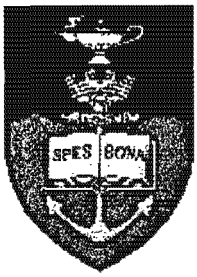

Soil chemical properties in pine plantations of different ages in the Eastern Escarpment region of South Africa

by

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Thesis submitted in partial fulfillment of the
requirements for the degree of
Master of Science
in
Environmental Geochemistry
Department of Geological Sciences
University of Cape Town
January, 1999

ABSTRACT

It is widely accepted that afforestation adversely affects soil chemical properties. A significant decrease in pH, base cation status and acid neutralising capacity (ANC), coupled with increasing acidity have been observed to occur in acid coniferous forest soils both in the Northern and Southern Hemispheres. International and local studies in Southern Africa have observed declining productivity over successive rotations in pine plantations. Increasing acidity loads in the Northern Hemisphere and their adverse effects on forest health have generated a search for chemical indices that would assist in pursuing thresholds beyond which forest vitality is damaged. A common and widely used chemical index is the Ca/Al ratio. The most common parameter adopted is the Ca/Al molar ratio in soil solutions. Recent studies in Southern Africa (Swaziland, Kwazulu-Natal) and in the Sabie area (Eastern Escarpment) have indicated that some forest compartments (*Pinus* sp.) may experience Ca/Al molar ratios dropping below unity. The value of unity is widely used and proposed as a threshold beyond which tree vitality may be adversely affected.

This study was conducted to determine the state of surface (0-20cm) soils underlying pine plantations of different ages in the Sabie area on the Eastern Escarpment of Southern Africa. The pine plantations were selected in areas overlying a uniform bedrock (shale), high altitude, high rainfall, north facing aspect and confined to 3 pine species (*P. elliottii*, *P. patula* and *P. taeda*). A composite sample was taken from each of 22 forest compartments varying in age (between 22 and 67 years) and rotation (first, second and third). In addition, the results of previous investigations of forest soils in the Eastern Escarpment region were considered in order to expand the array of forest compartment ages and the size of the overall data set used for statistical analysis, so that comparisons could be made.

Prior to analysis the soils were air dried and sieved (<2mm). Characterising the soil and investigation of the acidity status was conducted by analysis of pH (in water and KCl), organic carbon, acid neutralising capacity and exchangeable acidity and basic cations. All the pine forest surface soils are highly acidic. The acidification of natural soils under grassland is enhanced by afforestation and increases with increasing period of afforestation, predominantly within the first two decades. The pH levels (3.7-4.1 in KCl) dropped markedly in surface soils in the first two decades following afforestation. KCl-extractable acidity was observed to decline in a similar way for the first two decades. There is some indication of further acidification with plantation age beyond two decades, although the effect is not significant.

Base saturation levels do not exceed 25%, and exhibit a general drop in respect to afforestation of grassland soils. The depletion of basic cations (BC) from the exchange sites is evident as shown by a decline in the BC/acidity ratio, to values below unity, predominantly in the first decade following afforestation.

High levels of organic carbon were detected in the surface soils of the pine plantations studied (3.7-10%). The presence of organic matter is important in the context of Al complexation, which was confirmed by a significant correlation (r^2=0.59) between $CuCl_2$-extractable Al and organic carbon.

Soil solution composition was estimated based on the analysis of saturated paste extracts. The analysis included determination of pH (in the paste and in the extract), electrical conductivity (EC), dissolved organic carbon (DOC), monomeric Al, monomeric silica and major cations and anions. In addition, geochemical modelling (MINTEQA2) was used to calculate ion activities and saturation indices. Similarly to the solid phase, the soil solution was highly acidic with pH (saturated paste) levels ranging from 4.36 to 4.91. An important observation, and of utmost importance for future studies, was that of declining ionic strength of the soil solution with increasing plantation age (r^2=0.59).

Additional interesting observations were made of unexpectedly high levels of fluoride in solution (1.9-12 mg/l), which altered the detection of Al^{3+} and $Al(OH)_X^{3-X}$ concentrations in solution, and the calculation of alumino-silicate mineral solubility equilibria. The colorimetric method used for the detection of monomeric Al in solution probably excludes, to a large extent, F-complexed Al thus, posing great difficulty in the calculation of F-free monomeric Al activity in solution. Consequently, a more realistic approach was considered. In the process of calculating monomeric Al activities in solution (using MINTEQA2), the fluoride concentrations were thus, excluded. The inclusion of F in geochemical speciation calculations has indicated that the majority of Al species in solution are complexed to F and in addition, produced inconsistencies with respect to saturation indices of gibbsite, kaolinite and jurbanite. Evaluating the dissolution of Al in the absence of F offers the possibility that the dissolution of Al is controlled by Al-OM complexes (under pH 4.7) and by gibbsite (above pH 4.7).

The Ca/Al molar concentration ratio in solution was observed to drop in the soils following afforestation, and to reach, in some cases, levels below unity thus suggesting, that at some future time, forest health may be adversely affected. Ca/Al activity ratios calculated in the presence of F, were more than five orders of magnitude higher than activity ratio calculated in the absence of F.

High concentrations of NH_4^+ were detected in solution (4.8-36.5 mg/l) while other soluble forms of nitrogen were detected in significantly lower concentrations (NO_2^- <4 mg/l; NO_3^- - mostly undetected). The Abundance of NH_4^+-N coupled with smaller concentrations of NO_2^- may be the cause of the method used for the preparation of the saturated soil pastes and consequently interruption of biochemical processes such as nitrification taking place in the soil environment. Alternetively, the reason may be the loss of nitrogen from the F and H horizons (forest floor) to the upper mineral horizon in the form of NH_4^+-N, whereas the loss of nitrogen from the A horizon is mainly in the form of NO_3^--N.

High levels of dissolved organic carbon (DOC) were detected (53-193mg/l) and conform to the abundance of organic matter. A considerable anion deficit with respect to the charge balance of major ions in solution was assumed to be accounted for by negatively charged dissolved organic matter.

Comparing the Ca/Al ratio of the soil solution to the basic cations/acidity ratio of the exchange sites reveals similar trends (r^2=0.37 and r^2=0.39, respectively) with plantation age. As with acidity and pH, the Ca/Al ratio drops markedly in the first two decades following afforestation. Thus, strengthening the argument that the most prominent chemical changes in surface soils of these pine plantations occur within the first 20 to 30 years after the grasslands soils have been planted to trees.

ACKNOWLEDGEMENTS

The completion of this dissertation would have been impossible if it were not for the supervision and patience of Associate Professor Martin V. Fey. Additional acknowledgement should be given to Associate Professor James P. Willis for his constructive criticism. I am in debt to Dr Marian Tredoux for providing a peaceful working environment. I would also like to thank Mr Dawie du Toit and Mr Izak Holtzhausen for their kind hospitality, which is much appreciated. Proficient counsel was kindly given by Mr Ferdinand Leygonie. Keeping a good morale and the "lava flow" was easily accomplished thanks to my fellow class mates.

To the following people I express my gratitude for assisting in the initiation of the project and for their assistance: Mr & Mrs John McNamara of Mondi-forests offices in Sabie; Mrs Kim Olbrich and Ms Mieke van Tienhoven of the C.S.I.R. offices in Nelspruit; Mrs Colleen Carlson from the I.C.F.R. offices in Sabie; Mr Dan Saban and Mr Tom E. Nowicki. The project was partially sponsored by Eskom and Mondi-Forests .

Family and friends back home have provided moral and practical support that played an integral role throughout the year: this is very much appreciated.

Finally, I would like to dedicate this thesis to a very close and dear friend, Peter Allen-Frost, who, through a close and warm friendship, has greatly contributed both morally and practically, to many of my achievements thus far. It is most unfortunately that he has not lived to experience the "harvesting" of his support.

" When we are very young and know little,
mountains are mountains,
water is water,
and trees are trees.

When we scholar and become capable,
mountains are no longer mountains,
water is not water,
and trees are no longer trees.

When we have reached a fundamental understanding,
mountains are mountains again,
water is back to being water,
and trees are trees again."

(Zen, China)

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Background

Commercial pine plantations cover a vast amount of land in Southern Africa and are considered an important economic resource. Unfortunately, pine plantations are a source of ecological concern. Studies of commercial forest plantations conducted in Southern Africa have highlighted nutrient decline processes over second rotations and forest soil acidification following the conversion of grasslands into forest plantations. This is especially noticeable in the Eastern Escarpment of South Africa and the Natal Midlands (von Christen, 1964; du Toit, 1993; Nowicki, 1997).

Reports from Sweden (Johnson *et al.*, 1991) observed declining pH relating to stand age. Following these reports and a review by Cronan and Grigal (1995) concerning the Ca/Al ratio, it was the author's purpose, initially, to employ the concept of Ca/Al ratio and similar relationships in studying forest soils in the Eastern Escarpment of South Africa. The purpose of this study is to assist with future forest management strategies and to broaden the present knowledge of pine plantation ecology.

Over 100 years ago, declining productivity was observed in the second and third rotations of forest plantations. As early as 1869, reductions in the growth of spruce plantations were noticed in Germany and Switzerland (Pritchett and Fisher, 1987). These early studies estimated that the decline in yield was correlated to silviculture and soil degradation.

More than a century has passed since the first observations of declining yields following sequential rotations in plantations. Recently, further research has been carried out and produced some interesting findings. In the mid sixties and early seventies there was an increased interest in the issue of second rotation productivity (Pritchett and Fisher, 1987; Morris, 1986, Morris, 1995). The status of commercial plantation productivity, and the evidence of growth stress and tree mortality, has stimulated further research in forest ecology (Sverdrup and Warfvinge, 1993). Human activity (industry, silviculture) and some of its consequences (polluted precipitation) is believed to be an important contributor to the productivity and health of forest ecosystems (Pritchett and Fisher, 1987; Cronan and Grigal, 1995; Mayer, 1998). Reports from the Northern and Southern Hemispheres pointed out deficiencies in nitrogen, manganese, calcium, magnesium, potassium and phosphorus all related to successive rotations and age of afforestation (Clough, 1991; Brais *et al.*, 1995). Yet, some argue (Schutz, 1982; Larssen *et al.*, 1994) that there is no evidence of productivity decline in respect to second and third rotations, and that any problems that have arisen may be attributed to improper management. Furthermore, recent studies (Johnson, 1992; Adams *et al.*, in press) indicate some observations of nitrogen saturation in forests.

Intensive forestry research is aimed at providing meaningful measures for plantation management. Ulrich and Matzner (1983, cited in: de Vries, 1991 and Sverdrup and Warfvinge, 1993) suggested using the Ca/Al ratio of the soil solution as a measure of the growth response of trees to soil acidification. Relating the soil chemistry to the biology of trees is the main principle behind this ratio. Though widely acknowledged and used in many studies, this ratio is still under intensive study and debate.

In the local arena, South Africa is recognised as having relatively high levels of atmospheric pollution (Total sulphur dioxide emission in South Africa: $2.9*10^6$ ton/a), particularly in the eastern highlands of the country (van Tienhoven *et al.*, 1995). In the Mpumalanga province, situated in the eastern part of South Africa,

recent monitoring studies (Palmer monitoring station) have indicated increasing levels of SO_2 emissions, some 100km south-west of the town of Sabie where commercial forestry is abundant. Yet, the mean values of maximum atmospheric concentrations of surface SO_2 recorded for Palmer monitoring station (daily-51.2 mg/l; hourly-277 mg/l) do not exceed the guidelines issued by the Department of Environmental Affairs and Tourism (Rorich and Galpin, 1998). Indications of acidification induced by wet deposition are few though the issue of dry deposition requires further study. Piketh (1994, cited in van Tienhoven *et al.,* 1995) estimated the dry deposition of SO_4^{2-} over a forested area to be 0.109 keq/ha/a compared with 0.025 keq/ha/yr over grassland and at least 1 keq/ha/yr near industrial zones.

Changes in the chemical properties of South African forest soils, and in particular an increase in soil acidity, has already been reported (von Christen, 1964) and continues to occur (du Toit, 1993). Observations of growth stress in pine plantations in the Eastern Escarpment were reported by von Christen (1964). In a recent study by Morris (1995), declining yields of second rotations (2R) in comparison to first rotations (1R) were noted in Swaziland pine plantations which are situated 150km south-east of the city of Sabie in the Eastern Escarpment.

Other studies (Morris, 1986; Schutz, 1982; Clough, 1991) do not clearly indicate an overall trend in declining productivity in various forests in Southern Africa, but rather indicate nutrient depletion over stand age. This may introduce possible effects for site quality and successive rotations, indicating a potential for wider productivity problems in the future. Furthermore, some studies report processes of soil acidification, decline in pH, and changes in CECe and base saturation (BS) of local forest soils (Musto, 1992; du Toit, 1993; Nowicki, 1997). This study was proposed and performed in the light of the various forest studies mentioned above and conducted in this region.

Aims and key questions

The aim of this study is to investigate the change in certain chemical properties of surface soils in pine plantations of different ages. The phases studied are the exchangeable solid phase and the soil solution. Special attention is paid to acidic and basic cations on the exchange sites and in solution.

The hypothesis motivating this study is that there may be a correlation between the Ca/Al ratio in the soil solution and the age of the pine tree compartments. Three key questions are addressed:

1. What is the current status of the forest soils in the Eastern Escarpment of Southern Africa, with respect to possible processes of acidification and nutrient depletion from the upper mineral soil horizon?

2. Does the soil solution chemistry reflect a state of nutrient decline and an increase in phytotoxic ions (Al, Mn) over successive rotations and as the age of the plantation progresses?

3. To what extent can a relationship be drawn between the basic and acidic cation composition of the exchangeable phase, soil solution, various chemical ratios (Ca/Al, BC/Al) and period of afforestation?

CHAPTER 1. ACID-BASE PROPERTIES OF SOILS UNDER CONIFEROUS FORESTS: A LITERATURE REVIEW

1.1. Introduction

In recent years increasing acidification has been observed in pine forest soils of the Eastern Escarpment and the Natal Midlands of Southern Africa, especially after converting natural grasslands into commercial forest plantations (du Toit, 1993; Nowicki, 1997). Further observations were made regarding nutrient depletion and productivity decline following successive rotations (Morris, 1986, Morris, 1995), and of increasing air pollution in the Mpumalanga province, south of the Eastern Escarpment (Rorich and Galpin, 1998). Due to the complexity of forest ecosystems, it is not simple to evaluate, both quantitatively and qualitatively, the impact on forest health of various chemical factors, such as pH and ion concentration (exchangeable and soluble). Thus, it becomes necessary to identify a chemical parameter that could serve as an indicator of biological changes taking place in forests.

The aim of this review is to describe, in brief, the dynamics of acid mineral soils underlying coniferous forests. In addition, to address a specific and relatively novel chemical parameter, which may provide a valuable indication of long term effects on forest growth. The soil solution molar ratio of calcium to aluminium, and similar ratios, are suggested as measurable endpoints, beyond which increased damage to forest plantations may occur (de Vries, 1991; Cronan and Grigal, 1995). The use of the ratio reflects the relationship between ions required for plant growth and ions, which are believed to be non-essential and toxic (Sverdrup and Warfvinge, 1993).

A measurable endpoint constitutes the link between a stress factor, such as acidic input, and the assessment endpoint, which represents adverse health effects. Possible chemical endpoint criteria may be pH, acid neutralising capacity (ANC) or ion ratios (Barkman and Sverdrup, 1996).

1.2. Chemical properties of acid soils under coniferous forests

It is accepted that the increasing concentrations of Al and depletion of basic cations from the soil may adversely affect plant growth. Consequently, plant susceptibility to harmful agents such as pathogens and water stress may increase, as well as internal physiological damage associated with various toxic elements, such as Al, F and O_3, taken up by the plants (Pritchett and Fisher, 1987; Barkman and Sverdrup, 1996; Raven *et al.*, 1999). The effects are not only of soil on plants but are rather more dynamic and involve mutual effects between plants and their biological, physical and chemical surroundings. Pine forests are known to biochemically effect their immediate surroundings, for example through acidification processes of the forest floor (McBride, 1994; Scholes and Nowicki, 1998; Markewitz *et al.*, 1998).

1.2.1. Soil acidity

Soil acidification occurs naturally, it can be enhanced by human activity and for the past 60 years is known to occur in forest soils (McBride, 1994; Rodhe *et al.*, 1995; Drever, 1997). Some common chemical characteristics of acid soils under forests are low base saturation, abundance of acidic cations (especially Al), inhibition of biological processes such as nitrification, and increased eutrophication (de Vries, 1991; Sverdrup and Warfvinge, 1993; Barkman and Sverdrup, 1996). Among the various types of forests, pine forests are observed to produce a higher degree of soil acidity than that produced by grasslands (Jenny *et al.*, cited in Brady and Weil, 1999).

Increasing acidic inputs in the Northern Hemisphere and their adverse effects on the boreal forests, the natural habitat of pine forests, have motivated the development of methods and models such as SAFE and PROFILE, for assessing acidic loads and their effects on various plants and soils (Jonsson *et al.*, 1993; de Vries *et al.*, 1993; Warfvinge and Sverdrup, 1995). It is beyond the scope of this review to elaborate on the subject of acidic loads and inputs. Yet, it is important to acknowledge its existence since it constitutes an important factor in the identification of chemical indicators of forest vitality.

A common variable in the chemistry of acid soils is the pH. It affects chemical and biological processes, thereby influencing almost directly, the health of organisms living in an acidic medium such as acid soils underlying pine forests. Decreasing pH levels enhance the solubility of metals in the soil and consequently elevate their concentration in the soil solution (Drever, 1997). The fluxes of metals differ between tree species and between forests (Berggren *et al.*, 1990). Among the various metals, Al is of utmost importance, as it has substantial influence on the soil chemistry, and health of organisms which inhabit the soil environment. Al can be considered as a master chemical variable in many acidic soils.

1.2.2. Chemistry of Al in acid soils

Predicting the availability and activity of Al in forest soils is important since Al affects basic cation availability and hence, plant nutrition. In addition, at certain pH ranges, Al constitutes the main buffer substance and is affected by the presence of ligands such as complexes of fluorine, sulphur, organic functional groups, and hydrogen ion activity (Ulrich, 1986; Lindsay and Walthall, 1989; Schecher and Driscoll, 1995; Lawrence and David, 1996).

The solubility of Al in the soil solution is controlled by processes of dissolution and precipitation, and is not totally governed by Al on the exchange sites. Nevertheless, exchangeable Al constitutes an important buffer reserve of labile Al that, given the right circumstances (low pH, mineralogy), is easily solubilised and as previously noted, may affect the buffer capacity of the soils (Lindsay and Walthall, 1989, Brady and Weil, 1999).

As the pH rises, Al undergoes hydrolysis and its solubility decreases. At the same time, the presence of F is of great significance, since it forms strong complexes with Al, thereby reducing the activity of Al^{3+} in solution. Schecher and Driscoll (1995) indicate that the uncertainties involved in the speciation of Al in solutions are high. This would also be the case when the DOC (dissolved organic carbon) is taken into account. Schecher and Driscoll (1995) observed increasing uncertainties with respect to the determination of pH, ANC (acid neutralising capacity) and Al (total)

with increasing levels of DOC. These observations would be expected since soluble organic matter (represented by DOC) varies in its chemical nature as it consists of different functional groups with diverse charge and, consequently, metal complexing abilities (McBride, 1994; Lumsdon and Evans, 1995).

1.2.3. Al phytotoxicity in acid soils

Despite many uncertainties involved in the assessment of Al toxicity in soils, it is recognised as the most important factor limiting plant growth in acidic soils (Foy, 1984). In the soil environment Al interferes with biological activity and may adversely affect microbial breakdown of organic matter (Alexander, 1980; cited in Foy, 1984). It competes with basic cations on exchange sites of clays and organic matter and is favoured on these sites (McBride, 1994). The release of basic cations from exchange sites through exchange with Al, followed by leaching, greatly depletes the soil of basic cations. This, together with nutrient uptake by trees, adversely affects the ability of the soil to retain the cations, decreases its effectiveness as a source of nutrients for plants, and reduces the competence of the soil to neutralise incoming acidity. The presence of organic matter in the soil may increase the solubility of Al-organic complexes in solution, as Al is known to strongly bound to organic matter under highly acidic conditions, yet is known to simultaneously reduce the toxicity associated with free monomeric Al species in solution (McBride, 1994, Brady and Weil, 1999).

Al is known to interfere with plant cell division, to reduce DNA replication, ribosome distribution and protein synthesis and in addition to decrease root respiration (Foy, 1984; McLean and Brown, 1984; Taiz and Zaiger, 1991). The symptoms associated with Al toxicity are not easily identifiable, thereby adding to the difficulty involved in assessing growth stress, and in associating growth stress with Al and its species in solution. The use of geochemical speciation models and thermodynamic calculations to describe Al speciation and toxicity in soils has, to date, been both limited and of questionable integrity (Cronan and Grigal, 1995).

1.3. Effects of silviculture and afforestation on soil chemical status

Afforestation of natural soils and the nutrient status associated with it have been studied locally (Clough, 1991; du Toit, 1993; Nowicki, 1997) and internationally (Switzer and Nelson, 1972; Pritchett and Fisher, 1987; Miller, 1984). Nutrient depletion is known to result from leaching and plant uptake in the soil environment, and has been shown to persist with time. Nutrient loss is further magnified by silviculture (Khanna and Ulrich, 1984). For example, through harvesting, the soil is substantially depleted of essential nutrients for plant growth. The decrease of nutrient concentration in the soil solution results from the release of basic cations from the exchange sites into solution. Thereafter, the leaching through the soil column results in accumulation of the basic cations in lower horizons of the soil.

1.3.1. Nutrient depletion in forest soils

As previously discussed, the depletion of nutrients from the forest soil by leaching is a continuous process. The rates of nutrient depletion vary between trees of different ages. In Table 1.1, the transfer of some of the major nutrients in a forest ecosystem is described.

Comparing the rate of nutrient depletion from the soil to that of nutrient transfer from the tree ecosystem to the soil (Table 1.1), presents a process of nutrient loss of considerable magnitude and importance. The depletion of cations from the soil is equal in its magnitude to the input of cation from the organic horizon to the upper mineral horizon. For example, the transfer of Ca and Mg to the mineral soil accounts for 59 kg/ha/yr and 13.9 kg/ha/yr respectively. Yet, the soil is depleted of 35 kg/ha/yr and 10 kg/ha/yr of Ca and Mg respectively, whereas the requirements of the trees are 59kg/ha/yr and 17 kg/ha/yr of Ca and Mg respectively (Table 1.1). A similar situation was observed in other pine plantation studies (Switzer and Nelson, 1972; Miller, 1984; Johnson and Todd, 1987).

Table 1.1: *Estimated transfer rates for N, P, K, Ca and Mg in plantations of P. taeda at the age of 16 years (modified after Pritchett and Fisher,1987).*

Component	N	P	K	Ca	Mg
	kg / ha / yr				
Requirements of trees	117	20.6	65	59	17.0
Transfer within trees	17	0	18	0	0
Transfer to forest floor	68	8.3	28	35	8.9
Transfer to mineral soil	74	16.3	40	59	13.9
Additional transfer	26	4.3	5	0	3.1
Soil depletion	38	0.3	48	35	10.0

The throughfall and re-deposition of nutrients into the forest floor does not always meet the growth requirements of the trees. The state of nutrients in the soil is further worsened by loss *via* leaching. It is important to note, however, that the mineral soil is not the only source of nutrients for trees. The organic horizon and the canopy itself are common nutrient sources and receptors, the former serving mainly as a source, and the latter mainly as a receptor (Read, 1998; Raven *et al*, 1999). Thus, despite the depletion of nutrients from the soil's mineral horizon, trees may not necessarily suffer from nutrient shortage.

1.3.2. Nutrient uptake and retention by trees

Harvesting as a cause of nutrient depletion from soils underlying pine plantations has been observed for many years (Switzer and Nelson, 1972; Khanna and Ulrich, 1984; Miller, 1984; Pritchett and Fisher 1987; Scholes and Nowicki, 1998). The uptake levels of nutrients by some pine trees are presented in Table 1.2. From Table 1.2 it can be observed that the difference in the extent of nutrient loss due to harvesting differs between tree ages, pine species and within the pine species. Furthermore, the change in soil capital is reported to reach almost 100% with respect to some of the nutrients (Miller, 1984).

Table 1.2: *Annual and total uptake of nutrients, and removal by harvesting (Switzer and Nelson, 1972; Khanna and Ulrich, 1984; Miller, 1984; Pritchett and Fisher, 1987).*

Component	Age (y)	N	P	K	Ca	Mg
Annual uptake of elements				**kg / ha /yr**		
P. patula	18-20	146	12.4	78	108	⊗
Removal by harvesting						
P. elliottii	15	12-23	0.7-1.6	4.9-9.1	8.2-15	⊗
P. taeda	16	6.5-16	0.9-1.9	5-10	7-12	⊗
Total removal from soil				**kg/ ha**		
P. taeda	16	115-257	15-31	89-165	112-187	46
P. taeda	25	190	20	115	100	32
Soil - Total extractable cations						
P. taeda	Mature	⊗	5	224	1280	160

⊗ No data available.

Table 1.3 presents the relative contribution of nutrient sources to the requirements of a 20 year old *P. taeda* plantation ecosystem. Noteworthy is the fact that by the 20th year, the relative contribution of the soil in supplying nutrients is very low and most of the nutrient requirements are met by precipitation and internal cycling (Switzer and Nelson, 1972). This argument is further strengthened by Miller (1984), who points out that as the tree matures and the canopy is developed, the tree tends to increase its use of nutrients from atmospheric deposition.

In the case of a 20 year old *P. taeda* plantation ecosystem, the nutrient pool in the upper mineral horizon can be represented by the soil extractable cations (Table 1.2). Considering that by this age of a *P. taeda* plantation, the soil contributes very little to the nutrient pool, it is possible to assume that the extractable cations comprise the available pool for the next rotation.

Table 1.3 : *The relative contribution of nutrient sources to a 20th year requirement of a P. taeda plantation ecosystem (Switzer and Nelson, 1972).*

Nutrient sources	Contribution (%) to requirement of:					
	N	P	K	Ca	Mg	S
Litter decomposition	40	23	16	54	38	60
Canopy wash and leaching	5	9	50	24	16	0
Precipitation	16	6	12	39	16	88
Internal transfer	39	60	22	0	24	22
Soil	0	2	0	0	6	0
Total ①	100	100	100	117	100	170

① Values greater than 100 indicate soil accretion if root requirement and leaching losses are less than the excess indicated.

1.4. The Ca/Al ratio as an index of growth stress

In the past decade, numerous papers suggested possible interference of Al with the uptake of Ca in various plants. Some of the papers further suggest various ratios (Ca/Al, basic cations/Al) to indicate a probable growth stress (Khanna and Ulrich, 1984; de Vries, 1991, de Vries *et al.*, 1993; Sverdrup and Warfvinge, 1993; Warfvinge and Sverdrup, 1995; Lawrence *et al*, 1995; Walse *et al.*, 1996; Barkman and Sverdrup, 1996).

Cronan and Grigal (1995) presented a comprehensive review and analysis of the Ca/Al ratio as an indicator of growth stress in various plants. This ratio was examined in the soil solution and in various plant segments. Cronan and Grigal (1995) suggest that adverse effects on tree growth, is of a 50% risk when the soil solution Ca/Al molar ratio drops below unity. When the ratio is as low as 0.5, the associated risk level is 75% and when the ratio reaches 0.2 the risk of growth stress adversely affecting tree growth reaches almost 100%. They further suggest that the Ca/Al molar ratio in soils should be determined when the base saturation is under 15%, and if possible, should be accompanied by analysis of the Ca/Al ratio in plant tissues. The use of a 15% base saturation limit derives from observations made by Cronan and Schofield (1990, cited in Cronan and Grigal, 1995) where the highest concentrations of labile Al were observed in mineral horizons of forest soils having

base saturation levels under 15%. Cronan and Grigal conclude that the Ca/Al molar ratio, when used appropriately, can provide a valuable measurable endpoint to assess possible increased damage to a forest system. In addition, the Ca/Al ratio should be used to evaluate changes over time due to various processes (acid deposition, plantation management practices).

The Ca/Al molar ratio of unity is often used as a threshold which when dropped below one, it is believed the potential for growth stress rapidly increases. It is a ratio used both in the soil environment and as previously mentioned in plant segments (Cronan and Grigal, 1995). It is assumed that forests exhibiting a Ca/Al molar ratio greater than unity, are safe from acid related damage (Sverdrup and Warfvinge, 1993), especially in the presence of polluted atmospheric inputs. Comprehensive studies do note changes in Ca/Al ratios in forest ecosystems wchich may pose an increasing risk potential to those forests (Lyon and Sharpe, 1999), yet there is no significant reference in the literature of changes in the BC/Al ratio in trees and forest compartments of various and advanced ages.

Sverdrup and Warfvinge (1993) observed variations in the Ca/Al molar ratio with depth within acidified forest soils. Yet, the definitions used by Sverdrup and Warfvinge (1993) of the forest soil horizons are not very clear. They indicate the Ca/Al molar ratio to be high at the "top" of the soil (assumed by the author to be the O horizon and the forest floor). Thereafter it decreases down to the E (assumed by the author to be the upper mineral horizon) and B horizons, of acidified soils and subsequently generally increases again towards the C horizon. These changes in the Ca/Al ratio can create highly unfavourable conditions for tree growth and plantation management. For example the root system of the trees will prefer the upper mineral horizon of the soil thus retaining less standing stability of the bark and increasing the susceptibility of the tree for lodging (Sverdrup and Warvfinge, 1993). Sverdrup and Warfvinge (1993) conclude, similarly to Cronan and Grigal (1995), that the use of the BC/Al (which includes Ca/Al) ratio is a useful mean of evaluating growth decline in forests and that the general value of $BC/Al \geq 1$ is a useful critical value and indicator of forest health in European forests.

1.4.1. Other ratios in solution

Comprehensive studies regarding the (Ca+Mg+K)/Al ratio of various plants were conducted by Sverdrup and Warfvinge (1993) who produced some valuable data concerning plant health. The conclusions regarding that data were previously presented as part of the Ca/Al ratio discussion.

Apart from the various combinations of (basic cations)/Al ratios in the soil solution there are a few more significant ratios reported in the literature with respect to acid soils and plant health (Sverdrup and Warfvinge, 1993; de Vries, 1991). Some of these ratios are discussed below.

P/Al ratio – Phosphorus is an essential element for plant growth. Sverdrup and Warfvinge (1993) present studies showing possible growth stress reflected by the P/Al ratio. This is especially relevant in soils containing little or no excess of phosphorus. Data for Chinese tea (*Camellia sinensis*) indicates that P increases the tolerance of the plant to Al. Further support for effects of Al on solubility and availability of inorganic P is reported by Sumner *et al.* (1991), Pritchett and Fisher (1987), and Adams and Walker (1975).

$NH_4^+/(K^+ + Mg^{2+})$ – De Vries (1991) reported studies from the Netherlands where increasing concentrations of NH_4^+ and $NH_4^+/(K^+ + Mg^{2+})$ ratios were correlated with forest vitality. Increasing depositions of N enhance accumulation of NH_4^+ in the soil, which inhibits ectomycorrhyza growth. De Vries (1991) further reported studies by Boxman *et al.* (1988) where a strong decrease in the uptake of Ca^{2+} and Mg^{2+}, coupled with an increase of NH_4^+/K^+ (molar ratio), was noted in a greenhouse experiment on Corsican pines. A critical value of 5 was suggested for the $NH_4^+/(K^+ + Mg^{2+})$ ratio below which growth stress could be expected. Further support for this ratio is presented by Sverdrup and Warfvinge (1993) who indicated antagonistic effects between K^+ and NH_4^+, and by recent reports of N saturation of forest ecosystems (Johnson, 1992; Adams *et al.*, in press).

The various studies of BC/Al ratios in solution which have been discussed thus far have not indicated whether any observations were made regarding the BC/Al ratio in the solid/exchangeable phase. Although plant nutrition is more directly related to the availability of nutrients in solution, which constitutes the immediate available nutrient pool, the exchangeable phase constitutes the reserve pool of nutrients that provides elements for longer periods of time. Consequently, the exchangeable phase, has over a longer period of time, a significant effect on the dynamics of nutrients in the rhizosphere and subsequently plant health.

1.5. Acidification and nutrient status in pine forests of Southern Africa

In the beginning of this review, some indications were provided regarding the state of pine forest soils in Southern Africa. Recent studies indicate a drop in pH, base saturation and ANC (acid neutralising capacity), as well as changes in CECe (effective cation exchange capacity), that reflect a loss of basic cations and increasing levels of exchangeable Al dominating the CECe (Clough, 1991; du Toit, 1993; Nowicki, 1997).

Studies of forest productivity indicated similar trends of increase in exchangeable Al, decrease in exchangeable Ca and depletion of essential elements. This suggests the possibility of declining yield over successive rotations (Morris, 1986). These findings are in agreement with other observations regarding pine forest studies (Turner and Lambert, 1988).

With respect to the Ca/Al molar ratio, Nowicki (1997) observed Ca/Al molar ratios falling below unity (Ca/Al < 1) in some pine plantations in the Sabie area in the province of Mpumalanga. These observations were made in forest compartments on the Eastern Escarpment characterised by high elevation (1000-1800 m) and high rainfall (>1000 mm/yr).

1.6. Conclusions

Observations of acidification processes and declining productivity in pine plantations in Southern Africa have motivated the investigation of the relationship between coniferous forests and soil acidity status. Recent studies have suggested the use of an empirical ratio between the concentrations of Ca and Al in the soil solution and in plant segments (Cronan and Grigal, 1995). The inspiration behind the use of this ratio is to associate chemical processes taking place in the soil medium (such as acidification) with the biological response to the change in the chemical environment. Ideally, this will assist with predictions of forest growth and health status.

The chemistry of soils under pine plantations is widely discussed in the literature, especially in the context of acidic inputs (de Vries, 1991; Barkman and Sverdrup, 1996). A common chemical feature in acid soils is Al which is known to adversely affect plant growth and soil biota (Foy, 1984). It is favoured over basic cations on exchange sites and is recognised to have high affinity for ligands. The speciation of Al in solution and on the exchange sites is still the topic of many studies. The difficulty involved further increases in the presence of soluble organic matter (Schecher and Driscoll, 1995).

Employing the Ca/Al molar ratio of the soil solution as a complementary tool for assessing forest health has proved beneficial in many studies (Sverdrup and Warfvinge, 1993; Cronan and Grigal, 1995). No indications were provided in the literature examined to suggest the use of the Ca/Al ratio (and similar ratios) in investigating the solid phase. In addition, recent studies observed the Ca/Al molar ratio of the soil solution to drop below unity level in pine plantations in the Eastern Escarpment of South Africa (Nowicki, 1997).

CHAPTER 2. STUDY AREAS, SAMPLING AND STATISTICAL METHODS

2.1. Study area - general description

This section is based on Mondi-Forests (Ltd) and S.A.F.I. (Ltd) working plans for the Rhenosterhoek forest area and Mauchsberg forest area. The Rhenosterhoek area comprises the "Blyfstaanhoogte" and "Rhenosterhoek" plantations, whilst the Mauchsberg area comprises the "In die diepte" and "Grootfontein" plantations. Climatic data were obtained from the provincial statistics database (C.S.S., 1996).

The geographical terminology used in the various reports used in this study (S.A.F.I., 1957; S.A.F.I., 1973; S.A.F.I., 1979) requires some elaboration due to changes in provincial names. The study area (Sabie) currently falls under Mpumalanga Province. Previously, the study area fell under the Eastern Transvaal province, often referred to as a geographical unit as well. The Sabie district lies in the northern part of the Mpumalanga Province and the town of Sabie is the district capital (Figure 2.1). Detailed descriptions of the sampling sites are presented in Appendix A.

2.1.1. Climate

The study area falls within the semi-humid subtropical summer rainfall zone (October to April). The average number of rainy days is 90 (C.S.S., 1996). The rain ranges from heavy downpours to light penetrating showers. An appreciable amount of rain falls in the form of gentle drizzle and mist, which is typical of the area, hence the name "the mist belt" given to the area. The Grootfontein area is described (S.A.F.I., 1973) as not being typically "mist belt". In the rainy season, the soil is permanently well supplied with moisture, which, under these conditions, seldom rises by capillary forces to the surface. Moreover, during the rainy season precipitation exceeds evaporation. In winter (dry season), there is little rain and the dessication of the soil is accelerated by strong dry winds.

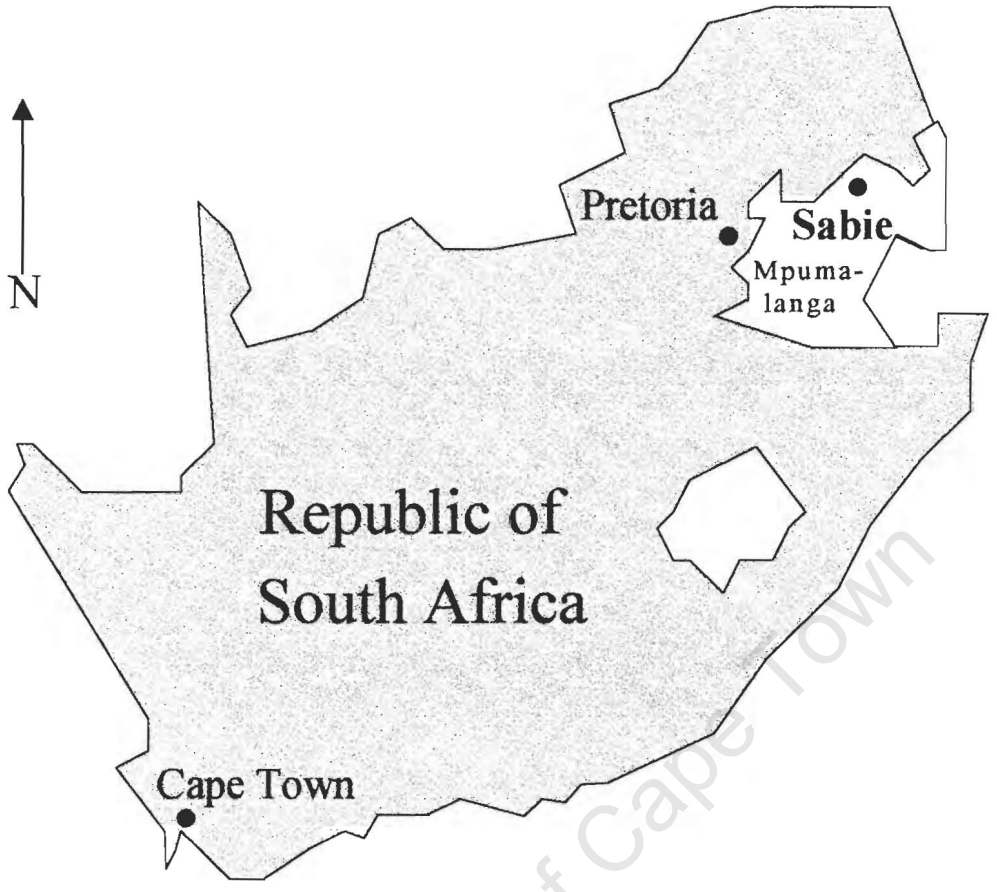

Figure 2.1: *Map of South Africa showing the position of Mpumalanga province.*

Table 2.1 presents the mean annual rainfall, and the maximum and minimum temperatures, recorded in the Eastern Transvaal-Mpumalanga region for the 1961-1990 period (C.S.S., 1996). Apparent from Table 2.1 is the considerable rainfall variation over Mpumalanga province. The average rainfall ranges from 500mm/a to almost 1500mm/a. Rabie *et al.* (1994) cite a lower precipitation limit of 750 mm/acre for commercial forestry. Mondi forests (1997) report a lower precipitation limit for softwood commercial plantation of more than 900 mm/a. Also important in this context are the maximum rainfall figures. These are for the Graskop area, which includes the Mauchsberg plantations. The Mauchsberg area is distinguished by its higher rainfall in comparison with the surrounding terrain in Mpumalanga. Optimum growth temperatures are reported to be between 15°C and 30°C (Rundel and Yoder, 1998). The vegetation is typical of dolomite and shale ground on hilly terrain (S.A.F.I., 1957), consisting mainly of grasslands (short and long grass). Trees occur in valleys and along mountain tops.

Table 2.1: *Temperatures and rainfall for the period of 1961-1990 (C.S.S., 1996)*

Mpumalanga	Annual	January	July	Annual	January	July
	Rainfall (mm)			Temperature (°C)		
Mean						
Nelspruit	767	127	10	19.9	24	14.8
Witrivier	687	102	14	21.1	24.8	16.7
Minimum	516	80	1	13.7	17.3	8
Maximum	1480	264	21	22.2	25.7	17.2

2.1.2. General geological and mineralogical background

The geological description of the area under study is based on the South African Geological Survey (S.A.C.S., 1980), and on reports produced by S.A.F.I. (1957, 1973, 1979) regarding specific plantations. Where discrepancies occur between the S.A.C.S. survey (1980) and the S.A.F.I. reports (1957, 1973, 1979), the S.A.C.S. description was preferred.

The area studied falls under the lithostratigraphic subdivision of the Transvaal sequence and the Pretoria group (S.A.C.S., 1980). The Pretoria group consists predominantly of quartzite and shale with a dominant volcanic unit, the Hekpoort andesitic formation (Figure 2.2). Minor conglomerates, as well as chemical and volcanic members are found.

Nowicki (1997) reports the clay content of the shales in forest soils of the Eastern Escarpment as being between 20% and 30%. In addition, the mineralogy of the clay was described to consisting mainly of kaolinite, chlorite, gibbsite and goethite.

The visual effect of afforestation on the landscape of the Eastern Escarpment can be observed in Figure 2.3. It can be seen from Figure 2.3 that forests have a great visual effect on the adjacent natural land comprising mainly of grasslands.

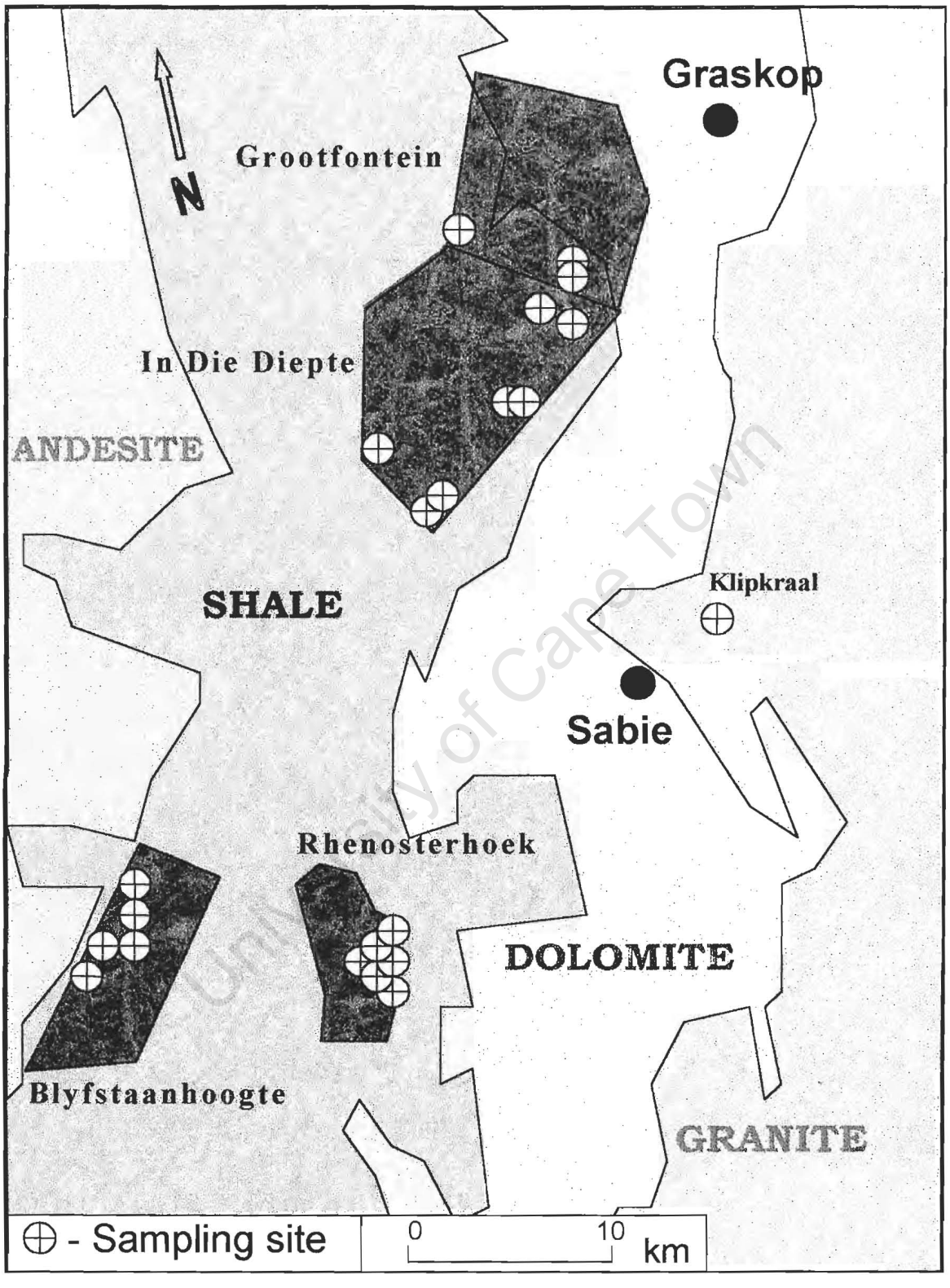

Figure 2.2: *Sampling sites and the basic geology of the Sabie area.*

Figure 2.3: *View from north west to south east from between compartments M27a and M47a, of the Rhenosterhoek Forest area.*

2.2. Rhenosterhoek forest area

The Rhenosterhoek forest area consists of the following plantations: Rhenosterhoek, Doornhoek and Blyfstaanhoogte. Afforestation at the Rhenosterhoek plantation commenced in 1944, at Doornhoek in 1949 and at Blyfstaanhoogte in 1957. The Rhenosterhoek plantation is 2127 hectares in extent, and the Blyfstaanhoogte plantation 3075 hectares. The plantations from which the samples were taken are described below.

2.2.1. Topography

Situated 30°35'E and 25°13'S, the forest area lies at the foothills of the Drakensberg mountain range, in the Eastern Transvaal escarpment area. The elevation is between 1400 and 2200 m above sea level. The area comprises two main drainage basins - the Nelspruit River and the Blyfstaanspruit River, both of which are part of the Crocodile River catchment area. On the northern and the western part of the Rhenosterhoek forest area, the topography is one of steep slopes levelling off towards the south east. The topographical features of the area are typical of the Eastern Transvaal. The terrain consists of irregular undulating gentle slopes, but becomes steep towards the northern, eastern and western boundaries, which run along the summits of the ridges.

2.2.2. Geology and soils

The underlying bedrock is predominantly dolomite and shale, with occasional quartzitic units of the Transvaal sequence. Diabase dykes and sills intrude all three bedrock types (Figure 2.2). The stratigraphic sequence dips to the west, with dolomite overlying quartzite of the Black Reef formation. The dolomitic terrain is deeply dissected with underground aquifers (S.A.F.I., 1957).

Shales of the basal Pretoria Group overlie the dolomites. The soils derived from the shale are predominantly clay loam. On the plateau, the soils are shallow to moderate in depth. The depth to the unweathered bedrock of the shale zone is reported to be between 10 and 15m (S.A.F.I., 1957), in the Rhenosterhoek-Doorenhoek area, and between 600 and 700m in the

Blyfstaanhoogte area (S.A.F.I., 1979). The shale in the Blyfstaanhoogte area is described as thinly bedded brown shale, very fissile in parts. The colour is slightly darker in the lower portions. Bands of micaceous, shaley sandstone are common throughout the area. The shale is generally highly jointed, and in some places highly ferruginous (S.A.C.S, 1980).

The soils of the area studied are typical of the "Mistbelt" and are derived from shale and quartzite of the Pretoria Group. The soils in the Rhenosterhoek plantation were described (S.A.F.I., 1957) as comprising mainly of a sandy loam and sandy clay. The soil texture of the Blyfstaanhoogte plantation was described as being a sandy loam- clay loam. Both plantations were reported (S.A.F.I., 1957) to be of low pH (4.4-4.9, in water suspension), adequate levels of nitrogen in the A and B mineral horizons, as well as low P and K (Appendix A).

2.2.3. Sampling sites

Eleven compartments were sampled. Six samples were taken from the Rhenosterhoek plantation (Appendix A) and five from the Blyfstaanhoogte plantation (Appendix A). The samples were labelled in a sequence specific to this study. The conversion of the official compartment identification to that used in this study is presented in Table 2.2.

2.3. Grootfontein forest area

The Grootfontein forest area is part of the Mauchsberg forest plantation area, and consists of the Grootfontein and in die diepte plantations (Appendix A). The terminology used in characterising the area in the various reports and maps is not consistent. This is due to changes in forest management and reporting policies over the years. Thus, the terminology needs to be standardised. Prior to 1978, the Grootfontein forest area comprised a single plantation: Grootfontein. From 1978 onwards, the references are to Grootfontein as including the Grootfontein plantation and In die diepte plantation. In this study the forest area will be referred to as the Mauchsberg area and the two

plantations will be referred to by their names: i.e. Grootfontein and In die diepte. As regards the history of afforestation in this area, commercial planting commenced in Grootfontein in 1948 and in In die diepte in 1959.

Table 2.2: *Site description - Rhenosterhoek forest area*

Plantation	Comp-artment No.	Sample labelling	Year established	Comp-artment age (y)	Present rotation No.	*Pinus* species
Rhenosterhoek	R-13	R-1	1946	52	2	®*p+e*
	R-15a	R-2	1946	52	2	*pat+ell*
	R-22	R-3	1947	51	3	*elliottii*
	R-23c	R-4	1945	53	3	*elliottii*
	R-23d	R-5	1945	53	2	*patula*
	R-24	R-6	1945	53	2	*patula*
Blyfstaanhoogte	M-27a	B-1	1958	40	2	*patula*
	M-47a	B-2	1976	22	1	*pat+ell*
	M-48b	B-3	1976	22	1	*patula*
	N-3b	B-4	1960	38	2	*patula*
	M-35a	B-5	1959	29	2	*patula*

® p -patula ; e - elliottii

2.3.1. Topography

The Mauchsberg forest area is situated behind the first range of hills west of the Drakensberg mountain range, and incorporates a portion of the Blyde River Canyon. The approximate geographical location is 30°45'E and 24°25'S. The topography of the plantation is rugged with steep, broken slopes, deep gorges and very little flat land. The plantation is bisected, roughly from south to north by the Blyde River with minor tributaries originating in gorges and running in all directions. The altitude varies from 1830 m above sea level in the south east corner, to 1280m at the Blyde River in the north of the forest area. The mountain slopes face predominantly east and west.

2.3.2. Geology and soils

The geological nature of this area is similar to that of the Rhenosterhoek area. Sediments of the Transvaal Group underlie most of the area of the study. The

soils derived from these rock types vary in depth. In the lower slopes, they are deep, rich and of dolomitic origin while on the higher areas the soils are shallow and are derived predominantly from shale, being poorer with respect to nutrient content.

2.3.3. Sampling sites

Ten compartments were sampled. Seven samples were taken from the In die diepte plantation and three from the Grootfontein plantation (Appendix A). The site description is presented in Table 2.3.

Table 2.3: *Site description - Mauchsberg forest area*

Plantation	Compa-rtment No.	Sample labelling	Year establi shed	Compa-rtment age (y)	Present rotation No.	*Pinus* species
Grootfontein	A-3a	G-1	1949	49	2	*⊛p+e*
	A-3b	G-2	1950	48	2	*pat+ell*
	E-3a	G-3	1955	43	2	*taeda*
In die diepte	L-1	I-1	1966	32	2	*taeda*
	M-20	I-2	1970	28	2	*pat+ell*
	M-22	I-3	1969	29	2	*patula*
	N-15	I-4	1972	26	1	*elliottii*
	N-16	I-5	1972	26	2	*elliottii*
	J-20	I-6	1964	34	2	*patula*
	P-4b	I-7	1973	25	1	*patula*

⊛p -patula ; e - elliottii

2.4. Klipkraal forest

The oldest site available for sampling was near Mondi's dam in the Klipkraal plantation (10km north east of Sabie). The plantation was established in 1931. The sampled compartment (R-15b) was never harvested, and the trees on this site are still of the first rotation (67 years of age). The geology of the site is predominantly granitic. It is of a western aspect and is some 400m lower than the average sampled site in the Rhenosterhoek and Mauchsberg forest area.

2.5. Sampling methods

Soil sampling was carried out at suitable sites where the pine plantations were of:

- A North-west to North-east aspect;
- Similar parent material (shale);
- Varied slopes;
- High altitude (1500-2000m);
- Maximum available spread of plantation age;

Twenty-two sites were selected to represent similar geological and geographical properties, with plantation age ranging between 22 and 67 years. One exception is a pine plantation chosen for its progressive age (67 years) despite its slightly different characteristics (granitic parent material, western slope, lower altitude). All sites were sampled within a time span of 48 hours. No substantial change in climate, liable to affect soil properties, was noted during the sampling period. The data and records of the various plantations and compartments were collected from Mondi regional offices in Sabie. The records were used to decide which of the compartments were to be sampled, and to obtain data regarding the history of each of the compartments.

Only topsoils were sampled for this study (0-20 cm). Any overlying organic material was removed. The reason being the assumption that most of the root mass (and root surface) responsible for water and nutrient uptake is in the topsoil (de Vries, 1991). In addition, it is the topsoil that is most sensitive to acid deposition, and thus most likely to reflect any change in the chemistry of the solid and aqueous phases in forest soils. Given the various silvicultural practices and disparate pattern of littering associated with the various pine species, the organic horizon was not sampled and was excluded from the samples. A composite soil sample was created according to the following method:

A sampling site, with an average size of 200 x 200m was selected. Four individual soil samples were obtained by removal of the upper organic horizon.

A hole, 20-25cm deep and 25cm wide, was dug. The soil was mixed in the hole and excavated. The four samples were consolidated, thoroughly mixed and a composite sample was taken (3-4 kg).

The samples were air-dried, sieved (2mm) and stored for further analysis. The soil samples were analysed by common methods of soil analysis. The main objective was characterising the chemistry of the exchangeable phase and the soil solution. All of the analytical work reported in this study was carried out on these 22 samples.

2.6. Statistical treatment

The relationship between surface soil chemical properties and age of these soils under commercial forestry is statistically evaluated by using a non-parametric, one way Anova test (Kruskal- Wallace). The reasoning behind the use of this statistical treatment is that there were sufficient samples (22) and the data could be evaluated while disregarding the distribution of the parent population. Most of the variables compared in this study were assumed not to be normally distributed. The assessment of a statistical treatment is done by obtaining the p-values, which provides an indication of whether the result is statistically significant or not (commonly a 95% confidence limit is used; i.e. $p \leq 0.05$).

Precision of the various methods used for the chemical analysis of the soil samples is evaluated by using mean, variance and standard deviation based on descriptive statistics. The relationship between various parameters (such as Ca/Al ratio and age of afforestation) is obtained by using non-parametric treatments such as the Shapiro-Wilks test for determining the distribution and obtaining trend lines (using Spearman r^2 criterion). All the statistical calculations are carried out using the STATISTICA software program (StatSoft Inc., 1995).

CHAPTER 3. SOIL CHARACTERISATION AND ACIDITY STATUS

3.1 Introduction

Understanding soil acidity status and the state of exchangeable cations enables us to evaluate the processes that are taking place in the forest environment and the potential effects they may have on forest productivity. An increase in soil acidity and exchangeable Al concentration and depletion of basic cations are known to occur in acid pine forest soils. Exchangeable Al constitutes an important buffered reserve of labile Al that can be made soluble by various processes and can be exchanged with basic cations.

This chapter presents the results of chemical analysis performed on the soil solid phase. Exchangeable cations, acidity and the acid neutralising capacity (ANC) were determined as a measure of understanding the present state of soil acidity and basic cations in the forest soils. Further calculations of effective cation exchange capacity and base saturation were conducted. Characterising the chemistry of the soil solution will be dealt with in Chapter 4.

3.2 Materials and methods

The study was based on analytical data for 22 samples of surface soil (0-20cm depth) taken from the upper mineral horizon of 5 pine plantations containing 22 different forest compartments, as presented in sections 2.2, 2.3 and 2.4. The samples were air dried and sieved to pass through 2mm.

Soil pH was determined in distilled water (pH_{water}) and 1M KCl (pH_{KCl}) at a soil: solution ratio of 1:2.5 using a Metrohm 691 pH meter. Soil suspensions were stirred, left for an hour to equilibrate, stirred again, and after 10 minutes pH was

measured. The pH value stated for each of the samples in the study represents the mean value of 3 measurements. Assuming that the pH data is not normally distributed (among the various samples) the Spearman R^2 and the Shapiro-Wilks distribution test were used for trend calculations (Statsoft Inc, 1995).

The determination of exchangeable acidity and cations was conducted by the following procedure. A suspension having a soil:solution (1M KCl) ratio of 1:10 was shaken for 10 minutes, centrifuged and the pH determined. The supernatant was passed through a 0.45μm membrane filter. A portion of the supernatant was diluted (1:9) and analysed for exchangeable Ca, Mg, Mn and Al by flame atomic absorption spectroscopy (FAAS). Exchangeable Mg and Mn were determined using an air/acetylene flame. Exchangeable Al and Ca were determined using a nitrous-oxide/acetylene flame. The remainder of the solution was used for exchangeable acidity determination. The supernatant was titrated to an end-point with 0.01M NaOH (phenolphthalein) (Rowell, 1994).

The acid neutralising capacity (ANC) of the soils was determined according to the method proposed by du Toit and Fey (1994). The detailed method is presented in Appendix B. ANC was calculated using the formula proposed by du Toit and Fey (1994) where:

$$ANC\ (cmol_c/l) = 9.624\ pH - 34.13.$$

In addition to the above methods, organic carbon (OC) was determined by the Walkley-Black wet oxidation procedure (Nelson and Sommers, 1982). Further details regarding the methods of analysis mentioned above are reported in Appendix B.

3.3 Results and discussion

3.3.1 Organic carbon (OC)

The levels of organic carbon found in the forest soils collection are relatively high (3.7-10%) with a mean value of 6.6. The high values recorded for organic carbon in the soil collection are not unexpected, since some pine forests (*P. patula, P. taeda*) are recognised to accumulate large amounts of organic matter (Morris, 1993; Dames, 1996). This pattern of accumulation is especially important in the absence of fire, which is the case in this study.

The importance of OC levels in coniferous forests lies with the tendency for litter (pine needles in particular) to be very acidic and to produce an acidic leachate (Parfitt *et al.*, 1997; Raven *et al.*, 1999), consequently enhancing acidification by introducing protons and other acid cations to the soil solution, thereby altering the acidity-alkalinity balance and promoting weathering of minerals (Miller, 1984; Pritchett and Fisher, 1987). Other possibilities do, however, exist. Ross and Bartlett (1992) indicate that the actual strength of organic matter acidity appears to be quite important and that the acidity generated is both a function of the formation of the organic matter and of the parent material. Furthermore, the leachate may not acidify as its acidification capacity is dependent on the ion concentration in solution and is independent of pH.

Another important feature of organic matter is its strong affinity for cation binding and especially relevant to this study is its bonding with Al (McBride, 1994; Brady and Weil, 1999). Aluminium is known to have a greater affinity for organic matter compared to other cations (Ross *et al.*, 1991). Organic matter alters the solubility of Al species in solution, it may decrease the phytotoxicity associated with free Al ions in solution and decrease the available pool of exchangeable Al (McBride, 1994; Brady and Weil, 1999). Hence, Al affects the CEC (cation exchange capacity) of the soils. The bonding of Al to organic matter reduces the potential of basic cations to attach to ligand groups on the organic matter and thus, the OM may contribute very little to the CEC of acid soils (Thomas and Hargrove, 1984).

In addition, Al has a reducing effect on the acidic strength of organic acids. For example, the organic acids may change their formation from a polyprotic acid to a weak monoprotic acid (Thomas and Hargrove, 1984). The extraction of Al from organic matter requires a forceful chemical measure of extraction, such as $CuCl_2$ (Juo and Kamprath, 1979).

3.3.2 Soil pH

Soil pH values in the soil collection indicate a generally highly acidic environment of the surface soil (Table 3.1). The soils studied present pH levels that are within the very bottom range of forest soils (Binkley and Richter, 1987). A lower pH in KCl than in water indicates a negatively charged clay surface with free exchangeable cations.

It is suggested that the buffering mechanism in this soil collection is controlled by the exchangeable Al (aluminosilicate surfaces) and hydroxo-Al compounds. The literature indicates various pH values in the acidic range for a buffering system dominated by Al (Khanna and Ulrich, 1984; McBride, 1994; Rowell, 1994). It is the author`s understanding that within the range of pH values observed in the soil collection, the buffering system is dominated by Al. A possible confirmation of this statement may be provided by a study by Bredenmeier *et al.* (1990) who studied Al buffering in certain pine forest soils in Europe. The buffering constituents were believed to include protons, Al^{3+}, interlayer Al and $n[Al(OH)_X^{(3-X)+}]$. Ulrich (1986) adds Al-hydroxosulphate as a buffering substance. The buffering substance suggested by Ulrich (1986), may not be present in the soil collection. It may, however, be considered in the cases where atmospheric pollution persists and sulphur emissions are on the increase. For example, at the Palmer monitoring station which is the nearest station to the Sabie forest area, situated some 100km south east of the city of Sabie, low altitude sulphur emissions have been observed in increasing levels (Rorich and Galpin, 1998).

Table 3.1: *Analytical data for the soil collection.*

Sample	pH KCl	pH water	Organic carbon (%)	KCl extractable ($mmol_c$/kg soil)					CECe ® ($mmol_c$/kg soil)	BS ④ (%)	ANC © ($mmol_c$/l)	$CuCl_2$ extractable ($mmol_c$/kg soil)
				Ca^{2+}	Mg^{2+}	Mn^{2+}	Al^{3+}	Acidity				Al^{3+}
K 1	3.90	4.50	3.7	1.36	2.96	0.04	32.0	25.5	36.4	11.9	28.4	88
I 1	3.90	4.80	10.4	2.17	3.76	0.17	43.7	46.5	49.8	11.9	39.0	384
I 2	3.95	4.90	3.8	3.77	3.07	0.61	25.5	24.5	33.0	20.8	41.9	99
I 3	3.80	4.60	8.3	2.45	3.63	<0.01	38.7	32.5	44.8	13.6	25.5	163
I 4	4.00	4.85	7.5	1.69	3.08	0.10	32.8	31.5	37.6	12.7	44.8	164
I 5	3.80	4.70	6.3	1.62	2.86	0.13	34.7	30.5	39.3	11.4	31.3	119
I 6	3.74	4.60	7.4	2.86	2.91	<0.01	38.5	35.5	44.3	13.0	34.2	171
I 7	3.90	4.80	5.9	3.11	3.01	<0.01	35.6	35.5	41.7	14.7	34.2	126
G 1	3.77	4.60	6.9	2.24	3.69	<0.01	57.3	55.5	63.2	9.39	25.5	128
G 2	4.10	4.90	8.3	2.00	3.43	0.23	29.1	20.5	34.7	15.7	57.3	106
G 3	3.76	4.25	4.3	2.53	3.72	0.04	41.5	41.5	47.8	13.1	23.6	69
R-1	3.90	4.80	6.4	3.62	3.20	0.08	31.2	32.5	38.1	17.9	36.1	93
R-2	3.85	4.60	6.6	1.89	2.65	<0.01	41.0	39.5	45.5	9.97	32.3	n.d.™
R-3	3.90	4.65	5.3	2.12	2.72	<0.01	33.4	30.5	38.2	12.7	35.1	103
R-4	3.75	4.45	7.2	2.55	3.22	<0.01	60.5	54.5	66.3	8.71	23.6	246
R-5	3.80	4.65	6.9	8.84	3.41	0.05	39.1	41.5	51.4	23.8	32.3	209
R-6	4.10	4.95	10.2	2.63	3.02	0.24	32.5	30.5	38.4	14.7	53.4	341
B 1	3.90	4.70	4.9	3.01	4.15	0.22	34.7	31.5	42.0	17.0	28.4	150
B 2	3.80	4.70	4.5	1.92	3.68	0.09	29.2	26.5	34.9	16.0	28.4	95
B 3	3.90	4.80	7.8	4.80	5.23	0.94	32.0	30.5	43.0	23.3	37.1	187
B 4	3.70	4.40	5.3	4.70	2.68	0.05	46.2	49.5	53.6	13.8	17.8	127
B 5	3.70	4.50	7.2	2.14	4.44	0.04	49.5	50.5	56.1	11.7	17.8	160

® Effective cation exchange capacity. Calculated as the sum of KCl extractable Ca, Mg, Mn and Al.
© Acid neutralising capacity.
™ Not determined.
④ Base saturation. Calculated as: 100 * (Basic cations) / CECe.

When evaluated alone, the pH levels do not exhibit any statistically significant relationship to age of plantation, age of stand or between the plantations. But, when incorporated with similar studies performed in the Eastern Escarpment (Nowicki, 1997) and in similar environments such as the Natal Midlands (du Toit, 1993), a decrease in pH_{KCl} was observed (Spearman $r^2 = 0.37$). In Figure 3.1, the pH_{KCl} values in forest soils of different ages and their adjacent grasslands in the Eastern Transvaal and the Natal Midlands are presented.

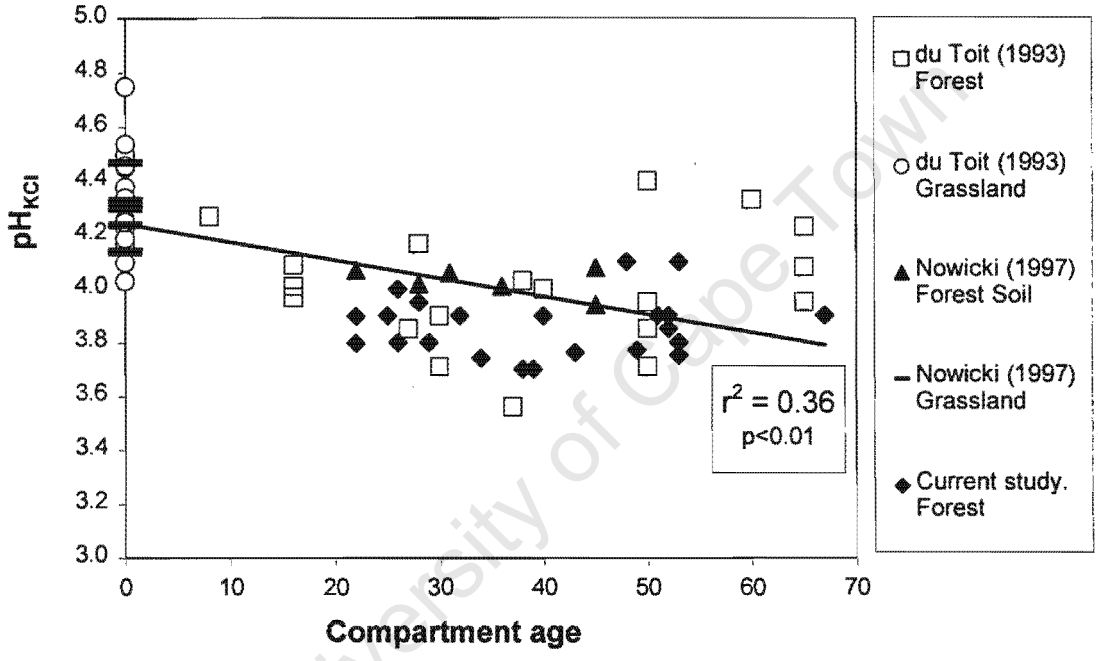

Figure 3.1: *pH_{KCl} values in forest soils of different ages and their adjacent Grasslands, in the Eastern Transvaal and the Natal Midlands.*

From Figure 3.1 it is clear that afforestation has affected the pH of the surface soils. Both areas (Natal Midlands and the Eastern Transvaal) exhibit pH levels, which are lower in the forest than in the adjacent grassland. In addition when observing the changes in pH with respect to the period of afforestation, a clear decline appears, mainly in the first 20 years of a forest compartment. The trend is similar when calculated linearly (r^2=0.37) or exponentially (r^2=0.36). It is the author`s understanding that the correlation is scientifically more viable when observed exponentially, since the most significant changes with respect to pH take place in the first 20 years. Thereafter the soil may have approached a state of

equilibrium beyond which no further decline in pH will occur. The trend discussed above conforms to the buffering system suggested for the soils analysed in this study and is a recognised phenomenon known to occur in forests (McBride, 1994).

3.3.3 Exchangeable acidity

Acidity values are between 20.5 and 55.5 $mmol_c/kg$ soil. Acidity levels (Table 3.1) are slightly higher than those of the exchangeable Al, which may suggest that Al and predominantly Al^{3+}, are the dominant forms of acidity in the soil (Thomas and Hargrove, 1984). This coincides with the buffer mechanism suggested for these soils (Section 3.3.2). Being in this buffer range, the soils are not expected to acidify any further (Johnson *et al.*, 1991).

Acidity determined in this study consists of the exchangeable acidity pool in the soil. It is beyond the scope of this study to determine the total (titratable) acidity. Yet, it may be added that as Thomas and Hargrove (1984) indicate, the ratio of exchangeable acidity / total acidity among clay minerals is the lowest with respect to kaolinitic clay minerals. This is probably the case in this study area since, as noted previously (section 2.1.2), kaolinite is believed to be the dominant mineral (Nowicki, 1997). In addition, the presence of organic matter is believed to contribute very little to the exchangeable pool of acidity.

A correlation between the acidity status and age of soils under commercial forest plantations indicates increasing acidity and compartment age (Figure 3.2). This relationship is important for long term monitoring and study of forested areas. From Figure 3.2 there is a clear indication that afforestation has influenced the state of acidity in the Eastern Escarpment soils by increasing acidity levels. During the first four decades, acidity increases with age of plantation. Noteworthy are the first 20 years of afforestation where a dramatic decline in acidity takes place. Thereafter (the first 2 to 4 decades), the soils may have reached a boundary beyond which further acidification is not likely to take place.

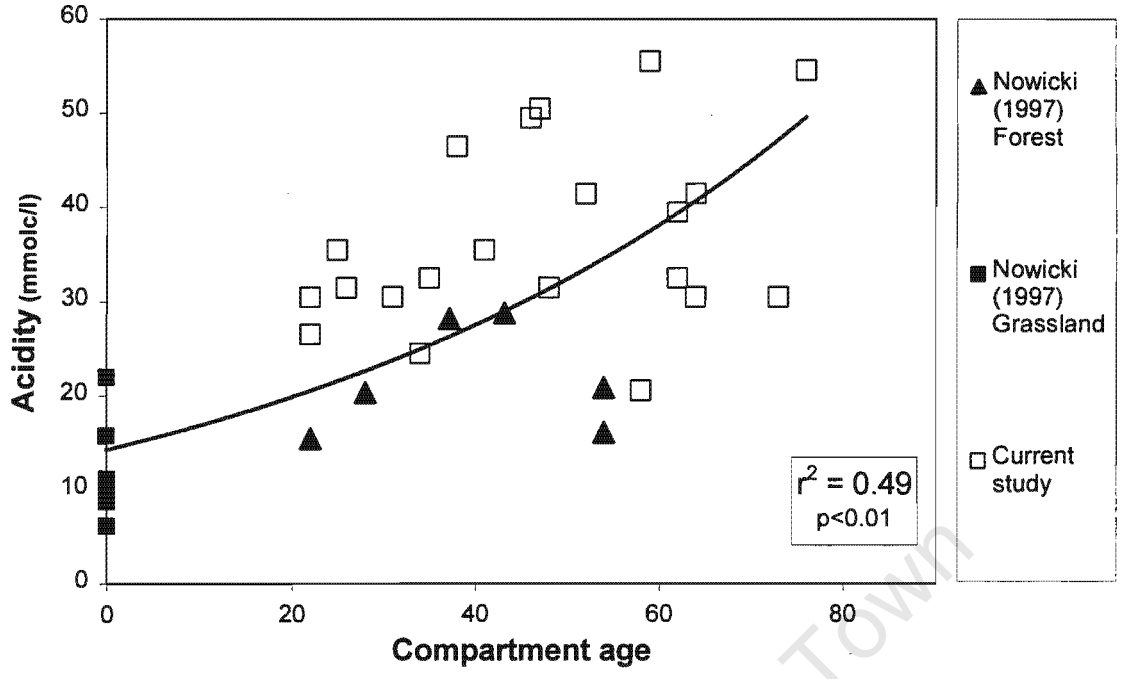

Figure 3.2: *Acidity status in surface soils from commercial forest plantations of different ages in the Eastern Escarpment.*

The values of exchangeable acidity found here suggest a state of acidification greater than that reported in recent studies of pine forest soils in the Eastern Escarpment (du Toit, 1993; Nowicki, 1997). Studies conducted in pine plantations elsewhere in South Africa also suggest acidity values which are generally lower than those obtained in the current study (Clough, 1991; Nowicki, 1997).

3.3.4 Exchangeable cations

The exchangeable cations data were presented earlier in Table 3.1. These ranged, for Ca^{2+}, from 1.36 to 8.84, for Mg^{2+} from 2.68 to 4.44, for Mn^{2+} from under 0.01 to 0.94, and for Al^{3+}, from 25.5 to 60.5 $mmol_c/kg$. Acidic cations, and especially exchangeable Al dominate the exchange complex, with base saturation levels being less than 25%. The change in KCl-extractable Al^{3+} concentration with pH_{KCl} is presented in Figure 3.3. This relationship is expected and is widely described and discussed in the literature (May, 1992; McBride, 1994; Schecher and Driscoll, 1995).

The concentration of exchangeable basic cations does not exhibit any significant relationship to the age of compartments. Johnson *et al.* (1991) point out that over a period of two decades or more, chemical changes such as a drop in pH, exchangeable bases and changes in N mineralisation do appear to be substantial in the soil environment. With respect to basic cations and pH, seasonal variations are generally observed and especially noted in surface soils of *P. taeda* plantations (Johnson *et al.*, 1991).

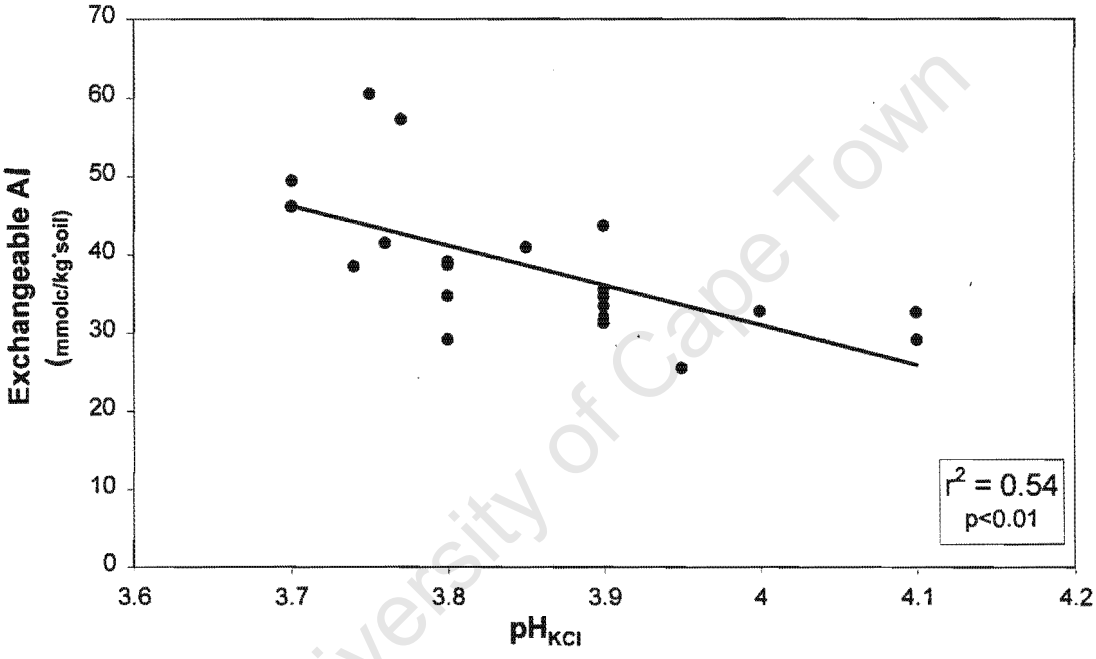

Figure 3.3: *Relationship between exchangeable Al (in aqueous solution of 1M KCl) and pH_{KCl}.*

Nevertheless, when the data from the current study were combined with those of previous and similar studies (du Toit, 1993; Nowicki, 1997), interesting relationships appear. When evaluating the change over time in the forest plantations with respect to the exchangeable basic cations/acidity ratio, a clear correlation is observed (Figure 3.4).

Figure 3.4 displays a sharp drop in exchangeable basic cations/acidity ratio as grasslands (age 0) are transformed into commercial forest plantations and as the age of the forests progresses. After the first 4 decades of afforestation, the system

seems to reach some form of equilibrium with respect to the exchangeable basic cations/acidity ratio. These results are not definite as the standard deviation is relatively high (especially during the first decade of afforestation). This is mainly due to the very few records available for the first decade and possibly insufficient records for the subsequent decades. The drop in BC/Acidity ratio is nevertheless marked following an exponential pattern as might be expected.

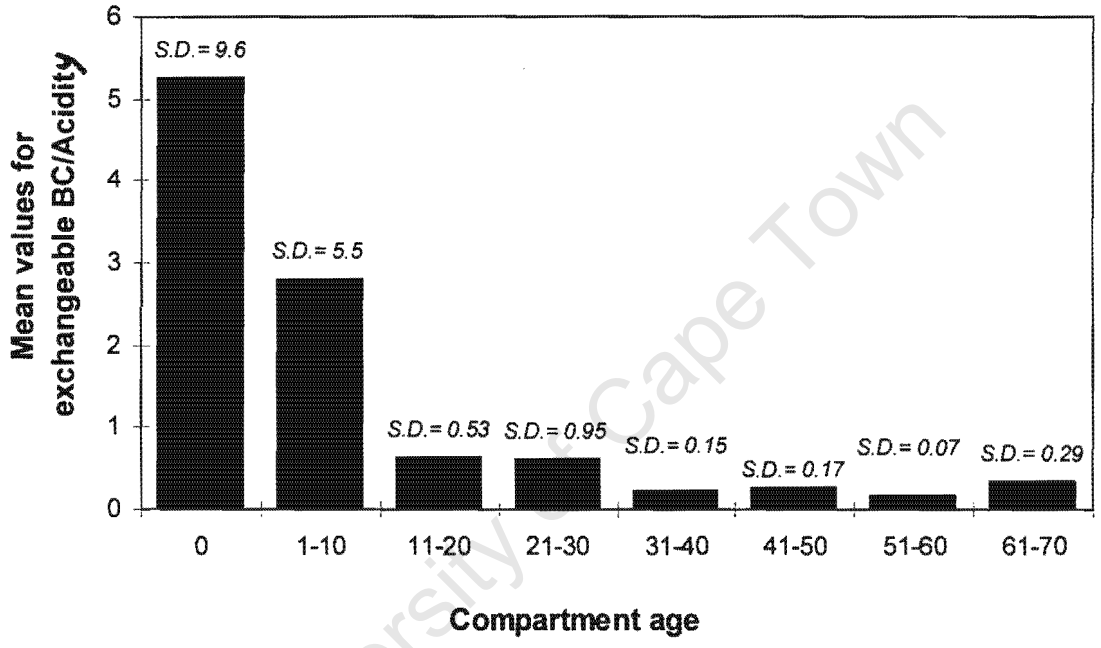

Figure 3.4: *Changes in exchangeable basic cations / acidity ratio in soils in relation to compartment age. The Age group of 0 to 10 consists of forest compartments and their adjacent grassland soils. (data source: current study, du Toit (1993) and Nowicki (1997)).*

Clough (1991) and Nowicki (1997) indicate increasing levels of exchangeable and organically bound Al in pine forest soils in comparison with adjacent indigenous forest and grassland. The levels of exchangeable Al presented by Clough (1991) are less than half of that observed in the soil collection under study. Nowicki (1997), presents equivalent levels of exchangeable acidity which are generally lower (20-46 $mmol_c/l$, mean: 25 $mmol_c/l$) than the equivalent levels found in this study (20.5-55.5 $mmol_c/l$, mean: 36 $mmol_c/l$).

Juo and Kamprath (1979) indicated that the extraction of Al by $CuCl_2$ yields more than twice the amount extracted by KCl. Juo and Kamprath (1979) stated that this reflected the fact that organically bound Al is extracted by this procedure. Similar results were observed in this study (Figure 3.5).

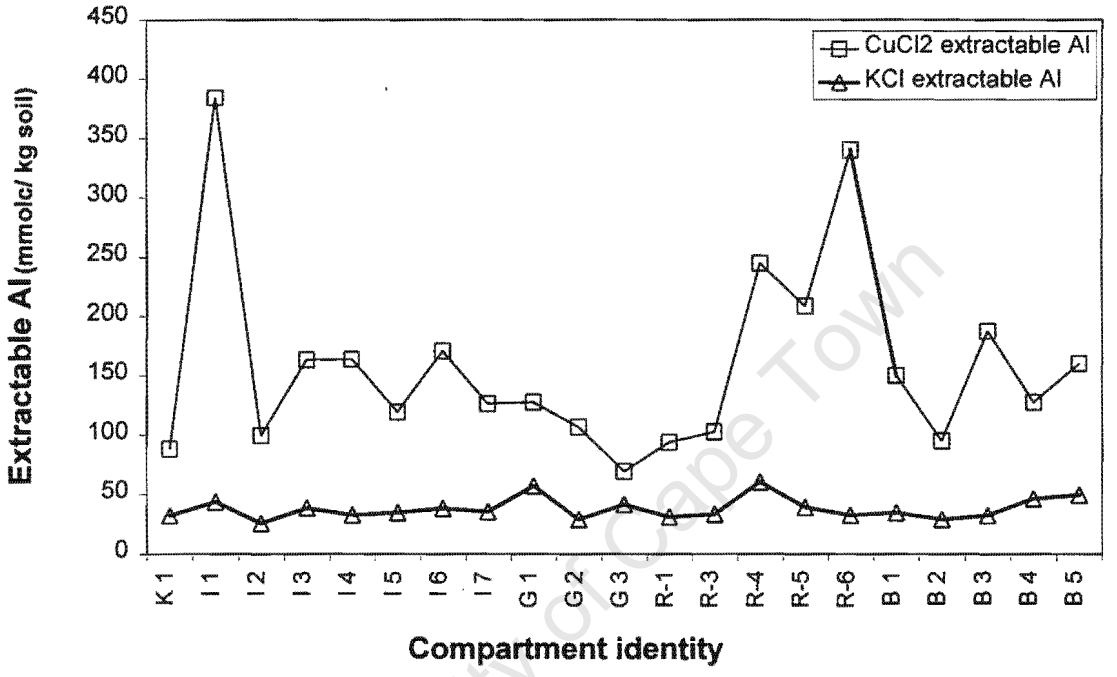

Figure 3.5: *Amount of Al extracted by 1M KCl and 1M $CuCl_2$ from the soil collection.*

Evidence for the claim that Al extracted by the $CuCl_2$ method is organically bound is confirmed in the significant correlation between organic carbon and the amount of Al extracted by the $CuCl_2$ (Figure 3.6).

The base saturation (Table 3.1) in the soil collection does not exceed 25% (mean: 14.4). This observation reflects a generally acidic environment as discussed in the preceding section.

Prior to any further discussion over the issue of base saturation (BS) it is important to consider some uncertainties that appear in the literature concerning the issue of BS. McBride (1994) points out that soils with variable charge minerals (highly weathered soils in particular) have low CEC. It is important to note that the

chemistry of Al in such soils may be controlled by processes such as precipitation and dissolution and not only cation exchange. Thus, McBride (1994, section 5.1b, p. 174) suggests that the use of BS should rather be replaced with separate measures of exchangeable basic and acidic cations, especially since phytotoxicity is better correlated with free Al^{3+} in solution (rather than BS). It is the author's view, however, that the use of BS is of importance to soil chemistry. The use of the BS concept proves beneficial in studying the dynamics of soil acidification (Warfvinge and Sverdrup, 1995), and especially since plant health depends on availability of cationic nutrients such as Ca and not solely on toxicity of Al. Toxicity of Al and availability of Ca are not necessarily covariant.

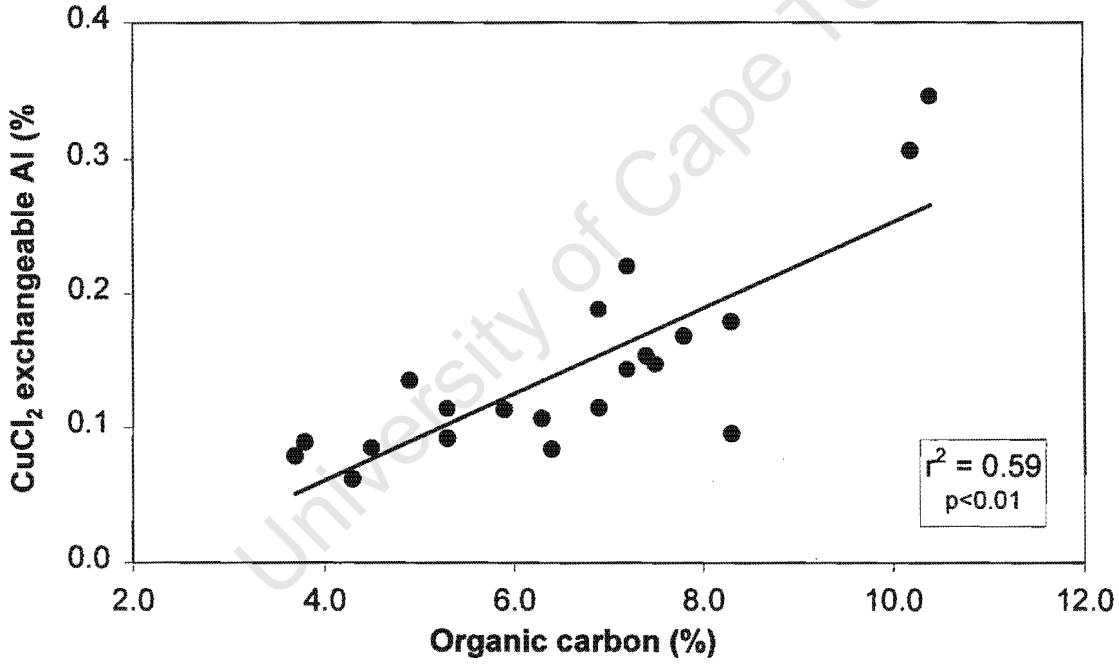

Figure 3.6: *Amount of Al removed by $CuCl_2$ in relation to the organic carbon (%) present in the soil collection.*

Comparing the results in this study and the study by Nowicki (1997) the BS levels for the pine forest soils are lower than BS levels reported for pine forest soils in the Southern Hemisphere (BS: 30-36%. Turner and Kelly, 1985) and in the Northern Hemisphere (BS: 62-98%. Johnson and Todd, 1987). The BS levels in

the present collection of pine forest soils are in agreement with previous studies conducted in the area (Nowicki, 1997), in which it was found that BS did not exceed 25% of CECe. Du Toit (1993) reports declining concentration of exchangeable basic cations, especially Ca, due to afforestation in the Natal Midlands. Incorporating the levels of BS from the data sets by Nowicki (1997) and du Toit (1993) into the data set of the current study, demonstrates a general overall decline in BS as result of afforestation of grasslands (Figure 3.7).

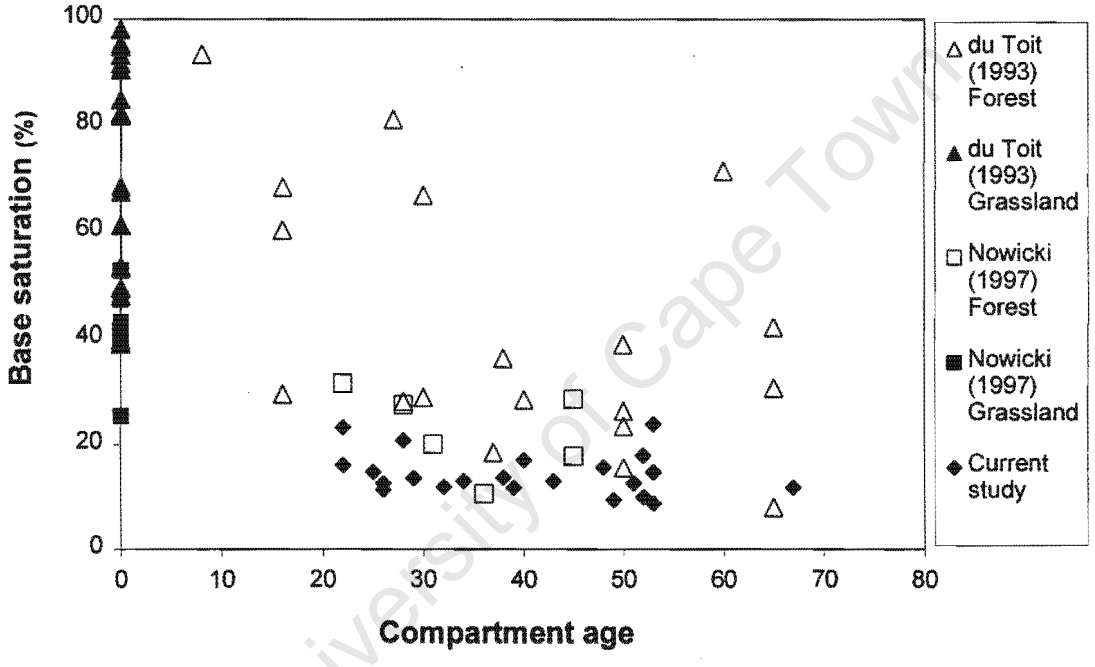

Figure 3.7: *State of base saturation (BS) in grassland soils and forest soils of different ages in the Eastern Escarpment and Natal Midlands.*

The levels of acid neutralising capacity (ANC) of the soil collection are between 17.8 and 57.3 $mmol_c/l$ (mean: 33mmolc/l). Shales are known to have a low to medium ability to neutralise acidity (Chadwick and Kuylenstierna, 1991).

The ANC was found to be inversely correlated with KCl extractable acidity (r^2 = 0.42; $p<0.01$). This result was expected, since the higher the acid neutralising capacity, the lower the acidity present. The ANC does not exhibit a significant

correlation with the total exchangeable basic cations (r^2 <0.01, p<1) but, a strong correlation between ANC and pH was observed (for pH_{KCl}: r^2 = 0.67, p<0.05). No clear trend could be observed between ANC and the period of afforestation.

3.4 Summary and conclusions

The pine forest surface soils of the Sabie area (Eastern Escarpment) are highly acidified. The acidification of these soils is well demonstrated when compared to early studies of grasslands and their adjacent forest compartments, conducted in the Eastern Escarpment area and in the Natal Midlands, thereby suggesting that a significant portion of the acidification process taking place is enhanced by afforestation.

A clear drop in pH is observed as grasslands are replaced by pine plantations and as the period of afforestation increases, especially during the first two decades. The levels of KCl-extractable acidity (exchangeable acidity fraction of the soil) exhibit a corresponding increase which, in the case of acidity continues to increase over the first four decades. Although ANC levels declined with a decrease in pH, no clear correlation was observed between ANC and period of afforestation. The KCl extractable cations are dominated by exchangeable Al (25.5-60.5 $mmol_c$/kg soil).

The mean values of the BC/acidity ratio in the soils declines following afforestation, to less than one (especially after the first 10 years of afforestation). Base saturation levels do not exceed 25%, and exhibit a general decrease in BS as grasslands are forested. The level of organic carbon found in the soils is relatively high (3.7-10%). Extraction by $CuCl_2$ yielded up to 10 times more Al than the KCl extraction, and a significant correlation (Spearman r^2= 0.59) was observed between $CuCl_2$ extractable Al and the content of organic carbon in the soil collection.

The soil collection under study covers a period of afforestation in the Sabie area, that ranges between 22 and 67 years. No data of previous studies regarding the first 20 years of afforestation was available. The importance of the first 20 to 40 years is exhibited in this study by the fact that no significant correlations and trends, regarding various soil chemical properties, were observed with respect to the period of afforestation. Therefore, it may be assumed that the upper mineral horizon experiences the most substantial chemical changes over the first two decades. Consequently, any further study aiming at providing any substantial chemical indices and trends should focus on these two first decades of afforestation.

CHAPTER 4. SOIL SOLUTION COMPOSITION

4.1 Introduction

This chapter investigates the chemical composition of saturated paste extracts, which can be considered a fair reflection of the soil solution (Sposito, 1989). An attempt is made to characterise the intensity of the chemical parameters of the soil solution as opposed to the quantity parameters dealt with in Chapter 3.

Interpreting the composition of the soil solution and assigning conclusions based on those interpretations is not simple. This is due to the fact that generally, the elemental concentration in the soil solution is relatively small in comparison with that on the solid phase (Lindsay, 1979). Due to the chemical sensitivity of the soil solution to mineral dissolution and ion exchange, it is however, a valuable index of relative changes in soil chemical status. Apart from a recent study by Nowicki (1997), there has been no systematic investigation of soil solution composition with respect to the effects of afforestation in Southern Africa.

4.2 Materials and methods

The soil samples were air dried and passed through a 2mm sieve. A 300 g subsample was wetted with deionised water to the point of saturation and allowed to equilibrate for 24 hours, before extracting the solutions under vacuum using a plastic Buchner funnel (Rowell, 1994). The saturated paste extract was then centrifuged and passed through a 0.45μm membrane filter. pH was measured both prior to extraction in the saturated paste, and after extraction in the supernatant.

Solution pH was measured using a Metrohm 691 pH meter and combination electrode. EC levels were measured using a Crison microCM 2201 conductivity meter. Major ions were determined by ion chromatography, using a Dionex DX300 ion chromatography (IC) system (Appendix B). Trace elements were determined

using a Perkin-Elmer ELAN-6000 inductively coupled plasma - mass spectrometer (ICP-MS) system. Prior to analysis by ICP-MS and IC, the samples were filtered (0.2μm) and diluted, to a concentration below 100μS/cm.

Aluminium was determined colorimetrically using the Cr-Azurol S (CAS) method of Kennedy and Powell (1986) (Appendix B). Dissolved monomeric silica (H_4SiO_4) was colorimetrically determined using the molybdosilicate method (Method No. 4500-Si D, Eaton *et al.*, 1995). Dissolved organic carbon analysis was conducted on 0.45μm filtered samples. The analysis was conducted using a variation of the persulphate oxidation method as found in Eaton *et al.* (1995) and described in detail in Appendix B.

Chemical speciation calculations were carried out for all solutions using the MINTEQA2 mathematical model (Alison *et al.*, 1991). The Davies equation option was selected for calculating activity coefficients.

4.3 Results and discussion

The chemical composition of the saturated paste extracts is presented in Table 4.1. Data reproducibility and precision are presented and discussed in Appendix C.

4.3.1 pH of the saturated paste

The pH levels of the saturated pastes range from 4.36 to 4.91, indicating a highly acidic environment which coincides with the state of soil acidity discussed in Chapter 3. The differences in pH values were observed to be generally higher in the supernatant than in the paste. The reason may lie with the suspension effect (greater ionic activity near the soil particles) and the variation of CO_2 concentrations between the soil:water suspension and the supernatant (McLean, 1982). The pH values discussed in this chapter are those of the saturated paste, since it can be assumed that the paste provides a better indication of the chemical characteristics of the solution phase in a saturated soil, than does the extracted, partially re-equilibrated supernatant.

Table 4.1: *Chemical composition of saturated paste extracts. Ion concentrations are in mg/l, EC levels are in µS/cm and pH levels are of the saturated paste prior to extraction.*

Sample	EC	pH	Na^+	NH_4^+	K^+	Mg^{2+}	Mn^{2+}	Ca^{2+}	Al^{3+}	F^-	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Si	DOC
K 1	110	4.50	13.9	6.2	7.9	8.0	<0.01	16.8	1.7	2.6	13.9	0.62	<0.01	<0.01	5.1	23.5	n.d ®
I1	181	4.64	11.5	25.1	14.0	12.2	<0.01	9.5	1.7	9.3	14.1	2.70	<0.01	<0.01	4.4	19.4	147
I2	153	4.86	13.4	8.4	8.7	3.6	7.76	37.4	1.4	4.8	13.2	1.90	<0.01	<0.01	8.2	16.5	86
I3	156	4.66	6.6	23.4	16.0	3.9	<0.01	10.7	2.0	3.9	7.0	1.10	<0.01	0.7	17.3	17.8	116
I4	130	4.65	11.2	14.2	3.9	4.7	1.62	16.5	1.3	5.3	9.8	0.88	<0.01	0.8	2.0	16.7	77
I5	146	4.49	14.1	13.1	6.2	8.1	<0.01	14.5	3.8	8.2	11.6	0.83	<0.01	<0.01	3.1	17.2	n.d
I6	145	4.63	27.6	30.3	12.1	9.7	<0.01	7.4	1.8	7.5	13.2	3.14	0.25	<0.01	5.1	24.2	131
I7	135	4.58	12.3	16.8	7.0	5.0	<0.01	3.2	2.2	3.6	5.0	1.00	<0.01	<0.01	2.0	16.9	131
G1	124	4.58	14.7	5.8	2.9	10.5	<0.01	12.3	2.1	6.3	11.8	1.85	0.21	<0.01	4.2	21.0	n.d
G2	76	4.91	9.3	6.2	1.9	3.0	<0.01	3.2	1.3	2.6	6.2	0.22	<0.01	<0.01	1.3	15.0	53
G3	151	4.62	29.2	6.2	5.6	7.9	<0.01	16.4	3.7	4.2	15.6	1.36	<0.01	1.4	3.8	23.3	n.d
R 1	115	4.72	8.0	13.4	7.8	3.1	<0.01	32.9	3.0	5.1	7.2	1.30	<0.01	<0.01	44.0	18.6	81
R 2	100	4.67	10.1	8.2	4.0	3.3	<0.01	5.1	1.4	4.3	6.3	1.20	<0.01	<0.01	7.4	28.4	n.d
R 3	79	4.78	7.4	4.8	2.9	2.1	<0.01	2.8	1.3	1.9	5.7	0.24	0.30	<0.01	3.5	30.1	44
R 4	89	4.53	5.9	6.4	5.2	2.8	<0.01	2.8	2.1	3.3	5.2	0.50	<0.01	<0.01	6.2	28.1	60
R 5	144	4.56	21.4	9.4	6.4	3.9	<0.01	3.6	1.6	5.8	15.8	1.55	<0.01	<0.01	6.5	25.5	n.d
R 6	111	4.82	9.8	14.0	11.8	3.6	3.50	1.9	1.3	4.5	10.4	1.12	<0.01	<0.01	4.6	20.1	77
B1	126	4.60	8.3	13.7	6.3	6.0	<0.01	6.9	1.9	6.2	6.1	1.54	<0.01	<0.01	7.7	18.7	130
B2	180	4.51	11.9	20.0	8.0	5.8	<0.01	3.9	1.8	8.4	10.6	2.14	<0.01	<0.01	9.0	19.4	n.d
B3	232	4.67	9.6	36.5	13.7	7.5	7.31	22.6	1.3	12.0	11.7	3.00	<0.01	<0.01	9.5	20.0	193
B4	152	4.38	13.7	6.5	4.6	5.7	<0.01	4.3	2.0	7.3	12.6	2.30	<0.01	<0.01	11.3	25.8	122
B5	116	4.36	9.2	8.9	5.3	5.7	<0.01	17.7	2.3	7.7	6.9	1.30	<0.01	<0.01	6.1	30.1	115

® Not determined.

4.3.2 General composition of the saturated paste extracts

The major anion and cation composition of the saturated paste extracts is summarised in Figures 4.1 and 4.2.

The chemical composition of the saturated paste extracts portrays a considerable excess of cations (up to 3.68 $mmol_c/l$). The acidic environment indicates that carbonates are likely to be present in insignificant concentrations. The presence of DOC levels (up to 193 mg/l), may provide a possible explanation for the high levels of cation excess. Dissolved organic matter is acknowledged to be high if it accedes 70 mg/l of C (Drever, 1997) and is widely recognised to have an overall anionic character (McBride, 1994). Thus, it is likely that the DOC may contribute substantially to the negative charge of the solutions investigated in the current study.

Additional major anions in solution which are present in a relatively similar order of magnitude are Cl^- (0.14-0.88 $mmol_c/l$), F^- (0.02-0.63 $mmol_c/l$) and SO_4^{2-} (0.07-0.92 $mmol_c/l$). The presence of F^- as a co-dominant anion to Cl^- and SO_4^{2-} in solution is unexpected, but may be related to the influence of parent material. Shale is known to contain fluorine in significant concentrations, though variation in the chemical compositions of a single type of rock may vary (Drever, 1997). The possibility of chemical variation within the shale may explain some observations made in previous studies in the Sabie area, where the absence of such significant amounts of fluorine in soil solutions (of surface soils) under pine plantations was noted (Nowicki, 1997).

In addition to the previous statement, fluoride was not detected in concentrations of similar magnitude in studies of pine forest soil solutions in the Northern Hemisphere (Binkley and Richter, 1987; Pritchett and Fisher, 1987; Ross and Bartlett, 1992; Bockheim and Langley-Turnbaugh, 1997).

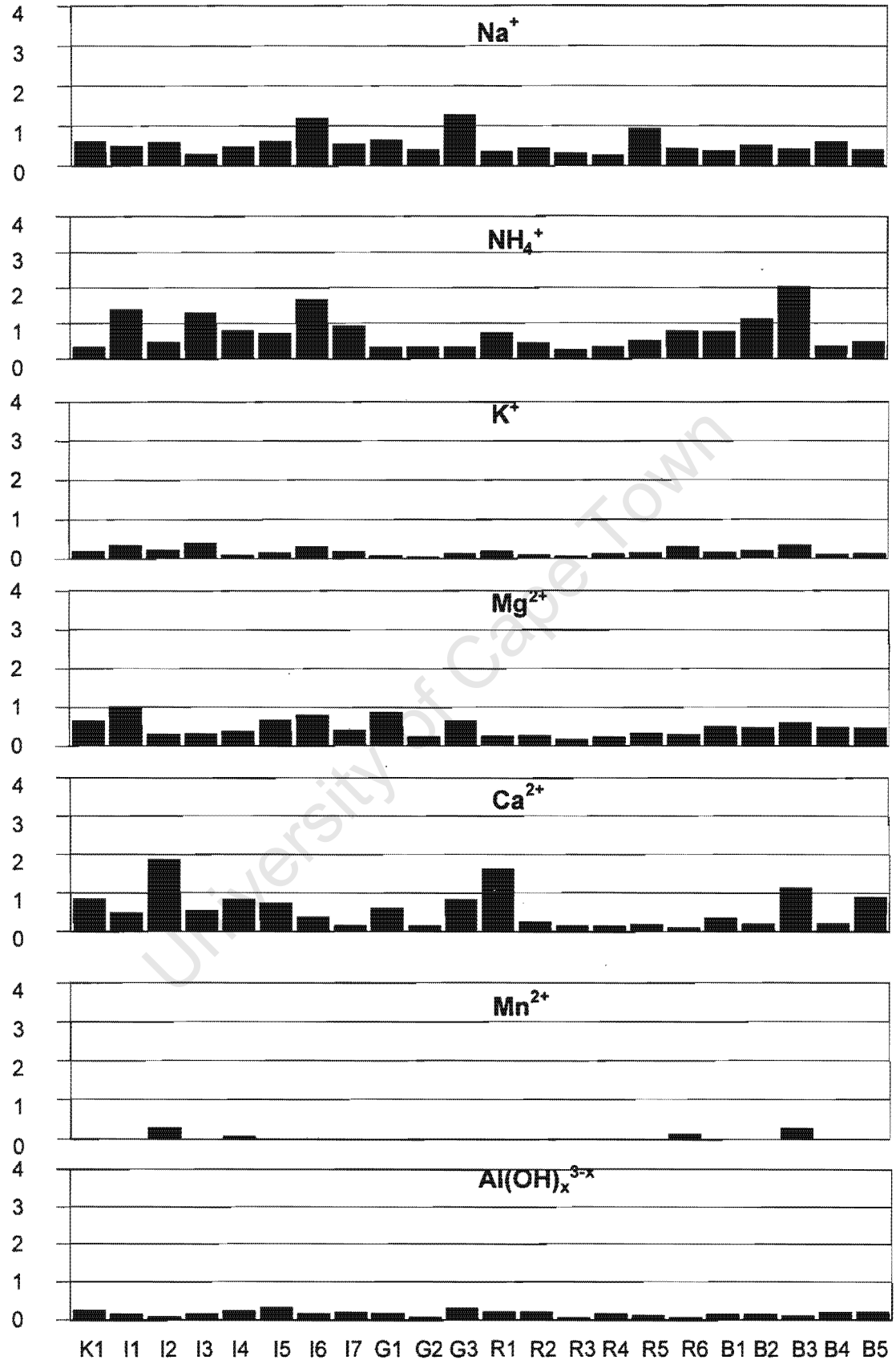

Figure 4.1: *Major cation composition of saturated paste extracts of the soil collection. Concentrations (Y axis) are presented in mmol$_c$/l.*

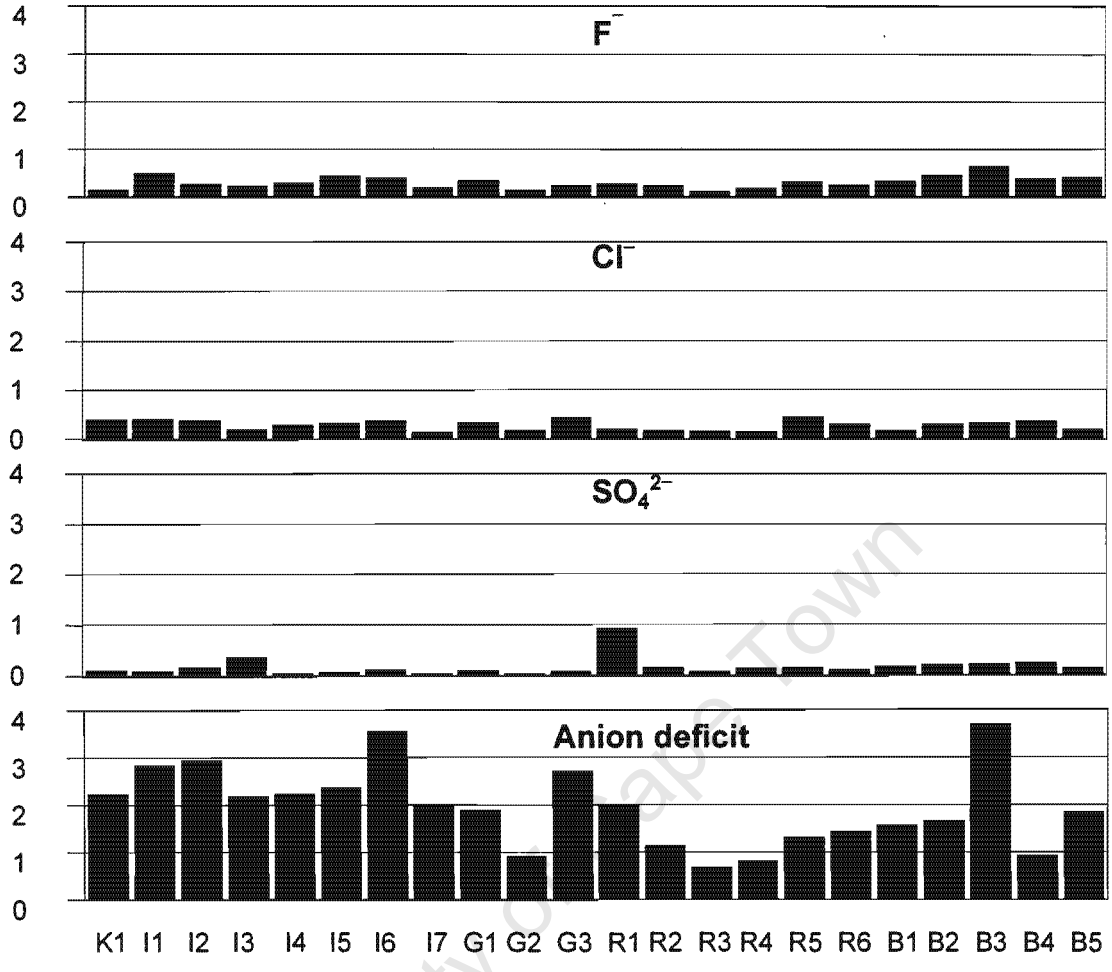

Figure 4.2: *Major anion composition of saturated paste extracts of the soil collection. Concentrations (Y axis) are presented in mmol$_c$/l. Anion deficit was calculated as the difference between the sum of inorganic cations (Figure 4.1) and anions.*

The importance of F^- in solution is magnified in the presence of Al under acidic conditions. The Al-F complexing is widely discussed in the context of acid soils (Gibson *et al.*, 1992; Schecher and Driscoll, 1995) and phytotoxicity (Nagata *et al.*, 1993; Stevens *et al.*, 1997). The complexation of Al with F dramatically affects the speciation of Al in solution. Consequently the monomeric Al determined by the Chrome-Azurol S (CAS) method, which according to Kennedy and Powell (1986) is likely to largely exclude Al-F complexes, underestimates the soluble Al present in solution.

Anionic compounds of nitrogen (NO_3^-, NO_2^-) were detected in very low concentrations that were orders of magnitude lower than that of NH_4^+ (Table 4.1). This suggests a possible inhibition of nitrification processes by the highly acidic environment (Tisdale *et al.*, 1985). The low concentrations of nitrite are in contradiction to previous studies conducted in pine plantations in the eastern escarpment where nitrate levels were observed to range between 0.02mmol$_c$/l to 2.65mmol$_c$/l, and were orders of magnitude similar to that of ammonium (Nowicki, 1997).

4.3.3 Electrical conductivity (EC)

The values of EC range from 76 to 232 μS/cm with a mean of 134 μS/cm (Table 4.1). The soil collection exhibits EC levels similar to those presented by Nowicki (1997) for forest soils studied in the same area (85-452 μS/cm, mean: 185).

The soil collection also exhibits a significant correlation between EC and the period of afforestation (Figure 4.3a). The correlation suggests a significant decrease in the ionic strength of the soil solution as the age of the plantation increases. This decrease indicates a state of decline in nutrient availability in surface soils of commercial pine forests. The decline in salinity can be attributed to leaching processes, presumably enhanced by the afforestation - induced acidity, taking place in the soil over a long period of time. Possible sources of anions in the soil solution could be decomposition of organic matter, soil respiration, fertiliser application, anthropogenic atmospheric emissions and marine inputs (Khanna and Ulrich, 1984).

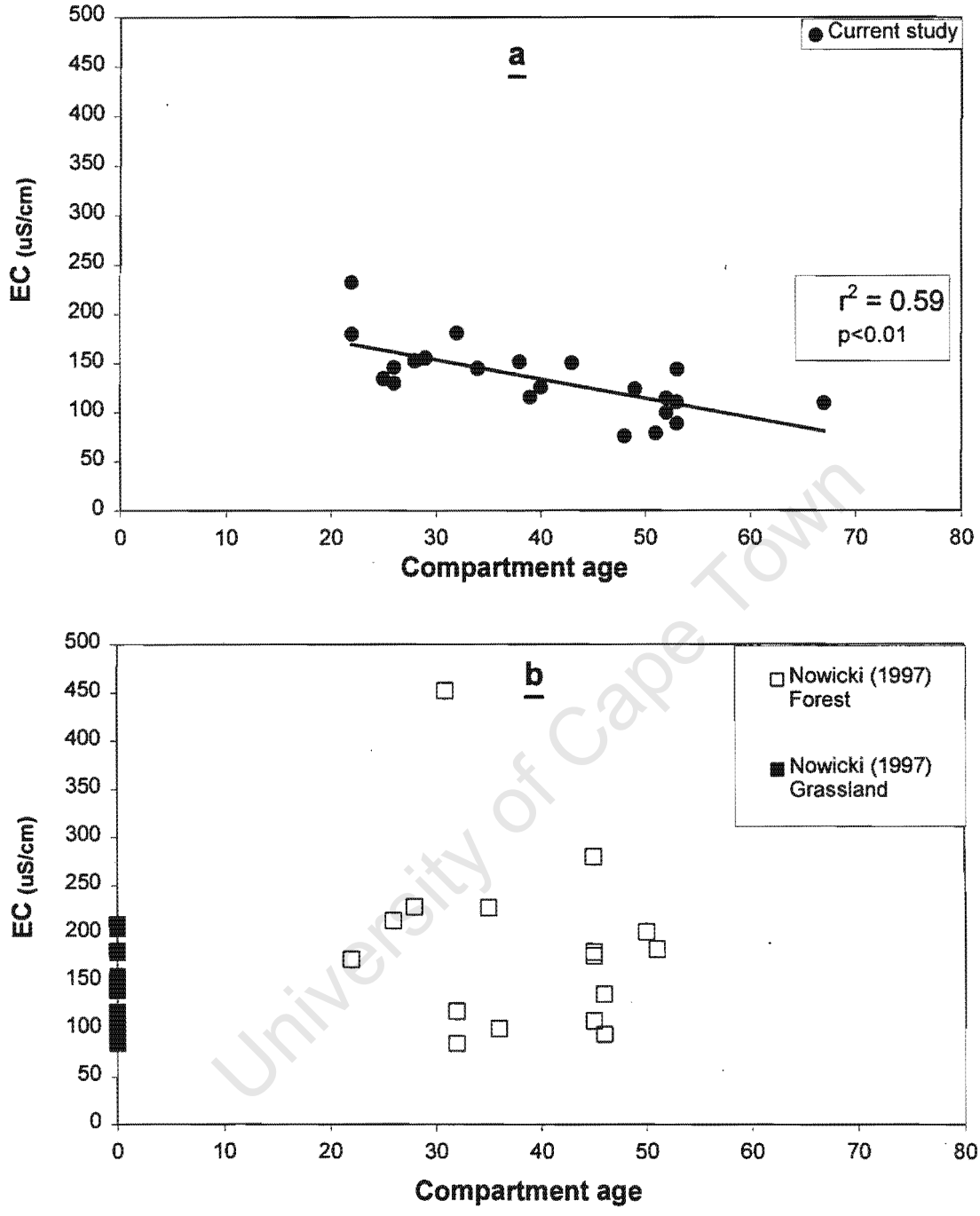

Figure 4.3: *EC levels in surface soils of pine forest soils of different ages and of their adjacent Grasslands.*

The decline in EC with period of afforestation should be carefully evaluated and preferably further investigated. When relevant data from a similar study in the Sabie area, conducted by Nowicki (1997) was plotted against compartment age, no correlation between EC and age of afforestation was evident (Figure 4.3b). It is important to note however, that the study conducted by Nowicki (1997) differs in

some respects from the current study, which may have caused the apparent lack of correlation between EC and compartment age. Nowicki (1997) compared grasslands to their adjacent forests and observed an EC decline with an increasing distance into the forest, though the observations were not statistically significant. An additional explanation may arise from the different site characteristics, such as altitude and aspect. In addition, out of the 16 samples presented in Figure 4.3b, four samples are repetitions (four sites sampled over two consecutive years).

4.3.4 Aluminium (Al)

Dissolved monomeric aluminium ($Al(OH)_x^{3-x}$) values range from 1.3 to 3.7 mg/l. Activity of Al^{3+}, calculated in the absence of F and DOC ranges from 12 to 62 μM and for monomeric Al activity from 31 to 91μM. Total dissolved Al (by ICP-MS) ranges from 0.11 to 1.41mg/l. The data concerning the total dissolved Al was disregarded since the it yielded Al concentrations (total dissolved Al) that were lower than those determined colorimetrically (monomeric Al) and such a difference can not be rationalised. A possible reason behind the low Al(total) concentration detected is the period of time (1 month) between the extraction of the saturated paste and the analysis by ICP-MS, in which increase in pH and precipitation processes have decreased the concentration of Al(total) in solution.

The method used for the determination of Al follows the colorimetric procedure suggested by Kennedy and Powell (1986). The main species of Al determined colorimetrically, and believed to exist in solution, is inorganic monomeric aluminium - $Al(OH)_x^{3-x}$ (Kennedy and Powell, 1986; Mulder *et al.* 1987). Kennedy and Powell (1986) indicate that interference by F reduces the accuracy of the Al determination by 94% for a sample containing dissolved concentrations of 0.5 mg/l Al and 1.9 mg/l F. Kennedy and Powell (1986) did not however, report the magnitude of interference at other concentration ranges of soluble F and Al.

Modelling (MINTEQA2) the distribution of Al species in the saturated paste was conducted in the presence of DOC and F and in their absence. In the presence of F and DOC, the saturated paste extracts exhibit a distribution of Al species dominated by the presence of F (Table 4.2).

Table 4.2: *Percent (%) distribution of aluminium species in solution calculated by MINTEQA2 in the presence of DOC and F.*

Sample	Al-Dom	AlF^{2+}	AlF_2^+	ALF_3	AlF_4^-
K-1	31	23	40	5	<1
I-1	<1	<1	3	76	11
I-2	<1	<1	29	67	4
I-3	<1	3	46	49	1
I-4	<1	<1	24	70	5
I-5	<1	<1	22	72	6
I-6	<1	<1	18	74	8
I-7	5	10	59	26	<1
G-1	<1	<1	28	68	4
G-2	3	6	55	36	<1
G-3	18	18	52	11	<1
R-1	<1	3	43	51	2
R-2	<1	<1	33	63	3
R-3	12	15	57	15	<1
R-4	6	12	60	30	<1
R-5	<1	<1	24	71	5
R-6	<1	<1	30	66	3
B-1	<1	<1	25	70	5
B-2	<1	<1	17	75	8
B-3	<1	<1	9	75	16
B-4	<1	<1	21	73	6
B-5	<1	<1	22	7	6
S.D.	11	8	17	23	4
Median	9	10	28	67	5
Mean	13	10	33	55	6

The distribution of Al species, when calculated in the presence of F, reveals less than one percent of free monomeric Al^{3+}. The Al^{3+} activity (0.2 to 1 μM) is orders of magnitude lower than that of the Al species presented in Table 4.2 such as AlF_3 (5.8 to 49 μM). From Table 4.2 it is clear that the speciation of Al in solution is dominated by the formation of various Al-F complexes that constitute almost 90% of all Al species in solution. A representative sample of speciation calculation is presented in Appendix E.

The speciation of Al calculated in the absence of DOC and F reveals, as expected, a different array of Al forms (Table 4.3). The Al^{3+} species is the dominant form of Al in solution comprising more than half of the Al species in solution. The hydrolysed species of Al ($Al(OH)_x^{3-x}$) are secondary in their dominance and, in general, comprise about one third of Al species in solution.

Table 4.3: *Percent (%) distribution of aluminium species in solution calculated by MINTEQA2 in the absence of DOC and F.*

Sample	Al+3	$Al(OH)^{2+}$	$Al(OH)_2^+$	$AlSO4^+$	$Al(OH)_3$
K-1	74	18	6	2	<1
I-1	79	15	4	2	<1
I-2	46	28	22	2	2
I-3	65	21	8	6	<1
I-4	68	22	9	<1	<1
I-5	75	18	6	1	<1
I-6	79	15	4	2	<1
I-7	79	16	4	<1	<1
G-1	74	18	6	2	<1
G-2	42	29	25	<1	3
G-3	75	18	6	1	<1
R-1	62	19	7	11	<1
R-2	58	25	13	3	1
R-3	33	29	32	<1	5
R-4	65	22	10	3	<1
R-5	66	22	9	2	<1
R-6	60	25	13	2	<1
B-1	66	22	9	3	<1
B-2	66	21	9	3	<1
B-3	68	21	8	3	<1
B-4	79	13	3	5	<1
B-5	79	15	4	2	<1
S.D.	13	5	7	2	2
Median	67	21	8	2	3
Mean	66	21	10	3	3

Another important component affecting Al is organic matter. Aluminium forms strong complexes with various functional groups inorganic ligands, which vary among soils. Organic acids are recognised, under certain conditions, to enhance the total solubility of Al, although quantifying the nature of alumino-organic complexes involves difficulties which are, to date, not completely solved or understood (Driscoll *et al.*, 1985; Lindsay and Walthall, 1989).

As previously discussed (Section 3.3.1), the soil collection contains high levels of organic matter, and therefore it is not surprising that the soil solutions contain quite high levels of DOC (44-193 mg/l) compared to other studies of forest soils such as that of Tipping *et al.* (1995) who found between 1 to 23 mg/l. They are, however, of similar magnitude to the DOC levels reported by Nowicki (1997; 50-490mg/l for his Eastern Escarpment soils).

Mineral saturation indices (SI) were also calculated using the MINTEQA2 program. The SI is commonly used to identify the possible minerals that may be in equilibrium with the soil solution (McBride, 1994). Accordingly, solutions exhibiting a positive SI for a particular mineral, are super-saturated with respect to that mineral. It is important to note that the modelling of mineral equilibria is in many cases indecisive and should be done with some reservation (May *et al.*, 1986).

The modelling was done in three different ways. Firstly, excluding DOC from the solution composition, secondly excluding DOC and F and finally including the full chemical composition. The solubility indices of four selected minerals (quartz, gibbsite, kaolinite and jurbanite) for the three modelling outputs are presented in Figure 4.4.

Observing the change in the saturation index of each of the minerals indicates that the soil solution, in all three modelling options is super saturated with respect to quartz, indicating its possible control over the dissolution of Si. Modelling the saturation index of gibbsite, kaolinite and jurbanite exhibits no significant change whether DOC is incorporated into solution or not, but the addition of F markedly changes the picture. At the presence of F the saturation indices of kaolinite, gibbsite and jurbanite vary dramatically and are for most are under saturated with respect to these minerals. When F is absent the solution is supersaturated with respect to kaolinite and gibbsite and slightly undersaturated with respect to jurbanite.

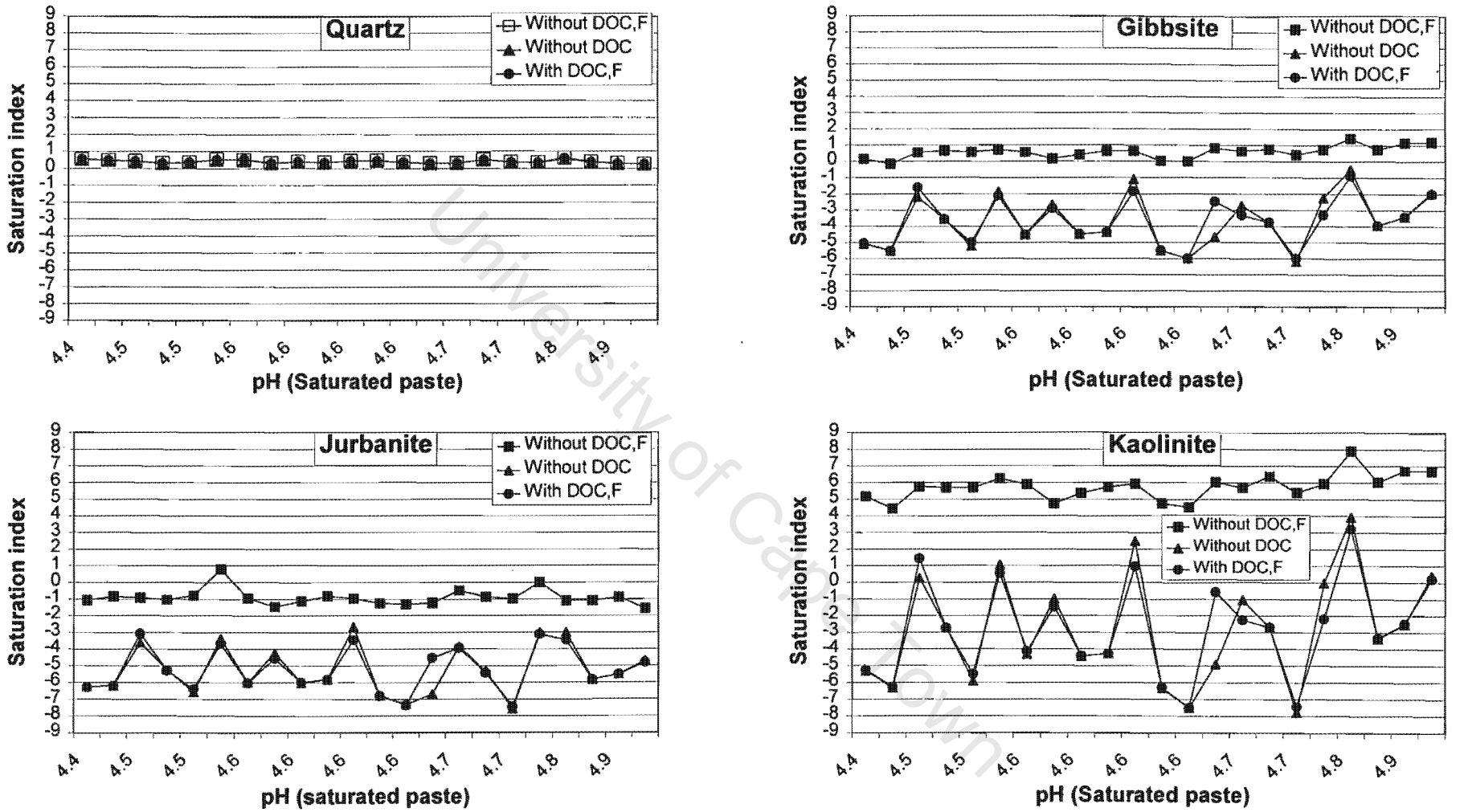

Figure 4.4: *Saturation indices of four selected minerals (quartz, kaolinite, gibbsite and jurbanite) for three various MINTEQA2 modeling outputs (With DOC&F, without DOC&F, Without DOC), at the pH range of the saturated pastes.*

Of the three Al-minerals presented in Figure 4.4, gibbsite is more likely to be in control of soluble Al levels. The reason being the slightly superasaturation (near equilibrium) condition which is consistent at the pH range of the solutions under study. Alternatively, Al dissolution may be due to the presence of Al-organic complexes. The likelihood of organic matter abundance and its strong complexation with Al was suggested by the organic carbon and $CuCl_2$-extractable Al levels discussed in Chapter 3.

A comparison is presented in Figure 4.5, as a function of pH, between the SI levels of gibbsite and those of Al-organic matter calculated according to Fey *et al.* (1998), based previous studies by Alison *et al.* (1990) and Cronan *et al.*, (1986). The calculation of the saturation index of Al-OM is based on the following equations:

$$SI\ (Al\text{-}OM\ complex) = \log (IAP) - \log K_{sp}$$

$$\log (IAP) = \log Al^{3+} + 0.6pH$$

$$\log K_{sp} = -2.52$$

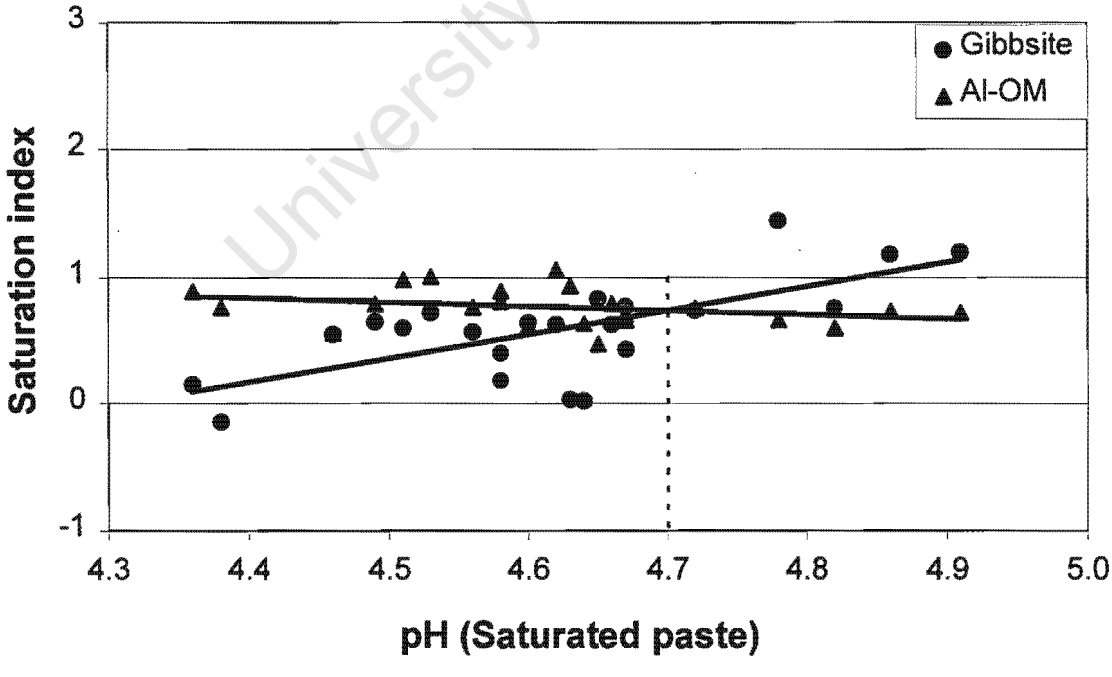

Figure 4.5: *Changes of soil solution saturation indices as a factor of pH (saturated paste) with respect to gibbsite and Al-OM complexes.*

The SI for gibbsite exhibits a general increase with the SI levels for Al-OM is less sensitive to pH, decreasing slightly with increasing pH levels. The crossing point between the two relationships suggests that below this pH, the solubility of Al is controlled by Al-organic matter complexes and above this pH by gibbsite. Such a result is generally consistent with other studies that suggest that under highly acidic conditions, the Al-OM complexes are likely to be the more abundant soluble forms of Al.

The consistency of gibbsite previously discussed suggests that the exclusion of F from the MINTEQA2 calculations, on the basis of formation of Al-F complexes preventing an accurate detection of soluble monomeric Al, was appropriate. Consequently, the exclusion of F from calculations of Al speciation may provide a better mean of calculating Al^{3+} activities.

4.3.5 Ca/Al ratio in the soil solution

The Ca/Al ratio of the soil solution ranges between 1.2 to 39 (as a molar ratio), and between 0.58 to 12.1 (as an equivalent ratio). When calculated in the absence of F and DOC, the Ca/Al activity ratio ranges between 0.98 to 20 for total monomeric Al and between 1.6 to 54 for Al^{3+}, which are similar to that calculated for the molar ratio. In the presence DOC and F, the Al^{3+} activity is strongly reduced, exhibiting Ca/Al activity ratios, which are orders of magnitude higher than those calculated without DOC and F.

A Ca/Al value of one has been suggested in the literature to represent a 50% risk for tree growth (Cronan and Grigal, 1995). When the values of Ca/Al ratio drop below unity, the risk for tree growth increases, and is reported to reach almost 100% at a ratio equivalent to two (Cronan and Grigal, 1995). Most studies of Ca/Al ratio have investigated the molar ratio of Ca/Al, and employ the concept of Ca/Al = 1 as a critical threshold value for forest health (de Vries, 1991; Sverdrup and Warfvinge, 1993). Figure 4.6 indicates a drop in the Ca/Al ratio when natural soils such as grasslands are transformed into commercial forests. In Figure 4.6a, the Ca/Al ratio calculated in units of $mmol_c/l$, has the value of less than one in some compartments.

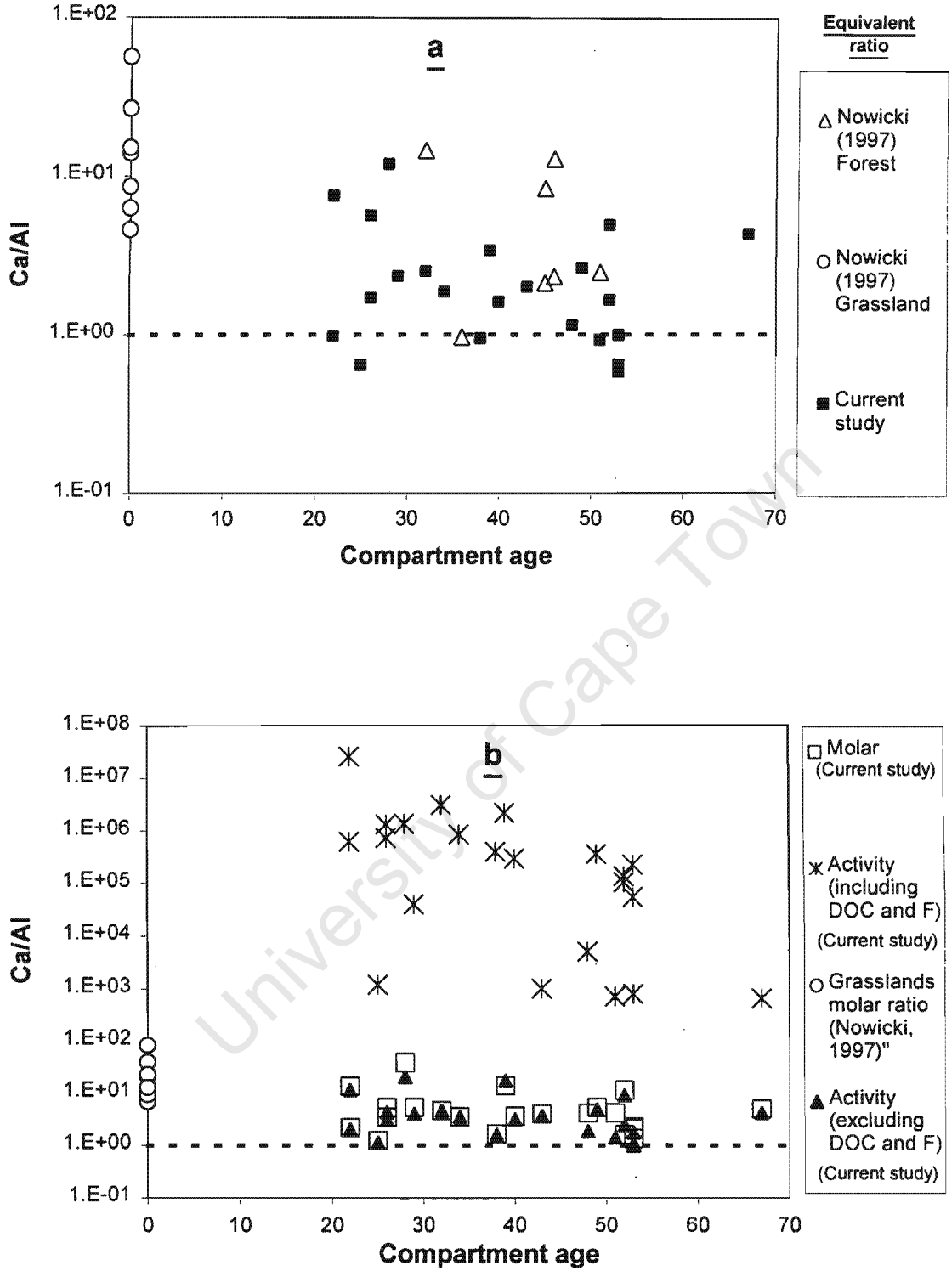

Figure 4.6: *Distribution of various Ca/Al ratios in soil solution of pine forest surface soils of different ages and of grasslands in the Sabie area. In Figure a, the Ca/Al is presented in mmol$_c$/l, and comprises of data by Nowicki (1997) for forest soils and grasslands and of the current study. Figure b consists of grassland soils data (Nowicki, 1997) and forest soil data (activity and molar ratios) of the current study.*

Using geochemical modelling (MINTEQA2) to calculate ion activities produced considerable higher Ca/Al ratios in the presence of DOC and F than in their absence. The Ca/Al activity ratios in the presence of DOC and F, presented in Figure 4.6, exhibits a convergence of ratios with increasing plantation age, the rate of decline is not statistically significant, and due to the complexity of evaluating Al in the presence of F, it would be presumptuous to assign trend lines and to draw definite conclusions regarding possible future effects on forest health.

In regard to phytotoxicity, Al-F complexes are potentially important with respect to the transport of Al. Studies of tea plants (*Camellia sinensis*) have found similar Al-F forms in tea branches and in solution (Nagata *et al.*, 1993). Further observations were made of $Al(OH)_X^{3-X}$ species maintaining higher phytotoxicity than AlF_X^{3-X} species (Stevens *et al.*, 1997). Although the studies discussed above are of crop plants, a similar situation may possibly occur in trees. Rowell (1991) reports that toxic levels of Al^{3+} activity for selected agricultural crops to range from 0.4 to 1μM. Thus, in terms of the a_{Al} in the soil solutions of the present study, there is no clear likelihood of Al toxicity. Further research is nevertheless vital for establishing whether Al-F complexes are likely to affect trees in general and conifers in particular.

4.3.6 Ammonium (NH_4^+)

The soil solution analysis (Table 4.1) showed relatively high levels of NH_4^+ (4.8-36.5 mg/l), and together with Na^+, these are the dominant cations in solution. Similar studies conducted in pine plantations in the Eastern Escarpment (Nowicki, 1997) indicate NH_4^+ levels (0.09-1.1 $mmol_c/l$) which are similar to those detected in this study (0.2-1.2 $mmol_c/l$).

The main N species recognised to be present in the forest floor include NH_4^+, NO_3^- and dissolved organic nitrogen (DON), of which the latter (DON), is believed to associate with humic substances and to represent the dominant form of N transport (Northup *et al.*, 1995). As the decomposition of organic matter proceeds, nitrogen compounds are released into the forest floor. Reaching the rhizosphere, N is taken

up in the form of DON, supplying the trees with the necessary N. In a controlled experiment of pine needle leachate, the loss of nitrogen from the F and H horizons (forest floor) to the upper mineral horizon was recorded to consist mainly of NH_4^+-N, whereas the loss of N from the A horizon was found to consist mainly of NO_3^--N (Parfitt *et al.*, 1997). This might explain the high concentrations of NH_4^+ and low concentrations of NO_3^- found in soil solutions.

An additional factor that is likely to influence the determination of nitrogen species in solution involves the procedure of saturated paste preparation. The soil samples are re-wetted after being air dried and are left for a period of 24 hours to allow chemical equilibration. Subsequently, the activity of nitrifying bacteria may be enhanced and processes such as dinitrification may take place, thus reducing, to an unknown extent, the potential for detecting nitrite and nitrate in solution, and may create favouring conditions for *Nitrosomonas* over *Nitrobacter*.

The present silvicultural policy applied in the plantations under study promotes accumulation of cuttings from pruning and thinning on the forest floor, and thus enhances the amount of organic matter in the forest floor and consequently the release of nitrogen species into the forest floor. Evaluating with greater accuracy the possible sources of nitrogen saturation in the soil collection would require further research involving nitrogen tracer techniques (Hauck, 1982; Drever, 1997).

4.3.7 Fluoride (F^-)

Soluble fluoride concentrations range from 1.9 to 12 mg/l. The forest soils exhibit high levels of F^- in comparison with previous studies of pine plantations in the Sabie area (Nowicki, 1997). When the type of underlying bedrock is taken into account (shale), the magnitude of fluoride levels found in this study are comprehensible. Drever (1997) presents typical concentrations of selected elements in various rocks and shows that shale contains Si, Al, Ti and Fe as major elements and F, Mn and Cs as additional abundant elements (>500 mg/kg). Granitic rocks (underlying bedrock of sample K1) are also recognised to have similar levels of fluoride (Drever, 1997). Consequently, in the context of this study

one would expect to find high levels of F in the soils under favourable conditions. Under acidic surroundings, the dissolution rate of most silicate minerals increases exponentially, with increasing hydrogen ion concentration. Leaching creates preferential conditions for mineral weathering and the dissolution of acidic cations, such as aluminium (Drever, 1997). As previously discussed, in the presence of F, the formation of Al-F complexes is strongly favoured. Thus, considering the fact that the elemental composition of shales may include F, and that the waters draining shales may promote Al dissolution, it would be very likely to detect F in solution and most probably in various forms of Al-F comprising an abundant form of monomeric Al in solution (Driscoll *et al.*, 1985; McBride, 1994). Previous sections discussed the complexation between F and Al and its chemical significance (sections 4.3.2 and 4.3.4).

The F ion and F complexes present possible toxic effects for plants. Plant uptake of F was observed to increase with increasing ionic strength of nutrient solutions (Stevens *et al.*, 1998). As already noted, however, F complexes strongly with Al and thus may reduce the phytotoxicity associated with soluble Al.

The dominant species of fluoride in solution calculated by MINTEQA2 modelling are F^- (mean: 33.5%) and AlF_3 (mean: 36.7%). Other F species, such as AlF_4^- and HF are present in only small concentrations (<5%). The levels of free F^- in acid soil solutions are reported to drop as the pH of the solution drops (Munns *et al.*, 1992; Schecher and Driscoll, 1995). Following the observations made in Chapter 3, where a decline in pH was observed in natural soils converted to forest plantations, it is reasonable to assume that a drop in pH would decrease the activity of free F^- in solution, since increased concentrations of free Al induced by a drop in pH may have promoted the formation of AlF_x complexes, at the expense of free F^-. This could also account for the observed reduction of free F^- with increasing plantation age.

As previously discussed, F^- is the dominant ligand bound to Al in solution. However, fluoride may not always have this effect on the detection of Al^{3+} in solution. Moore and Ritchie (1988) have found that although adding F^- to acid soil solutions increased total concentrations of Al, it did not decrease the Al^{3+} concentrations in all cases. These findings were later confirmed by Gibson *et al.* (1992).

4.3.8 Dissolved organic carbon (DOC)

The DOC levels in the saturated paste extracts range from 53 to 193mg/l. In conjunction with the organic carbon levels presented in Chapter 3, and with the high anionic charge deficit, being probably accounted for by DOC, the soil collection exhibits a strong "organic" signature. Consequently, and as previously indicated (section 4.3.4), DOC may have a dominant influence on the dissolution of Al with respect to mineral saturation indices. In addition, the DOC found in the soil collection constitute a dominant portion of the anions in solution, and as such, may affect pH control, enhance acidification, mineral weathering, nitrogen mineralisation and, as a result, various processes involved in the nitrogen cycle (Parfitt *et al.*, 1997; Drever, 1997).

Nowicki (1997), while studying various pine forests in South Africa, demonstrated a correlation between DOC and excess cation charge in solution, suggesting that dissolved organic anions account for the apparent deficit of negative charge. Adopting this concept in the current study has yielded poor results that prevented the formation of a statistically meaningful trend such as that generated by Nowicki (1997). The reasons may lie with the limited amount of samples analysed for DOC and with chemical changes that may have taken place during storage (±4°C) in the sample solutions prior to the DOC determination. Nevertheless, it is the author's understanding that the anion deficit can be attributed (in the absence of analytical errors) to the presence of negatively charged soluble organic matter (McBride, 1994). This assumption was used as a basis for incorporating DOC into the geochemical modelling.

MINTEQA2 modelling is based on studying metal interactions with Suwannee River fulvic acid (Lumsdon and Evans, 1995). The model treats dissolved organic matter as a complex material consisting of various types of monoprotic acid sites. The concentration of these ligand sites is normally distributed with respect to their log *K* values for protons or metals. The nature of the geochemical modelling does not necessarily represent in an accurate manner of DOC speciation in solutions. For example, the model is generally restricted to predetermined ionic strength at which the modelling parameters were determined, as they do not consider electrostatic effects resulting from polyelectrolite behaviour of humic macromolecules (Lumsdon and Evans, 1995).

DOC is an important nutritional source for heterotrophic microbial activity that forms NH_4^+-N (Parfitt *et al.*, 1997). Yet, when an attempt is made to quantify the dissolved organic acids in solution, some difficulties arise. For example, in the process of re-wetting dry soils, organic compounds greatly increase their solubility in comparison to their solubility in the soil prior to sample excavation in the field (Bartlett and James, 1980).

4.4 Comparing the Ca/Al ratio between the soil solution and the exchange sites

Combining the observations regarding the exchangeable phase and the soluble phase results in an interesting association between the two phases. In Figure 4.7, a summary of the BC/AC ratios is presented. This summary consists of the solution Ca/Al molar ratio and the BC/AC ratio of the exchangeable phase as observed in various local studies (du Toit, 1993; Nowicki, 1997). The comparison between the Ca/Al ratio in solution to the BC/acidity on the exchange sites was done due to the lack of data regarding exchangeable Al and Ca in some of the previous studies, thus preventing the calculation of the Ca/Al ratio of the solid phase. It is not a fortuitous comparison, since the aim is to show the possible changes taking place in the soil environment with respect to the state of acidity and basic cations and to point out some possible trends that may occur.

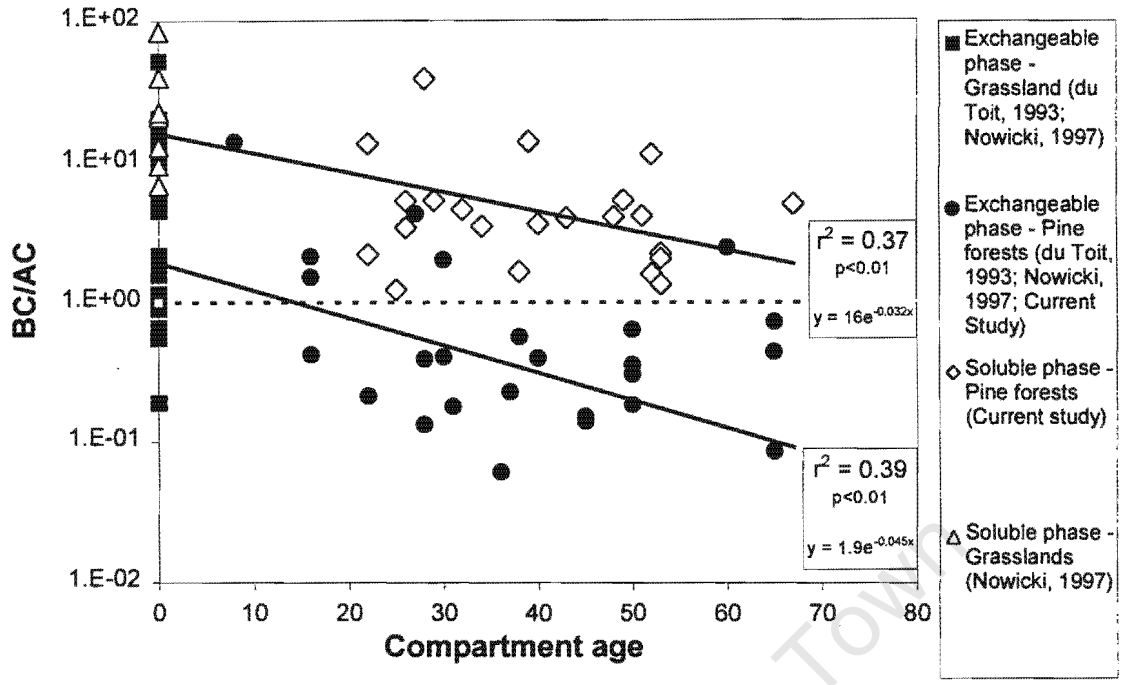

Figure 4.7: *BC/AC ratio on the exchangeable sites and Ca/Al molar ratio in soil solutions of forest compartments of different ages and of natural grasslands in the Eastern Escarpment and the Natal Middlands.*

It can be seen from Figure 4.7 that the quantity (solid phase) and intensity (soil solution) of the BC/acidity ratio decreases with increasing plantation age. Both the soluble phase and the solid phase exhibit similar trends. Although not statistically significant (r^2<0.4) they do, however, emphasise the importance of the first 2 to 3 decades of afforestation since that period of time was not covered by this study and consequently no significant trends were able to be calculated. Further studies are necessary to establish the rate of BC/acidity decline in the first two decades of afforestation. An important observation from Figure 4.7 is the difference between the solid phase and the soluble phase with respect to unity level suggested in the literature as a threshold for forest health. The exchangeable phase has clearly dropped below unity, yet the soluble phase is still above unity. A possible reason for the higher levels of Ca/Al ratio in solution in comparison with the solid phase is due to the presence of F. The fluoride ion complexes strongly with Al, thereby reducing the pool of F-free monomeric Al in solution, consequently creating higher ratios of Ca/Al which do not account for the monomeric Al-F complexes in solution.

4.5 Conclusions

Interesting trends have appeared of declining levels of ionic strength in solution as the period of afforestation increases (r^2 = 0.59), and of a ~~clear~~ drop in the Ca/Al ratio as grassland soils are converted to forests, coupled with indications of Ca/Al ratios falling below unity in some forest compartments. Activity ratios of Ca/Al were calculated under different conditions showing a state of decline with plantation age when DOC and F are included in the calculation, and an over all drop in Ca/Al ratio when DOC and F are excluded, indicating a markedly depletion of basic cations from the soil solution over the first two decades following afforestation. Further study and monitoring is necessary for following the changes in the Ca/Al ratio since ratios falling below unity are associated with growth stress and consequently reduction in productivity.

Monomeric Al is present in concentrations (1.3-3.8 mg/l) which may be considered low in such an environment. Yet, due to the overwhelming mass dominance of F over Al in solution and the strong complexing potential of F with Al, it is reasonable to expect lower levels of monomeric Al than might have been otherwise anticipated. The concentrations of soluble monomeric Al would normally be dominated by Al-F species, and the colorimetric method used for the determination of soluble monomeric Al is thereby likely to underestimate the total dissolved Al concentrations in solution. Consequently, Al activity calculations are probably performed in a better manner when the Al-F complexation reactions are excluded. This finding may be confirmed through the calculations of mineral solubility equilibria. The exclusion of F from the calculations of the mineral solubility equilibria proved beneficial in the sense that the Al-minerals (gibbsite, kaolinite and jurbanite) have shown greater consistency at the absence of F than in the presence of F. Further calculations in the absence of F have indicated that gibbsite may control Al solubility in the studied solutions whereas under the higher acidic conditions of the studied solutions, Al-organic matter complexes may dominate the solubility of Al.

The soil solution contains surprisingly high levels of F^- (1.9-12 mg/l) and NH_4^+ (4.8-36.5 mg/l). The high levels of F found in solution are believed to originate from the underlying bedrock (shale). Abundance of NH_4^+-N coupled with smaller concentrations of NO_2^- may be the cause of the method used for the preparation of the saturated soil pastes and consequently interruption of biochemical processes such as nitrification taking place in the soil environment. Low pH and certain organic acids are known to inhibit nitrification processes and alter the balance between the two main bacterial communities responsible for nitrification. Thus, altering the balance between the intermediate, and the end products of nitrification. This is exhibited in this study by the relative abundance of NO_2^- over NO_3^-.

Bearing in mind the high levels of organic carbon found in the solid phase (Chapter 3), it was not surprising to find high levels of DOC in the soil solution (53-193 mg/l). Based on the assumption that anionic deficit can be attributed to the presence of negatively charged soluble organic matter, the anionic deficit was ascribed to DOC, thus adding to the observations of a strong organic matter signature in the upper mineral horizon of the studied pine plantations.

CHAPTER 5. GENERAL DISCUSSION AND CONCLUSIONS

5.1 Soil chemical status under pine plantations in the eastern highlands of Southern Africa

The aim of this study was to evaluate the state of acidity and basic cations in soils underlying pine forests of different ages in the Sabie area (Eastern Escarpment). The hypothesis that was set maintained that chemical changes take place in the forest soils with increasing plantation age.

The objectives of this study were, for the most part, achieved. Some important trends were pinpointed: statistically significant tendencies indicating various chemical changes taking place as the period of afforestation progresses. The most dominant observation was a decrease in the soil solution ionic strength (EC) with increasing plantation age (r^2=0.59). Yet, these results are not conclusive in the sense that the most important change in the form of a substantial drop in EC, appears to be taking place in the first 2 to 3 decades following afforestation. A strong decline, yet with no clear trend, of basic cations and an increase in acidity with a growing period of afforestation were observed - especially during the first two decades of a plantation.

The pine plantations of the current study cover compartment ages between 22 and 76 years, thus the first two decades of afforestation were not studied. While it can be argued that, as a result, important studies and observations are missing, this study looked and incorporated data from studies previously conducted in the Eastern Escarpment and the Natal Midlands (du Toit, 1993; Nowicki, 1997).

Following world-wide studies on the use of basic cation/Al ratios in soil solutions as an index of forest vitality, and in conjunction with data of previous studies conducted locally, some interesting observations were made: A similar decline in the basic cation/acidity ratio on the exchange sites and the Ca/Al molar concentration of the soil solution were observed to take place as the period of afforestation increased. Although the trends observed were not statistically significant, they strengthened the assumption that the most distinct depletion of basic cations, both from the solid phase and from the solution, occur in the first 2 to 3 decades following afforestation.

A basic cation/acidity ratio below unity was observed on the soil exchange sites of almost all the soil samples. Whereas, the Ca/Al molar concentration ratio of the soil solution was observed to fall below unity in only a few of the plantations. The low levels of Ca/Al concentration ratio on the exchange sites and in solution might indicate possible future problems with respect to forest productivity. Further research into the Ca/Al ratio is recomended both from a soil chemical perspective and from a botanical one.

Unexpectedly high levels of F in solution have adversely affected the determination of F-free monomeric Al species in solution thereby influencing the calculation of Al activity, speciation and mineral solubility. Nevertheless, it is assumed that in the absence of F, gibbsite dominates the solubility of Al and at higher acidic conditions, Al-organic matter complexes dominates the solubility of Al.

The high levels of NH_4^+ need to be carefully evaluated. Not only in terms of the methods used for the soil solution preparation and extraction, but also because they suggest the possibility of nitrogen saturation occurring in the surface soils of the pine forests under study.

5.2 Practical implications of the current study

Pine plantations exhibiting Ca/Al ratios below unity should be carefully observed for any growth stress, and preferably, productivity data should be gathered and assessed in order to establish the best available silvicultural application.

Soil amelioration programs should be carefully formed and implemented since the acidity status may change between the various plantations and compartments. Most important is the further consideration of growth response studies, specifically in terms of acidification and Al-F complexes of the various pine species.

Any future afforestation programs of natural grasslands should consider the results of the previous studies of the soils underlying pine plantations in order to form the best economical and ecological viable plans regarding species, rotation, and their suitability for various soil types and bedrocks.

The presence of relatively high organic carbon both in solution and as solid organic matter should be evaluated in conjunction with NH_4^+ since silviculture has a vital impact on the accumulation of litter on the forest floor. Decomposition of organic matter can alter various chemical and biological processes taking place in the soil environment, such as microbial activity, acidification, which can be induced by the presence of nitrogen and by the accumulation of organic matter (such as pine needles).

5.3 Future studies

As previously mentioned, further research would require the study of the first 20 years of a plantation. A possible extension of plantation age study could be made up to the first 40 years. The reason being, as stated previously, that the most prominent chemical changes on the solid phase and in solution probably take place during the first 2 to 4 decades, with a strong possibility that the most significant changes in the soil chemical properties take place in the first 2 decades.

Furthermore, consideration should be given to the soil chemical changes between the upper organic horison and its underlying mineral horison. Especially since there is a greater tendency for an organic carbon loss with depth in forest soils than in natural grasslands (Brady and Weil, 1999). The author further recomends studying soil physical properties in a comparison of forests and their adjacent grasslands in view of their hydrological implications.

The overall effect of species should be studied since some observations were made concerning the effect of species on the soil chemical properties. For example, *P. patula* is known to accumulate higher levels of organic matter on the forest floor in comparison with *P. elliottii* and *P. taeda* (Dames, 1996). The accumulation may also arise due to growth at high altitudes, thus a more detailed understanding is required. Studying the effects of species should involve sampling forest compartments of similar species and similar age. The use of analytical methods and modelling should carefully consider the presence of high levels of F^- and DOC in solution, especially when Al is analysed. A proposed sampling design plan for further studies is described in Appendix F.

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APPENDIX A1: RHENOSTERHOEK PLANTATION

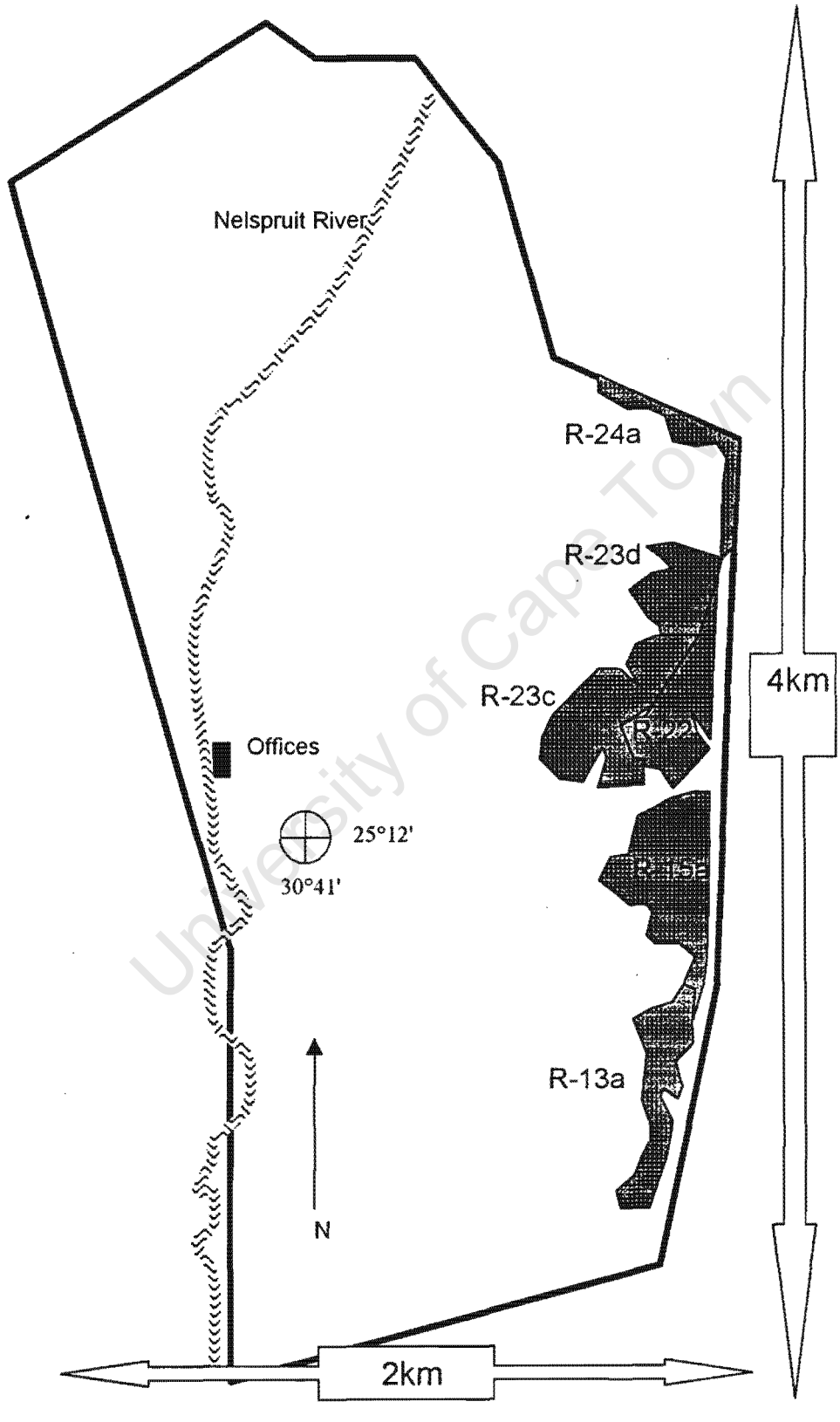

Figure A1: *Schematic map of the Rhenosterhoek plantation*

APPENDIX A.2: BLYFSTAANHOOGTE PLANTATION

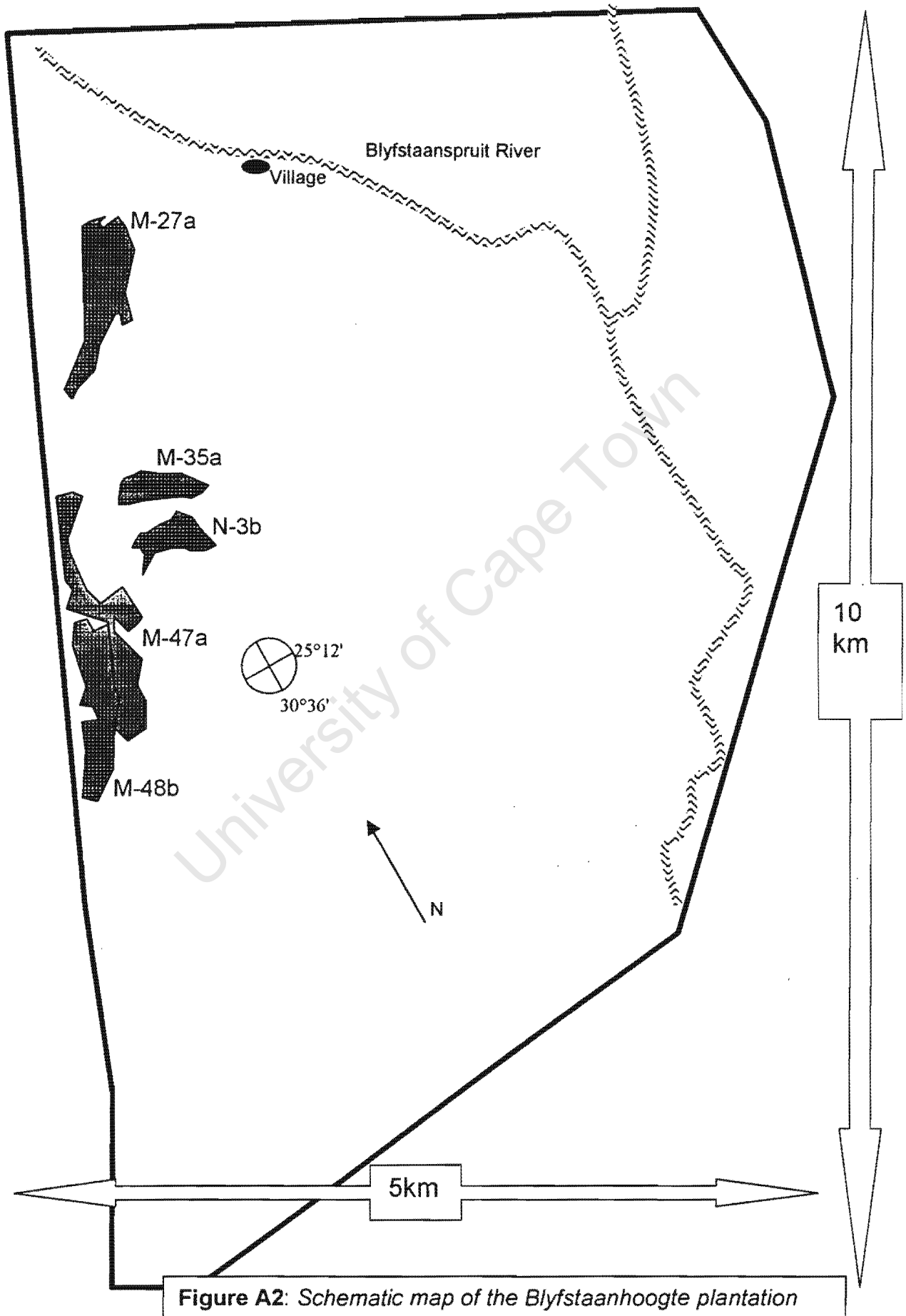

Figure A2: *Schematic map of the Blyfstaanhoogte plantation*

APPENDIX A.3: GROOTFONTEIN PLANTATION

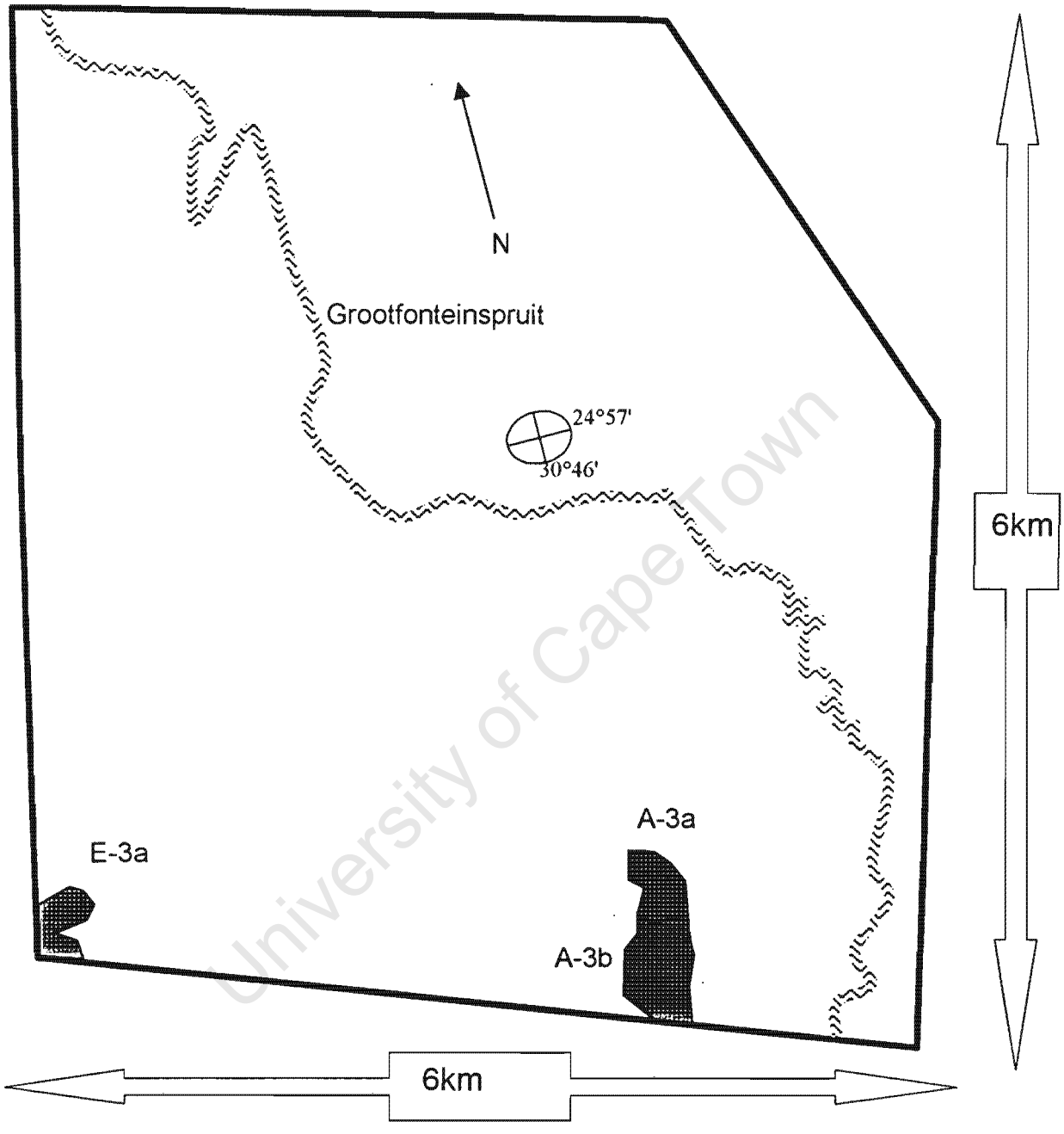

Figure A3: *Schematic map of the Grootfontein plantation*

APPENDIX A.4. IN DIE DIEPTE PLANTATION

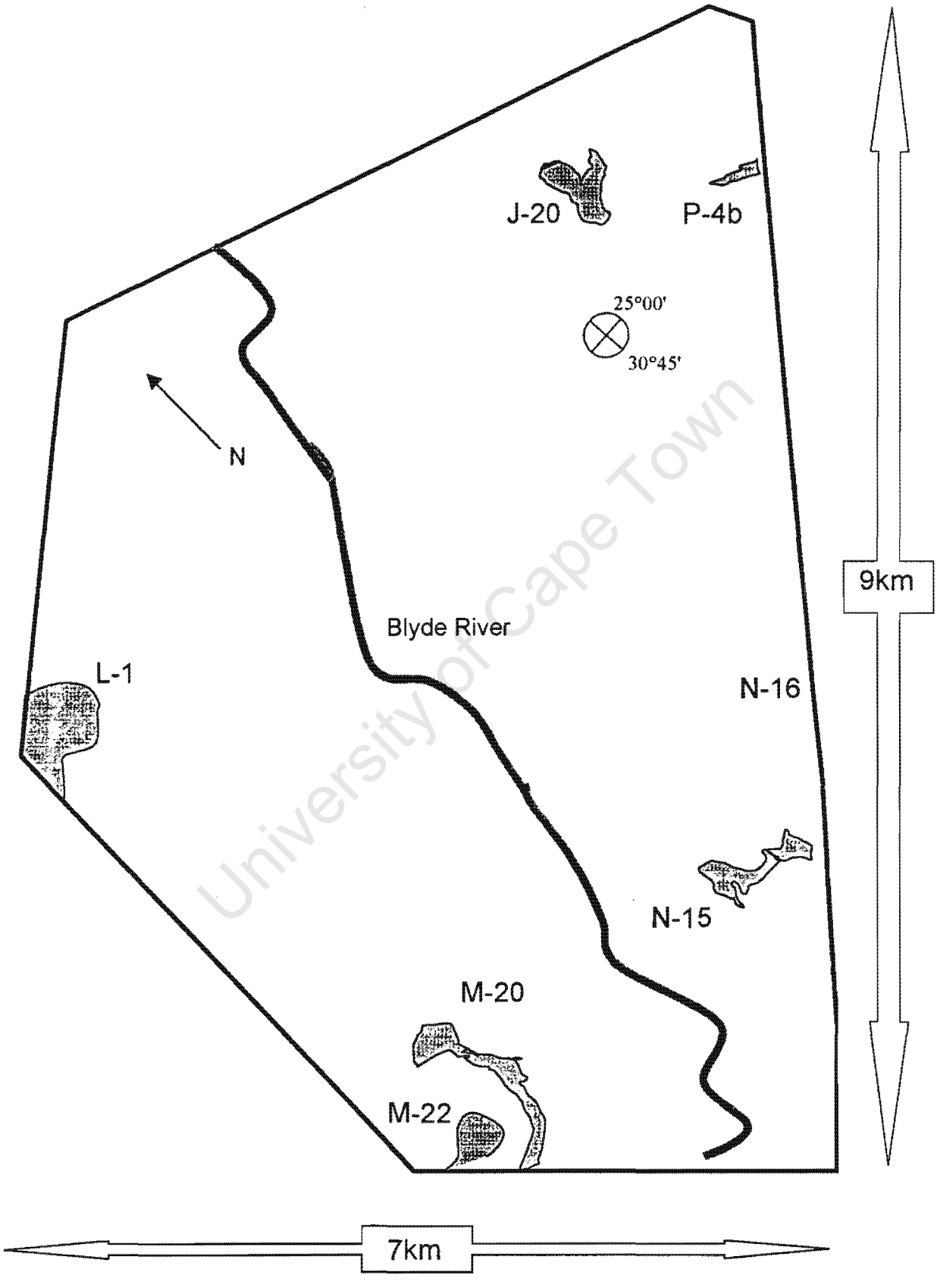

Figure A4: *Schematic map of the In Die Diepte plantation*

Appendix A.5

Table A.1: *Soil profile description for two selected pits in P. patula plantations in the Rhenosterhoek area (S.A.F.I, 1957).*

Profile	Species	Geol. Form.	Horizon	Colour	Depth In cm	pH (water suspension)	Soil reaction	% N (as N)	% P (as P_2O_5)	% K (as K_2O)	Soil texture		
											% Clay	% Silt	% Sand
1	*P. patula*	Pretoria Series	A	Red Brown	8	4.5	Strongly acid	0.186	2	0.012	30	32	38
			B	Red Brown	8-21	4.9	Acid	0.091	<1	0.006	26	22	52
			C	Light Brown	21-36	4.8	Acid	0.042	<1	0.008	34	32	34
2	*P. patula*	Pretoria Series	A	Brown	10	4.4	Strongly acid	0.18	<1	0.006	14	36	50
			B	Red Brown	10-26	4.8	Acid	0.1	<1	0.006	20	66	14
			C	Light Brown	26-43	4.7	Strongly acid	0.044	<1	0.006	22	34	44

APPENDIX B: ANALYTICAL METHODS

B.1. Introduction

The soil collection was sieved and air dried. The process of air drying the soil may cause an increase in the surface acidity, exchangeable and soluble Mn^{2+}, and the solubility and oxidizability of the organic matter (Bartlett and James, 1980). In addition the drying may alter exchangeable potassium (K), increase variability in pH ($CaCl_2$), and significantly increase the cation exchange capacity (CEC) and the anion exchange capacity (AEC) (Harada *et al.*, 1980, cited in Bartlett and James, 1980).

Bartlett observed an increase in exchangeable Ca^{2+} and Mg^{2+}, variability in exchangeable K and a decrease in exchangeable Mn^{2+}, after rewetting the soils.

B.2. $CuCL_2$ extractable Al

The method used for determining $CuCl_2$ extractable Al follows the procedure suggested by Juo and Kamprath (1979). 3g of soil and 30ml of 1M $CuCl_2$ were added to a polyethylene centrifuge tube. For Al-kaolinite, Juo and Kamprath (1979) suggested successive extractions of Al, indicating that the first extraction removes the majority of the Al, though further extractions produce additional, yet limited, amounts of Al. Thus, a single two hour shaking following a single extraction should be sufficient for extracting Al bound to organic matter. However, the author has conducted the method with some modifications of the shaking sequence. The samples were shaken for 2 hours, stored overnight in a fridge (±4°C), and shaken again for two hours. Thereafter the procedure follows Juo and Kamprath (1979). The samples were centrifuged, filtered (0.45 μm) and sent for FAAS (flame atomic absorption spectroscopy) using a N_2O burner. Also, the $CuCl_2$ solutions were not diluted, since the FAAS method used 1M $CuCl_2$ as an eluent solution to reduce background noise.

The results have produced Al concentrations which are between 1.6 and 10 times higher (mean: 4.2) than the Al concentration determined by the KCl extraction of Al. Juo and Kamprath (1979) indicated that the Al concentration produced by the $CuCl_2$ extraction were generally more than twice as much as that extracted by the KCl. It is the author's opinion that the modification used in this study proved adequate, and represents a possible improvement on the method suggested by Juo and Kamprath (1979) with respect to Al-kaolinite.

B.3. FAAS - Flame atomic absorption spectroscopy

The method used for determining exchangeable Al^{3+}, Ca^{2+}, Mg^{2+} and Mn^{2+} follows the method by Barnhisel *et al.* (1982). 3 gr of soil and 30ml of 1M KCl were added to a polyethylene centrifuge tube. The tube was shaken for 2 hours, centrifuged, filtered (0.45 μm), diluted (1:9) and sent for FAAS analysis at the department of Chemical Engineering at the University of Cape Town. Exchangeable Mg^{2+} and Mn^{2+} were determined using an air/acetylene flame type. Exchangeable Ca^{2+} and Al^{3+} were determined using a N_2O/acetylene flame type.

Interferences. Intereferences with exchangeable Mg^{2+} determination involved a general absorbance enhancement of 15%, which was caused ionisation suppression due to alkali metals. Interferences with exchangeable Mn^{2+} detection are not common when using an oxidising air/acetylene flame. Interferences with exchangeable Ca^{2+} detection arises mainly due to the Ca^{2+} ion itself. This is overcome by the use of a more readily ionised element such as potassium. Interferences with the detection of exchangeable Al^{3+} involve the partial ionisation of Al^{3+}. This is avoided by adding a potassium chloride solution. For all samples, a 1000mg/l solution of KCl was used to eliminate possible interferences and background "noise".

B.4. Acid neutralising capacity (ANC)

The acid neutralising capacity of the soils was determined according to the method proposed by du Toit *et al.* (1994). The following procedure was performed. A mixture consisting of 0.01 moles of HOAc, 0.001 moles of KOAc and 0.1 moles of $CaCl_2$ was made up to 1 litre and adjusted to pH 3.5 with HCl. 15ml of the buffer solution was added to 5ml of soil, shaken for 15min, centrifuged and allowed to settle for 15 min. Thereafter the pH of the supernatant suspension was recorded. The technique for calculating the ANC was conducted using the formula proposed by du Toit and Fey (1994), where:

1) ANC ($cmol_c/l$) = 9.624 pH – 34.13.
2) ANC of 1 $cmol_c/l$ = 1 ton of $CaCO_3$/ ha (20 cm deep) = 0.5kg/m^3 $CaCO_3$.

B.5. Organic carbon

Organic carbon was determined using the "Walkley Black" method following the procedure of Nelson and Sommers (1982). The analyses were conducted by the Agricultural Research Institute - Infruitec, Stellenbosch. This method provides an approximate estimate of organic carbon in the soil. The procedure involves oxidising the carbon by treating it with hot mixtures of $K_2Cr_2O_7$ and H_2SO_4. After the reaction, the excess $Cr_2O_7^{2-}$ is titrated with $Fe(NH_4)_2(SO_4^{2})_2(H_20)_6$. The reduced $Cr_2O_7^{2-}$ is assumed to be equivalent to the organic carbon present in the sample.

B.6. Monomeric soluble Al

Aluminium was determined colorimetrically using the Cr-Azurol S (CAS) method proposed by Kennedy and Powell (1986). The method determines monomeric Al species in solution ($Al(OH)_x^{3-X}$). The lower limit of detection is approximately 0.075 mg/l. According to Kennedy and Powell (1986), adding fulvic acid to a 0.5 mg/l Al

solution did not affect absorbency readings, indicating that Al-organic complexes in solution can also be determined by this method. The analysis was carried out within 15 minutes of the saturated paste extraction.

B.7. Cation and anion concentrations

Cation (K^+, Na^+, NH_4^+, Ca^{2+}, Mn^{2+} and Mg^{2+}) and anion (F^-, Cl^- NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) concentrations within soil solutions of saturated paste extracts were determined by ion chromatography (IC). Analyses were performed on a Dionex 300 ion chromatograph within the Department of Geological Sciences at the University of Cape Town.

The samples were initially filtered through a 0.22 μm Millipore filter membrane to remove suspended solids. They were thereafter diluted with M_Q deionised water, to obtain values under 100 μS/cm. Prior to analysis, the samples were passed through a Dionex onguard-P cartridge, containing a polyvinylpyrrolidone (PVP) polymer.

The column used for anion separation was a Dionex AS14, preceeded by a Dionex AG4A guard column using an eluent comprising 3.5 mM Na_2CO_3 and 1.7mM $NaHCO_3$ eluent. The rate of flow of the eluent was 2ml/min and the sample loop volume was 50μl. An anion micro-membrane supressor was fitted.

Cations were separated using a Dionex CS12A cation exchange column, preceeded by a Dionex CG12A guard column using a 22mM MSA (methanesulphonic acid) eluent. The eluent flow rate was 1ml/min and sample loop volume of 25μl. Detection was conducted according to conductivity using chemical eluent suppression. A cation self-regenerating suppressor (CSRS) was fitted. Four standards were analysed prior to measuring the sample solutions.

B.8. Trace element concentrations

Trace element concentrations were determined for soil solutions of saturated paste extracts using an ELAN 6000 ICP-MS (inductive coupled plasma mass spectrometry), within the Department of Geological Sciences at the University of Cape Town. The elements analysed were: Li, B, Al, Ti, V, Cr, Mn, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Mo, Cd, Cs, Ba, Nd, Tl, Pb and U. All samples were filtered though a 0.22 μm Millipore filter and then diluted (1:1) with 2% of HNO_3, to a total aliquot volume of 30ml. Prior to analysis, 100μl of an internal standard (Rh) solution was added to each sample for purposes of instrument calibration and drift corrections. The internal standard solution was made up of 3ppm Rh in 2% HNO_3. Trace elements concentrations are presented in Table B.1.

In order to assess accuracy during sample measurements, two standards of the U.S.A National Institute of Standard Technology (NIST 1640 and NIST 1643d) were run at the beginning of the analytical session. The precision of trace element detection for the NIST standards is reported in Appendix C.

B.9. Dissolved organic carbon determination

Dissolved organic carbon (DOC) analysis was conducted by the Environmentek analytical services unit (Stellenbosch), a division of the C.S.I.R. The method involved some adaptations introduced by the C.S.I.R., for the Persulphate-Ultraviolet oxidation method (Louw M., personal communication, 1998). This method is appropriate for determining DOC levels ranging from 0.1 to 20 mg/l as C. Higher concentrations would require diluting of the samples.

Principle

The method implements an automated Persulphate-Ultraviolet oxidation method, using colorimetric detection of the CO_2 thus generated. Organic carbon is oxidised to CO_2 by persulphate in the presence of ultraviolet light. The CO_2 produced, diffuses through a gas-permeable membrane, and is measured by the decrease in absorbance of a phenolpthalein solution. Inorganic carbon is first removed by acidifying the sample to pH 2 or less for the purpose of converting the inorganic carbon species to CO_2, and then purifying the sample with a purified gas (N_2) to strip off the CO_2.

Samples need to be filtered through a 0.45μm filter. If unstable, samples are to be acidified. Standards are processed and calibration curves are determined.

Interferences

Persulphate oxidation of organic molecules is slowed in the presence of chloride due to the preferential oxidation of chloride. At a concentration of 0.1% Cl^-, oxidation of organic matter may be inhibited completely. To remove this interference, hydroxylamine ammonium chloride is added.

Table B.1: *Trace element composition of the soil solution (saturated paste extracts) from 22 surface soils under pine plantations of different ages in the Sabie area, Mpumalanga. Concentrations are reported in µg/l.*

Sample	Li	B	Al	Ti	V	Cr	Mn	Ni	Cu	Zn	As	Se	Rb	Sr	Zr	Mo	Cd	Cs	Ba	Nd	Tl	Pb	U
K 1	1.1	22	1407	5	3.0	9.0	375	7.5	18	50	0.9	4.4	26	37	8.4	0.4	0.2	0.1	35	0.9	0.1	44	0.3
I 1	0.5	14	540	3	6.6	3.8	1024	5.7	13	18	1.0	5.8	43	23	1.6	0.3	0.3	0.4	50	0.6	0.1	2	0.2
I 2	1.1	23	113	21	3.6	0.2	3189	18.7	43	64	1.1	3.3	18	114	1.3	0.2	0.3	0.3	81	0.2	0.3	20	0.5
I 3	0.7	36	699	8	2.5	5.2	108	2.3	8	19	1.0	5.3	37	31	5.1	0.5	0.1	0.4	27	1.0	0.2	1	0.3
I 4	0.5	12	168	8	1.7	2.6	838	22.2	6	34	0.8	3.9	21	66	0.9	0.6	0.2	0.4	64	0.3	0.1	2	0.3
I 5	5.5	10	3066	41	3.7	6.4	885	7.7	13	54	1.1	6.4	31	70	2.9	0.3	0.4	0.3	99	2.9	0.2	21	0.9
I 6	0.5	12	580	2	2.3	7.9	444	7.3	10	51	1.0	5.2	21	20	3.2	0.6	0.5	0.3	48	0.7	0.1	14144	0.3
I 7	0.4	11	1034	2	2.1	3.7	346	9.4	125	794	0.7	3.4	25	22	2.1	0.1	0.3	0.2	42	2.8	0.1	3	0.7
G 1	0.7	10	916	6	1.6	15.0	354	15.2	12	47	0.8	3.7	17	28	5.2	0.9	0.4	0.2	56	2.5	0.1	1	0.3
G 2	0.4	12	147	2	1.5	3.2	424	2.6	10	61	0.9	5.2	10	15	0.8	0.5	0.2	0.2	22	0.2	0.1	1	0.1
G 3	1.7	24	741	4	3.4	5.8	576	32.2	20	50	1.3	3.3	12	38	6.0	9.7	0.3	0.2	110	1.7	0.1	2	0.4
R 1	0.7	16	320	20	3.0	3.1	330	6.5	7	86	1.0	4.8	27	64	3.2	0.8	3.3	0.3	32	0.3	0.2	2	0.2
R 2	0.7	27	414	3	2.0	2.7	149	5.4	7	34	0.8	3.3	22	20	3.3	0.3	0.3	0.2	32	0.4	0.1	2	0.3
R 3	0.6	17	332	2	1.2	4.7	102	3.9	10	20	0.7	3.3	9	15	3.6	0.2	0.2	0.1	20	1.6	0.1	1	0.2
R 4	0.7	13	936	2	2.2	6.6	135	4.6	7	14	0.7	3.3	14	13	7.8	0.3	0.1	0.2	28	1.4	0.1	2	0.3
R 5	0.7	13	558	3	1.9	2.7	437	4.7	5	17	0.7	4.2	14	19	2.7	0.4	0.1	0.2	42	0.3	0.1	1	0.1
R 6	0.6	12	366	1	3.9	2.7	1078	13.6	12	41	0.9	4.7	15	11	1.1	0.3	3.8	0.4	31	1.2	0.1	1	0.1
B 1	1.4	21	412	5	2.5	12.0	530	12.8	41	1138	1.5	3.8	15	23	3.5	0.3	0.3	0.3	35	1.4	0.2	5	0.1
B 2	1.2	20	432	3	2.9	11.1	435	23.0	14	27	1.0	3.7	22	20	3.7	2.5	0.2	0.5	59	1.1	0.3	1	0.2
B 3	2.5	69	1340	10	4.6	21.8	2004	25.6	22	111	2.0	5.7	43	40	2.4	14.9	1.2	114.8	54	1.0	0.5	5	0.2
B 4	2.7	19	1271	3	4.9	8.3	353	14.1	26	61	1.0	2.7	19	34	7.9	2.0	0.8	0.6	87	4.6	0.1	3	0.3
B 5	2.1	18	648	21	1.8	3.9	326	12.7	16	25	0.9	2.8	28	178	5.9	0.2	0.2	0.4	70	1.7	0.2	0	0.3

APPENDIX C: PRECISION AND REPRODUCIBILITY OF DATA

C.1. pH determination

pH measurements were conducted using a Metrohm 691 pH meter with a 3M KCl combined electrode (glass indicator electrode and a reference electrode). The pH meter was calibrated prior to analysis, using buffer solutions of pH 7 and pH 4. pH measurements were taken at room temperature, ± 20°C. In Table C.1, duplicate measurements are reported using basic statistical interpretation of pH measurements for the saturated paste extracts, pH_{KCl} and pH_{water}. The S.D. values in Table C.1 indicate adequate analytical precision.

An interesting observation is the variation in pH between that of the saturated paste and that of the extract. The pH levels in the paste were predominantly lower than those recorded in the extract (Figure C.1).

The reason for the increase in pH between the paste and the extract may be attributed to the contact of the extract with atmospheric pressure of CO_2. The soils are poorly buffered and the contact with the atmosphere during the process of extraction exposes the solution to atmospheric CO_2. Thermodynamically, water exposed to atmospheric CO_2 at 25°c will have a pH of 5.7 (Krauskopf, 1967). Therefore, the extracts may form weak carbonic acids that elevate the pH of the solutions.

Another possible explanation for the variation between the pH levels of the pastes and those of the extracts is the fact that, in the process of rewetting the soils (after they were air dried), the pH was most likely to be affected, and as Bartlett and James (1980) observed, the pH of the soils may rise or drop after rewetting. It was further noticed that most of the extracts exhibited a further increase in pH at the second repetition of pH measurements (Figure C.2).

Table C.1: *Data summary of duplicate pH measurements in saturated pastes, prior to extraction.*

Sample	Reading 1	Reading 2	Reading 3	Mean	S.D.	% RSD
		KCl				
K 1	3.86	3.94		3.90	0.06	1.45
I 1	3.88	3.92		3.90	0.03	0.73
I 5	3.71	3.88		3.80	0.12	3.17
I 7	3.97	3.97		3.97	0.00	0.00
G 3	3.75	3.76		3.76	0.01	0.19
R 3	3.92	3.87		3.90	0.04	0.91
R 4	3.78	3.71		3.75	0.05	1.32
R 5	3.81	3.80		3.81	0.01	0.19
B 2	3.76	3.83		3.80	0.05	1.30
B 4	3.68	3.73		3.71	0.04	0.95
		Water				
I 2	4.95	4.84		4.90	0.08	1.59
I 3	4.62	4.57		4.60	0.04	0.77
I 4	4.84	4.85		4.85	0.01	0.15
G 1	4.57	4.64		4.61	0.05	1.07
G 2	4.75	5.04		4.90	0.21	4.19
R 1	4.82	4.77		4.80	0.04	0.74
R 2	4.6	4.6		4.60	0.00	0.00
B 1	4.7	4.7		4.70	0.00	0.00
B 3	4.79	4.8		4.80	0.01	0.15
B 5	4.42	4.48		4.45	0.04	0.95
		Paste				
K 1	4.43	4.49		4.46	0.04	0.95
I 1	4.65	4.62		4.64	0.02	0.46
I 2	4.89	4.82		4.86	0.05	1.02
I 3	4.66	4.66		4.66	0.00	0.00
G 1	4.56	4.6		4.58	0.03	0.62
R 1	4.71	4.72		4.72	0.01	0.15
R 2	4.66	4.68		4.67	0.01	0.30
R 3	4.78	4.78		4.78	0.00	0.00
B 1	4.6	4.6		4.60	0.00	0.00
B 2	4.52	4.49		4.51	0.02	0.47
		Extract				
K 1	4.6	5.15	5.80	5.18	0.60	11.59
I 1	4.71	4.92		4.82	0.15	3.08
I 3	4.73	4.78		4.76	0.04	0.74
I 6	4.47	4.5		4.49	0.02	0.47
G 2	5.03	5.4	5.61	5.35	0.29	5.49
R 1	4.73	4.75		4.74	0.01	0.30
R 2	4.78	4.75		4.77	0.02	0.45
R 5	4.72	4.8		4.76	0.06	1.19
B 1	4.71	4.82	5.12	4.88	0.21	4.35
B 3	4.69	4.84		4.77	0.11	2.23
B 4	4.43	4.64		4.54	0.15	3.27

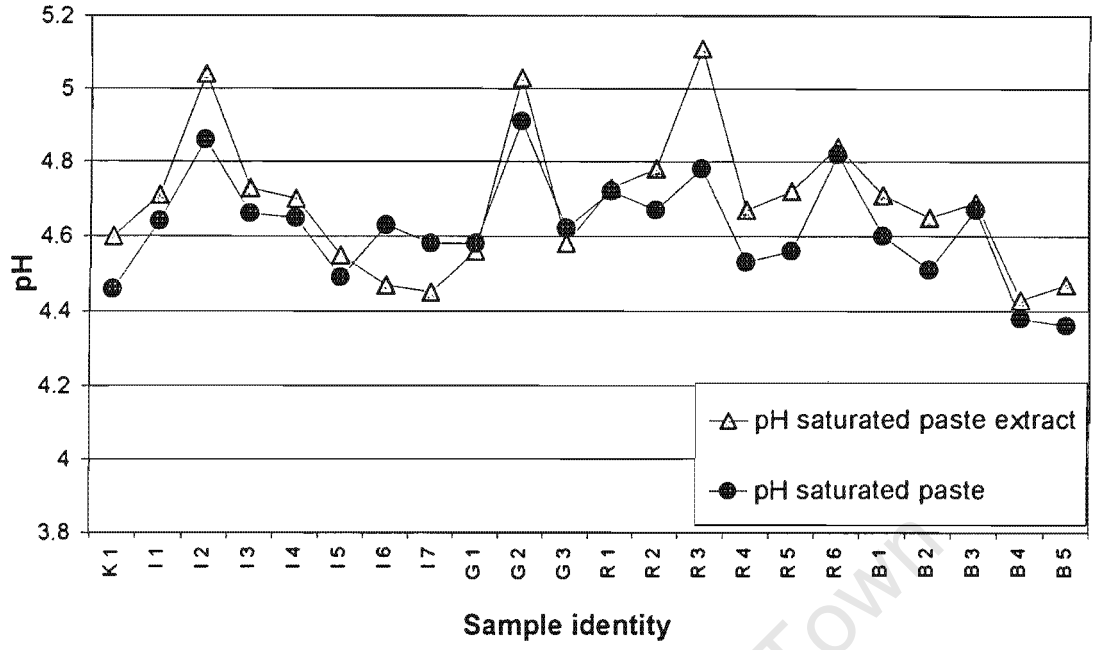

Figure C.1: *pH values of saturated pastes and extracts of 22 surface soils under pine plantations of different ages in the Sabie area, Mpumalanga.*

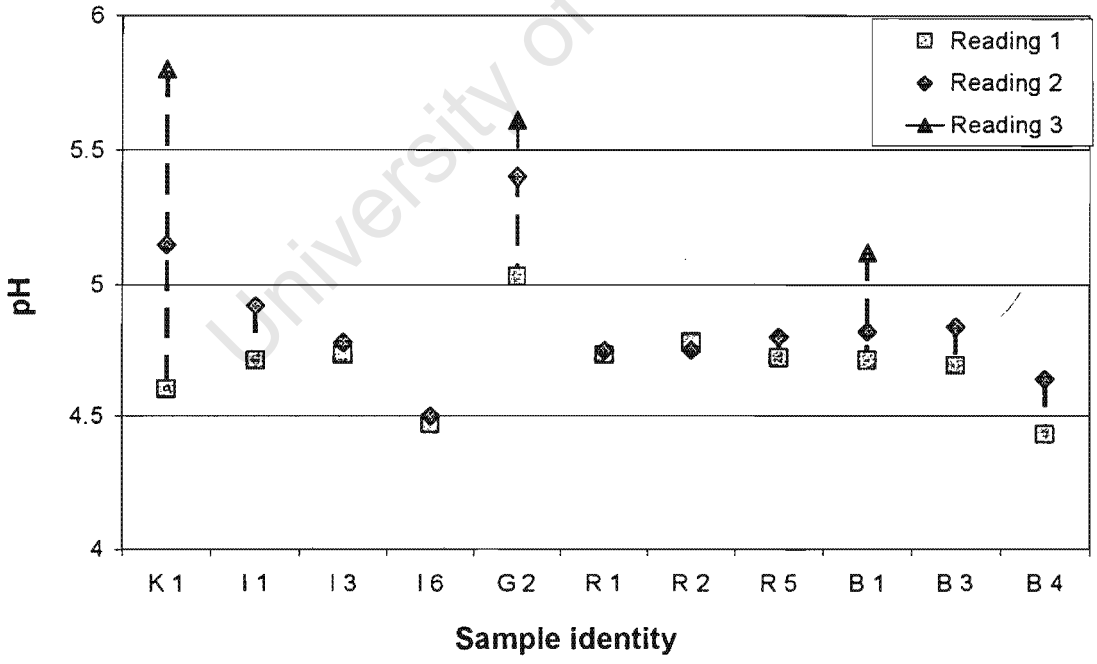

Figure C.2: *pH values of three successive measurements in extracts of soil solution for 11 surface soils under pine plantations of different ages in the Sabie area, Mpumalanga.*

By observing the changes in pH values over successive measurements in saturated paste extracts (Figure C.2) it was assumed that the pH values of the saturated pastes presented more appropriate pH values for the soil solution.

C.2. Electrical conductivity (EC)

The ionic strength of the soil solutions was determined by calculating the EC of the saturated paste extracts. EC measurements were conducted by using a Crison microCM 2201 conductivity meter. The conductivity meter consists of a conductivity cell (cell constant: C=1.03/cm) and a temperature probe for automatic temperature compensation. In Table C.2 the values of EC measurements as recorded for duplicate readings of 11 saturated paste extracts are presented. The S.D. does not exceed 10%, indicating adequate precision levels.

Table C.2: *Duplicate electrical conductivity readings for 11 saturated paste extracts from surface soils under pine plantations of different ages in the Sabie area, Mpumalanga*

Sampl	Reading	Reading	Mea	S.D	%
K 1	106	113	110	4.9	4.52
I 2	148	157	153	6.3	4.17
I 4	126	133	130	4.9	3.82
I 5	144	147	146	2.1	1.46
G 2	75	76	76	0.7	0.94
R 2	98	102	100	2.8	2.83
R 4	86	91	89	3.5	3.99
R 5	140	147	144	4.9	3.45
B 1	125	126	126	0.7	0.56
B 2	181	180	181	0.7	0.39
B 3	230	234	232	2.8	1.22

C.3. Exchangeable Cations by FAAS

Exchangeable cations were examined using a VARIAN Spectra 10-20 at the Department of Chemical Engineering, University of Cape Town. In Table C.3, the results from duplicate measurements of selected samples are presented. Also presented are the standards as they were determined before, during, and at the end of the analysis.

The analysis of exchangeable cations by FAAS presents relatively adequate precision. Some samples, however, present precision levels which are unsatisfactory. As can be seen in Table C.3, the % RSD levels which exceed 10% are in sample I4 with respect to Mn^{2+} and Ca^{2+}, in samples G2 and R5 with respect to Mn^{2+}, in sample B3 with respect to Ca^{2+}, and in the 50 mg/l standard for $CuCl_2$ Al extraction procedure. The Mn^{2+} levels were very low and thus the effectiveness of determination is reduced.

C.4. Acid neutralising capacity (ANC)

The acid neutralising capacity was determined according to the methods suggested by du Toit and Fey (1993). The pH measurements for the calculation of ANC are reported in Table C.4. From Table C.4 it can be observed that the % RSD does not exceed 10%. The second readings are all higher than the first. A possible explanation is a temperature change of 2°C that took place during the period of pH measuring. Apart from this, the calibration of the pH electrode may have been affected, though calibration was conducted before every set of readings and the calibration curve slope was observed to be between 93% and 97%. Nevertheless, the precision is believed to be adequate for the purposes of this study.

C.5. Ion chromatography (IC)

Ion concentration for saturated paste extracts were determined using a Dionex 300 Ion Chromatograph IC. Precision and data reproducibility are reported in Table C.5.

Table C.3: *Results of four duplicate analysis and three standards of exchangeable cations determined by FAAS.*

Sample		KCl extractable				$CuCl_2$ extractable
		Ca^{2+}	Mg^{2+}	Mn^{2+}	Al^{3+}	Al^{3+}
		mg/l				mg/l
I 4	Reading 1	0.308	0.318	0.031		143.0
	Reading 2	0.368	0.340	0.026		151.0
	Reading 3					145.7
	Mean	0.338	0.329	0.029		146.6
	S.D.	0.042	0.015	0.004		4.1
	%RSD	12.6	4.60	12.4		2.8
G 2	Reading 1	0.416	0.398	0.115		
	Reading 2	0.388	0.346	0.011		
	Mean	0.402	0.372	0.063		
	S.D.	0.020	0.036	0.074		
	% RSD	4.9	9.8	116.7		
R 5	Reading 1	1.887	0.354	0.018		
	Reading 2	1.657	0.359	0.010		
	Mean	1.772	0.357	0.014		
	S.D.	0.163	0.003	0.006		
	% RSD	9.18	0.932	40.4		
B 3	Reading 1	0.492	0.560	0.252		
	Reading 2	1.433	0.586	0.263		
	Mean	0.963	0.573	0.258		
	S.D.	0.665	0.018	0.008		
	% RSD	69.1	3.17	3.0		
R 4	Reading 1					217
	Reading 2					224
	Reading 3					198
	Mean					213
	S.D.					13.3
	% RSD					6.3
Standards			1 mg/l (Mg)		25 mg/l (Al)	50 mg/l (Al)
	Reading 1		0.91		21.5	47.4
	Reading 2		0.85		22.3	45.9
	Reading 3				24.3	38.9
	Mean		0.88		22.7	44.05
	S.D.		0.04		1.45	4.53
	% RSD		4.82		6.38	10.3

Table C.4: *pH readings for the determination of ANC from 22 surface soils under pine plantations of different ages in the Sabie area, Mpumalanga.*

Sample	Reading 1	Reading 2	Mean	S.D.	%RSD
K 1	3.81	3.86	3.84	0.04	0.92
I 1	3.75	4.18	3.97	0.30	7.67
I 2	3.76	3.95	3.86	0.13	3.49
I 3	3.61	3.99	3.80	0.27	7.07
I 4	3.79	4.23	4.01	0.31	7.76
I 5	3.63	4.06	3.85	0.30	7.91
I 6	3.67	4.09	3.88	0.30	7.65
I 7	3.66	4.12	3.89	0.33	8.36
G 1	3.81				
G 2	4.14				
G 3	3.79				
R 1	3.68	4.15	3.92	0.33	8.49
R 2	3.64	4.08	3.86	0.31	8.06
R 3	3.66	4.17	3.92	0.36	9.21
R 4	3.53	4.02	3.78	0.35	9.18
R 5	3.63	4.12	3.88	0.35	8.94
R 6	3.85	4.25	4.05	0.28	6.98
B 1	3.84				
B 2	3.84				
B 3	3.93				
B 4	3.73				
B 5	3.73				

From Table C.5, it can be observed that the % RSD varies. In some cases it reaches up to 140 %. Yet, the variation was observed to be high when the concentrations of the samples were low, thus increasing the error associated with the detection of ions. A possible source of error originated from diluting the samples to EC levels that were too low for adequate detection by IC, and thereby reaching the detection limits of the Dionex column. In the case of sample B3, the third reading was disregarded due to exceptionally high levels of Ca^{2+} and Mn^{2+}, and was assumed to be associated with an operational analytical error originating from low eluent levels.

Table C.5: *Precision and data reproducibility for four soil solutions (saturated paste extracts) and standards determined for major ion concentration by IC.*

Sample		Na^+	NH_4^+	K^+	Mg^{2+}	Mn^{2+}	Ca^{2+}	F^-	Cl^-	NO_2^-	Br^-	PO_4^{3-}	SO_4^{2-}
I 1	Reading 1	11.60	34.90	14.80	11.20		9.35	6.50	13.90	2.50			4.10
	Reading 2	11.40	19.00	12.50	15.90		9.75	12.60	14.50	3.70			4.75
	Reading 3	11.40	21.40	14.50	9.80		9.40	8.80	14.00	1.40			4.49
	Mean	11.47	25.10	13.93	12.30		9.50	9.30	14.13	2.53			4.45
	S.D.	0.12	8.57	1.25	3.20		0.22	3.08	0.32	1.15			0.33
	%RSD	1.01	34.15	8.97	25.98		2.29	33.12	2.27	45.41			7.36
G 2	Reading 1	10.50	5.74	2.60	3.15		3.54	2.51	6.10	0.00		0.34	5.40
	Reading 2	8.21	6.65	1.10	2.94		2.95	2.60	6.25	0.22		0.36	3.06
	Mean	9.36	6.20	1.85	3.05		3.25	2.56	6.18	0.11		0.35	4.23
	S.D.	1.62	0.64	1.06	0.15		0.42	0.06	0.11	0.15		0.01	1.65
	%RSD	17.31	10.39	57.33	4.88		12.86	2.49	1.72	141.42		3.64	39.12
R 5	Reading 1	20.50	9.64	6.27	3.50		3.89	5.75	15.80	1.60	0.26		6.36
	Reading 2	22.20	9.09	6.42	4.39		3.24	5.80	15.90	1.47	0.00		6.55
	Mean	21.35	9.37	6.35	3.95		3.57	5.78	15.85	1.54	0.13		6.46
	S.D.	1.20	0.39	0.11	0.63		0.46	0.04	0.07	0.09	0.18		0.13
	%RSD	5.63	4.15	1.67	15.95		12.89	0.61	0.45	5.99	141.42		2.08
B 3	Reading 1	9.89	37.80	13.55	6.54	3.97	23.20	12.20	11.74	3.00			9.91
	Reading 2	9.58	34.80	13.66	6.42	4.40	22.10	11.80	11.70	3.00			8.96
	Reading 3	9.45	37.00	14.02	9.20	0.00	75.20	9.40	10.00	1.30			11.30
	Mean	9.64	36.53	13.74	7.39	2.79	40.17	11.13	11.15	2.43			10.06
	S.D.	0.23	1.55	0.25	1.57	2.43	30.34	1.51	0.99	0.98			1.18
	%RSD	2.34	4.25	1.79	21.28	86.94	75.55	13.60	8.91	40.34			11.70
Standard 1	Concentration	12.50	2.50	2.50	2.50	2.50	12.50						
	Reading	13.10	2.59	2.63	2.78	2.61	13.60						
	Mean	12.80	2.55	2.57	2.64	2.56	13.05						
	S.D.	0.42	0.06	0.09	0.20	0.08	0.78						
	%RSD	3.31	2.50	3.58	7.50	3.04	5.96						
Standard 2	Concentration	12.50	2.50	2.50	2.50	2.50	12.50						
	Reading	13.20	5.81	2.30	2.32	2.55	12.33						
	Mean	12.85	4.16	2.40	2.41	2.53	12.42						
	S.D.	0.49	2.34	0.14	0.13	0.04	0.12						
	%RSD	3.85	56.33	5.89	5.28	1.40	0.97						

C.6. Trace element determination by ICP-MS

Trace element concentrations were determined using an ELAN 6000 ICP-MS. In Table C.6, the precision measurements of the NIST standards (Suwannee River samples: NIST 1640 and NIST 1643b) are presented. These standards were analysed prior to the analysis of the soil solution samples.

Table C.6: *Trace element concentrations and precision analysis of two standards determined by ICP-MS, prior to trace element analysis of soil solutions.*

Element	NIST-1640	Published	Published deviation	Deviation	NIST-1643d	published	Published deviation	Deviation
		µg/l		%		µg/l		%
Li	50.7	50.7	1.40	0.00	17.0	16.5	0.55	1.49
B	284.0	301.1	6.10	-2.92	134.0	144.8	5.20	-3.87
Al	69.1	52.0	1.50	14.12	128.0	127.6	3.50	0.16
Ti	6.8				26.3			
V	13.3	13.0	0.37	1.18	36.7	35.1	1.40	2.23
Cr	36.6	38.6	1.60	-2.66	19.3	18.5	0.20	2.04
Mn	120.0	121.5	1.10	-0.62	38.7	37.7	0.83	1.36
Ni	27.9	27.4	0.80	0.90	59.4	58.1	2.70	1.11
Cu	87.8	85.2	1.20	1.50	21.4	20.5	3.80	2.15
Zn	57.9	53.2	1.10	4.23	71.5	72.5	0.65	-0.68
As	26.3	26.7	0.41	-0.70	55.8	56.0	0.73	-0.20
Se	22.5	22.0	0.51	1.21	12.2	11.4	0.17	3.26
Rb	1.9	2.0	0.02	-1.78	11.7	13.0		-5.26
Sr	121.0	124.2	0.70	-1.31	295.0	294.8	3.40	0.03
Zr	0.2				0.0			
Mo	46.9	46.8	0.26	0.16	116.0	112.9	1.70	1.35
Cd	22.9	22.8	0.96	0.24	6.5	6.5	0.37	0.15
Cs	0.1				4.7			
Ba	145.0	148.0	2.20	-1.02	505.0	506.5	8.90	-0.15
Nd	0.3				①n.d.			
Tl	n.d.				7.6	7.3	0.25	2.22
Pb	29.6	27.9	0.14	2.97	19.8	18.2	0.64	4.35
U	0.8				0.0			

① Not detected.

The highest deviation in the analysis of the standards was observed for Al (14%), whereas all the other elements were detected more precisely (<5%). This may add to the findings concerning Al in solution discussed in Chapter 4, where the determination of soluble Al was suggested to be inaccurate and underestimated.

Precision analysis has been performed on three random samples. The precision and data reproducibility are reported in Table C.7. The precision for Al and Mn determinations proves sufficient despite the 14 % deviation presented in Table C.6. Nevertheless, as mentioned in Chapter 4, the samples were stored for a month prior to ICP-MS analysis and may therefore have undergone chemical changes, such as precipitation and pH increase, that may have reduced the solubility of Al and Mn in solution.

Table C.7: *Precision and data reproducibility of three soil solutions (saturated paste extracts) determined for selected trace element concentrations by ICP-MS. Results are reported in µg/l.*

Sample	R 5					I 3					B 4				
	Reading 1	Reading 2	Mean	S.D.	RSD %	Reading 1	Reading 2	Mean	S.D.	RSD %	Reading 1	Reading 2	Mean	S.D.	RSD %
Li	0.66	0.72	0.69	0.04	6.15	0.68	0.64	0.66	0.03	4.29	2.76	2.70	2.73	0.04	1.55
B	12.84	13.14	12.99	0.21	1.63	35.20	37.00	36.10	1.27	3.53	19.32	19.59	19.46	0.19	0.98
Al	567	549	558	12.73	2.28	682	716	699	24.04	3.44	1296	1245	1270.50	36.06	2.84
Ti	4.35	2.34	3.35	1.42	42.49	7.66	7.52	7.59	0.10	1.30	3.18	2.61	2.90	0.40	13.92
V	1.86	1.83	1.85	0.02	1.15	2.48	2.48	2.48	0.00	0.00	4.98	4.83	4.91	0.11	2.16
Cr	2.13	3.18	2.66	0.74	27.96	5.26	5.16	5.21	0.07	1.36	8.31	8.31	8.31	0.00	0.00
Mn	435	438	436	2.12	0.49	108	108	108	0.42	0.39	354.00	351	352.50	2.12	0.60
Ni	4.68	4.77	4.73	0.06	1.35	2.24	2.32	2.28	0.06	2.48	14.04	14.22	14.13	0.13	0.90
Cu	4.35	5.10	4.73	0.53	11.22	7.22	8.20	7.71	0.69	8.99	24.93	27.96	26.45	2.14	8.10
Zn	15.84	17.67	16.76	1.29	7.72	19.00	19.44	19.22	0.31	1.62	58.80	62.70	60.75	2.76	4.54
As	0.72	0.75	0.74	0.02	2.89	1.00	0.92	0.96	0.06	5.89	0.93	0.96	0.95	0.02	2.24
Se	4.38	3.96	4.17	0.30	7.12	5.42	5.08	5.25	0.24	4.58	2.70	2.76	2.73	0.04	1.55
Rb	13.95	13.92	13.94	0.02	0.15	36.60	37.40	37.00	0.57	1.53	18.96	18.84	18.90	0.08	0.45
Sr	18.69	18.42	18.56	0.19	1.03	30.40	31.00	30.70	0.42	1.38	34.50	33.90	34.20	0.42	1.24
Zr	2.79	2.64	2.72	0.11	3.91	5.00	5.16	5.08	0.11	2.23	7.95	7.77	7.86	0.13	1.62
Mo	0.33	0.36	0.35	0.02	6.15	0.42	0.50	0.46	0.06	12.30	0.78	3.18	1.98	1.70	85.71
Cd	0.11	0.11	0.11	0.01	5.81	0.12	0.13	0.12	0.01	8.05	0.84	0.84	0.84	0.00	0.00
Cs	0.17	0.18	0.18	0.01	3.63	0.36	0.36	0.36	0.00	0.00	0.57	0.57	0.57	0.00	0.00
Ba	41.10	42.00	41.55	0.64	1.53	27.20	26.40	26.80	0.57	2.11	88.20	85.80	87.00	1.70	1.95
Nd	0.30	0.30	0.30	0.00	0.00	1.02	1.02	1.02	0.00	0.00	4.62	4.53	4.58	0.06	1.39
Tl	0.10	0.12	0.11	0.01	9.69	0.14	0.16	0.15	0.01	6.56	0.13	0.13	0.13	0.00	3.29
Pb	0.78	0.93	0.86	0.11	12.41	0.82	0.92	0.87	0.07	8.13	3.00	3.33	3.17	0.23	7.37
U	0.13	0.13	0.13	0.00	1.63	0.30	0.32	0.31	0.01	4.56	0.33	0.30	0.32	0.02	6.73

C.7. Soluble Al

Soluble Al was determined colorimetrically using the method of Kennedy and Powell (1986). The analytical precision regarding the colorimetric method used is reported in Table C.8.

Table C.8: *Analytical precision of Al determined colorimetrically according to the method of Kennedy and Powell (1986), for seven soil solutions (saturated paste extracts) of surface soils under pine plantations of different ages in the Sabie area, Mpumalanga.*

Sample	Reading 1	Reading 2	Mean	S.D.	%RSD
K 1	1.74	4.39	3.07	1.88	61.18
I1	1.70	1.74	1.72	0.03	1.79
I3	2.04	1.35	1.70	0.49	29.01
I4	1.30	1.35	1.33	0.03	2.32
I5	3.83	1.30	2.57	1.78	69.51
R1	3.00	1.52	2.26	1.05	46.23
B2	1.78	1.87	1.83	0.06	3.37

The precision of the analyses varies and suggests that the method used may not be adequate in the context of this study. The method involves a timed reaction that requires a spectrophotometric reading within the first 15 minutes after the last reagent was added. The samples were taken through the procedure immediately after the soil solutions were extracted from the saturated pastes. As noted before, the pH of the pastes changed in a rapid manner and the soil solutions became more alkaline, thus reducing the solubility of Al.

The stability of colour in the solutions deteriorated with time and consequently produced Al concentrations that are underestimated. The method was performed within the required time span of 15 minutes. The colour was observed to deteriorate with time, yet the loss of colour is more prominent after the first 20 to 30 minutes from the last addition of reagents. Standards were analysed before and after each set of samples, and indicated the

accuracy of the photometer. Therefore, due to the consistency of the instrument and the standards, and the inconsistency in Al measurements in solution, it is suggested that rapid changes take place during the process of preparing the samples for Al determination, probably due to the changes in pH and solubility equilibria of Al.

C.8. Silica concentrations

Silica concentrations were determined using the molybdosilicate method (Eaton *et al.*, 1995). Results from duplicate analyses of silica in solution are presented in Table C.9 As can be seen from Table C.9, the reproducibility of data is adequate and indicates sufficient precision of the method in use.

Table C.9: *Analysis precision of Si determined colorimetrically according to the method of Eaton et al. (1995), for six soil solutions (saturated paste extracts) of surface soils under pine plantations of different ages in the Sabie area, Mpumalanga.*

Sample	Reading 1	Reading 2	Mean	S.D.	%RSD
I 4	11.57	11.14	11.36	0.31	2.69
G 2	9.97	10.00	9.99	0.02	0.20
R 3	22.94	20.10	21.52	2.01	9.34
R 4	18.77	18.70	18.74	0.05	0.27
R 5	19.97	17.00	18.49	2.10	11.37
B 3	13.37	13.30	13.34	0.05	0.38

APPENDIX D: PINE ECOLOGY WITH RESPECT TO THE STUDIED SPECIES

D.1. Introduction

The ecology of pines is described in many papers and textbooks (Vidakovic, 1991; Richardson and Rundel, 1998; Raven *et al.*, 1999). This section will briefly describe the ecological aspects of pine and introduce some of the fundamental concepts of the biology and physiology of the three studied pine species: *P. patula, P. elliottii and P. taeda*.

It is important to note that the natural habitat of pine is in the Northern Hemisphere, characterised by rainy, cold winters and relatively dry, hot summers. The characteristics of the area of this study are fundamentally different; a rainy summer season and a dry winter season. Pines are known to be light-dependant (yet, exhibit low shade tolerance), water efficient and fast growing trees. Some of the significant characteristics of *Pinus* sp. are:

- An ability to inhabit nutrient poor soils. In temperate and tropic regions, pines are usually associated with acidic, nutrient poor soils (Keeley and Zedler, 1998).
- Needle longevity is well correlated with the state of nutrients and the water supply (Richardson and Rundel, 1998).
- Serotiny (Agee, 1998).
- Enhancement of soil acidity and depletion of available nutrients (Scholes and Nowicki, 1998).

High levels of genetic variation, reproductive capacity and facultative selfing, have been identified as being major contributors to the succession of pines in non-native environments (Ledig, 1998). Variations with respect to these contributors are found among and within pine populations. Therefore, the ability of the pines to adjust to a change in the environment is elevated.

Rundel and Yoder (1998) point out some further distinctive features of pines. When the capacity is evaluated per unit of projected area, the pine trees have high capacity rate. The variation in photosynthetic capacity between pine species can be significant, though variation within species can vary as well. For example the photosynthetic rate of *P. taeda* can be twice or even four times higher than that of *P. elliottii* (Rundel and Yoder, 1998). Overall, conifer species experience an annual rate of photosynthetic decline between 30% and 50%.

Mycorrhyzal pine status.

The ectomycorrhyza are formed predominantly in the organic horizon of an acid forest soil profile, where nitrification is inhibited (Read, 1998). Read (1998) further indicates that there is increasing evidence of further functions promoted by the ectomycorrhyza, such as enhancing the resistance of the tree to potentially toxic metal ions and to the roots, which can be harmful at low pH. The abundance and variety of innoculum in commercial plantations, is known to be very low in comparison with the natural habitat of pines (Read, 1998).

D.2. P. patula

P. patula is a tropical pine that grows in high elevations (greater than 3500m), with high rainfall (1200-2000 mm/a). The height of *P.patula* is between 12 to 20m. The crown is broadly conical. A distinguishing design in *P. patula* is its needle morphology and longevity. The needles hang downwards. In its natural habitat (tropical mountains and coastal fog zones), this needle structure aids the condensation and dripping of fog moisture. In terms of needle longevity, *P. patula* has the highest needle litter fall of the three studied species, which exhibits itself in the depth of the litter layer. It has an average litter layer thickness of 10cm, notably greater than that generated by *P. elliottii* (5cm) and *P. taeda* (6cm) (Dames, 1996).

D.3. P. elliottii

P. elliottii is a tropical fast growing species that may grow up to 20-30 m in height and 60-90cm in diameter. Naturally found at low elevations (under 100m), *P. elliottii* requires abundant moisture in the soil and moderate climatic conditions for growth. Individual variations between trees are found in high stem volume, crown width, branch and bark thickness, wood specific gravity, resistance to disease and insects, response to fertilisation, and flower production and properties of seeds and needles (Vidakovic, 1991).

D.4. P. taeda

P. taeda is a tropical Pine. This is a fast growing tree with an average height up to 30m, and a diameter of up to 1m. Its maximum natural altitude distribution is 250m in moderately warm regions. Genetic variation exists in pest resistance, crown development, flowering and to a lesser extent in stem growth and width (Vidakovic, 1991). The presence of mycorrhyza significantly increases carbon fixation in *P. taeda,* even when no enhancement of mineral nutrients is involved (Read, 1998).

APPENDIX E: MINTEQA2 MODELLING OUTPUT

Following is an example of a MINTEQA2 modelling output. The example describes one of the possible full output files available by MINTEQA2 as exhibited by running sample I1 of the In Die Diepte plantation.

```
                                  PART 1 of OUTPUT FILE
  PC MINTEQA2 v3.10    DATE OF CALCULATIONS:  2-DEC-98  TIME: 13: 4:35


I-1
with doc

--------------------------------------------------------------------------------
 Temperature (Celsius):  22.00
 Units of concentration: MG/L
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 The maximum number of iterations is: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

--------------------------------------------------------------------------------
    330  0.000E-01   -4.50 y
    500  1.107E+01   -3.32 y
    490  2.600E+01   -2.84 y
    410  1.364E+01   -3.46 y
    460  7.310E+00   -3.52 y
    470  1.020E+00   -4.73 y
    150  7.390E+00   -3.73 y
     30  1.720E+00   -4.20 y
    270  9.250E+00   -3.31 y
    180  1.405E+01   -3.40 y
    491  2.700E+00   -4.23 y
    732  4.450E+00   -4.33 y
    770  1.940E+01   -3.69 y
    145  1.000E-03   -3.00 y

 H2O has been inserted as a COMPONENT
  3   1
  330      4.5000      0.0000
```

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	NAME	ACTIVITY GUESS	LOG GUESS	ANAL TOTAL
330	H+1	3.162E-05	-4.500	0.000E-01
500	Na+1	4.786E-04	-3.320	1.107E+01
490	NH4+1	1.445E-03	-2.840	2.600E+01
410	K+1	3.467E-04	-3.460	1.364E+01
460	Mg+2	3.020E-04	-3.520	7.310E+00
470	Mn+2	1.862E-05	-4.730	1.020E+00
150	Ca+2	1.862E-04	-3.730	7.390E+00
30	Al+3	6.310E-05	-4.200	1.720E+00
270	F-1	4.898E-04	-3.310	9.250E+00
180	Cl-1	3.981E-04	-3.400	1.405E+01
491	NO2-1	5.888E-05	-4.230	2.700E+00
732	SO4-2	4.677E-05	-4.330	4.450E+00
770	H4SiO4	2.042E-04	-3.690	1.940E+01
145	DOM	1.000E-03	-3.000	1.000E-03
2	H2O	1.000E+00	0.000	0.000E-01

Charge Balance: UNSPECIATED

Sum of CATIONS= 3.471E-03 Sum of ANIONS = 3.835E-03

PERCENT DIFFERENCE = 4.983E+00 (ANIONS - CATIONS)/(ANIONS + CATIONS)

IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:

Mn+2	Log activity guess:	-4.73
Al+3	Log activity guess:	-4.32
SO4-2	Log activity guess:	-4.34
H4SiO4	Log activity guess:	-3.69

PART 3 of OUTPUT FILE

PC MINTEQA2 v3.10 DATE OF CALCULATIONS: 2-DEC-98 TIME: 13: 4:39

PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY	RESIDUAL
0	SO4-2	4.633E-05	7.581E-06	-4.33536	7.576E-06
1	SO4-2	4.633E-05	2.362E-07	-4.37850	2.316E-07
2	H4SiO4	2.019E-04	-2.467E-07	-3.69494	2.265E-07
3	SO4-2	4.633E-05	3.616E-07	-4.49330	3.569E-07
4	SO4-2	4.633E-05	-2.984E-08	-4.49655	2.520E-08
5	SO4-2	4.633E-05	-1.230E-08	-4.49627	7.670E-09
6	F-1	4.869E-04	5.274E-08	-3.58469	4.044E-09

ID	NAME	ANAL MOL	CALC MOL	LOG ACTVTY	GAMMA	DIFF FXN
145	DOM	1.000E-03	6.415E-04	-3.46137	0.538798	-5.677E-10
500	Na+1	4.816E-04	4.815E-04	-3.35168	0.924151	-9.417E-11
490	NH4+1	1.442E-03	1.441E-03	-2.87562	0.924151	-2.819E-10
410	K+1	3.489E-04	3.488E-04	-3.49168	0.924151	-6.822E-11
460	Mg+2	3.007E-04	2.804E-04	-3.68921	0.729411	-2.545E-10
470	Mn+2	1.857E-05	1.844E-05	-4.87115	0.729411	-1.444E-11
150	Ca+2	1.844E-04	1.179E-04	-4.06553	0.729411	-2.373E-10

30	Al+3	6.375E-05	5.585E-11	-10.56127	0.491686	-2.740E-12
270	F-1	4.869E-04	2.816E-04	-3.58469	0.924151	-6.358E-11
180	Cl-1	3.963E-04	3.963E-04	-3.43621	0.924151	-7.751E-11
491	NO2-1	5.870E-05	5.870E-05	-4.26565	0.924151	-1.148E-11
732	SO4-2	4.633E-05	4.374E-05	-4.49615	0.729411	-3.436E-11
770	H4SiO4	2.019E-04	2.019E-04	-3.69440	1.001254	1.377E-12
2	H2O	0.000E-01	-3.063E-10	-0.00003	1.000000	0.000E-01
330	H+1	0.000E-01	3.422E-05	-4.50000	0.924151	0.000E-01

Type I - COMPONENTS AS SPECIES IN SOLUTION

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK
330	H+1	3.422E-05	3.162E-05	-4.50000	0.92415	0.034
500	Na+1	4.815E-04	4.450E-04	-3.35168	0.92415	0.034
490	NH4+1	1.441E-03	1.332E-03	-2.87562	0.92415	0.034
410	K+1	3.488E-04	3.223E-04	-3.49168	0.92415	0.034
460	Mg+2	2.804E-04	2.045E-04	-3.68921	0.72941	0.137
470	Mn+2	1.844E-05	1.345E-05	-4.87115	0.72941	0.137
150	Ca+2	1.179E-04	8.599E-05	-4.06553	0.72941	0.137
30	Al+3	5.585E-11	2.746E-11	-10.56127	0.49169	0.308
270	F-1	2.816E-04	2.602E-04	-3.58469	0.92415	0.034
180	Cl-1	3.963E-04	3.663E-04	-3.43621	0.92415	0.034
491	NO2-1	5.870E-05	5.424E-05	-4.26565	0.92415	0.034
732	SO4-2	4.374E-05	3.190E-05	-4.49615	0.72941	0.137
770	H4SiO4	2.019E-04	2.021E-04	-3.69440	1.00125	-0.001
145	DOM	6.415E-04	3.456E-04	-3.46137	0.53880	0.269

Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK
3302701	HF2 -	1.202E-08	1.111E-08	-7.95427	0.92415	3.749
3302702	H2F2 AQ	3.964E-10	3.968E-10	-9.40137	1.00125	6.767
1453300	H DOM	2.771E-04	2.146E-04	-3.66838	0.77448	3.981
1450300	Al DOM	3.997E-09	3.984E-09	-8.39965	0.99685	5.201
1451500	Ca DOM	6.577E-05	6.253E-05	-4.20392	0.95077	2.922
1454600	Mg DOM	1.564E-05	1.487E-05	-4.82760	0.95077	1.922
3300020	OH-	2.734E-10	2.527E-10	-9.59745	0.92415	-14.063
3307700	H3SiO4 -	6.982E-10	6.453E-10	-9.19025	0.92415	-9.962
3307701	H2SiO4 -2	4.005E-17	2.921E-17	-16.53440	0.72941	-21.703
7702700	SiF6 -2	1.721E-13	1.255E-13	-12.90126	0.72941	30.438
3304900	NH3 AQ	1.936E-08	1.939E-08	-7.71253	1.00125	-9.337
4907320	NH4SO4 -	5.922E-07	5.473E-07	-6.26177	0.92415	1.144
4603300	MgOH +	8.832E-12	8.162E-12	-11.08819	0.92415	-11.865
4602700	MgF +	3.512E-06	3.245E-06	-5.48872	0.92415	1.819
4607320	MgSO4 AQ	1.132E-06	1.133E-06	-5.94579	1.00125	2.239
1503300	CaOH +	5.786E-13	5.347E-13	-12.27185	0.92415	-12.672
1507320	CaSO4 AQ	5.443E-07	5.450E-07	-6.26364	1.00125	2.298
1502700	CaF +	1.976E-07	1.826E-07	-6.73852	0.92415	0.946
5007320	NaSO4 -	7.552E-08	6.979E-08	-7.15618	0.92415	0.726
5002700	NaF AQ	1.875E-08	1.878E-08	-7.72637	1.00125	-0.791
4107320	KSO4 -	7.418E-08	6.855E-08	-7.16399	0.92415	0.858
303300	AlOH +2	9.933E-12	7.245E-12	-11.13994	0.72941	-4.942
303301	Al(OH)2 +	2.360E-12	2.181E-12	-11.66133	0.92415	-10.066
303302	Al(OH)4 -	1.395E-16	1.289E-16	-15.88963	0.92415	-23.294
302700	AlF +2	1.002E-07	7.312E-08	-7.13595	0.72941	7.147
302701	AlF2 +	8.028E-06	7.419E-06	-5.12964	0.92415	12.635

302702	AlF3 AQ	4.847E-05	4.853E-05	-4.31395	1.00125	17.001
302703	AlF4 -	7.149E-06	6.607E-06	-5.18001	0.92415	19.754
307320	AlSO4 +	9.568E-13	8.842E-13	-12.05344	0.92415	3.038
307321	Al(SO4)2 -	2.396E-15	2.214E-15	-14.65473	0.92415	4.933
303303	Al(OH)3 AQ	8.672E-14	8.682E-14	-13.06136	1.00125	-16.001
4701800	MnCl +	2.157E-08	1.994E-08	-7.70035	0.92415	0.641
4701801	MnCl2 AQ	1.981E-12	1.984E-12	-11.70256	1.00125	0.040
4701802	MnCl3 -	3.544E-16	3.275E-16	-15.48477	0.92415	-0.271
4703300	MnOH +	9.243E-12	8.542E-12	-11.06845	0.92415	-10.663
4703301	Mn(OH)3 -1	7.295E-27	6.742E-27	-26.17124	0.92415	-34.766
4702700	MnF +	2.682E-08	2.478E-08	-7.60584	0.92415	0.884
4707320	MnSO4 AQ	7.516E-08	7.525E-08	-7.12347	1.00125	2.243
3307320	HSO4 -	9.753E-08	9.013E-08	-7.04512	0.92415	1.985
3302700	HF AQ	1.143E-05	1.144E-05	-4.94146	1.00125	3.143

Type III - SPECIES WITH FIXED ACTIVITY

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
2	H2O	-3.063E-10	-9.514	0.000	0.000
330	H+1	-3.228E-04	-3.491	4.500	0.000

PART 4 of OUTPUT FILE

PC MINTEQA2 v3.10 DATE OF CALCULATIONS: 2-DEC-98 TIME: 13: 4:39

PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

DOM				
	64.2	PERCENT BOUND IN SPECIES #	145	DOM
	27.7	PERCENT BOUND IN SPECIES #	1453300	H DOM
	6.6	PERCENT BOUND IN SPECIES #	1451500	Ca DOM
	1.6	PERCENT BOUND IN SPECIES #	1454600	Mg DOM
Na+1	100.0	PERCENT BOUND IN SPECIES #	500	Na+1
NH4+1	100.0	PERCENT BOUND IN SPECIES #	490	NH4+1
K+1	100.0	PERCENT BOUND IN SPECIES #	410	K+1
Mg+2	93.3	PERCENT BOUND IN SPECIES #	460	Mg+2
	5.2	PERCENT BOUND IN SPECIES #	1454600	Mg DOM
	1.2	PERCENT BOUND IN SPECIES #	4602700	MgF +
Mn+2	99.3	PERCENT BOUND IN SPECIES #	470	Mn+2
Ca+2	63.9	PERCENT BOUND IN SPECIES #	150	Ca+2
	35.7	PERCENT BOUND IN SPECIES #	1451500	Ca DOM
Al+3	12.6	PERCENT BOUND IN SPECIES #	302701	AlF2 +
	76.0	PERCENT BOUND IN SPECIES #	302702	AlF3 AQ
	11.2	PERCENT BOUND IN SPECIES #	302703	AlF4 -
F-1	57.8	PERCENT BOUND IN SPECIES #	270	F-1
	3.3	PERCENT BOUND IN SPECIES #	302701	AlF2 +
	29.9	PERCENT BOUND IN SPECIES #	302702	AlF3 AQ
	5.9	PERCENT BOUND IN SPECIES #	302703	AlF4 -
	2.3	PERCENT BOUND IN SPECIES #	3302700	HF AQ
Cl-1	100.0	PERCENT BOUND IN SPECIES #	180	Cl-1
NO2-1	100.0	PERCENT BOUND IN SPECIES #	491	NO2-1
SO4-2	94.4	PERCENT BOUND IN SPECIES #	732	SO4-2
	1.3	PERCENT BOUND IN SPECIES #	4907320	NH4SO4 -
	2.4	PERCENT BOUND IN SPECIES #	4607320	MgSO4 AQ
	1.2	PERCENT BOUND IN SPECIES #	1507320	CaSO4 AQ

H4SiO4	100.0	PERCENT BOUND IN SPECIES # 770	H4SiO4
H2O	89.3	PERCENT BOUND IN SPECIES #3300020	OH-
	2.9	PERCENT BOUND IN SPECIES #4603300	MgOH +
	3.2	PERCENT BOUND IN SPECIES # 303300	AlOH +2
	1.5	PERCENT BOUND IN SPECIES # 303301	Al(OH)2 +
	3.0	PERCENT BOUND IN SPECIES #4703300	MnOH +
H+1	10.6	PERCENT BOUND IN SPECIES # 330	H+1
	85.8	PERCENT BOUND IN SPECIES #1453300	H DOM
	3.5	PERCENT BOUND IN SPECIES #3302700	HF AQ

PART 5 of OUTPUT FILE

PC MINTEQA2 v3.10 DATE OF CALCULATIONS: 2-DEC-98 TIME: 13: 4:39

---------- EQUILIBRATED MASS DISTRIBUTION ----------

IDX	NAME	DISSOLVED		SORBED		PRECIPITATED	
		MOL/KG	PERCENT	MOL/KG	PERCENT	MOL/KG	PERCENT
145	DOM	1.000E-03	100.0	0.000E-01	0.0	0.000E-01	0.0
500	Na+1	4.816E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
490	NH4+1	1.442E-03	100.0	0.000E-01	0.0	0.000E-01	0.0
410	K+1	3.489E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
460	Mg+2	3.007E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
470	Mn+2	1.857E-05	100.0	0.000E-01	0.0	0.000E-01	0.0
150	Ca+2	1.844E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
30	Al+3	6.375E-05	100.0	0.000E-01	0.0	0.000E-01	0.0
270	F-1	4.869E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
180	Cl-1	3.963E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
491	NO2-1	5.870E-05	100.0	0.000E-01	0.0	0.000E-01	0.0
732	SO4-2	4.633E-05	100.0	0.000E-01	0.0	0.000E-01	0.0
770	H4SiO4	2.019E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
2	H2O	3.063E-10	100.0	0.000E-01	0.0	0.000E-01	0.0
330	H+1	3.228E-04	100.0	0.000E-01	0.0	0.000E-01	0.0

Charge Balance: SPECIATED

Sum of CATIONS = 3.151E-03 Sum of ANIONS 3.192E-03

PERCENT DIFFERENCE = 6.499E-01 (ANIONS - CATIONS)/(ANIONS + CATIONS)

EQUILIBRIUM IONIC STRENGTH (m) = 5.442E-03

EQUILIBRIUM pH = 4.500

DATE ID NUMBER: 981202
TIME ID NUMBER: 13043999

PART 6 of OUTPUT FILE

PC MINTEQA2 v3.10 DATE OF CALCULATIONS: 2-DEC-98 TIME: 13: 4:40

Saturation indices and stoichiometry of all minerals

ID #	NAME	Sat. Index	Stoichiometry in [brackets]
2003000	ALOH3(A)	-7.643	[1.000] 30 [3.000] 2 [-3.000] 330
6003000	ALOHSO4	-7.327	[-1.000] 330 [1.000] 30 [1.000] 732 [1.000] 2
6003001	AL4(OH)10SO4	-24.442	[-10.000] 330 [4.000] 30 [1.000] 732 [10.000] 2
6041000	ALUM K	-17.822	[1.000] 410 [1.000] 30 [2.000] 732 [12.000] 2
6041001	ALUNITE	-15.793	[1.000] 410 [3.000] 30 [2.000] 732 [6.000] 2 [-6.000] 330
6015000	ANHYDRITE	-3.953	[1.000] 150 [1.000] 732
2003001	BOEHMITE	-5.849	[-3.000] 330 [1.000] 30 [2.000] 2
2046000	BRUCITE	-11.674	[1.000] 460 [2.000] 2 [-2.000] 330
2077000	CHALCEDONY	-0.137	[-2.000] 2 [1.000] 770
8646000	CHRYSOTILE	-24.035	[-6.000] 330 [3.000] 460 [2.000] 770 [1.000] 2
8246000	CLINOENSTITE	-9.871	[-1.000] 2 [1.000] 460 [1.000] 770 [-2.000] 330
2077001	CRISTOBALITE	-0.066	[-2.000] 2 [1.000] 770
2003002	DIASPORE	-4.118	[-3.000] 330 [1.000] 30 [2.000] 2
8215000	DIOPSIDE	-17.270	[-2.000] 2 [1.000] 150 [1.000] 460 [2.000] 770 [-4.000] 330
6046000	EPSOMITE	-6.025	[1.000] 460 [1.000] 732 [7.000] 2
8646003	SEPIOLITE(C)	-16.578	[-0.500] 2 [2.000] 460 [3.000] 770 [-4.000] 330
4215000	FLUORITE	-0.251	[1.000] 150 [2.000] 270
8046000	FORSTERITE	-21.732	[-4.000] 330 [2.000] 460 [1.000] 770
2003003	GIBBSITE (C)	-6.001	[-3.000] 330 [1.000] 30 [3.000] 2
3003000	Al2O3	-17.103	[2.000] 30 [3.000] 2 [-6.000] 330
6015001	GYPSUM	-3.712	[1.000] 150 [1.000] 732 [2.000] 2
4150000	HALITE	-8.363	[1.000] 500 [1.000] 180
8450000	MAGADIITE	-10.412	[-1.000] 330 [-9.000] 2 [1.000] 500 [7.000] 770
6050001	MIRABILITE	-9.944	[2.000] 500 [1.000] 732 [10.000] 2
8646001	PHLOGOPITE	-58.147	[-10.000] 330 [1.000] 410 [3.000] 460 [1.000] 30 [3.000] 770
2077002	QUARTZ	0.358	[-2.000] 2 [1.000] 770
8646004	SEPIOLITE(A)	-19.242	[-0.500] 2 [2.000] 460 [3.000] 770 [-4.000] 330
2077003	SIO2(A,GL)	-0.643	[-2.000] 2 [1.000] 770
2077004	SIO2(A,PT)	-0.955	[-2.000] 2 [1.000] 770
8646002	TALC	-22.161	[-4.000] 2 [3.000] 460 [4.000] 770 [-6.000] 330
6050002	THENARDITE	-11.025	[2.000] 500 [1.000] 732
8215001	TREMOLITE	-50.398	[-8.000] 2 [2.000] 150 [5.000] 460 [8.000] 770 [-14.000] 330
2047003	PYROCROITE	-11.128	[-2.000] 330 [1.000] 470 [2.000] 2
4147000	MNCL2, 4H2O	-14.324	[1.000] 470 [2.000] 180 [4.000] 2
6047000	MNSO4	-12.152	[1.000] 470 [1.000] 732
8450001	ANALCIME	-10.191	[1.000] 500 [1.000] 30 [2.000] 770 [-1.000] 2 [-4.000] 330
8603000	HALLOYSITE	-10.801	[2.000] 30 [2.000] 770 [1.000] 2 [-6.000] 330

8603001	KAOLINITE	-7.500	[2.000]	30	[2.000]	770	[1.000]	2			
			[-6.000]	330							
8415000	LEONHARDITE	-25.057	[-1.000]	2	[-16.000]	330	[2.000]	150			
			[8.000]	770	[4.000]	30					
8450002	LOW ALBITE	-9.718	[1.000]	500	[1.000]	30	[3.000]	770			
			[-4.000]	330	[-4.000]	2					
8450003	ANALBITE	-10.651	[1.000]	500	[1.000]	30	[3.000]	770			
			[-4.000]	330	[-4.000]	2					
8641000	MUSCOVITE	-14.691	[1.000]	410	[3.000]	30	[3.000]	770			
			[-10.000]	330							
8415001	ANORTHITE	-22.533	[1.000]	150	[2.000]	30	[2.000]	770			
			[-8.000]	330							
8603002	PYROPHYLLITE	-7.302	[2.000]	30	[4.000]	770	[-4.000]	2			
			[-6.000]	330							
8415002	LAUMONTITE	-18.802	[1.000]	150	[2.000]	30	[4.000]	770			
			[-8.000]	330							
8415003	WAIRAKITE	-23.306	[1.000]	150	[2.000]	30	[4.000]	770			
			[-8.000]	330	[-2.000]	2					
2015000	LIME	-28.207	[-2.000]	330	[1.000]	150	[1.000]	2			
2015001	PORTLANDITE	-17.969	[-2.000]	330	[1.000]	150	[2.000]	2			
2046001	PERICLASE	-16.468	[-2.000]	330	[1.000]	460	[1.000]	2			
3046000	SPINEL	-25.809	[-8.000]	330	[1.000]	460	[2.000]	30			
			[4.000]	2							
4250000	CRYOLITE	-10.553	[1.000]	30	[3.000]	500	[6.000]	270			
8215002	WOLLASTONITE	-11.901	[-1.000]	2	[-2.000]	330	[1.000]	770			
			[1.000]	150							
8215003	P-WOLLSTANIT	-12.763	[-1.000]	2	[-2.000]	330	[1.000]	770			
			[1.000]	150							
8015001	CA-OLIVINE	-31.882	[-4.000]	330	[1.000]	770	[2.000]	150			
8015002	LARNITE	-33.393	[-4.000]	330	[1.000]	770	[2.000]	150			
8015007	CA3SIO5	-63.550	[-6.000]	330	[1.000]	770	[3.000]	150			
			[1.000]	2							
8015003	MONTICELLITE	-24.089	[-4.000]	330	[1.000]	770	[1.000]	150			
			[1.000]	460							
8015005	AKERMINITE	-40.251	[-1.000]	2	[-6.000]	330	[2.000]	770			
			[2.000]	150	[1.000]	460					
8015004	MERWINITE	-56.616	[-8.000]	330	[2.000]	770	[1.000]	460			
			[3.000]	150							
8441000	KALSILITE	-12.801	[-4.000]	330	[1.000]	770	[1.000]	30			
			[1.000]	410							
8441001	LEUCITE	-10.029	[-2.000]	2	[-4.000]	330	[2.000]	770			
			[1.000]	30	[1.000]	410					
8441002	MICROCLINE	-7.844	[-4.000]	2	[-4.000]	330	[3.000]	770			
			[1.000]	30	[1.000]	410					
8441003	H SANIDINE	-8.304	[-4.000]	2	[-4.000]	330	[3.000]	770			
			[1.000]	30	[1.000]	410					
8450004	NEPHELINE	-14.073	[-4.000]	330	[1.000]	770	[1.000]	30			
			[1.000]	500							
8015006	GEHLENITE	-45.635	[-10.000]	330	[2.000]	30	[1.000]	770			
			[2.000]	150	[3.000]	2					

APPENDIX F: A PROPOSED SAMPLING DESIGN PLAN FOR FURTHER STUDIES

F.1. Introduction

The following discussion defines a possible way to address further research in forest soils. The plan is based on forming genuine homogenous areas to be sampled, through the use of discriminating analysis. The plan incorporates the variables used in this study, but can easily be modified for other variables that are assumed to affect forest health and soil chemical properties.

F.2. Setting a hypothesis

The first step, prior to setting a hypothesis, is the setting of logical discriminating variables should be determined. For example:

1. Geology
2. Age of plantation
3. Tree species
4. Elevation

These reasoning behind the discrimination is based on the assumed relative importance, for instance: the bedrock may be assumed to have the most significant influence on the chemical analysis and consequently the productivity of the plantation, thereafter the age of the compartment presented by the rotation. Following discriminating variables could be the tree species, elevation, productivity data and the various tree ages.

These variables are initially assumed to have the most significant influence on the hypothesis. Thereafter, a hypothesis is proposed. With respect to the current study, a few possible hypotheses may arise, for example:

Seeking possible effects of afforestation on soil chemical properties overlying different bedrocks (shale ,granite, dolomite). Thus aiming at providing possible effects on the soil chemical properties that may arise due to afforestation over the different geological formations. Ultimately, creating a fit between tree species and the geological bedrock, with the possibility of adding other factors such as climate and situation, and eventually creating an economically based plan for future planting programs.

F.3. Setting the sampling area

A geographical domain is set, for example, a certain forest area. It is important that the area chosen would be adequate for testing the hypothesis. Variables, chemical and others (age, productivity, type of rock, tree species, climate, physical properties of the forest) are chosen according to their relative importance. The relative importance is determined according to the assumed ability of the variables to affect the soil chemical properties and consequently the hypothesis. For example: to what extent does each of the variables may affect forest productivity. Subsequently, the area chosen to be sampled must be homogenous with respect all of these variables; i.e. similar underlying bedrock, similar species, same age group, etc. Thus, a list of areas is prepared of which each and every one of them would be solely tested for the hypothesis. A designated area may contain a uniform bedrock with different compartments, where each compartment consists of a specific species. Alternatively a forest area of a single species, overlying various bedrocks can be chosen.

F.4. First sampling set

The sampling plan generated should be based upon a regular grid that would provide a systematic manner of collecting the specimen and forming the samples. A set of specimen is taken from the field. For example, from underlying bedrock, various soil horizons, plant segments of various trees.

The samples are analysed chemically and the data produced is tested statistically. The aim of the statistical treatment is to determine whether the discriminating factors are contributing to the hypothesis. A possible way of reaching such conclusions would be by using geostatistical methods such as spatial analysis for each of the discriminating factors and testing other possible variables that were not previously considered. The aim is to determine which of the discriminating variables, initially chosen, present a variability that could be assigned to the hypothesis. For example the results from the soils analysis is compared to the tree species, to productivity data with the aim to either accept (statistically, at first) the fact that the soil chemical composition varies according to tree species or age - such as was the case in the current study where the ionic strength of the soil solution was observed to decline with plantation age. Alternatively, discriminating variables showing no correlation at all, are discarded. It is important to analyse and observe variables which are different from those set initially, since some of them may alter the definition of homogenous areas and consequently change the sampling pattern. If necessary, the hypothesis should be modified.

F.5. Second sampling set

Confident maps are generated based on the various chemical (and other) variables, within the above defined homogenous areas.. These maps would serve as a base for evaluating the confidence of the samples taken and consequently would provide the means for setting a new discriminating set of variables that are assumed to have an impact on the modified hypothesis. For example productivity data shows a statistically significant correlation with the soil type or elevation or rainfall. The confident maps are used simultaneously to form a new and optimum grid for specimens to be collected.

A second set of specimen is collected and chemically analysed. The samples are taken within the newly defined homogenous areas based upon pre-selected confident limits.

The results are tested statistically. Similarly to the first set. Spatial analysis would be useful for forming new grids and contour maps of the various factors and chemical properties. This would assist in generating conclusions regarding the hypothesis. For example, using those maps to match pine species to soil types, bedrocks, elevation etc. and perhaps even finding new possibilities of rotation between species corresponding to types of bedrock, soil or elevation.

F.6. Summary

The proposed plan for future studies of pine plantations regarding soil chemistry consists of two main phases each containing threesteps. In brief these steps are:

Phase A

1. Setting a hypothesis
2. Collecting samples based on the discriminating factors assumed to affect the hypothesis
3. Testing the hypothesis according to the sample analysis
    3.1. Homogenous areas are redefined
    3.2. The hypothesis is re-evaluated, and modified

Phase B

1. A second set of samples is taken based predetermined confidence maps
2. The samples are analysed and tested statistically according to the new set of discriminating variables
3. Once the data is tested statistically and a scientific reasoning is based, predictions can be made of the possible effects of the variables on the modified hypothesis