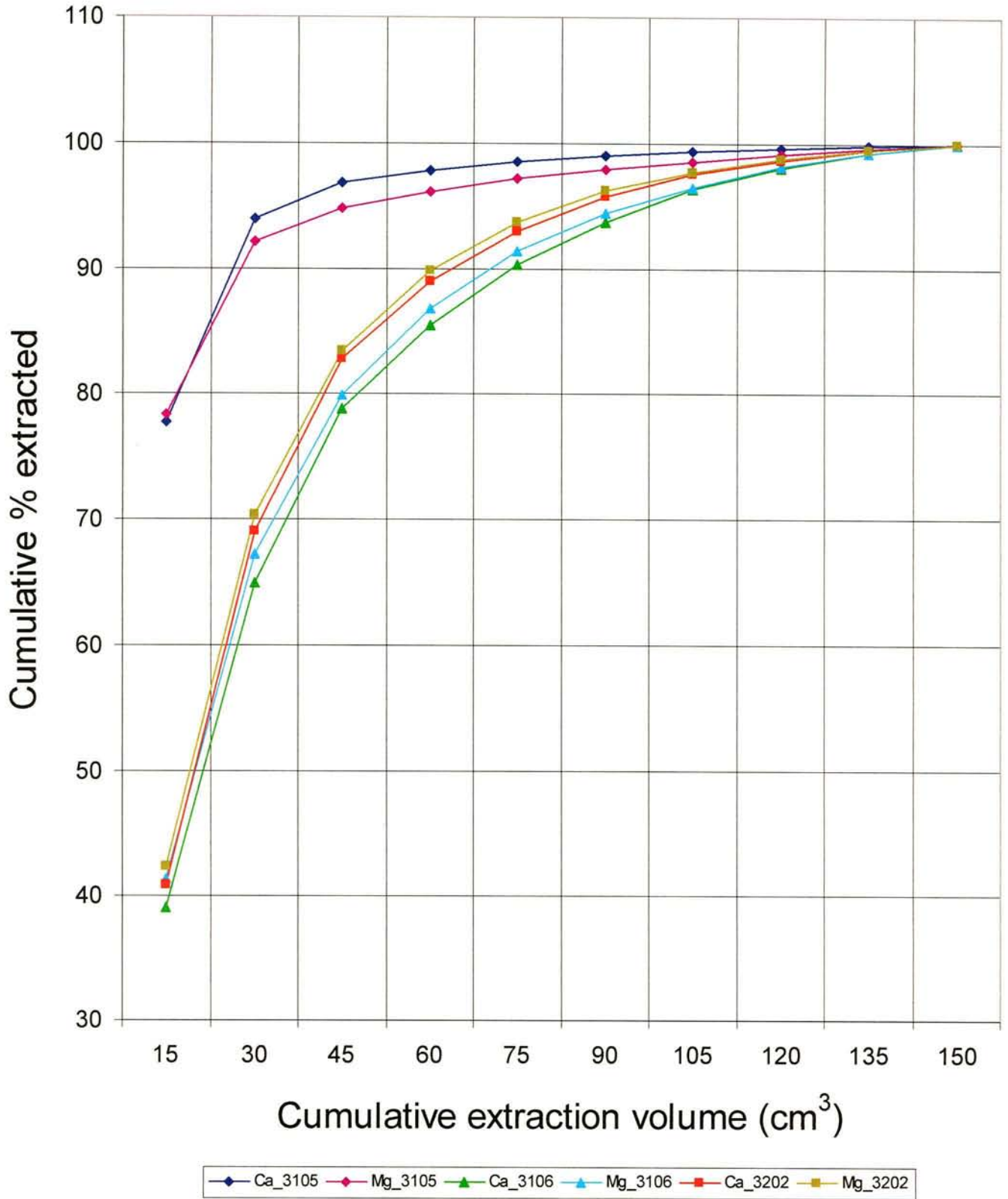


Figure 7.4 Fractional extraction of Ca and Mg with 0.1M HCl from two selected Western Cape structured, high Mg:Ca ratio soil samples (3106, 3202) and from a normal soil sample (3105).

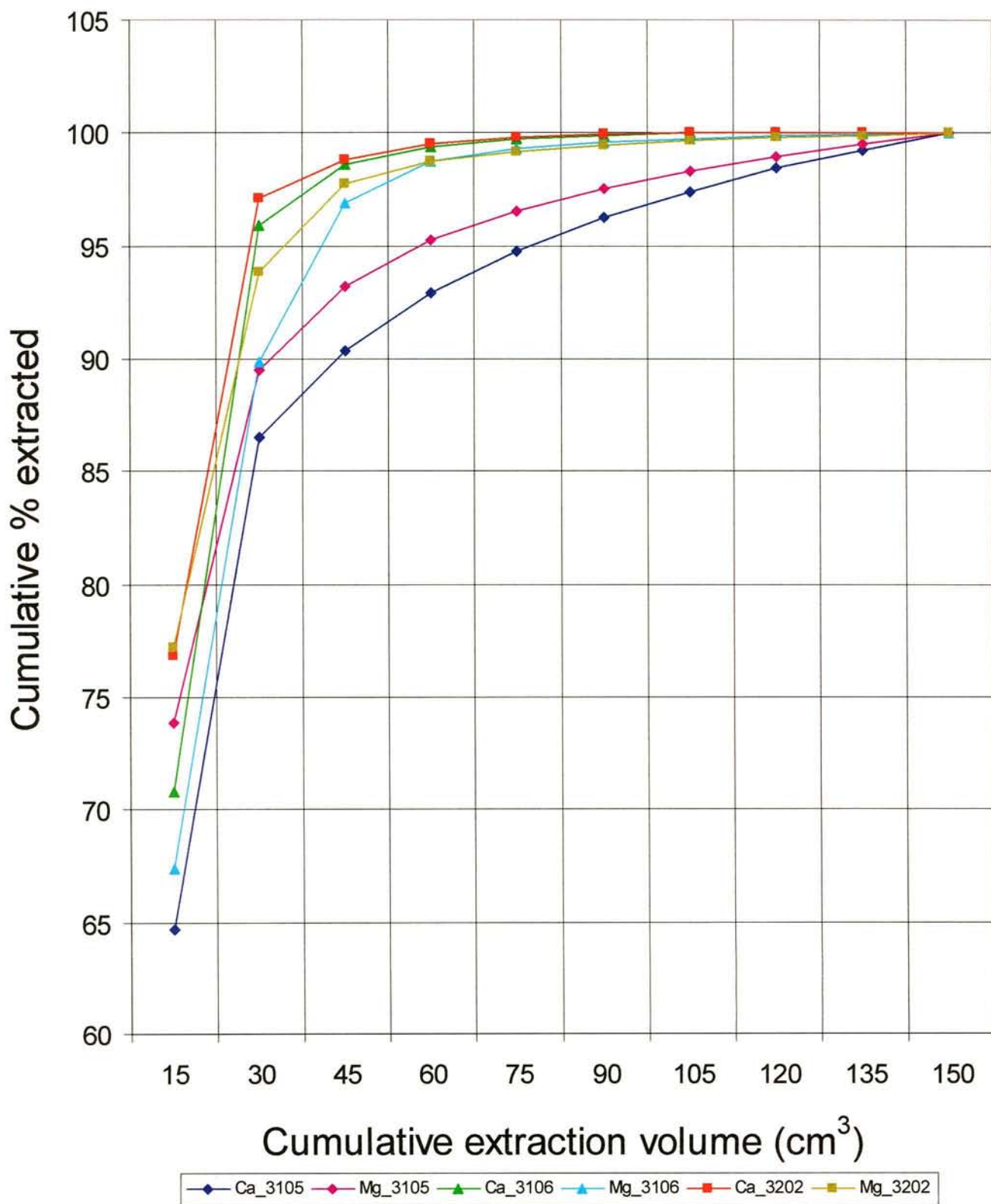


Figure 7.5 Fractional extraction of Ca and Mg with 0.2M NH₄OAc, buffered at pH 7, from two selected Western Cape structured, high Mg:Ca ratio soil samples (3106, 3202) and from a normal soil sample (3105).

The 0.1M HCl extracting solution resulted in an extraction curve (Figure 7.4) of similar shape to that given by 0.2M NH_4OAc from the organic (Figure 7.1) and normal (Figure 7.2) soil samples. The curves reflected some measure of Ca release from all three samples during all of the ten extraction cycles, in contrast to the 0.2M NH_4OAc extractions which indicated abrupt Ca release endpoints in the case of the structured, high Mg:Ca ratio subsoils (Appendix IX A).

The 0.1M HCl extractant removed less Ca and Mg from the Mg-rich samples (3106, 3202) (Table 7.4) after 10 extractions than did the 0.2M NH_4OAc (Table 7.3). This may explain the abrupt termination of Ca release from the structured soils, which were extracted with 0.2M NH_4OAc (Appendix IX A). However, the converse was true for the normal (topsoil) sample 3105 (Table 7.4). Why more Ca was extracted from sample 3105 by the 0.1M HCl than the 0.2M NH_4OAc is unclear but may reflect the presence in sample 3105 of some residual calcium carbonate or calcium-containing minerals. The levels of Mg extracted by both methods were similar. From Figure 7.4 and Figure 7.5 it is apparent that Ca and Mg was extracted with greater ease from sample 3105 using 0.1M HCl as a extractant. As was the case in this trial, Stout (1982) found that more Mg was extracted from lighter-textured soils, and less from heavier-textured soils, where a double acid method was used than where the extractant was NH_4OAc . In accordance with the liotropic series for monovalent cations ($\text{Li} < \text{Na} < \text{H}_3\text{O}^+ < \text{K} < \text{NH}_4^+ < \text{Rb} < \text{Cs}$) (Talibudeen, 1981), NH_4^+ should exchange for other cations more readily than H_3O^+ . Clays certainly display a stronger affinity for NH_4^+ than for H_3O^+ in exchange reactions (Gilbert & Laudelout, 1965). Talibudeen (1981) referred to NH_4^+ as "the perfect displacing cation". For these reasons NH_4OAc should be more effective than HCl as an extracting solution, especially in view of the limited time which was allowed for contact between solution and soil, and because the concentration of the NH_4OAc solution was double that of the HCl.

The principle components of the clay fractions of samples 3105, 3106 and 3202 consisted of kaolinite and mica (Table 7.2). This fact provides no explanation for the rapid depletion of Ca by fractional leaching of the structured, high Mg:Ca ratio samples. Neither does it explain why Mg continued to be extractable long after Ca had ceased to be present in the leachates. If it were assumed that Mg and Ca were equally well buffered by the exchange complex, then both should be depleted at the same rate. Figure 7.3 shows that this was not the case.

It is most probable that the initial Ca levels in the structured, high Mg:Ca ratio samples was low and that the Ca was very poorly buffered, with the result that the available Ca was released quickly and the Ca levels soon decreased below the detection capabilities of the atomic absorption spectrophotometer. In contrast to this assumption was the fact that Mg, though present at similar and lower levels in the other samples, was not depleted as rapidly or as completely. It is clear that the structured, high Mg:Ca ratio samples released both Ca and Mg more rapidly (were more poorly buffered) than did the organic and normal soils (Table 7.3). Precisely why Ca and Mg were equally poorly buffered in the structured, high Mg:Ca ratio soils is unclear in view of the fact that the literature is unambiguous in asserting that soil exchange systems show a preference for Ca over Mg. Tucker (1985) found that clay subsoils which

contain very little organic matter bear very high percentages of their active cations in exchangeable (but poorly buffered) form. This is the most probable reason for the high extractability of both Ca and Mg from the structured, high Mg:Ca ratio subsoils and, if Ca was assumed to be originally present in lower quantities than Mg, would explain the higher exchange ratio on the Mg-rich samples and to a lesser extent in the topsoil samples. Since it appears that most of the Mg in the Mg-rich structured subsoils is readily exchangeable, the explanation for the lack of acid neutralising capability of Mg might be explained by a different mechanism than the presence of brucite interlayers. McBride (1978) found that Mg readily co-precipitated with Al to form an amorphous Mg-Al gel. The liming of acid soils could produce such gel-like material (Grove *et al.*, 1981). This might be the explanation for the lower neutralising capacity of Mg where acid soils contain large amounts of Mg.

7.4 Conclusions

Sequential extraction trials provided no definite evidence for the existence in the structured, high Mg:Ca ratio soils of a brucite interlayered mineral that might have been capable of delivering Mg from structural reserves into exchangeable form. The ease with which Ca and Mg were extractable from the structured, high Mg:Ca ratio soils was apparently linked to the low organic matter content of those soils.

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8. CONCLUSIONS

Aspects investigated in this study were factors which affect the prediction of lime requirement by the Eksteen method. Analyses were carried out on a population of sandy soils, high organic matter soils and structured soils having high exchangeable Mg:Ca ratios, in addition to normal soils. The following conclusions were reached:

1. The R:pH relationship determined in this trial differed from the standard Eksteen R:pH relationship. The standard Eksteen curve gives R-values of 5.0 and 10.0 at pH_{KCl} levels of 5.0 and 5.5, respectively, and these values are widely used for advisory purposes. In contrast, the corresponding R-values for the present population of normal soils, were 4.3 and 7.2. These results indicate that inappropriate R-values may be used for some soil groups. This is a potential source of error, and it is suggested that the R:pH relationship which is currently used for advisory purposes should be refined through further research.
2. The over prediction of lime requirement for organic-rich topsoils, which is an acknowledged characteristic of the Eksteen method, was found to stem from the large pH-dependant acidity component that is associated with organic matter. Further, it was found that the pH-dependant acidity contributed by mineral components was limited and differed between soil groups. The pH-dependant acidity, which was mainly attributed to organic material, could be accounted for by adjusting the total extracted acidity (H), as routinely determined, using an organic matter correction factor (OMCF). The OMCF has a value of $0.202 \text{ cmol}_c \text{ kg}^{-1} \text{ pH unit}^{-1} \%C^{-1}$. Total extracted acidity (H) is corrected with the OMCF before the lime requirement is calculated by the Eksteen method (it is suggested to use the R-values for normal soils) in the following manner:

$$H_{\text{OMCF}} = H - \{(7 - \text{field } \text{pH}_{\text{KCl}}) \times \%C \times \text{OMCF}\}$$

3. Because of a lack of material capable of acting as a buffer for chemical exchange processes (clay and organic matter) the Eksteen method for lime requirement determination cannot be effectively applied to pale coloured sandy soils. It is suggested that these soils be limed, on an equivalent basis, to their total extracted acidity (H). The H must be corrected for residual lime by the determination of Ca and Mg in the 0.1M HCl extract. H should not be corrected unless Ca+Mg exceeds $1.5 \text{ cmol}_c \text{ kg}^{-1}$. This correction can be carried out in the following manner:

$$H_{\text{corrected}} = H - \{(\text{Ca} + \text{Mg}) - 1.5\}$$

After H is corrected, where necessary, the lime requirement can be calculated on the basis that $1 \text{ cmol}_c \text{ kg}^{-1}$ of H equals $1.61 \text{ t calcitic lime ha}^{-1} 15 \text{ cm}^{-1}$ soil depth (for a soil bulk density of 1500 kg m^{-3} and corrected for 70% lime purity).

4. The neutralising capacity of Mg in structured, high Mg:Ca ratio subsoils is not equivalent to that of Ca. This lower neutralising capacity of Mg leads to under estimation of the lime requirement by the Eksteen method. The extend of this under-liming depends on the level of Mg in the soils, and on the ratio of Mg to Ca. It was found that Mg was only half as effective as Ca in neutralising acidity. The Eksteen formula can be adapted to incorporate this effect, as follows:

$$x = \frac{RH - (Ca + 0.5Mg)}{R + 1} \times F$$

(It is suggested to use the R-values for normal soils)

5. No evidence was found to support the hypothesis that the high exchangeable Mg levels noted in the structured, high Mg:Ca ratio subsoils were due to release from semi-crystalline brucite interlayers. Most of the Mg in these soils was readily extractable, and sequential extractions revealed no tendency toward sustained release.
6. The occurrence of high, and possibly toxic, levels of Al was only observed in the present soil population at soil pH_{KCl} levels lower than approximately 4.7. The presence of Al at higher pH levels was negligible. The presence of organic matter had a negative effect on exchangeable Al levels.

Agricultural significance

This research confirms earlier observations that the Eksteen method for determining lime requirements is inaccurate when applied to sandy soils, soils with high organic matter contents and structured soils having high exchangeable Mg:Ca ratios. Partial explanations were provided for the anomalous lime requirements calculated for those soils by the Eksteen method. Of greatest practical importance, however, is the fact that methods were devised by which the Eksteen method can be adapted for use with soils having characteristics which previously rendered the method inapplicable.

Recommendations for further research

This research was carried out on a limited soil population. The adaptations made to the Eksteen method in this investigation must be tested on a wider soil population for further refinement and verification.

Appendix I. Particle size analysis of the 78 experimental soil samples.

Sample number	Clay (%)	Silt (%)	Fine Sand (%)	Medium Sand (%)	Coarse Sand (%)
	< 0.002 mm	0.02 - 0.002 mm	0.2 - 0.02 mm	0.5 - 0.2 mm	0.5 - 2 mm
1101	5.6	15.0	52.2	25.0	2.2
1102	8.4	11.2	56.0	23.0	1.4
1103	8.2	11.4	56.2	23.0	1.2
1104	33.4	18.8	33.8	7.4	6.6
1105	20.2	20.4	44.8	11.8	2.8
1106	35.8	32.8	29.8	1.0	0.6
1107	33.6	26.6	36.0	2.2	1.6
1108	17.2	31.2	41.8	5.6	4.2
1109	13.2	34.6	42.2	5.4	4.6
1110	32.8	34.8	26.2	4.0	2.2
1111	25.2	27.4	36.8	8.4	2.2
1112	12.2	21.2	57.6	7.8	1.2
1113	9.4	22.4	56.0	11.0	1.2
1114	9.2	15.0	60.2	13.4	2.2
1201	8.8	12.2	53.8	21.0	4.2
1202	11.8	12.0	53.0	18.6	4.6
1203	24.0	12.6	46.6	12.8	4.0
1204	21.0	34.8	38.4	4.8	1.0
1205	25.2	36.2	33.8	3.8	1.0
1206	39.8	29.0	28.4	2.4	0.4
1207	32.8	24.0	36.2	5.6	1.4
1208	25.2	23.6	41.2	9.2	0.8
1209	31.8	20.4	39.0	8.4	0.4
1210	25.0	20.2	43.6	10.8	0.4
1211	28.2	35.8	30.6	3.4	2.0
1212	33.4	34.6	28.2	2.6	1.2
1213	40.8	28.4	28.0	1.8	1.0
1214	16.6	27.8	51.2	3.6	0.8
1215	19.8	21.0	53.6	4.4	1.2
1216	28.0	16.0	51.0	4.4	0.6
1217	19.8	25.8	50.6	3.8	1.0
1218	24.8	28.0	43.4	2.4	1.4
1219	24.8	20.6	51.0	3.6	0.0
2101	1.3	1.5	6.1	15.5	75.6
2102	3.0	1.6	18.8	27.6	49.0
2103	3.9	4.2	18.5	31.8	41.6
2104	4.6	15.5	20.2	29.7	30.0
2105	1.4	7.0	16.1	35.6	39.9
2106	2.4	1.5	28.7	28.2	39.2
2107	1.4	6.6	19.1	23.3	49.6
2108	1.3	5.1	18.1	34.1	41.4
2201	0.5	2.2	11.5	22.4	63.4
2202	1.8	4.6	25.4	30.7	37.5
2203	2.8	6.0	23.8	38.3	29.1
2204	1.4	1.0	19.9	33.7	44.0
2205	1.6	4.8	23.4	35.7	34.5
2206	1.6	6.6	22.2	46.2	23.4
2207	1.7	8.7	20.2	40.3	29.1
2208	0.8	1.4	18.0	35.6	44.2
2209	0.7	1.3	19.3	34.1	44.6
3101	12.0	12.6	65.0	5.6	4.8
3102	41.0	19.4	33.2	2.2	4.2
3103	12.8	15.2	12.2	15.4	44.4
3104	39.8	4.4	35.4	8.6	11.8
3105	12.8	14.2	54.4	10.0	8.6
3106	72.8	10.8	13.4	1.6	1.4
3107	13.2	19.2	53.8	8.2	5.6
3108	36.0	11.2	41.0	7.6	4.2
3109	13.0	14.2	57.8	8.6	6.4
3110	62.2	13.4	20.0	2.6	1.8
3111	9.0	11.2	56.8	9.8	13.2
3112	77.0	14.0	7.8	0.8	0.4
3201	10.0	8.0	49.8	7.1	25.1
3202	44.0	7.0	26.4	8.2	14.4
3203	17.6	15.2	49.2	7.6	10.4
3204	37.2	14.0	26.2	5.2	17.4
3205	11.8	12.6	52.0	10.6	13.0
3206	65.2	10.8	19.4	1.4	3.2
3207	9.2	10.8	53.6	10.0	16.4
3208	60.8	14.4	18.4	3.0	3.4
3209	16.2	15.4	53.0	3.6	11.8
3210	67.8	11.4	16.8	1.8	2.2
3211	20.8	16.0	50.0	8.4	4.8
3212	48.4	10.8	29.0	5.4	6.4
4101	51.8	27.2	21.0	0.0	0.0
4102	52.8	34.2	11.8	0.8	0.4
4103	41.2	46.8	9.4	1.2	1.4
4104	43.8	32.6	23.4	0.2	0.0

Appendix II. pH, resistance, organic carbon content, total acidity, exchangeable bases, CEC and T-value of the experimental soil samples.

Sample no.	Lime status	pH		Resistance (Ω)	C (%)	Total ¹ Acidity (cmol _e kg ⁻¹)	Exchangeable bases ² (cmol _e kg ⁻¹)				CEC (cmol _e kg ⁻¹)	T-value
		H ₂ O	KCl				Ca	Mg	K	Na		
1101	unlimed	5.49	4.44	5300	2.04	3.11	1.54	0.33	0.32	0.03	8.89	5.32
1102	unlimed	5.16	4.39	18600	1.68	3.22	0.04	0.06	0.09	0.01	6.35	3.43
1103	unlimed	5.06	4.44	18700	1.66	3.11	0.07	0.05	0.06	0.02	7.00	3.31
1104	unlimed	5.52	4.39	13400	0.62	3.01	0.08	0.23	0.07	0.09	6.65	3.47
1105	unlimed	5.46	4.19	4400	1.86	3.63	0.99	0.43	0.32	0.04	8.02	5.42
1106	unlimed	5.37	3.96	7900	2.23	5.81	0.54	0.55	0.43	0.44	12.73	7.76
1107	unlimed	5.36	4.06	12700	1.71	5.19	0.81	0.42	0.17	0.06	11.43	6.64
1108	unlimed	5.63	4.54	3100	2.57	3.11	2.50	1.07	0.63	0.06	10.56	7.37
1109	unlimed	5.85	4.90	1850	3.75	2.49	3.93	1.91	0.78	0.38	12.33	9.50
1110	unlimed	5.31	4.04	7350	2.23	5.29	1.32	0.74	0.59	0.45	11.61	8.40
1111	unlimed	5.31	4.07	10000	1.92	4.77	0.72	0.75	0.45	0.12	9.89	6.81
1112	unlimed	5.30	4.30	3950	1.85	4.67	1.58	0.49	0.07	0.22	10.30	7.03
1113	unlimed	5.19	4.36	8500	1.70	4.05	0.67	0.39	0.04	0.05	8.96	5.21
1114	unlimed	5.34	4.55	9900	2.68	2.70	0.29	0.20	0.03	0.04	5.70	3.26
1201	limed	6.80	6.15	1980	1.61	0.42	4.92	0.42	0.39	0.16	7.59	6.30
1202	limed	6.33	5.25	3825	1.20	1.35	2.39	0.23	0.47	0.13	6.25	4.57
1203	limed	5.50	4.58	2460	0.91	2.28	0.92	0.16	0.27	0.06	5.15	3.69
1204	limed	6.71	6.12	500	2.61	0.52	7.42	2.26	1.90	0.17	13.71	12.28
1205	limed	6.43	5.53	1100	2.20	1.25	6.25	2.41	0.65	0.17	13.07	10.73
1206	limed	5.86	4.46	2640	1.32	3.11	2.81	1.62	0.23	0.28	10.60	8.05
1207	limed	5.67	4.18	5900	1.16	3.84	1.09	1.18	0.15	0.12	10.13	6.39
1208	limed	5.76	4.82	1390	2.37	2.91	3.57	0.95	0.44	0.14	11.47	8.00
1209	limed	5.00	4.13	5550	2.14	5.09	0.35	0.26	0.20	0.06	10.36	5.96
1210	limed	5.12	4.26	6050	2.46	4.57	0.25	0.22	0.12	0.05	9.64	5.21
1211	limed	6.30	5.50	1380	2.51	1.25	6.03	1.69	0.41	0.27	12.26	9.65
1212	limed	5.86	4.91	2540	1.85	2.49	3.78	1.83	0.31	0.16	12.69	8.57
1213	limed	5.34	4.18	8400	1.66	5.19	0.57	0.62	0.09	0.08	11.85	6.55
1214	limed	5.49	4.42	2380	2.70	3.63	2.09	1.11	0.55	0.09	10.60	7.47
1215	limed	5.16	4.18	6450	1.51	4.05	0.73	0.43	0.12	0.06	8.79	5.38
1216	limed	5.16	4.18	5620	0.68	3.32	0.18	0.42	0.08	0.09	6.50	4.09
1217	limed	5.63	4.78	1160	2.81	2.70	2.08	2.41	0.14	0.20	11.60	7.53
1218	limed	5.57	4.43	2140	2.00	3.32	2.02	2.00	0.07	0.21	10.23	7.62
1219	limed	5.45	4.17	4550	0.43	2.18	0.26	0.93	0.02	0.17	5.01	3.56
2101	unlimed	4.87	3.85	14000	0.19	0.62	0.04	0.12	0.01	0.01	1.23	0.79
2102	unlimed	5.17	4.48	24200	0.91	1.87	0.01	0.05	0.02	0.01	2.97	1.97
2103	unlimed	5.57	4.78	16500	0.16	0.73	0.10	0.36	0.01	0.03	1.32	1.23
2104	unlimed	4.69	4.13	980	1.27	2.91	0.01	0.12	0.04	0.36	4.81	3.43
2105	unlimed	5.03	4.21	11200	0.53	1.66	0.03	0.04	0.03	0.04	2.25	1.80
2106	unlimed	5.41	4.50	6500	2.71	3.11	0.71	0.37	0.06	0.03	6.05	4.28
2107	unlimed	4.93	3.77	8350	1.43	2.91	0.21	0.16	0.06	0.02	4.58	3.37
2108	unlimed	5.19	4.33	6800	1.21	1.45	0.66	0.20	0.13	0.02	2.50	2.46
2201	unlimed	5.98	5.51	5800	0.25	0.31	0.55	0.13	0.06	0.01	1.27	1.07
2202	limed	6.30	5.35	7250	0.82	0.73	0.91	0.53	0.14	0.02	3.08	2.33
2203	limed	5.29	4.19	11300	0.60	1.56	0.20	0.17	0.04	0.01	2.69	1.99
2204	limed	7.04	6.77	2540	0.84	0.21	2.30	0.68	0.26	0.02	3.37	3.46
2205	limed	7.83	7.07	4470	0.92	0.10	2.97	0.49	0.03	0.03	3.60	3.61
2206	limed	5.96	5.32	6150	2.05	1.35	2.31	0.78	0.11	0.03	6.09	4.57
2207	limed	5.42	4.77	7750	0.45	0.52	0.49	0.18	0.02	0.01	1.95	1.21
2208	limed	6.93	6.44	11200	0.17	0.10	0.57	0.11	0.01	0.01	0.75	0.79
2209	limed	6.95	6.63	14600	0.08	0.10	0.28	0.07	0.01	0.00	0.65	0.46
3101	unlimed	5.66	4.63	1870	0.53	1.04	1.02	1.06	0.27	0.08	3.84	3.46
3102	unlimed	6.05	4.87	1310	0.26	1.04	0.49	3.25	0.08	0.44	6.39	5.30
3103	unlimed	5.62	4.86	2790	0.99	0.93	1.75	0.55	0.21	0.06	4.47	3.49
3104	unlimed	6.11	5.24	2760	0.10	0.73	1.17	4.84	0.15	0.18	8.34	7.06
3105	unlimed	6.04	5.04	2930	0.77	0.73	1.73	0.60	0.18	0.05	4.16	3.29
3106	unlimed	6.53	5.28	1790	0.21	0.83	0.90	9.66	0.12	0.74	13.33	12.25
3107	unlimed	5.52	4.78	1450	1.47	1.25	1.69	1.31	0.21	0.16	5.69	4.62
3108	unlimed	6.30	5.80	590	0.02	0.31	0.57	3.92	0.07	0.69	6.38	5.56
3109	unlimed	6.29	5.21	2350	1.18	0.83	1.63	1.56	0.19	0.15	4.96	4.36
3110	unlimed	5.06	4.21	420	0.11	1.97	0.36	7.07	0.09	0.88	11.31	10.38
3111	unlimed	5.58	5.02	3125	0.88	0.83	1.60	0.62	0.26	0.13	4.10	3.45
3112	unlimed	6.31	5.79	1850	0.17	0.42	0.81	9.89	0.11	0.73	12.93	11.95
3201	limed	6.14	5.43	1780	0.97	0.73	2.51	0.73	0.23	0.08	5.03	4.28
3202	limed	6.31	5.36	2480	0.13	0.73	1.19	5.52	0.18	0.28	9.49	7.90
3203	limed	6.31	5.29	1950	0.68	0.73	1.86	1.23	0.12	0.15	5.34	4.09
3204	limed	6.32	5.21	1890	0.08	0.73	1.72	2.50	0.10	0.29	6.81	5.33
3205	limed	5.75	4.96	2200	0.48	0.73	1.71	0.50	0.10	0.09	4.21	3.12
3206	limed	6.44	5.30	1770	0.12	0.73	0.89	8.80	0.10	0.95	12.49	11.47
3207	limed	6.80	6.50	2140	0.79	0.10	3.66	0.45	0.12	0.08	4.02	4.41
3208	limed	6.25	5.53	1410	0.15	0.62	1.13	7.03	0.11	0.65	10.74	9.54
3209	limed	5.27	4.64	1820	0.45	0.93	1.27	0.96	0.08	0.16	4.13	3.39
3210	limed	5.42	4.18	1680	0.25	2.28	0.76	6.98	0.09	0.75	12.89	10.87
3211	limed	5.94	4.83	2360	0.58	0.93	1.18	1.36	0.10	0.30	4.58	3.88
3212	limed	6.30	5.36	2000	0.15	0.73	0.95	4.43	0.09	0.40	9.09	6.60
4101	unlimed	5.41	4.11	8300	0.31	6.54	0.02	0.47	0.24	0.15	10.02	7.42
4102	unlimed	5.56	3.90	10000	0.37	7.58	0.07	0.23	0.14	0.15	10.94	8.18
4103	unlimed	5.24	3.59	7200	0.27	10.38	0.01	0.25	0.09	0.07	13.19	10.81
4104	unlimed	5.20	3.75	8300	0.20	10.38	0.01	0.25	0.13	0.05	13.16	10.82

¹ determined at pH 7 (Eksteen acidity)

Appendix III. KCl extractable acidity, extractable aluminium and mean pH-dependant acidity of the experimental soil samples.

Sample no.	Soil group	Lime status	1N KCl ¹			ICP-Al ²	SSPDA ³	ΔpH ⁴	mean pH-dependant acidity (ΔH) (cmol _e kg ⁻¹ pH unit ⁻¹)
			H	Al	Total				
			(cmol _e kg ⁻¹)						
1101	organic	unlimed	0.73	0.88	1.60	0.87	1.51	2.56	0.590
1102	organic	unlimed	1.20	1.60	2.80	1.74	0.42	2.61	0.161
1103	organic	unlimed	0.60	1.75	2.35	2.03	0.76	2.56	0.297
1104	structured	unlimed	0.39	1.78	2.16	2.28	0.85	2.61	0.325
1105	organic	unlimed	0.29	1.50	1.79	1.59	1.84	2.81	0.655
1106	organic	unlimed	0.41	3.19	3.60	3.55	2.21	3.04	0.727
1107	organic	unlimed	0.41	2.99	3.40	3.43	1.79	2.94	0.609
1108	organic	unlimed	0.15	0.35	0.50	0.27	2.61	2.46	1.061
1109	organic	unlimed	0.10	0.10	0.20	0.04	2.29	2.10	1.090
1110	organic	unlimed	0.43	2.73	3.16	3.33	2.13	2.96	0.719
1111	organic	unlimed	0.35	2.50	2.85	3.20	1.92	2.93	0.655
1112	organic	unlimed	0.18	1.73	1.90	2.12	2.77	2.70	1.026
1113	organic	unlimed	0.24	2.16	2.40	2.70	1.65	2.64	0.625
1114	organic	unlimed	0.14	1.36	1.50	1.87	1.20	2.45	0.490
1201	organic	limed	0.09	0.06	0.15	0.00	0.27	0.85	0.318
1202	organic	limed	0.10	0.10	0.20	0.08	1.15	1.75	0.657
1203	organic	limed	0.15	1.10	1.25	1.35	1.03	2.42	0.426
1204	organic	limed	0.04	0.06	0.10	0.00	0.42	0.88	0.477
1205	organic	limed	0.04	0.06	0.10	0.00	1.15	1.47	0.782
1206	organic	limed	0.20	0.46	0.65	0.47	2.46	2.54	0.969
1207	organic	limed	0.30	1.63	1.93	1.75	1.92	2.82	0.679
1208	organic	limed	0.16	0.07	0.23	0.08	2.69	2.18	1.232
1209	organic	limed	0.45	2.95	3.40	3.86	1.69	2.87	0.589
1210	organic	limed	0.45	2.50	2.95	2.89	1.62	2.74	0.591
1211	organic	limed	0.05	0.05	0.10	0.01	1.15	1.50	0.767
1212	organic	limed	0.15	0.05	0.20	0.08	2.29	2.09	1.096
1213	organic	limed	0.45	3.10	3.55	3.45	1.64	2.82	0.582
1214	organic	limed	0.29	0.76	1.05	0.80	2.58	2.58	1.000
1215	organic	limed	0.32	2.46	2.78	2.85	1.27	2.82	0.450
1216	structured	limed	0.33	1.95	2.28	2.17	1.05	2.82	0.371
1217	organic	limed	0.13	0.13	0.25	0.11	2.45	2.22	1.104
1218	organic	limed	0.28	0.70	0.98	0.85	2.35	2.57	0.912
1219	structured	limed	0.37	1.13	1.50	1.23	0.68	2.83	0.240
2101	sandy	unlimed	0.19	0.11	0.30	0.15	0.32	3.15	0.102
2102	sandy	unlimed	0.30	1.10	1.40	1.14	0.47	2.52	0.187
2103	sandy	unlimed	0.13	0.40	0.53	0.45	0.21	2.22	0.092
2104	sandy	unlimed	0.36	1.50	1.85	1.70	1.06	2.87	0.369
2105	sandy	unlimed	0.38	0.77	1.15	0.85	0.51	2.79	0.183
2106	sandy	unlimed	0.40	0.95	1.35	1.30	1.76	2.50	0.704
2107	sandy	unlimed	0.50	0.75	1.25	0.74	1.67	3.23	0.515
2108	sandy	unlimed	0.20	0.13	0.33	0.15	1.13	2.67	0.421
2201	sandy	limed	0.08	0.03	0.10	0.00	0.21	1.49	0.141
2202	sandy	limed	0.08	0.03	0.10	0.01	0.63	1.65	0.382
2203	sandy	limed	0.20	0.50	0.70	0.62	0.86	2.81	0.306
2204	sandy	limed	0.03	0.03	0.05	0.00	0.16	0.23	0.696
2205	sandy	limed	0.05	0.02	0.07	0.00	0.03	-0.07	-0.464
2206	sandy	limed	0.08	0.03	0.10	0.01	1.25	1.68	0.744
2207	sandy	limed	0.11	0.05	0.16	0.04	0.37	2.23	0.164
2208	sandy	limed	0.07	0.03	0.09	0.00	0.01	0.56	0.018
2209	sandy	limed	0.07	0.03	0.09	0.00	0.01	0.37	0.027
3101	normal	unlimed	0.13	0.08	0.20	0.06	0.84	2.37	0.354
3102	structured	unlimed	0.08	0.08	0.15	0.04	0.89	2.13	0.418
3103	normal	unlimed	0.08	0.02	0.10	0.01	0.83	2.14	0.388
3104	structured	unlimed	0.07	0.03	0.10	0.01	0.63	1.76	0.357
3105	normal	unlimed	0.08	0.03	0.10	0.00	0.63	1.96	0.321
3106	structured	unlimed	0.05	0.10	0.15	0.02	0.68	1.72	0.395
3107	normal	unlimed	0.10	0.03	0.13	0.01	1.13	2.22	0.507
3108	structured	unlimed	0.04	0.02	0.05	0.00	0.26	1.20	0.217
3109	normal	unlimed	0.06	0.02	0.08	0.00	0.76	1.79	0.422
3110	structured	unlimed	0.32	1.01	1.33	1.12	0.65	2.79	0.231
3111	normal	unlimed	0.06	0.04	0.10	0.01	0.73	1.98	0.369
3112	structured	unlimed	0.05	0.03	0.08	0.00	0.35	1.21	0.285
3201	normal	limed	0.08	0.03	0.10	0.00	0.63	1.57	0.401
3202	structured	limed	0.05	0.03	0.08	0.00	0.66	1.64	0.399
3203	normal	limed	0.05	0.02	0.06	0.00	0.67	1.71	0.392
3204	structured	limed	0.08	0.02	0.09	0.00	0.64	1.79	0.358
3205	normal	limed	0.08	0.03	0.10	0.01	0.63	2.04	0.309
3206	structured	limed	0.05	0.03	0.08	0.00	0.66	1.70	0.385
3207	normal	limed	0.05	0.02	0.06	0.00	0.04	0.50	0.080
3208	structured	limed	0.07	0.03	0.09	0.00	0.53	1.47	0.361
3209	normal	limed	0.13	0.06	0.19	0.07	0.74	2.36	0.315
3210	structured	limed	0.27	1.06	1.33	1.14	0.96	2.82	0.339
3211	normal	limed	0.09	0.06	0.15	0.03	0.78	2.17	0.359
3212	structured	limed	0.04	0.02	0.05	0.00	0.68	1.64	0.415
4101	structured	unlimed	0.96	6.59	7.55	7.50	-1.01	2.89	-0.349
4102	structured	unlimed	1.10	6.95	8.05	7.49	-0.47	3.10	-0.152
4103	structured	unlimed	1.69	9.76	11.45	11.59	-1.07	3.41	-0.314
4104	structured	unlimed	1.58	10.02	11.60	11.25	-1.22	3.25	-0.375

¹ 1N KCl extractable acidity and its exchangeable H and Al components

² 1N KCl extractable Al determined in the leachate by inductively coupled plasma emission spectroscopy

³ soil-specific pH-dependant acidity (difference between the Eksteen acidity and the total 1N KCl acidity)

⁴ ΔpH

Appendix IV. Combined results for the 0.1M HCl, 0.2M NH₄OAc and 0.2M NaCl extractions of Ca, Mg, Na and K for the experimental soil samples.

Sample no.	Soil group	Lime status	Ca			Mg			K		Na	
			HCl	NH ₄ OAc	NaCl	HCl	NH ₄ OAc	NaCl	HCl	NH ₄ OAc	HCl	NH ₄ OAc
1101	organic	unlimed	2.46	1.54	2.13	0.42	0.33	0.35	0.20	0.20	0.03	0.02
1102	organic	unlimed	0.55	0.04	0.05	0.19	0.06	0.09	0.07	0.08	0.02	0.01
1103	organic	unlimed	0.96	0.07	0.05	0.13	0.05	0.05	0.03	0.05	0.02	0.02
1104	structured	unlimed	0.59	0.08	0.11	0.32	0.23	0.24	0.03	0.05	0.09	0.09
1105	organic	unlimed	1.87	0.99	1.36	0.53	0.43	0.47	0.26	0.28	0.05	0.04
1106	organic	unlimed	1.99	0.54	1.50	0.71	0.55	0.60	0.17	0.22	0.05	0.05
1107	organic	unlimed	1.23	0.81	0.83	0.49	0.42	0.51	0.04	0.07	0.06	0.05
1108	organic	unlimed	3.50	2.50	3.37	1.15	1.07	1.12	0.53	0.59	0.06	0.06
1109	organic	unlimed	7.80	3.93	5.43	2.23	1.91	1.86	0.78	0.78	0.08	0.08
1110	organic	unlimed	1.62	1.32	1.15	0.74	0.74	0.73	0.45	0.50	0.05	0.05
1111	organic	unlimed	1.09	0.72	0.71	0.41	0.75	0.38	0.30	0.33	0.05	0.04
1112	organic	unlimed	2.76	1.58	2.46	0.58	0.49	0.53	0.05	0.07	0.08	0.07
1113	organic	unlimed	0.96	0.67	0.53	0.35	0.39	0.30	0.02	0.04	0.04	0.04
1114	organic	unlimed	0.84	0.29	0.32	0.28	0.20	0.23	0.01	0.03	0.04	0.04
1201	organic	limed	10.05	4.92	4.93	1.12	0.42	0.37	0.18	0.21	0.14	0.13
1202	organic	limed	3.44	2.39	2.63	0.35	0.23	0.15	0.05	0.07	0.13	0.13
1203	organic	limed	1.34	0.92	1.05	0.20	0.16	0.12	0.04	0.06	0.07	0.06
1204	organic	limed	15.39	7.42	8.50	3.26	2.26	2.20	1.47	1.42	0.19	0.17
1205	organic	limed	11.24	6.25	7.51	2.86	2.41	2.43	0.33	0.37	0.18	0.17
1206	organic	limed	3.94	2.81	3.09	1.69	1.62	1.57	0.15	0.20	0.14	0.14
1207	organic	limed	1.90	1.09	1.62	1.24	1.18	1.18	0.09	0.15	0.12	0.12
1208	organic	limed	6.33	3.57	5.16	1.09	0.95	1.02	0.41	0.44	0.16	0.14
1209	organic	limed	0.99	0.35	0.72	0.31	0.26	0.29	0.17	0.20	0.08	0.06
1210	organic	limed	0.96	0.25	0.49	0.31	0.22	0.22	0.09	0.12	0.09	0.05
1211	organic	limed	11.73	6.03	7.65	2.29	1.69	1.83	0.41	0.41	0.23	0.21
1212	organic	limed	6.76	3.78	5.12	2.14	1.83	1.94	0.11	0.15	0.15	0.16
1213	organic	limed	1.27	0.57	1.17	0.69	0.62	0.66	0.06	0.09	0.08	0.08
1214	organic	limed	3.69	2.09	2.99	1.27	1.11	1.11	0.56	0.55	0.10	0.09
1215	organic	limed	1.11	0.73	0.87	0.46	0.43	0.47	0.10	0.12	0.06	0.06
1216	structured	limed	0.54	0.18	0.29	0.80	0.42	0.73	0.02	0.04	0.09	0.09
1217	organic	limed	8.69	2.08	5.02	2.60	2.41	2.28	0.12	0.14	0.21	0.20
1218	organic	limed	4.15	2.02	2.72	2.09	2.00	1.93	0.05	0.07	0.20	0.21
1219	structured	limed	0.62	0.26	0.31	0.96	0.93	0.90	0.01	0.02	0.16	0.17
2101	sand	unlimed	0.35	0.04	0.05	0.08	0.12	0.13	0.00	0.01	0.00	0.01
2102	sand	unlimed	0.33	0.01	0.03	0.06	0.05	0.06	0.02	0.02	0.01	0.01
2103	sand	unlimed	0.38	0.10	0.03	0.07	0.36	0.04	0.00	0.01	0.03	0.02
2104	sand	unlimed	0.31	0.01	0.04	0.15	0.12	0.12	0.03	0.03	0.41	0.36
2105	sand	unlimed	0.31	0.03	0.13	0.06	0.04	0.09	0.01	0.02	0.04	0.04
2106	sand	unlimed	1.28	0.71	0.67	0.43	0.37	0.34	0.05	0.06	0.05	0.03
2107	sand	unlimed	0.86	0.21	0.60	0.21	0.16	0.21	0.03	0.03	0.03	0.02
2108	sand	unlimed	1.42	0.66	1.03	0.23	0.20	0.23	0.04	0.04	0.03	0.02
2201	sand	limed	2.20	0.55	0.54	1.00	0.13	0.13	0.08	0.06	0.02	0.01
2202	sand	limed	3.31	0.91	1.15	2.20	0.53	0.57	0.08	0.08	0.02	0.02
2203	sand	limed	0.61	0.20	0.30	0.23	0.17	0.19	0.03	0.04	0.02	0.01
2204	sand	limed	5.44	2.30	1.99	2.10	0.68	0.67	0.26	0.26	0.03	0.02
2205	sand	limed	7.20	2.97	2.50	2.23	0.49	0.47	0.03	0.03	0.09	0.03
2206	sand	limed	6.26	2.31	2.89	1.68	0.78	0.79	0.09	0.10	0.04	0.03
2207	sand	limed	1.35	0.49	0.60	0.30	0.18	0.20	0.01	0.02	0.01	0.01
2208	sand	limed	1.67	0.57	0.61	0.43	0.11	0.13	0.00	0.01	0.01	0.01
2209	sand	limed	0.79	0.28	0.29	0.18	0.07	0.09	0.00	0.01	0.01	0.00
3101	normal	unlimed	1.53	1.02	1.05	1.12	1.06	1.08	0.27	0.27	0.08	0.07
3102	structured	unlimed	0.83	0.49	0.48	3.02	3.25	2.79	0.04	0.08	0.52	0.05
3103	normaal	unlimed	3.02	1.75	1.87	0.67	0.55	0.63	0.21	0.21	0.07	0.06
3104	structured	unlimed	1.29	1.17	0.98	4.33	4.84	4.45	0.11	0.15	0.26	0.18
3105	normaal	unlimed	2.80	1.73	1.87	0.73	0.60	0.80	0.19	0.18	0.06	0.05
3106	structured	unlimed	1.04	0.90	0.89	7.75	9.66	10.75	0.04	0.12	0.77	0.74
3107	normaal	unlimed	2.88	1.69	1.93	0.39	1.31	1.81	0.22	0.21	0.18	0.16
3108	structured	unlimed	0.90	0.57	0.62	3.97	3.92	3.95	0.05	0.07	0.73	0.69
3109	normaal	unlimed	2.79	1.63	1.93	1.90	1.56	1.93	0.22	0.19	0.18	0.15
3110	structured	unlimed	0.70	0.36	0.41	5.98	7.07	7.48	0.02	0.08	0.62	0.88
3111	normaal	unlimed	2.51	1.60	1.69	0.71	0.62	0.83	0.24	0.23	0.11	0.09
3112	structured	unlimed	1.02	0.81	0.81	8.43	9.89	10.02	0.05	0.11	0.81	0.73
3201	normaal	limed	3.81	2.51	2.42	0.96	0.73	1.14	0.22	0.23	0.13	0.08
3202	structured	limed	1.31	1.19	1.10	4.84	5.52	5.48	0.08	0.15	0.22	0.21
3203	normaal	limed	2.91	1.86	1.96	1.49	1.23	1.55	0.11	0.12	0.17	0.15
3204	structured	limed	1.97	1.72	1.57	2.48	2.50	2.48	0.07	0.10	0.31	0.29
3205	normaal	limed	2.35	1.71	1.63	0.61	0.50	0.64	0.09	0.09	0.09	0.09
3206	structured	limed	0.98	0.89	0.89	7.44	8.80	8.56	0.04	0.10	1.22	0.95
3207	normaal	limed	7.08	3.66	3.39	0.57	0.45	0.72	0.14	0.12	0.09	0.08
3208	structured	limed	1.30	1.13	1.09	6.42	7.03	7.21	0.05	0.11	0.67	0.65
3209	normaal	limed	1.94	1.27	1.41	1.08	0.96	1.28	0.06	0.08	0.17	0.16
3210	structured	limed	1.07	0.76	0.77	6.13	6.98	6.93	0.04	0.09	0.75	0.75
3211	normaal	limed	1.73	1.18	1.18	1.60	1.36	1.57	0.07	0.07	0.19	0.19
3212	structured	limed	1.16	0.95	0.84	4.25	4.43	4.13	0.05	0.09	0.44	0.40
4101	structured	unlimed	0.38	0.02	0.09	0.57	0.47	0.39	0.00	0.03	0.08	0.09
4102	structured	unlimed	0.43	0.07	0.12	0.35	0.23	0.27	0.02	0.03	0.08	0.07
4103	structured	unlimed	0.35	0.01	0.04	0.36	0.25	0.28	0.02	0.03	0.19	0.07
4104	structured	unlimed	0.39	0.01	0.03	0.38	0.25	0.30	0.01	0.03	0.09	0.05

Appendix V. Analysis of variance of data presented in Appendix IV.

Analysis of variance for Ca

Source	Sum of squares (Type I)	d.f.	Mean square	F-ratio	P-value
MAIN EFFECTS					
A: Soil group	215.811	3	71.937	28.80	0.0001
B: Lime status	116.046	1	116.046	46.46	0.0001
C:Extraction method	70.142	2	35.071	14.04	0.0001
INTERACTIONS					
AB	56.518	3	18.839	7.54	0.0001
AC	17.535	6	2.922	1.17	0.3239
BC	12.212	2	6.106	2.44	0.0894
ABC	7.293	6	1.216	0.49	0.8178
Corrected Total	1174.027	233			

Analysis of variance for Mg

Source	Sum of squares (Type I)	d.f.	Mean square	F-ratio	P-value
MAIN EFFECTS					
A: Soil group	462.907	3	154.302	64.72	0.0001
B: Lime status	12.162	1	12.162	5.10	0.0250
C:Extraction method	0.172	2	0.086	0.04	0.9646
INTERACTIONS					
AB	2.438	3	0.813	0.34	0.7958
AC	5.193	6	0.866	0.36	0.9016
BC	1.053	2	0.527	0.22	0.8020
ABC	1.014	6	0.169	0.07	0.9986
Corrected Total	1094.717	233			

Analysis of variance for K

Source	Sum of squares (Type I)	d.f.	Mean square	F-ratio	P-value
MAIN EFFECTS					
A: Soil group	1.70058	3	0.56686	18.67	0.0001
B: Lime status	0.00396	1	0.00396	0.13	0.7188
C:Extraction method	0.01385	1	0.01385	0.46	0.5007
INTERACTIONS					
AB	0.10811	3	0.03604	1.19	0.3176
AC	0.00878	3	0.00293	0.10	0.9619
BC	0.00005	1	0.00005	0.00	0.9682
ABC	0.00037	3	0.00012	0.00	0.9996
Corrected Total	6.68496	155			

Analysis of variance for Na

Source	Sum of squares (Type I)	d.f.	Mean square	F-ratio	P-value
MAIN EFFECTS					
A: Soil group	3.12006	3	1.04002	43.44	0.0001
B: Lime status	0.06991	1	0.06991	2.92	0.0900
C:Extraction method	0.01540	1	0.01540	0.64	0.4241
INTERACTIONS					
AB	0.08288	3	0.02763	1.15	0.3302
AC	0.01177	3	0.00392	0.16	0.9206
BC	0.00001	1	0.00001	0.00	0.9835
ABC	0.00033	3	0.00011	0.00	0.9996
Corrected Total	7.41131	155			

Appendix VI. Chemical analysis of the experimental soils studied in terms of the Eksteen lime requirement determination.

Sample no.	Soil group	Lime status	pH (KCl)	%C	H	Ca (cmol _c kg ⁻¹)	Mg	R-value	Mg:Ca ratio
1101	organic	unlimed	4.44	2.04	3.11	2.46	0.42	0.93	0.17
1102	organic	unlimed	4.39	1.68	3.22	0.55	0.19	0.23	0.35
1103	organic	unlimed	4.44	1.66	3.11	0.96	0.13	0.35	0.14
1104	structured	unlimed	4.39	0.62	3.01	0.59	0.32	0.30	0.54
1105	organic	unlimed	4.19	1.86	3.63	1.87	0.53	0.66	0.28
1106	organic	unlimed	3.96	2.23	5.81	1.99	0.71	0.47	0.36
1107	organic	unlimed	4.06	1.71	5.19	1.23	0.49	0.33	0.40
1108	organic	unlimed	4.54	2.57	3.11	3.50	1.15	1.50	0.33
1109	organic	unlimed	4.90	3.75	2.49	7.80	2.23	4.03	0.29
1110	organic	unlimed	4.04	2.23	5.29	1.62	0.74	0.45	0.46
1111	organic	unlimed	4.07	1.92	4.77	1.09	0.41	0.31	0.38
1112	organic	unlimed	4.30	1.85	4.67	2.76	0.58	0.72	0.21
1113	organic	unlimed	4.36	1.70	4.05	0.96	0.35	0.32	0.37
1114	organic	unlimed	4.55	2.68	2.70	0.84	0.28	0.42	0.34
1201	organic	limed	6.15	1.61	0.42	10.05	1.12	26.61	0.11
1202	organic	limed	5.25	1.20	1.35	3.44	0.35	2.80	0.10
1203	organic	limed	4.58	0.91	2.28	1.34	0.20	0.67	0.15
1204	organic	limed	6.12	2.61	0.52	15.39	3.26	35.86	0.21
1205	organic	limed	5.53	2.20	1.25	11.24	2.86	11.28	0.25
1206	organic	limed	4.46	1.32	3.11	3.94	1.69	1.81	0.43
1207	organic	limed	4.18	1.16	3.84	1.90	1.24	0.82	0.65
1208	organic	limed	4.82	2.37	2.91	6.33	1.09	2.55	0.17
1209	organic	limed	4.13	2.14	5.09	0.99	0.31	0.26	0.31
1210	organic	limed	4.26	2.46	4.57	0.96	0.31	0.28	0.32
1211	organic	limed	5.50	2.51	1.25	11.73	2.29	11.22	0.20
1212	organic	limed	4.91	1.85	2.49	6.76	2.14	3.57	0.32
1213	organic	limed	4.18	1.66	5.19	1.27	0.69	0.38	0.54
1214	organic	limed	4.42	2.70	3.63	3.69	1.27	1.36	0.34
1215	organic	limed	4.18	1.51	4.05	1.11	0.46	0.39	0.41
1216	structured	limed	4.18	0.68	3.32	0.54	0.80	0.40	1.48
1217	organic	limed	4.78	2.81	2.70	8.69	2.60	4.18	0.30
1218	organic	limed	4.43	2.00	3.32	4.15	2.09	1.88	0.50
1219	structured	limed	4.17	0.43	2.18	0.62	0.96	0.72	1.54
2101	sandy	unlimed	3.85	0.19	0.62	0.35	0.08	0.70	0.23
2102	sandy	unlimed	4.48	0.91	1.87	0.33	0.06	0.21	0.17
2103	sandy	unlimed	4.78	0.16	0.73	0.38	0.07	0.62	0.18
2104	sandy	unlimed	4.13	1.27	2.91	0.31	0.15	0.16	0.46
2105	sandy	unlimed	4.21	0.53	1.66	0.31	0.06	0.22	0.18
2106	sandy	unlimed	4.50	2.71	3.11	1.28	0.43	0.55	0.34
2107	sandy	unlimed	3.77	1.43	2.91	0.86	0.21	0.37	0.25
2108	sandy	unlimed	4.33	1.21	1.45	1.42	0.23	1.14	0.16
2201	sandy	limed	5.51	0.25	0.31	2.20	1.00	10.32	0.45
2202	sandy	limed	5.35	0.82	0.73	3.31	2.20	7.54	0.66
2203	sandy	limed	4.19	0.60	1.56	0.61	0.23	0.54	0.37
2204	sandy	limed	6.77	0.84	0.21	5.44	2.10	35.93	0.39
2205	sandy	limed	7.07	0.92	0.10	7.20	2.23	94.28	0.31
2206	sandy	limed	5.32	2.05	1.35	6.26	1.68	5.88	0.27
2207	sandy	limed	4.77	0.45	0.52	1.35	0.30	3.16	0.22
2208	sandy	limed	6.44	0.17	0.10	1.67	0.43	20.95	0.26
2209	sandy	limed	6.63	0.08	0.10	0.79	0.18	9.72	0.22
3101	normal	unlimed	4.63	0.53	1.04	1.53	1.12	2.55	0.73
3102	structured	unlimed	4.87	0.26	1.04	0.83	3.02	3.70	3.66
3103	normal	unlimed	4.86	0.99	0.93	3.02	0.67	3.96	0.22
3104	structured	unlimed	5.24	0.10	0.73	1.29	4.33	7.69	3.37
3105	normal	unlimed	5.04	0.77	0.73	2.80	0.73	4.84	0.26
3106	structured	unlimed	5.28	0.21	0.83	1.04	7.75	10.58	7.48
3107	normal	unlimed	4.78	1.47	1.25	2.88	0.39	2.61	0.13
3108	structured	unlimed	5.80	0.02	0.31	0.90	3.97	15.72	4.42
3109	normal	unlimed	5.21	1.18	0.83	2.79	1.90	5.65	0.68
3110	structured	unlimed	4.21	0.11	1.97	0.70	5.98	3.39	8.55
3111	normal	unlimed	5.02	0.88	0.83	2.51	0.71	3.87	0.28
3112	structured	unlimed	5.79	0.17	0.42	1.02	8.43	22.51	8.25
3201	normal	limed	5.43	0.97	0.73	3.81	0.96	6.54	0.25
3202	structured	limed	5.36	0.13	0.73	1.31	4.84	8.43	3.69
3203	normal	limed	5.29	0.68	0.73	2.91	1.49	6.04	0.51
3204	structured	limed	5.21	0.08	0.73	1.97	2.48	6.10	1.26
3205	normal	limed	4.96	0.48	0.73	2.35	0.61	4.06	0.26
3206	structured	limed	5.30	0.12	0.73	0.98	7.44	11.53	7.61
3207	normal	limed	6.50	0.79	0.10	7.08	0.57	76.47	0.08
3208	structured	limed	5.53	0.15	0.62	1.30	6.42	12.45	4.94
3209	normal	limed	4.64	0.45	0.93	1.94	1.08	3.25	0.56
3210	structured	limed	4.18	0.25	2.28	1.07	6.13	3.16	5.73
3211	normal	limed	4.83	0.58	0.93	1.73	1.60	3.58	0.92
3212	structured	limed	5.36	0.15	0.73	1.16	4.25	7.41	3.67
4101	structured	unlimed	4.11	0.31	6.54	0.38	0.57	0.14	1.51
4102	structured	unlimed	3.90	0.37	7.58	0.43	0.35	0.10	0.82
4103	structured	unlimed	3.59	0.27	10.38	0.35	0.36	0.07	1.01
4104	structured	unlimed	3.75	0.20	10.38	0.39	0.38	0.07	0.98

Appendix VII. Over-estimation of lime requirement ($\text{t ha}^{-1} 15 \text{ cm}^{-1}$) over a range of organic carbon contents and pH values, calculated from the organic matter correction factor (OMCF)* on an equivalent basis assuming a soil bulk density of 1500 kg m^{-3} and lime purity of 70%.

Organic carbon (%)	Field pH_{KCl}										
	3.50	3.75	4.00	4.25	4.50	4.75	5.00	5.25	5.50	5.75	6.00
0.5	0.57	0.53	0.49	0.45	0.41	0.37	0.32	0.28	0.24	0.20	0.16
1.0	1.14	1.06	0.97	0.89	0.81	0.73	0.65	0.57	0.49	0.41	0.32
1.5	1.71	1.58	1.46	1.34	1.22	1.10	0.97	0.85	0.73	0.61	0.49
2.0	2.27	2.11	1.95	1.79	1.62	1.46	1.30	1.14	0.97	0.81	0.65
2.5	2.84	2.64	2.44	2.23	2.03	1.83	1.62	1.42	1.22	1.02	0.81
3.0	3.41	3.17	2.92	2.68	2.44	2.19	1.95	1.71	1.46	1.22	0.97
3.5	3.98	3.70	3.41	3.13	2.84	2.56	2.27	1.99	1.71	1.42	1.14
4.0	4.55	4.22	3.90	3.57	3.25	2.92	2.60	2.27	1.95	1.62	1.30
4.5	5.12	4.75	4.39	4.02	3.66	3.29	2.92	2.56	2.19	1.83	1.46
5.0	5.69	5.28	4.87	4.47	4.06	3.66	3.25	2.84	2.44	2.03	1.62
5.5	6.25	5.81	5.36	4.91	4.47	4.02	3.57	3.13	2.68	2.23	1.79
6.0	6.82	6.34	5.85	5.36	4.87	4.39	3.90	3.41	2.92	2.44	1.95

*OMCF = $0.202 \text{ cmol}_c \text{ kg}^{-1} \text{ pH unit}^{-1} \%C^{-1}$

Appendix VIII. Calculation of the effective Mg contents of the experimental soils, and of the ratios of effective Mg content to soil Mg content.

Sample no.	Lime status	pH _{KCl}	H	Ca	Mg	x* (t ha ⁻¹ 15 cm ⁻¹)	Effective Mg (cmol _c kg ⁻¹)	Effective Mg: soil Mg ratio
				(cmol _c kg ⁻¹)				
3102	unlimed	4.87	1.04	0.83	3.02	2.56	1.42	0.47
3104	unlimed	5.24	0.73	1.29	4.33	0.84	2.25	0.52
3106	unlimed	5.28	0.83	1.04	7.75	0.17	4.59	0.59
3108	unlimed	5.80	0.31	0.90	3.97	-0.46	2.27	0.57
3110	unlimed	4.21	1.97	0.70	5.98	5.05	3.14	0.53
3112	unlimed	5.79	0.42	1.02	8.43	-1.56	5.19	0.62
3202	limed	5.36	0.73	1.31	4.84	0.66	2.58	0.53
3204	limed	5.21	0.73	1.97	2.48	1.22	0.78	0.32
3206	limed	5.30	0.73	0.98	7.44	-0.08	4.44	0.60
3208	limed	5.53	0.62	1.30	6.42	-0.25	3.69	0.57
3210	limed	4.18	2.28	1.07	6.13	6.01	3.02	0.49
3212	limed	5.36	0.73	1.16	4.25	0.91	2.24	0.53
Average =								0.53

*lime requirement calculated by the Eksteen formula using an R-value of 11.2

Example: Calculation of the effective Mg content of sample no. 3106 using the R-value of normal soils which is 7.2:

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

$$\text{Mg} = 7.2 \times 0.83 - 1.04 - [0.17 \times (7.2 + 1)] \div 4$$

$$\text{Mg} = 5.976 - 1.04 - 0.3485$$

$$\text{Mg} = 4.59 \text{ cmol}_c \text{ kg}^{-1}$$

Appendix IX A. The results of fractional extractions of selected experimental soil samples using 0.2M NH_4OAc as extracting solution. Ca and Mg was extracted and determined in 10 consecutive extractions with 15 cm^3 of NH_4OAc .

Organic soil samples

Extraction no.	Ca (mg dm^{-3})			Mg (mg dm^{-3})		
	Sample no.			Sample no.		
	1105	1204	1211	1105	1204	1211
1	73.20	437.50	386.50	22.45	87.60	80.20
2	34.85	233.50	201.50	7.12	41.30	37.10
3	7.11	119.00	104.20	2.60	17.50	15.15
4	4.94	79.80	66.80	1.46	9.83	7.80
5	3.41	58.60	47.00	0.89	6.51	4.64
6	2.81	43.75	35.30	0.69	4.58	3.36
7	2.36	34.15	33.75	0.55	3.20	2.47
8	1.88	27.20	23.65	0.41	2.49	1.98
9	1.61	9.45	8.47	0.36	2.31	1.75
10	1.55	8.62	7.60	0.35	2.08	1.49

Normal soil samples

Extraction no.	Ca (mg dm^{-3})			Mg (mg dm^{-3})		
	Sample no.			Sample no.		
	3105	3111	3209	3105	3111	3209
1	151.20	120.40	118.20	36.80	28.40	56.40
2	51.20	47.10	34.70	7.81	8.29	11.88
3	8.85	10.46	6.39	1.85	2.75	2.91
4	5.96	6.94	4.23	1.01	1.34	1.50
5	4.38	4.99	2.71	0.66	0.83	0.99
6	3.47	3.84	2.07	0.49	0.58	0.69
7	2.77	3.18	1.59	0.39	0.45	0.53
8	2.38	2.57	1.26	0.31	0.35	0.45
9	1.92	2.19	1.09	0.27	0.29	0.39
10	1.72	1.83	0.86	0.25	0.24	0.32

Structured soil samples

Extraction no.	Ca (mg dm^{-3})					Mg (mg dm^{-3})				
	Sample no.					Sample no.				
	3106	3110	3112	3202	3206	3106	3110	3112	3202	3206
1	95.20	33.60	88.20	123.40	102.00	605.00	424.00	661.00	388.50	658.00
2	33.70	11.65	32.10	32.60	22.40	201.25	144.75	214.75	83.70	129.40
3	3.59	1.06	1.88	2.74	1.35	63.40	39.25	40.10	19.47	20.61
4	1.06	0.29	0.52	1.12	0.45	16.42	8.83	9.80	5.23	4.56
5	0.51	0.00	0.14	0.44	0.10	5.40	3.76	3.39	2.19	1.89
6	0.18	0.00	0.04	0.25	0.00	2.44	1.82	1.97	1.37	1.09
7	0.16	0.00	0.00	0.10	0.00	1.40	1.10	1.13	1.00	0.79
8	0.00	0.00	0.00	0.00	0.00	0.91	0.71	0.83	0.68	0.59
9	0.00	0.00	0.00	0.00	0.00	0.68	0.45	0.66	0.51	0.45
10	0.00	0.00	0.00	0.00	0.00	0.53	0.37	0.52	0.45	0.37

Appendix IX B. The results of fractional extractions of selected experimental soil samples using 0.1M HCl as extracting solution. Ca and Mg was extracted and determined in 10 consecutive extractions with 15 cm³ of HCl.

Extraction no.	Ca (mg dm ⁻³)			Mg (mg dm ⁻³)		
	Soil group/Sample no.			Soil group/Sample no.		
	Normal 3105	Structured 3106	Structured 3202	Normal 3105	Structured 3106	Structured 3202
1	242.50	43.70	60.70	38.75	327.50	183.0
2	50.40	29.00	41.80	6.85	205.00	121.5
3	9.00	15.50	20.35	1.32	100.20	56.6
4	3.24	7.52	9.08	0.66	54.80	27.6
5	2.12	5.36	6.04	0.50	35.80	16.8
6	1.42	3.82	4.06	0.38	23.80	10.7
7	1.24	2.92	2.62	0.30	16.80	6.6
8	0.96	1.96	1.76	0.28	12.80	4.6
9	0.68	1.26	1.20	0.26	8.60	3.2
10	0.40	0.90	0.76	0.18	6.30	2.2