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THE IMPACT OF PLANTATIONS OF *PINUS* SPP. ON THE CHEMICAL PROPERTIES OF SOILS AND STREAM WATERS IN SOUTH AFRICAN UPLAND CATCHMENTS

by

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ABSTRACT

Studies of forest ecosystems have indicated that internal sources constitute a significant component of the acid load to forest soils and can result in significant decreases in soil pH, acid neutralising capacity and base status. Despite this, the possibility that these processes can result in a significant transfer of acidity to drainage solutions and consequently to associated surface waters has, to a large extent, been discounted due to the self limiting nature of "natural" acidification processes which purportedly do not involve significant concentrations of the strong acid anions NO_3^-, SO_4^{2-} and Cl^-. In South Africa, extensive plantations of *Pinus* spp. (pine) are developed in mountainous regions that were previously covered by grassland or fynbos (macchia) vegetation and are mostly not believed to be influenced by significant atmospheric pollution. Thus, a good opportunity exists to study the effects of afforestation without the superimposed influence of acid deposition. This thesis documents the results of a regional investigation of the geochemical impact of pine afforestation in South Africa. The study focuses specifically on factors relating to the transfer of soil acidity to drainage waters. The key questions that are addressed are: 1) to what extent is soil acidification, as previously documented for plantations in the eastern seaboard region of southern Africa, prevalent in other forestry areas within South Africa?; 2) in the absence of acid deposition, can afforestation cause enhanced concentrations of strong acid anions in soil solutions and drainage waters, and can this lead to the transfer of large quantities of acidity from forest soils to surface waters?; 3) does afforestation-induced acidification lead to increased concentrations of environmentally important metals such as Al and Mn in soil solutions and surface waters?; and 4) how does afforestation affect the quantity of dissolved organic matter in soils and streams?

The effect of afforestation was assessed by comparing the properties of bulk topsoil samples taken from under forest with those of equivalent samples taken in adjacent undisturbed land. Water samples were taken from streams draining pine plantations and equivalent grassland or fynbos catchments. Sampling was carried out in four regions: i.e. the eastern escarpment in Mpumalanga, the midlands of KwaZulu-Natal, the southern Cape and the western Cape. These cover a range of climatic, botanical and geological conditions. In all cases, the pine plantations are developed on well leached soils occurring mostly in areas of high rainfall. Soil samples were air-dried and sieved (< 2 mm) prior to analysis and soil solution compositions were estimated based on the composition of saturated paste extracts.

The soils are texturally variable with clay contents ranging from < 2 % to approximately 55 %. They are mostly rich in organic carbon (up to 12 %) and display bulk chemical and mineralogical properties that are consistent with a high degree of leaching. The clay fraction is dominated by kaolinite, quartz, pedogenic chlorite and gibbsite. All of the soils investigated are naturally acidic (pH_{KCl} from 3.1 to 4.5 in virgin soils). Differences in soil pH and exchangeable base cation and acidity concentrations for paired forest and virgin soils show that the acidifying effect of pine plantations, as previously documented for the eastern seaboard region (which includes the eastern escarpment and midlands areas), is prevalent in the southern and western Cape as well. In most cases, however, rates of acidification in the latter regions are less than ~ 0.4 $kmol_c\ ha^{-1}\ yr^{-1}$, and they are generally lower than those observed in the eastern seaboard. The latter range up to ~ 2 $kmol_c\ ha^{-1}\ yr^{-1}$ and are comparable to rates of acidification in northern hemisphere forests that are impacted by moderate levels of acid deposition. The data suggest that biomass uptake of basic cations can, in most cases, account for the observed rates of acidification. Lower acidification rates in the Cape regions are associated with low forest productivity levels and reflect a combination of pedological and climatological factors.

Data obtained for saturated paste extracts indicate that, in general, afforestation results in increased concentrations of strong acid anions in soil solutions. In the maritime Cape regions, concentrations of soluble Cl^- are considerably enhanced in forest soils (~ 1 to 3 $mmol_c\ L^{-1}$) relative to those in their fynbos counterparts (generally < 0.75 $mmol_c\ L^{-1}$). This probably results from enhanced interception and evaporative concentration of sea salt. Saturated paste extracts from most forest soils in the eastern seaboard region have dramatically higher NO_3^- concentrations (~ 0.2 to 2.7 $mmol_c\ L^{-1}$) than those of adjacent grassland soils (< 0.1 $mmol_c\ L^{-1}$). While the sample preparation and saturated paste extraction procedures are likely to affect the concentration of soluble NO_3^-, the data suggest that the pine plantations may have a considerable impact on N dynamics that could lead to the leaching of NO_3^- from forest soils. The high concentrations of soluble NO_3^- may be related to relatively high levels of N deposition that are evident in parts of the eastern seaboard, but the most prominent impact of afforestation is likely to stem from an associated modification of the N cycle. The concentrations of soluble SO_4^{2-} range from ~ 0.1 to 0.75 $mmol_c\ L^{-1}$ and are not strongly influenced by afforestation. Considerable increases in the levels of phosphate extractable SO_4^{2-} are evident in all clay-rich soils, however, indicating that SO_4^{2-} is accumulating at a much higher rate in topsoils under forest than in those under adjacent grassland. The concentrations

of soluble strong acid anions in both forest and virgin soils of this study are comparable to those observed in soil solutions of forest ecosystems in the northern hemisphere that are subject to considerable inputs of atmospheric pollutants. In the long term, the effect of these high solute levels on drainage waters is likely to be offset, to a large extent, by reduced leachate volumes. Under conditions of high discharge, however, the concentration of strong acid anions in drainage waters may be raised considerably. In view of the aforegoing, this effect would be enhanced by pine afforestation.

Estimated concentrations of organic anions in saturated paste extracts (based on an observed correlation between dissolved organic carbon and excess positive charge) mostly range from 0.4 to 1.5 $mmol_c L^{-1}$. Colour variations and apparent charge density differences suggest that there are broad regional differences in the chemical nature of dissolved organic matter but that these parameters are not markedly influenced by afforestation. The effect of afforestation on the concentration of DOC is variable and is related to the original concentration in the virgin soil. Most of the eastern seaboard soils display reduced DOC levels under forest whereas in the Cape regions, afforestation generally increases the concentration of DOC. This is reflected in the DOC concentrations of surface waters in the western Cape.

The pH of saturated paste extracts from forest soils ranges from approximately 3.7 to 5 and is consistently lower (by between 0.2 and 1.2 pH units) than that of the equivalent virgin soils. These differences are accompanied by a considerable enhancement of the concentration of soluble monomeric Al which, in the forest soils, ranges from 0.014 to 1 $mmol_c L^{-1}$ (0.13 to 9 $mg L^{-1}$). Taken in conjunction with the strong acid anion data, the changes in pH and Al concentration indicate that pine afforestation considerably enhances the potential for acidification of drainage waters.

Under certain conditions, the changes observed in soil solutions are reflected in the composition of surface waters. Forest streams in the eastern escarpment and western Cape show reduced pH (from ≥ 6.5 to ≤ 5.5) and alkalinity, increased concentrations of strong acid anions and, in some cases, enhanced levels of Al compared to those observed in equivalent streams draining undisturbed catchments. In the eastern escarpment, acidified forest streams show Al concentrations of up to 0.32 $mg L^{-1}$ (levels in equivalent grassland streams are below the detection limit of 0.075 $mg L^{-1}$). In the western Cape, stream waters are naturally acidic (pH between 4.3 and 6.0) and have high concentrations of DOC and Al (up to 0.4 $mg L^{-1}$).

Nonetheless, acidification has led to further pH reductions and in some cases has considerably enhanced the concentration of Al (up to 1.3 $mg\,L^{-1}$). All of the above-described compositional changes are associated with conditions of high discharge and occur in forest streams that drain catchments underlain by quartzitic parent materials with low buffering capacity.

Speciation calculations indicate that a large proportion (~ 20 to 80 %) of the dissolved Al in soil solutions and stream waters is organically bound and the very high concentrations of Al in the western Cape are associated with darkly coloured solutions with high concentrations of DOC. Relationships between Al^{3+} activity and pH, as well as calculated saturation indices, support control of Al solubility by equilibria involving solid-phase $Al(OH)_3$, Al-sulphates and Al-organic matter. Due to the uncertainties associated with modelling of Al-DOM interactions, however, deductions based on calculated Al^{3+} activities can only be regarded as tentative. Data obtained for saturated paste extracts suggest that, under certain conditions, afforestation causes dramatically enhanced concentrations of soluble Mn^{2+} (up to 0.9 $mmol_c\,L^{-1}$). This effect is not widespread, however, and appears to be dependent on a combination of relatively high inherent Mn^{2+} concentrations and increased solute levels. Variations in the redox status of saturated pastes, and the acid conditions prevailing in both forest and virgin soils, might be expected to play an important role in controlling Mn^{2+} solubility.

Increased concentrations of strong acid anions in soil solutions are accompanied by substantially enhanced levels of base cations (particularly Na^{+}, Mg^{2+} and Ca^{2+}). Thus, despite the considerable increase in acidity under forest, reductions in the proportion of base cations in solution ([Base Cations]/[Base Cations + Al^{3+} + H^{+} + Mn^{2+}]) are mostly small. This reflects the combined effect of increased solute concentrations under forest and the high relative affinity of acid cations for exchange surfaces which results in a preferential displacement of base cations into solution. It is only in certain forest soils with very low base saturation of the exchange complex that the proportion of base cations in solution drops below 90 %.

The findings of this study have important implications with respect to forest productivity and the potential environmental impact of pine afforestation. Continued reduction of the concentration of exchangeable bases and the Ca/Al ratio in soil solutions is likely to lead to nutrient deficiency and Al toxicity problems that may impact on tree growth. In addition, it is apparent that, under certain conditions, afforestation may present a threat to surface water quality, in that it increases the potential for leaching of strong acid anions, acidity and environmentally important metals such as Al and Mn.

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1. INTRODUCTION

Over the last two decades intensive research into the effects of acid deposition in northern Europe and North America has highlighted the problem of soil acidification, a phenomenon which impacts on terrestrial and aquatic ecosystems due to the critical role of soil as a medium for plant growth and as a mediator of associated surface water chemistry (Reuss and Johnson, 1986; Cresser and Edwards, 1987). The most prominent manifestations of soil acidification are decreased Ca/Al ratios, other nutrient imbalances and deficiencies which detrimentally affect the soil's capacity to support plant growth, and increased H^+ and Al concentrations in associated surface water bodies which can have major impacts on aquatic ecosystems. A further important consequence of acidification is the enhanced solubility and mobility of certain trace metals, which can lead to elevated and possibly toxic concentrations in associated drainage waters (Bergkvist, 1987; Berggren *et al.*, 1990; Vesely, 1994).

Studies of forest ecosystems have indicated that internal sources can make up a significant if not dominant component of the acid load to forest soils (even in areas affected by acid deposition) and can result in significant decreases in soil pH, acid neutralising capacity and base saturation (Morris, 1986; Ulrich, 1986; Bredemeier *et al.*, 1990; Johnson *et al.*, 1991; du Toit, 1993). However, the possibility that these processes can result in a significant transfer of acidity to drainage solutions and consequently to associated surface waters has, to a large, extent been discounted due to the purported self limiting nature of "natural" acidification processes (Nilsson *et al.*, 1982). It is generally argued that in acidic soils protonation of the weak acidic anions involved in natural acidification (i.e. bicarbonate and natural organic anions) precludes leaching of acidic cations from exchange sites into soil solutions and drainage waters and that the strong acid anions required to facilitate leaching can be derived only from atmospheric pollution (Ulrich, 1986; Reuss and Johnson, 1986; Reuss *et al.*, 1987; de Vries and Breeuwsma, 1987). However, recent chemical data for soil solutions from a number of apparently unpolluted afforested areas in South Africa indicate that elevated concentrations of strong acid anions (Cl^-, SO_4^{2-} and NO_3^-) are present (Fey and Netch, 1994), suggesting that the effect of afforestation on the anion suite in associated drainage waters should be investigated further.

In northern Europe and America where the majority of acidification studies has been carried out, evaluation of the impact of forests on the chemical properties of soils has been complicated in many cases by overprinted acid deposition effects and by the close spatial and temporal association between air pollution impacts (which are most prominent in "naturally" acidic forest soils) and afforestation. In South Africa, a good opportunity exists to study the chemical effects of afforestation without the superimposed influence of atmospheric deposition of pollutants. Extensive commercial plantations of exotic *Pinus* and *Eucalyptus* species have been developed in mountainous regions of South Africa which were previously covered by grassland or, in the case of the southern and south-western Cape, by fynbos (scrub or macchia) vegetation. These are relatively high rainfall areas and are typically underlain by leached, naturally acidic soils which are particularly sensitive to further acidification associated with anthropogenic influences. With the exception of the eastern escarpment and possibly the northern parts of KwaZulu-Natal, the afforested areas are very remote from any major sources of atmospheric pollution.

1.1. AIMS AND KEY QUESTIONS

The aim of this study is to evaluate the effects of afforestation on the chemistry of sensitive upland soils and associated surface waters in a range of environments within South Africa. The study focuses on the chemistry of soil solutions and drainage waters, primarily with a view to determining the extent to which afforestation affects the quality of associated surface waters. Four key questions are addressed:

1. Acidification of soils by forestry is well documented for the eastern seaboard regions of Southern Africa (Morris, 1986; du Toit, 1993). Are acidification processes prevalent in other forestry areas of Southern Africa and how are rates of acidification influenced by factors such as climate, original vegetation type and the chemical nature of soils prior to afforestation?

2. Through processes such as the enhanced concentration of solutes through evapotranspiration, increased interception of atmospheric salts and deep-rooted phytocycling, it may be possible for plantations of exotic tree species not only to acidify

soils but also to significantly enhance the concentrations of strong acid anions (Cl^-, SO_4^{2-} and NO_3^-) in soil solutions and drainage waters. To what extent does this take place and can it lead to the displacement of large quantities of acidic cations from the soil exchange complex, thereby acidifying drainage solutions and associated surface waters?

3. Soil acidification involves the stripping of base cations (through leaching and/or biomass aggradation) and enhancement of exchangeable Al concentration, and may lead to enhanced solubility of a number of trace metals (e.g. Mn, Be and Zn; Vesely, 1994). In acidified forest soils, do these processes result in soil solutions and drainage waters which are depleted in base cations and which contain higher concentrations of Al, Mn and other environmentally important metals relative to equivalent soils and waters occurring in association with natural vegetation?

4. Soil acidification and changes in vegetation type and biomass quantity associated with afforestation are likely to have a major influence on soil organic matter. How does this affect the quantity of dissolved organic matter in soil solutions and drainage waters, and what are the implications with respect to the mobility and speciation of environmentally important metals (e.g. Al)?

1.2. RESEARCH STRATEGY

The effect of afforestation was assessed using the "modified historic" (retrospective) approach whereby the chemistry of forest soils and associated surface water was compared with that of adjacent undisturbed (virgin) ecosystems. This strategy has been used extensively to evaluate afforestation impacts (e.g. Turner and Kelly, 1985; Morris, 1984; Johnson *et al.*, 1991) and should be valid, provided it can be demonstrated that the afforested and undisturbed sites differ only with respect to vegetation cover and, therefore, that any compositional differences directly reflect the influence of forestry. The study focuses on the impact of *Pinus* (pine) species only, as pine plantations are prevalent in all of the major forestry areas in South Africa and, in the Cape regions, these are the only tree species which are cultivated on a large scale for forestry purposes.

A "two-pronged" approach was employed, whereby the influence of afforestation on water quality was assessed by means of soil solution studies, as well as by direct sampling and analysis of stream waters. Due to logistical constraints and the limited duration of the project, it was not possible to undertake a comprehensive water sampling programme and most streams were only sampled once. Thus the stream water study is limited in that temporal variations in water composition are not accounted for. However, due to the critical role played by soil as a mediator of associated surface water chemistry (Reuss and Johnson, 1986; Cresser and Edwards, 1987), soil solution and drainage water studies provide an indirect but possibly more representative means of investigating the influence of afforestation on water quality and, in conjunction with stream water data, enable a clearer evaluation to be made of the main processes influencing stream water chemistry in upland catchments.

1.3. THESIS OUTLINE

The first phase of this study involved a literature review on soil and water acidification processes in forest ecosystems, the results of which are presented in the next chapter. Study areas, sampling and statistical methods are described in Chapter 3. Research methods and findings relating to the chemical nature of the soils and stream waters, regional variations and afforestation impacts are reported in Chapters 4 to 7. These are arranged in what is regarded as a logical progression from research pertaining to the inherent characteristics of the soil solid phase (Chapter 4), to that dealing with the composition of the cation exchange complex (Chapter 5) and ultimately to work which investigates the attributes of, as well as processes affecting, the aqueous phase in soils and streams (Chapters 6 and 7, respectively). The latter two sections are particularly important in that they address the key questions relating to the effect of afforestation on the composition of soil solutions and surface waters. However, the work presented in Chapters 4 and 5 is also highly relevant to the aims of this study in that: 1) a thorough understanding of the soil solid phase and cation exchange complex forms an important basis for the interpretation of soil solution data; 2) data relating to the soil solid phase provide an indication of the validity of forest-virgin comparisons; and 3) data are presented for areas in which afforestation impacts on soil acidity have not previously been evaluated.

2. SOIL AND WATER ACIDIFICATION IN FOREST ECOSYSTEMS

2.1. INTRODUCTION

Soil acidity, its causes and its amelioration have been the subject of intense research and debate since the early part of this century (e.g. Veitch, 1904; Hartwell and Pember, 1918; Bradfield 1923; Corrie, 1926), primarily due to its importance with respect to agriculture. As a result, a very large body of literature pertaining to these subjects has been published and is reviewed in several recent publications (e.g. Thomas and Hargrove, 1984; Ulrich and Sumner, 1991). A comprehensive review of the literature on soil acidity is beyond the scope of this study which focuses on acidification processes related to forestry and, in particular, on the transfer of acidity to soil solutions and surface waters. Interest in these aspects of soil acidity has, to a large extent, evolved over the last two and a half decades as a result of the increased awareness of, as well as research into, the impacts of acid deposition in northern Europe and parts of North America (e.g. Hutchinson and Havas, 1980; Ulrich and Pankrath, 1983; Kennedy, 1986; van Breemen *et al.*, 1996.). This work has highlighted the sensitivity of naturally acidic forest soils to further acid inputs and has led to a fairly clear understanding of the dominant soil acidification processes in forest ecosystems (Reuss and Johnson, 1986; Richter, 1986; Bredemeier *et al.*, 1990; Verstraten *et al.*, 1990; Johnson *et al.*, 1991). Similarly, much progress has been made towards a better understanding of how soil acidification processes influence the composition of drainage waters and a number of quantitative models have been developed to predict the impact of acid deposition on the acidity of streams and lakes (Christophersen *et al.*, 1982; Cosby *et al.*, 1985; Gherini *et al.*, 1985; Reuss, 1991). Research on the subject of water acidification is, however, largely restricted to ecosystems that are impacted by acid deposition and the extent to which surface waters draining forested catchments can be acidified in the absence of anthropogenic inputs is not clearly understood. A key question in this regard relates to the availability of mobile strong acid anions in forest ecosystems, as research has clearly indicated that the transfer of soil acidity to drainage waters is dependent on the supply of these ions (Reuss and Johnson, 1986).

In this chapter, acidification processes occurring in forest ecosystems are reviewed. While the issue of acid deposition is addressed, emphasis is placed on processes which are inherent to forest ecosystems and which could potentially lead to surface water acidification in unpolluted areas.

2.2. SOIL ACIDITY: CONCEPTS AND DEFINITIONS

Soil acidity can be viewed in terms of intensity, quantity and capacity factors. *Intensity* factors relate primarily to the concentrations of ions in soil solution. The pH of a soil is the most important measure of the intensity of acidity and reflects the concentration of H^+ ions in aqueous solutions which are in equilibrium with the solid phase of the soil. The most commonly measured factors reflecting the *quantity* of acidity or alkalinity contained within a soil, are exchangeable and total acidity/alkalinity and total concentrations of exchangeable base cations. *Capacity* factors reflect the relationship between quantity and intensity factors. In the context of soil acidification, they reflect the extent to which a soil can accommodate added acidity or alkalinity without associated changes in pH, i.e. they reflect the soil's buffer capacity. The main sources of buffering in soils are mineral dissolution (all minerals, with the exception of sulphides, have acid neutralising capacity) and ion exchange (Ulrich, 1986; Sparks, 1995). In non-calcareous soils, ion exchange is the dominant short-term buffering mechanism. Thus cation exchange capacity (CEC) is the most important capacity factor in these soils and the relative quantities of exchangeable acidic and basic cations (i.e. the base or acid saturation of the exchange complex) provide an indication of the degree of acidification. The acidity of a cation is dependent on the degree to which it hydrolyses in solution, which in turn is primarily a function of its charge/size ratio or ionic potential (Thomas and Hargrove, 1984). Cations with high ionic potentials hydrolyse to generate hydronium ions thereby lowering solution pH. This can be represented by the generalised reaction:

$$M(H_2O)_n \rightleftharpoons [M(H_2O)_{2n-x}(OH)_x]^{n-x} + xH_3O^+,$$

where M is a cation with a valency of n. In soils, the most important acidic cations are Al^{3+} and Fe^{3+}.

The acidity of soils is commonly expressed in terms of exchangeable and non-exchangeable fractions. Exchangeable acidity is defined as that which can be displaced from the solid phase by a neutral salt solution (typically 1M KCl or 0.01M $CaCl_2$ is used) and reflects the relative quantities of readily exchangeable acidic and basic cations present. In most soils, Al is by far the most important component of exchangeable acidity and it is only in extremely acid soils

(pH < 4) and in soils with very high organic matter contents, that significant quantities of exchangeable H^+ occur (Thomas and Hargrove, 1984; Sparks, 1995; Ross *et al.*, 1996). Exchangeable acidity constitutes the more strongly acidic fraction of soil acidity and is effectively neutralised at pH values of 5.5 and above (Thomas and Hargrove, 1984). Non-exchangeable acidity is calculated by subtracting the exchangeable acidity from the total acidity determined by titration of a soil suspension with a strong base (usually NaOH or $Ca(OH)_2$) to a pH of approximately 8. The dominant constituents giving rise to non-exchangeable acidity are organic matter and hydrated Al and Fe oxides (Thomas and Hargrove, 1984).

Strictly speaking, acid soils are those which have pH values less than 7, but problems associated with acidification generally only occur when the soil pH drops below approximately 5.5 (Sumner *et al.*, 1991) and/or when total exchangeable acidity exceeds ~ 15 % of the cation exchange capacity (Sposito, 1989). The ecological effects of soil acidification arise partly because under these conditions Al^{3+} ions are mobilised (Bache, 1986; Adams *et al.*, 1990; McBride, 1994), due to dissolution of aluminosilicates and Al-hydroxide (primarily gibbsite) phases (Lindsay, 1979; McBride, 1994; Ritchie, 1995), and dissociation of Al-organic matter complexes (Bloom *et al.*, 1979; Berggren and Mulder, 1995). Thus, the availability of Ca^{2+} and Mg^{2+} to plants can be severely limited as a result of replacement of exchangeable bases by H^+ and Al^{3+}. In the presence of strong acid anions, Al concentrations in the soil solution can be raised to toxic levels and high Al/(Base Cation) ratios result in nutrient deficiency (Sumner *et al.*, 1991; Sverdrup *et al.*, 1993; Cronan and Grigal, 1995). Other potentially phytotoxic elements such as Mn and B may be solubilised under acidic conditions and may contribute to the above-mentioned plant stresses (Adams and Walker, 1975; Sumner *et al.*, 1991). Certain key nutrient elements (e.g. P and Mo) are less soluble under acidic conditions and, therefore, may become deficient (i.e. unavailable to plants) in acid soils. A further detrimental effect of soil acidification is to inhibit beneficial bacterial transformations of some nutrients (especially nitrogen). In addition to these effects on terrestrial ecosystems, soil acidity can have a major impact on the composition and consequently the quality of associated surface waters (Cronan and Schofield, 1979; Seip, 1980; Reuss and Johnson, 1985; Cresser and Edwards, 1987).

2.3. SOIL ACIDIFICATION AS A NATURAL PROCESS

Soil acidification is a naturally occurring process associated with soil formation. It occurs as a result of leaching of base cations, liberated by hydrolytic exchange and dissolution reactions (Table 2.1), and their replacement with the acidic cations H^+, Al^{3+} and to a lesser extent Mn^{2+} (Sposito, 1989; Fey *et al.*, 1990). The prime driving force of soil acidification is the addition of protons which displace base cations from the soil exchange complex and drive dissolution reactions. In the natural environment the dominant sources of protons are carbonic and natural organic acid dissociation, soil nitrogen transformations (mineralisation, nitrification) and excess cation uptake by biomass with accompanying release of protons (Bredemeier *et al.*, 1990; van Breemen *et al.*, 1996) (Table 2.1). In stable ecosystems, biomass uptake and nitrogen transformations are balanced by acid consuming or neutralising processes, i.e. the return of dead biomass with accompanying base cations to the soil, denitrification and NO_3^- uptake by plants (Binkley and Richter, 1987; Ulrich, 1991).

Table 2.1: Potential sources of acidity and associated reactions (adapted from Bredemeier et al. 1990). The first five sources may arise out of natural processes, whereas the last three are associated with atmospheric deposition of acidifying pollutants and/or N fertilisation.

Proton source	Generalized reactions
Assimilation of surplus inorganic cations over anions in organic matter	$R\text{-}OH + M^+ \rightarrow R\text{-}OM + H^+$ (M^+ = nutrient cation)
Generation and protolysis of organic acids	$R\text{-}OH \rightarrow R\text{-}O^- + H^+$ (pK_a ~2.5 - 5.5)
Preferential uptake of NH_4^+ over NO_3^-	$R\text{-}OH + NH_4^+ \rightarrow R\text{-}NH_2 + H_2O + H^+$ (H^+ source) $R\text{-}OH + H^+ + NO_3^- \rightarrow R\text{-}NH_2 + H_2O$ (H^+ sink)
Carbonic acid dissociation	$CO_2 + H_2O \rightarrow H^+ + HCO_3$ (pK_a ~ 6.3)
Disruption of ecosystem-internal nitrogen cycle, net nitrification and nitrate leaching	$R\text{-}NH_2 + O_2 \rightarrow R\text{-}OH + H^+ + NO_3^-$
Buffering of deposited H^+ in the forest canopy with subsequent restoration of foliar buffer capacity and H^+ excretion to the soil	
Nitrification of deposited NH_4^+	$NH_4^+ + 2O_2 \rightarrow 2H^+ + NO_3^- + H_2O$ (H^+ source)
Direct flux of free H^+ to the soil in throughfall	$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$ $HNO_3 \rightarrow H^+ + NO_3^-$

Net acidification of soils only occurs when there is a permanent export of basic components, i.e. the solubilised basic cations, out of the soil. This can only occur by cation leaching, or if natural biogeochemical cycles are disrupted in such a way that proton generating processes are decoupled from those resulting in proton consumption (Ulrich, 1986; Binkley and Richter, 1987; van Breemen, 1991). In the context of acidification by leaching of base cations (as opposed to biomass uptake), it is important to note that the process is as much dependent on proton addition as on the complementary supply of mobile acidic anions to accompany base cations out of the soil (Reuss and Johnson, 1986; de Vries and Breeuwsma, 1987; Reuss *et al.*, 1987; McBride, 1994). This concept is discussed further in section 2.6.

The extent to which soils can be acidified over the long term depends on the rate of acid input relative to the rate at which weathering can supply bases, as well as on the strength of the acids involved. Natural factors which influence the relative rates of acid input and base production generally coincide with those implicated in soil formation processes and include: *soil parent material* - the basicity and weatherability of soil parent materials determines the extent and rate of acid buffering; *climate* - the amount of precipitation relative to evapotranspiration determines the extent of leaching which can take place; *topography* - bases are generally translocated from highlying areas to adjacent lowlands; *vegetation* - vegetation type and biomass quantity has a major influence on soil acidity due to base cation uptake, formation of organic acids and fixation and mineralisation of nitrogen (e.g. Jarvis and Duncan, 1976; Williams *et al.*, 1978; Crampton, 1982; Miles, 1985; Binkley and Valentine, 1991).

In soils of moderate to high pH values (i.e. above ~ 5) and base status, CO_2 dissolution and the consequent formation of carbonic acid constitutes a major source of protons and, in areas where rainfall significantly exceeds evapotranspiration, will result in high rates of soil acidification due to bicarbonate leaching (van Breemen *et al.*, 1984). In acid soils with pH values below approximately 5, very limited carbonic acid dissociation takes place. In the absence of anthropogenic influences, therefore, further leaching of these soils is governed primarily by the supply and dissociation of natural organic acids (Reuss and Johnson, 1986; Ulrich, 1986; van Breemen, 1991). This is a slow process whereby mobile organic acid anions (primarily fulvates) leach cations (initially base cations, followed by Al and Fe) from the upper soil horizons, ultimately leading to the formation of podzolised soils (Krug and Frink, 1983; Khanna and Ulrich, 1984; Ulrich, 1986; Cresser and Edwards, 1987). Due to the slow

nature of the process and the crucial involvement of organic matter, acidification is generally limited to the upper soil horizons (i.e. O and E horizons)(Ugolini *et al.*, 1977; Krug and Frink, 1983; Ulrich, 1991). Nonetheless, this process can result in very low pH values (~ 3.5) in the upper organic and mineral soil horizons (e.g. Cresser and Edwards, 1987 and references cited therein).

2.4. ANTHROPOGENIC ACIDIFICATION PROCESSES

Anthropogenic processes can greatly intensify soil acidification either by addition of acidic or potentially acidic components, or by disruption of natural proton and base cation cycles by export of bases in harvested biomass. The most important anthropogenic sources of acidity are atmospheric deposition, agriculture and forestry.

Atmospheric deposition of the oxidation products of sulphur and nitrogen derived from industrial sources and, in some cases, of ammonia derived from agricultural activities, constitutes a major source of acidity and its effect on soils and waters has been intensively studied over the last two decades (eg. Hutchinson and Havas, 1980; Ulrich and Pankrath, 1983; Reuss and Johnson, 1986; Kennedy, 1986; Cresser and Edwards, 1987; Hornung and Skeffington, 1993; van Breemen *et al.*, 1996). The most important components of acid deposition are sulphuric and nitric acid in wet deposition and dry deposition of gaseous oxides of sulphur (primarily SO_2) and nitrogen (NO_x) which are converted to their respective acids (i.e. H_2SO_4 and HNO_3) in the soil environment (Reuss and Johnson, 1986). The degree to which these acids and, more specifically, the dissociated strong acid anions exceed base cations present in atmospheric deposition, determines the acidifying potential of the system. In certain areas, notably those in which intensive livestock farming is practised, ammonium (NH_4^+) and ammonia (NH_3) in wet and dry deposition, respectively, constitute a major source of acidity (Verstraten *et al.*, 1990; Lee and Caporn, 1993). These compounds are rapidly oxidised in the soil environment resulting in nitric acid generation. The impacts of acid deposition occur as a result of direct inputs of acidic components into soils, as well as indirectly by processes, such as canopy leaching and direct uptake by plants of NH_4^+ in excess of NO_3^-, which result in proton release by plant roots (Ulrich, 1986; Bredemeier, 1987; Verstraten *et al.*, 1990).

In very acid soils, the ratio of basic to acidic cations is in many cases close to or lower than that of typical acid deposition and the effect of the latter on soil acidity is unlikely to be significant (Krug and Frink, 1983; Johnson *et al.*, 1988a). However, in these soils, significant atmospheric inputs of SO_4^{2-} and NO_3^-, together with associated protons and other cations, have a major impact on the acidity of soil solutions and associated surface waters (see section 2.6).

Soil acidification associated with *agriculture* occurs as a result of base cation uptake, as well as by application of ammoniacal fertilisers and their consequent oxidation to produce protons. With the exception of ammonium sulphate which generates more protons than it does NO_3^- ions, proton production by fertilizer oxidation is generally balanced by plant uptake of associated NO_3^- and net soil acidification only occurs as a result of harvesting or excessive fertiliser application (Fey *et al.*, 1990). Thus, the degree of acidification associated with agriculture depends to a large extent on the type and amounts of fertilizers and liming agents being used, as well as on the farming system being employed.

The acidifying effect of *forestry* stems largely from the net accumulation of base cations in forest biomass and the associated release of protons into the soil. Other important processes which influence the acidifying potential of forests include the addition of acid-generating litter with a low ash alkalinity, the fixing of nitrogen by certain tree species and clear-felling with associated rapid oxidation of organic matter. These and other relevant processes impacting on the chemistry of forest soils, as well as evidence relating to the extent to which they have affected soil and associated water chemistry are discussed in the following sections.

2.5. ACIDIFICATION OF SOIL BY FORESTRY

2.5.1. Introduction

The association of acidification processes with forests, as a consequence of afforestation (natural and anthropogenic) as well as changes from deciduous to coniferous species dominance, is well recognized (e.g. Salisbury 1922; Lutz and Chandler 1946; Ovington and Madgwick 1957; Williams *et al.*, 1978). However, in the context of the relatively recent upsurge in awareness of, and research into, acid deposition and its ecological effects, it has become increasingly important to evaluate the extent of this acidification and the possible

contribution that it makes to the observed widespread acidification of surface waters in northern Europe and America. In their natural range, coniferous species in general, and pines in particular, typically occur in marginal environments (Delcourt and Delcourt, 1987; Richardson and Bond, 1991). They are often developed on naturally acidic, nutrient-poor soils (Wilde, 1958; Fitzpatrick, 1980; Delcourt and Delcourt, 1987) and, because of their adaptation to these conditions, commercial pine plantations are in many cases developed in similar environments which are unsuitable for agriculture. Thus pine afforestation commonly, although by no means exclusively, occurs on naturally acidic, poorly-buffered soils which are particularly sensitive to further acid inputs. Assessment of afforestation impacts in these environments is often complicated by the commonly observed geographical coincidence of afforested areas with those in which the effects of acid deposition are most prominent. In order to elucidate the acidifying effects of forestry, a clear understanding of the relevant chemical and biochemical processes taking place in forest ecosystems, as well as a careful evaluation of available evidence relating to the actual impacts of these processes, is essential.

2.5.2. Acidification processes in forests

Soil acidification in forest ecosystems is primarily related to phytocycling of nutrients and accompanying protons, those of particular importance being nitrogen, sulphur and the base cations (primarily Ca^{2+} and Mg^{2+})(Binkley and Richter, 1987; Johnson *et al.*, 1991). More specifically, the disruption of these nutrient cycles by vegetation changes and forest management practices is the prime cause of soil acidification (Morris, 1984; Ulrich, 1986; Johnson and Todd, 1987; Bredemeier, 1987). Changes in the quantity and/or acid strength of soil organic matter may result in significant pH reductions in forest soils (Krug and Frink, 1983; Binkley and Sollins, 1990), but have no direct role in soil acidification, i.e. these changes do not directly influence soil ANC (van Breemen *et al.*, 1984). However, the introduction of polyphenol-rich and relatively base cation and nitrogen-poor litter (e.g. under pine forests), can lead to enhanced generation of soluble humic and fulvic acids which may leach from the soil, thereby contributing to soil acidification processes (Swift *et al.*, 1979; Khanna and Ulrich, 1984). The relative importance of cation leaching as opposed to biomass uptake as a cause of acidification depends on factors which may limit the generation or mobility of organic acids (e.g. high clay content), and on those which influence the rate of biomass accumulation and the degree to which nutrient cycles are disrupted (e.g. by whole-

tree harvesting). Other phenomena associated with forestry which are likely to impact on soil chemical processes and which may play a role in soil and water acidification, are the enhanced interception of precipitation and significantly enhanced evapotranspiration, particularly when compared to grassland and heath-type ecosystems. These processes are discussed in more detail in section 2.6 below.

A distinction can be made between acidification associated with "natural" colonization of areas previously covered by other vegetation types and that associated with commercial forestry. A number of acidification processes may operate in the former case. Net accumulation of base cations in biomass occurs temporarily during the aggradation phase of forest development and may occur due to retarded litter decay processes and resultant net litter accumulation on the forest floor (Alban, 1982; Gholz *et al.*, 1985; Richter 1986; Billet *et al.*, 1993; Morris, 1995). Nitrogen fixation by certain tree species (e.g. certain *Alnus*, *Eucalyptus* and *Acacia* species) can lead to NO_3^- production in excess of plant requirements, resulting in NO_3^- leaching and associated soil acidification (van Miegroet and Cole, 1985; Johnson *et al.*, 1991). Depending on the nature of the original vegetation, the addition of pine litter may result in enhanced leaching of organic acids, as described above (Khanna and Ulrich, 1984). Preferential uptake of ammonium-nitrogen (i.e. high NH_4^+/NO_3^- uptake ratios) by pine species, as suggested by hydroponic experiments (Keltjens and van Loenen, 1989), and soil nitrogen studies (Arnold, 1992), may contribute to acidification by significantly enhancing the net uptake of positively charged ionic species with associated release of protons into the soil (Arnold, 1992).

In the case of commercial pine plantations, export of nutrient cations in harvested biomass (Feller and Kimmins, 1984; Ulrich, 1986; Richter, 1986; Johnson and Todd, 1987; Johnson *et al.*, 1988a; Morris, 1992) and rapid oxidation of forest litter following clearfelling (with associated NO_3^- leaching; Bormann and Likens, 1979; Mitchell *et al.*, 1989), intensifies acidification processes significantly. Thus, intense soil acidification by forests is primarily linked to commercial forestry activities as well as to forest recovery or succession (Rosenqvist, 1978; Krug and Frink, 1983; Johnson *et al.*, 1991). The role of base cation uptake is particularly important in acid soils with low base saturation. Due to ion exchange considerations, leaching of bases from these soils is severely limited, even in the presence of acid deposition, and further soil acidification occurs primarily through the uptake and export of base cations in harvested biomass (Johnson *et al.*, 1991).

The relative effect of different tree species will depend on factors such as tree growth-rate, relative accumulation rates of base cations, degree of nitrogen fixation, the ash alkalinity of tree litter and the spatial distribution of roots. These factors, particularly growth rate, are in turn dependent to varying degrees on "external" variables such as climate. Nonetheless, all other factors being equal, tree species which accumulate base cations (particularly Ca^{2+}) to a greater extent than pines (e.g. oak and aspen species)(Alban 1982; Johnson and Todd, 1987) and species which are capable of fixing large amounts of nitrogen, would be expected to have a more prominent effect than pine species on the acidity and nutrient status of underlying mineral soil. However, studies of plantation ecosystems suggest that, while species differences are evident, rates of uptake, accumulation and release (in throughfall and litterfall) of nutrients are primarily governed by growth rate (Miller, 1984), which is largely a function of climate and original soil nutrient status. Organic matter may have an important influence on the degree of acidification under different species. Fenwick and Knapp (1982) report a dramatic decrease in soil pH together with incipient podzolisation following partial replacement of an oak woodland by pine and larch (Figure 2.1). The oak woodland is underlain by sandy, acid brown soils (original pH of 6). It appears, therefore, that in sandy soils with limited buffering capacity, the nature of the pine litter may play a prominent role, with the leaching of organic acids generated in the mor horizon leading to podzolisation and acidification of the underlying mineral soil (Khanna and Ulrich, 1984; Wardenaar and Sevink, 1992). Binkley and Sollins (1990) document evidence indicating that the higher acid strength of organic matter associated with coniferous tree species has a dominant influence on soil pH in certain forest ecosystems of northwestern U.S.A.

The addition of organic matter can ameliorate soil acidity and the extent to which this occurs is proportional to the ash alkalinity or base cation content of the tree litter (Noble and Randall 1996; Pocknee and Sumner, 1997). Thus, the low ash alkalinity of pine litter (Noble and Randall, 1996), as well as the general lack of bioturbation in the acidic forest floor (Fenwick and Knapp 1982, Wardenaar and Sevink, 1992), may further contribute to soil acidity by limiting the extent to which the acidifying effect of net base cation uptake in forest biomass is neutralised by the reincorporation of alkalinity in the form of organic matter.

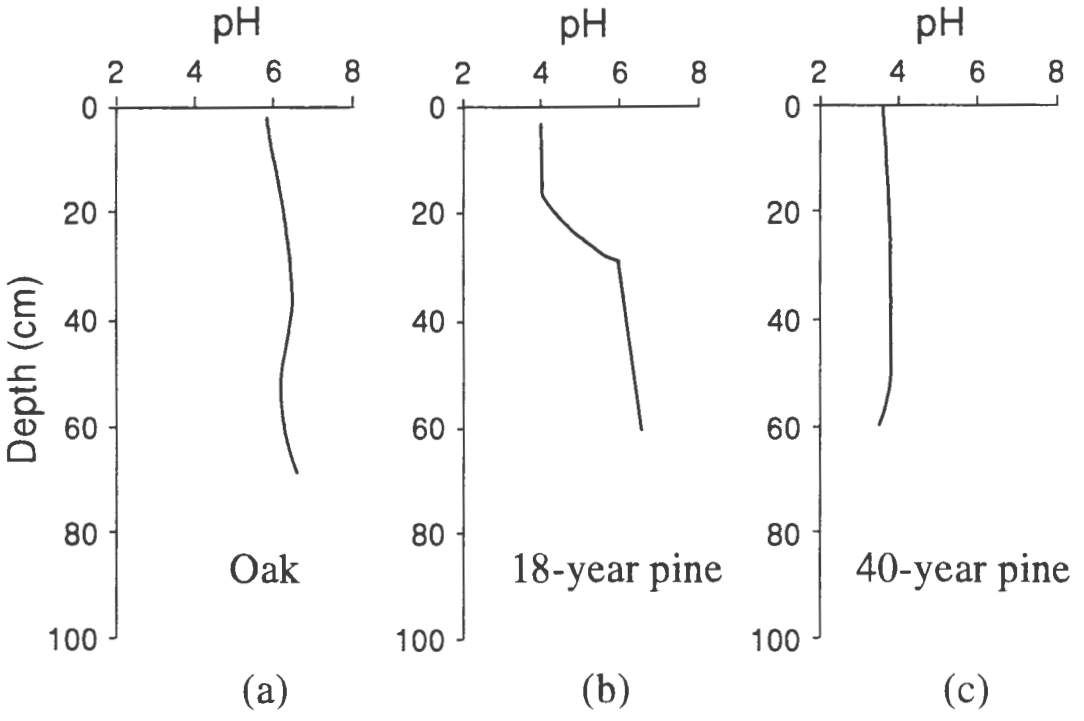

Figure 2.1: *pH profiles for acid brown soils developed under oak woodland which has been partially replaced by pine at Simon's Copse, Surrey, England. a) undisturbed oak woodland; b) 18-year old pine; c) 40-year old pine. Reproduced from Fenwick and Knapp (1982).*

2.5.3. Evidence of afforestation impacts

Numerous studies of the extent and rates of acidification by forests have been undertaken, particularly over the last two decades. These can be subdivided into two broad groups, i.e. those based on historical evidence and those based on the measurement and calculation of proton and/or nutrient budgets.

The historic approach involves evaluating changes in soil properties with time and is based either on comparisons of soil chemical data obtained for single forested areas over lengthy time periods, on studies of soil chemical differences within forest chronosequences, or on a comparison of data for forested and adjacent undisturbed areas of similar climate, parent material and topography (the "modified historic approach"). Studies in northern Europe and North America (e.g. Hallbäcken, 1992; Johnson *et al.*, 1991 and references cited therein), in Australasia (Davis and Lang, 1991) and in southern Africa (Morris, 1984; Clough, 1991; Musto, 1992; du Toit, 1993) have demonstrated significant decreases in soil pH and base status as a result of commercial forestry (Table 2.2). The highly variable nature of results

obtained from these studies stems from a number of factors including differences in tree species, climate, topography, parent materials and pre-afforestation acidity status. Additional examples of documented base cation depletion under forests are presented in Chapter 5 and are discussed in relation to the findings of this study.

*Table 2.2: Examples of changes in topsoil pH and exchangeable base cation concentration (EBC) as determined by historical studies on forest soils. ∆ - idicates the decrease in a parameter. * - S.E. U.S.A. and Swedish sites are significantly impacted by acid deposition. References: 1 - Amundson and Tremback, 1989; 2 - Johnson et al., 1991; 3 - Brand et al., 1986; 4 - Binkley et al., 1989; 5 - Hallbäcken, 1992; 6 - du Toit, 1993; 7 - Morris, 1984.*

Locality	Species	Years	∆pH	∆pH yr^{-1} (x10)	pH_{final}	∆EBC(%)	Ref.
W. USA	*Pinus radiata*	~100	1.5	0.15	~5.5#	-	1
USA	*Eucalyptus saligna*	6	1.0	1.67	4.9#	-	2
Canada	*Pinus resinosa*	45	0.7	0.15	5.3#	-	3
S.E. USA*	*Pinus taeda*	20	0.3-0.8	0.15-0.4	-	30-80	4
Sweden*	*Picea* spp.	57	0.77	0.14	3.77#	~80	5
RSA	*Pinus patula*	>45	0.34	0.07	4.02+	76	6
RSA	*Acacia mearnsii*	>45	0.54	0.12	3.78+	42	6
RSA	*Eucalyptus* spp.	>45	0.29	0.06	4.25+	78	6
Swaziland	*Pinus patula*	27	0.15	0.05	3.79+	~50	7

- medium for pH measurement unspecified /+ - pH measured in 1M KCL

Proton budget calculations are carried out by measuring the concentrations of important chemical species in all of the major biogeochemical compartments of the soil-plant system, as well as the fluxes between these compartments, and by applying charge and mass balance principles. The extent to which excess loss of base cations (i.e. that which is not balanced by a parallel transfer of anions) to leaching and plant uptake is not fully compensated by their return in throughfall or litterfall is taken as a quantitative estimation of internal proton production (van Breemen *et al.*, 1984; Bredemeier, 1987; Verstraten *et al.*, 1990). Examples of data generated by this type of study are given in Table 2.3. These indicate that in acid soils proton additions associated with net biomass uptake of nutrient cations range from ~ 0.7 to ~ 1.5 kmol H^+ ha^{-1} yr^{-1} and can constitute a significant proportion of the total acid load, even in areas which are subject to very high levels of acid deposition (e.g. N.W. Germany, N.E. U.S.A.).

Table 2.3: *Examples of estimated net annual proton inputs (in kmol ha^{-1} yr^{-1}) based on proton budget and flux calculations. Rates are given for proton production associated with: biomass cation uptake (int-H^+); bicarbonate leaching (HCO_3^-); and atmospheric deposition of acidity (ext-H^+). The latter includes indirect proton additions associated with acid deposition induced canopy leaching and excess uptake of deposited NH_4^+ relative to NO_3^-. References: 1 - Verstraten et al., 1990; 2 - Bredemeier, 1987; 3 - van Breemen et al., 1984; 4 - Richter, 1986.*

Locality	Species	int-H^+	HCO_3^-	ext-H^+	Ref.
Netherlands	Mixed deciduous	1.9	-	3.3	1
N.W. Germany	*Fagus* spp.	1.05	-	1.55	2
N.W. Germany	*Picea* spp.	1.14	-	4.42	2
N.W. Germany	*Pinus* spp.	0.68	-	1.12	2
N.W. Germany	*Quercus* spp.	1.48	-	2.56	2
Sweden	*Pinus* and *Picea* spp.	1.0	0.7	1.7	3
N.E. USA	Mixed hardwoods	1.0	0.1	1.4	3
S. USA	Various	0.83-1.44	0.3-0.75	1.0	4

Johnson and coworkers have used a similar approach to study nutrient cycling in general, and base cation loss in particular, in forest ecosystems of the U.S.A. (Johnson and Todd, 1987; Johnson *et al.*, 1988a; Johnson and Todd, 1990). Nutrient fluxes have been obtained primarily by direct measurement of soil solution composition (multiplied by estimated soil water fluxes), biomass uptake, throughfall and litterfall. These studies confirm that base cation removal by whole-tree harvesting (0.4 to 1.2 $kmol_c\ ha^{-1}\ yr^{-1}$) makes up a significant, and in some cases dominant, component of base cation loss, particularly in acid soils (Johnson *et al.*, 1988a). Biomass uptake of base cations, and particularly of Ca^{2+}, appears to be more prominent in mixed deciduous (predominantly oak) forests of south-eastern U.S.A. (Alban, 1982; Johnson and Todd, 1990) than in northern coniferous forests (Johnson *et al.*, 1988a). However, in view of uncertainties regarding rotation ages and variable original soil acidity levels. the significance of this difference is not clear.

It is clear from the above-described evidence that there can be little doubt regarding the acidifying effects of forests and that over long time periods this can result in pools of exchangeable acidity which are very large (~ 100 to 300 kmol ha^{-1}) relative to annual acid fluxes (Table 2.3) (Rosenqvist, 1978; Richter, 1986; McBride, 1994). However, the extent to

which these processes can detrimentally affect associated drainage waters has not been conclusively established and is strongly linked to the question of strong acid anion generation by "natural" processes (i.e. processes other than the deposition of atmospheric pollutants) (Reuss *et al.*, 1987).

2.6. ACIDIFICATION OF SOIL SOLUTIONS AND ASSOCIATED SURFACE WATERS

2.6.1. Ion exchange and cation leaching

Soil acidification is generally accompanied by increased alkalinity in associated surface water due to the leaching of base cations together with bicarbonate and, in areas affected by acid deposition, with SO_4^{2-} and NO_3^-, (e.g. van Breemen *et al.*, 1984; Reuss *et al.*, 1987). However, naturally occurring acidic soils with low base status and large quantities of exchangeable acidity, such as those typically developed under forests, are incapable of buffering additional acid inputs by base cation exchange. Ion-exchange considerations require that proton or other cation inputs to these soils primarily displace Al ions from exchange sites, resulting in decreased pH and alkalinity, as well as increased Al concentrations in soil solutions (Driscoll, 1985; Reuss, 1991). In addition to phytotoxicity effects associated with high Al/(base cation) ratios in soil solution (Cronan and Grigal, 1995), this results in acidic drainage solutions which can cause significant decreases in the pH and alkalinity as well as significant increases in the Al content of associated surface waters (Driscoll, 1985; Reuss and Johnson, 1986; Bricker, 1986), resulting in major impacts on aquatic ecosystems (Cresser and Edwards, 1987; Charles, 1990; Ormorod, 1993). Recent work on acid deposition impacted forests in northeastern U.S.A. suggests that Al, mobilised by strong acid inputs to the mineral soil, can be transported into the forest floor as a result of biocycling and water table fluctuations (Lawrence *et al.*, 1995). This is believed to cause permanent loss of exchangeable Ca in the forest floor due to preferential formation of strong Al-organic matter complexes, and may have significant implications with respect to forest nutrition. Acidification of soils also enhances the solubility of trace metals such as Mn, B, Cu, As, Cd, Zn and Pb (Bergkvist, 1987; Berggren *et al.*, 1990; Sumner *et al.*, 1991; Marschner *et al.*, 1992; Vesely, 1994) which may be leached into associated fresh waters, potentially raising concentrations to levels which are toxic to aquatic organisms.

2.6.2. The role of mobile anions

Charge balance considerations require that cations in soil solution or drainage water must be accompanied by anions. As discussed in section 2.3, bicarbonate, the dominant "natural" anion in soil solutions, has a negligible concentration at pH values lower than approximately 5 and is therefore not available to facilitate cation leaching in very acid soils. Carboxyl functional groups of dissolved humic and fulvic acids typically have pK_a values ranging from ~ 3.5 to > 5 (Oliver *et al.*, 1983; Cronan and Aiken, 1985; Perdue, 1985). Thus under conditions favouring the generation and mobility of these acids, organic anions (i.e. humates and fulvates) may contribute substantially to the acidification of soil solutions and associated surface waters. Waters acidified as a result of organic anion leaching are typically highly coloured and generally occur in association with peats (Moore, 1988; Mitchell, 1990), very sandy tropical soils (Janzen, 1974), or other environments in which podzolisation is a dominant process (Reeve and Fergus, 1983; Midgley and Schafer, 1992). However, in most acid soils, leaching of organic anions is likely to be limited by relatively high pK_a values and by processes which significantly reduce their mobility, such as metal complexation and co-precipitation in subsoils (Ugolini *et al.*, 1977; Cronan *et al.*, 1978; McDowell and Wood, 1984) or the formation of clay organic matter complexes (Kononova, 1966; Schnitzer, 1986). Recent work by Dosskey and Bertsch (1997) demonstrated the strong retention of dissolved organic matter (DOM) in deep sandy Ultisol E horizons, suggesting that the mobility of organic anions is limited in a wider variety of soils than previously envisaged. Thus, the transfer of large quantities of acidity to soil solutions generally requires inputs of mobile strong acid anions, i.e. SO_4^{2-}, NO_3^- or Cl^- (Ulrich, 1986; Reuss *et al.*, 1987). Acidification of soil solutions and consequently of associated surface waters is, therefore, governed primarily by processes controlling the supply and mobility of these anions in forest ecosystems.

2.6.3. Acid deposition

In areas impacted by atmospheric pollution, acid inputs of SO_4^{2-} and NO_3^- constitute a major source of strong acid anions and have been implicated in the observed widespread acidification of surface waters in northern Europe and parts of North America (Cronan and Schofield, 1979; Henrickson, 1979; Bricker, 1986; Reuss and Johnson, 1986; Brakke *et al.*, 1987; Cresser and Edwards, 1987). The impact of acid deposition, both on soil acidity and soil solution composition, is mediated by immobilisation and uptake of these anions within the soil-plant system.

In the case of *sulphate*, atmospheric inputs often significantly exceed plant requirements and its mobility is governed primarily by abiotic processes. Mechanisms which may influence SO_4^{2-} mobility include adsorption, incorporation into organic matter (Strickland and Fitzgerald, 1984; Schindler *et al.*, 1986) and, in the case of acid soils, precipitation of Al sulphates and hydroxysulphates (Nordstrom, 1982; Ulrich, 1986; Reuss and Johnson, 1986; Courchesne and Hendershot, 1990). However, most studies of soils that have been impacted by acid deposition suggest that adsorption, mainly by sesquioxide minerals and amorphous Fe and Al compounds, is the dominant process controlling SO_4^{2-} mobility in the soil environment (Johnson *et al.*, 1982; Johnson *et al.*, 1986; Harrison *et al.*, 1989; Mitchell *et al.*, 1989; David *et al.*, 1991a; Barton *et al.*, 1994; Rustad *et al.*, 1996). Sulphate sorption may occur by reversible processes such as electrostatic bonding to positively-charged colloid surfaces (Nodvin *et al.*, 1986; Sposito, 1989) and outer-sphere complexation to protonated hydroxyl groups or to a surface metal cation (Sposito, 1989). However, several studies have demonstrated the presence of significant quantities of irreversibly-sorbed SO_4^{2-} (Harward and Reisenauer, 1966; Harrison *et al.*, 1989), indicating that, in certain soils, inner-sphere complexation is an important mechanism of SO_4^{2-} retention. This occurs primarily in soils with high concentrations of Fe and Al oxides and hydroxides (mostly hematite, goethite and gibbsite). The surfaces of these minerals acquire a net positive charge at low pH, and SO_4^{2-} sorption occurs largely by ligand exchange with protonated surface hydroxyl groups (Mott, 1981; Sposito, 1989).

Sulphate immobilisation by adsorption can ameliorate the impact of acid deposition (Cosby *et al.*, 1986). This is particularly prevalent in highly weathered sesquioxidic soils (Johnson *et al.*, 1979; Johnson and Todd, 1983), but also occurs in certain young soils which are rich in amorphous Fe and Al oxyhydroxides (Johnson *et al.*, 1986). Even in these soils, however, continued inputs can lead to saturation of the SO_4^{2-} sorption capacity (Wright and Hauhs, 1991), leading to renewed SO_4^{2-} leaching and acidification of drainage waters (Ryan *et al.*, 1989). In addition, the reversal of soil and water acidification following reductions in acid inputs may be delayed significantly by the release and consequent leaching of accumulated (reversibly sorbed) SO_4^{2-} (Reuss and Johnson, 1986; Harrison *et al.*, 1989; Wright and Hauhs, 1991).

Nitrogen is an important, and in many cases limiting, nutrient in forest ecosystems (Binkley and Richter, 1987; Johnson, 1992) and atmospheric inputs are usually small in relation to internal pools and fluxes (Switzer and Nelson, 1972; Johnson, 1992). Unlike SO_4^{2-}, NO_3^- is not readily adsorbed on soil colloid surfaces (Parfitt, 1978; Johnson *et al.*, 1986), and leaching of deposited NO_3^- or other nitrogen compounds is limited primarily by plant and microbial uptake (Vitousek *et al.*, 1979; Reuss and Johnson, 1986; Boring *et al.*, 1988). Thus significant NO_3^- leaching and associated acidification of soil solutions and surface waters will only take place if biological nitrogen requirements are exceeded, i.e. when nitrogen saturation occurs. There is a growing amount of evidence which suggests that many forest ecosystems in northern Europe and North America are approaching or have reached nitrogen saturation (Bormann *et al.*, 1977; Cole and Rapp, 1981; van Breemen *et al.*, 1987; Johnson and Lindberg, 1991; Durka *et al.*, 1994). Evidence suggests that, at least in some cases, nitrogen saturation is related to acidification-induced forest decline (Durka *et al.*, 1994).

The commonly observed correlation between lake acidification and SO_4^{2-} concentrations in northern Europe and America (Brakke *et al.*, 1987; Reuss *et al.*, 1987), as well as palaeolimnological evidence relating the onset of lake acidification to that of atmospheric pollution in the post-industrial revolution period (e.g. Battarbee, 1990; Renberg *et al.*, 1990a), are generally accepted as strong evidence implicating atmospheric deposition as the prime cause of fresh-water acidification (Reuss *et al.*, 1987; Brakke *et al.*, 1987; Kreiser *et al.*, 1993). While in many cases the evidence appears to be irrefutable, it is often difficult to separate, both spatially and temporally, the onset of acid deposition from that of commercial afforestation and successional land use changes from agriculture or pastoral use to unmanaged acidifying heath vegetation and forests (Batterbee, 1990). It is generally accepted that acidification associated with these land use changes has sensitised the soils to acid deposition, thereby significantly exacerbating the latter's impacts on drainage waters (Reuss and Johnson, 1986). Very few studies, however, have successfully investigated the possibility that, in the absence of acid deposition, changes in land use and particularly, the afforestation of acid-sensitive upland soils, may result in acidification of surface waters and associated chemical changes. Limnological investigations of the effect of forestry on lake waters (e.g. Kreiser *et al.*, 1990; Anderson and Korsman, 1990; Renberg *et al.*, 1990a; Renberg *et al.*, 1990b) have generally been inconclusive, largely due to the critical complicating effects of high background acid deposition and local variations in biomass production, climate and soil properties. However, data presented by Flower *et al.* (1990) for a loch in north-west Scotland,

indicate a significant decrease in lake-water pH (from 5.3 to 4.6) over a period of four years following afforestation of the catchment region which was initiated approximately ten years prior to the first pH measurement. Lake-water pH values have remained low despite decreased levels of SO_4^{2-} in atmospheric deposition and in lake waters, suggesting that the observed acidification in the forested catchment cannot be ascribed entirely to enhanced interception of acid SO_4^{2-} deposition.

2.6.4. Internal sources of strong acid anions in forest ecosystems

Annual cycling of most nutrients (including base cations, N- and S-compounds) in forest ecosystems greatly exceeds fluxes into or out of the system (Switzer and Nelson, 1972; Cole and Rapp, 1981; Miller, 1984), even in the presence of intense acid deposition. Thus *internal* sources of strong acid anions in forest ecosystems relate primarily to disruption of nutrient cycles. Due to the high concentration of nitrogen in plant biomass relative to that of sulphur (S/N ~ 1/10 to 1/30) or chlorine (Cl/N ~ 1/300), the former is generally the dominant anion involved in these processes and is regarded by Ulrich (1986) as the only potentially available strong acid anion in natural systems. Nitrate differs from SO_4^{2-} or Cl^- in that its fate is governed almost exclusively by biologically-mediated transformations and fluxes (Johnson *et al.*, 1986; Binkley and Richter, 1987). The conceptual model of Johnson (1992) (Figure 2.2) illustrates some of the complexities of the nitrogen cycle and highlights the importance of plant uptake, litterfall, microbial immobilisation and mineralisation as the dominant processes controlling nitrogen fluxes in forest ecosystems. The potential for NO_3^- leaching is governed primarily by the extent to which mineralisation and nitrification rates exceed the rate of nitrogen removal by plant and microbial uptake, denitrification and, to a lesser extent, immobilisation by non-biological sorption of NH_4^+ to soil colloid surfaces (Vitousek *et al.*, 1979; Johnson, 1992). These processes are, in turn, dependent on factors such as temperature, soil moisture content, pH and the C:N ratio of soil organic matter (Edmonds and McColl, 1989).

In a study of 19 forested sites in the U.S.A., Vitousek *et al.* (1979) have demonstrated that, despite significant variations in mineralisation and nitrification rates between sites, nitrogen losses to drainage waters were minimal prior to any forest disturbance. This may not apply to forests which include a large component of nitrogen fixing species such as red alder (Binkley *et al.*, 1982; van Miegroet and Cole, 1984). Rapid oxidation of forest litter following

harvesting can cause dramatic increases in NO_3^- supply while at the same time reducing plant uptake to very low levels (Vitousek *et al.*, 1979). Thus harvesting generally results in extensive NO_3^- leaching, with associated pH decline, loss of alkalinity and enhancement of Al concentrations in soil solutions and drainage waters (Bormann and Likens, 1979; Martin *et al.*, 1984; Mitchell *et al.*, 1989). The degree to which this occurs is variable, however, and factors such as low temperatures, dry conditions and weed growth may significantly reduce the impacts of harvesting on NO_3^- levels in soil solution (Nohrstedt *et al.*, 1994; Smethurst and Nambiar, 1995; Munsen and Timmer, 1995).

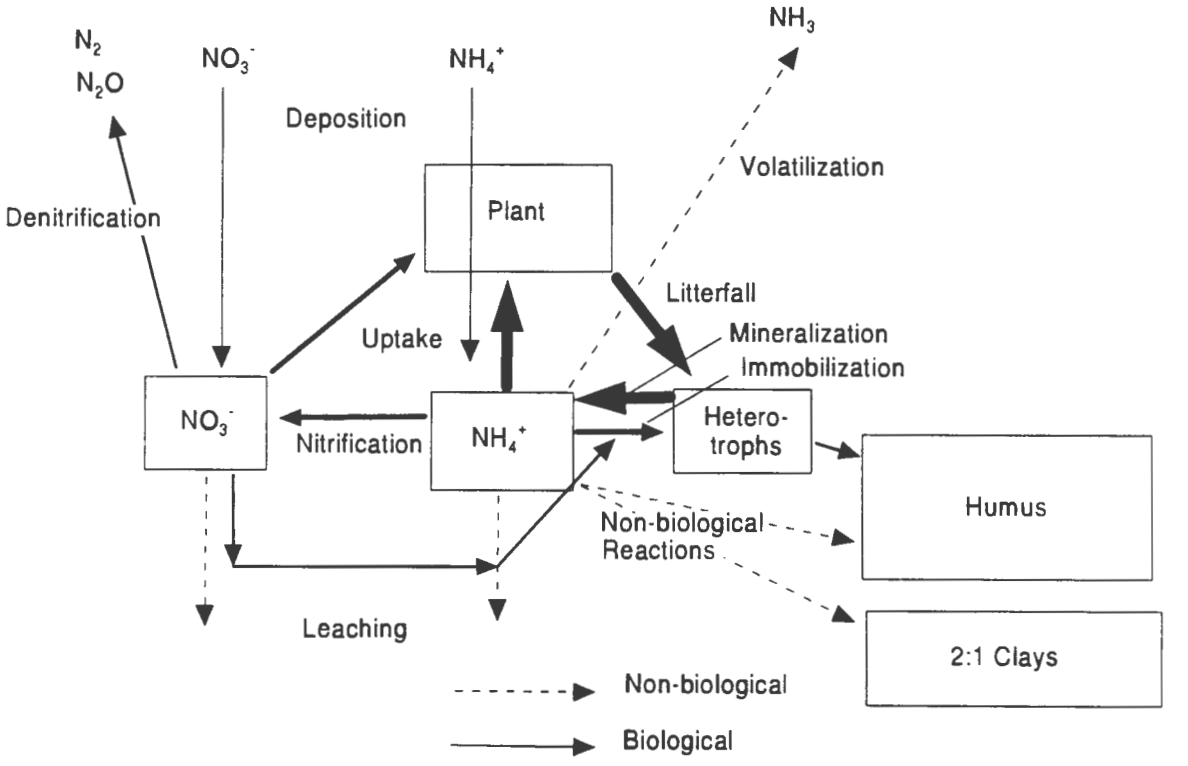

Figure 2.2: *Schematic representation of the nitrogen cycle. Reproduced from Johnson (1992).*

2.6.5. Atmospheric salt inputs

Displacement of acidity from the soil exchange complex can be achieved, in the absence of *acid* inputs, by addition of soluble *salts* of strong acid anions (Johnson *et al.*, 1986; Richter *et al.*, 1988; David *et al.*, 1991b). The cationic component of the salt displaces exchangeable H^+ and Al^{3+} which are accompanied in the soil solution and drainage waters by the anionic component. This effect is particularly evident in naturally leached, acidic soils in which minor increases in electrolyte concentration (i.e. ~ 0.3 to ~ 0.6 $mmol_c\ L^{-1}$) can cause significant decreases in the pH of soil solutions (by ~ 0.3 units) (Richter *et al.*, 1988).

In unpolluted areas, Cl^- is by far the most important strong acid anion in atmospheric deposition. Chloride is not influenced to any significant extent by abiotic or biotic soil chemical processes (Johnson *et al.*, 1986). Thus inputs of Cl^- salts to acidic forest soils will cause acidification of soil solutions and, in environments where precipitation exceeds evapotranspiration, will induce leaching of acidity. Although Cl^- is likely to be the dominant anion in unpolluted deposition, SO_4^{2-} salts are also likely to be present in significant quantites, particularly in regions with a maritime influence. Work by Miller *et al.* (1996) indicated that at least 50 % of the SO_4^{2-} impacting on a peatland area in northern Scotland was ocean-derived. These authors predicted that the development of forests in this area would lead to increased interception of atmospheric SO_4^{2-} and consequently would have a considerable impact on the composition of drainage waters.

Enhanced interception of precipitation and atmospheric aerosols, as well as enhanced evapotranspiration associated with forests, may play a key role in the context of the above-described processes and are especially important in coastal or near-coastal regions which receive large inputs of sea salt (Cresser and Edwards, 1987). The effects of these processes will be particularly prominent in situations where forests have replaced a previous vegetation community which is less interceptive and/or transpiritive in nature. Episodic acidification and enhancement of Al concentrations resulting from sea salt inputs have been widely reported for lakes, streams and soil solutions (Langan, 1987; Sullivan *et al.*, 1988; Wright *et al.*, 1988; Heath *et al.*, 1992; Hindar *et al.*, 1994; Pedersen and Bille-Hansen, 1995). Data for coniferous forest ecosystems being monitored as part of the EXMAN project, demonstrate that Cl^- inputs at sites with a marine influence can significantly exceed SO_4^{2-} deposition at severely polluted sites in Germany and Holland (Farrell *et al.*, 1994)(Table 2.4). Because of the acid nature of these forest soils, the high salt inputs cause acid soil leachates (A horizon soil solution pH of 3.8 - 4.2; B horizon soil solution pH of 4.11 - 4.56) with high Al concentrations (up to 0.9 $mmol_c\ L^{-1}$) and Ca/Al ratios lower than one (Farrell *et al.*, 1994). Pedersen and Bille-Hansen (1995) document extreme enhancement of salt concentrations in soil solutions, together with reduced pH and dramatic increases in Al concentration (to > 2.2 $mmol_c\ L^{-1}$), associated with episodes of high salt deposition and low surplus water percolation at spruce and beach stands in Denmark. Salt inputs to these sites have led to the leaching of 0.2 to 0.6 $kmol_c\ Al\ ha^{-1}\ yr^{-1}$ below 90 cm in the soil profiles, and the high salt and Al concentrations in soil solutions are believed to be important factors contributing to reduced vitality of Norway spruce ecosystems in Denmark. In addition to impacts on forest productivity, recent evidence indicates that these episodic salt "events" can have dramatic effects on aquatic

ecosystems (Hindar *et al.*, 1994). While inputs of sea salt to acid soils commonly result in acidity "flushes", the continued input of basic cations (particularly Mg) may ultimately have an ameleorative effect on the soil, provided that cation inputs exceed removal by the forest biomass.

Table 2.4: Water and ion fluxes ($mol_c\ ha^{-1}\ yr^{-1}$) in precipitation and throughfall at EXMAN control plots in northern Europe (data obtained from Farrell et al. 1994). Fluxes are the product of volume-weighted mean concentration and total water flux. Non-marine SO_4^{2-} is calculated from the seawater ratio of SO_4^{2-} to Mg^{2+} (0.532 mol SO_4^{2-}/ mol Mg^{2+}). The EXMAN sites were selected to cover a wide range of deposition loads. Klosterhede (Denmark) and Ballyhooly (Ireland) are coastal sites with significant marine salt input. Acid deposition is highest at Solling (Germany) and lowest at Ballyhooly. High rates of NH_4^+ deposition at Kootwijk (Netherlands) derive primarily from agriculture.

	Water flux (mm)	H^+	NH_4^+	NO_3^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cl^-	SO_4^{2-}	SO_4^{2-} (non-marine)
Precipitation											
Klosterhede	980	340	340	490	150	410	52	1880	2340	980	762
Kootwijk	852	176	734	330	141	139	21	504	675	625	551
Högwald	785	132	441	328	190	74	76	93	102	446	407
Solling	1068	380	837	580	230	112	83	429	430	880	820
Ballyhooly	1022	33	290	107	182	376	68	2684	2377	428	228
Throughfall											
Klosterhede	723	340	940	660	780	1840	720	7130	7810	2230	1251
Kootwijk	544	46	2101	724	328	286	383	835	1175	1879	1727
Högwald	456	32	1488	676	359	151	368	103	228	1096	1016
Solling	801	1240	1480	1250	1120	367	673	909	1120	3310	3115
Ballyhooly	576	32	565	207	428	761	635	3533	4354	871	466

The importance of interception enhancement by the forest canopy, and the extent to which this is influenced by vegetation type, was highlighted in a study by Miller *et al.* (1990). Monitoring of inputs and outputs from two forested catchments indicated that Sitka spruce (*Picea sitchensis*) enhanced the interception and crown leaching of solutes to a considerably greater extent than did Norway spruce (*P. abies*), and that this had led to higher concentrations of Na^+, Cl^- and SO_4^{2-} in output streams from the Sitka spruce catchment.

In areas with high evapotranspiration rates, salt concentrations of soil solutions are likely to increase as a result of evaporative concentration. Afforestation of low-biomass ecosystems such as grassland and fynbos will lead to a considerable enhancement of this effect and the possibility that this may influence solution acidity is being investigated in this study. High salt concentrations generated by evaporative concentration may have a detrimental impact on tree growth due to induced elevation of soil-solution Al concentrations and possibly, in extreme cases, due to high salinity. The impact of these enhanced concentrations on soil drainage waters will be offset by reduced leaching caused by evapotranspiration, and total outputs should not exceed inputs. However, evaporative concentration may, over extended time periods, lead to significant accumulation of soluble salts in forest soils, with potential for acid salt flushes during periods of unusually high rainfall, or during the first leachate pulse following the dry season.

2.6.6. Hydrological flow paths

Hydrological flow paths and the extent to which percolating water interacts with the soil through which it is moving are of critical importance with respect to the relationship between soil acidification and associated surface water quality (Krug and Frink, 1983; van Breemen *et al.*, 1984). Shallow flow paths, generally prevalent during periods of high discharge, facilitate interaction between drainage water and the upper, more acidic soil horizons. This results in greater acidification of associated surface waters than would occur under conditions of low discharge and deeper flow whereby acidified soil solutions can be neutralised by interaction with more alkaline subsoils, saprolite or parent materials (Krug and Frink, 1983; Cresser and Edwards, 1987). The importance of flow paths is highlighted by data presented by Verstraten *et al.* (1990) for a deciduous forest ecosystem in the Netherlands. Despite considerable acid inputs (~ 5.2 $kmol_c\ ha^{-1}\ yr^{-1}$) which have resulted in soil solution Al concentrations of 0.05 - 2 $mmol_c\ L^{-1}$ and pH values significantly lower than 5 in the upper organic and mineral soil horizons, underlying calcareous soil and parent material neutralises drainage solutions which have no observable acidifying effect on associated surface water.

2.7. SUMMARY

Forest soils, particularly those developed under coniferous species, are typically acidic. In the case of natural forests, this is partly due to the fact that coniferous species tend to colonise, and are adapted to, marginal habitats, often with naturally acidic, nutrient-poor soils.

Processes such as biomass accumulation of bases during the aggradational phase of forest development, the transfer of nutrients from the mineral soil to accumulating litter layers, preferential uptake of ammonium nitrogen, and nitrogen fixation in excess of plant requirements with associated NO_3^- leaching, contribute to further acidification of mineral soils under most forest types. Commercial forestry activities significantly exacerbate the acidifying effect of forests, primarily due to the permanent export of nutrients in harvested biomass, but also as a result of litter oxidation and associated NO_3^- leaching following harvesting. Studies of forest ecosystems indicate that these processes can cause considerable build-up of exchangeable acidity with an associated loss of exchangeable bases and acid neutralising capacity, even in areas which are not subject to significant acid deposition inputs.

Although this intense acidification can, and has, led to problems of Al toxicity and nutrient imbalances in forest ecosystems, the degree to which soil solutions and associated surface waters are acidified, depends to a large extent on the supply of the mobile strong acid anions (SO_4^{2-}, NO_3^- and Cl^-). In polluted areas, deposition of acid SO_4^{2-} and NO_3^- is a major strong acid anion source and has been implicated in the widespread acidification of surface waters in northern Europe and parts of North America. In the absence of acid deposition, the transfer of soil acidity to soil solutions and surface waters can occur due to NO_3^- leaching or due to the input of atmospheric salts derived from precipitation and dry deposition of aerosols. Nitrate leaching occurs primarily as a result of rapid oxidation of forest litter following clearfelling and is therefore largely a feature of commercial plantations. In maritime environments, the impact of salt deposition can be very severe. In these regions, intermittent acidification of soil solutions and surface waters as a result of "salt episodes" is well documented and has led to major impacts on forest and aquatic ecosystems. Although these effects are likely to be less dramatic in areas with lower atmospheric salt inputs, they may occur to some extent due to enhanced interception and evaporative concentration of atmospheric salts by forests.

3. STUDY AREAS, SAMPLING AND STATISTICAL METHODS

3.1. STUDY AREAS

Soil and water samples were taken in four regions within South Africa (Figure 3.1). These are: the *eastern escarpment* in Mpumalanga province; the *midlands* region of southern KwaZulu-Natal; the area between the towns of George and Knysna in the *southern Cape*; and the *western Cape* in the vicinity of Cape Town.

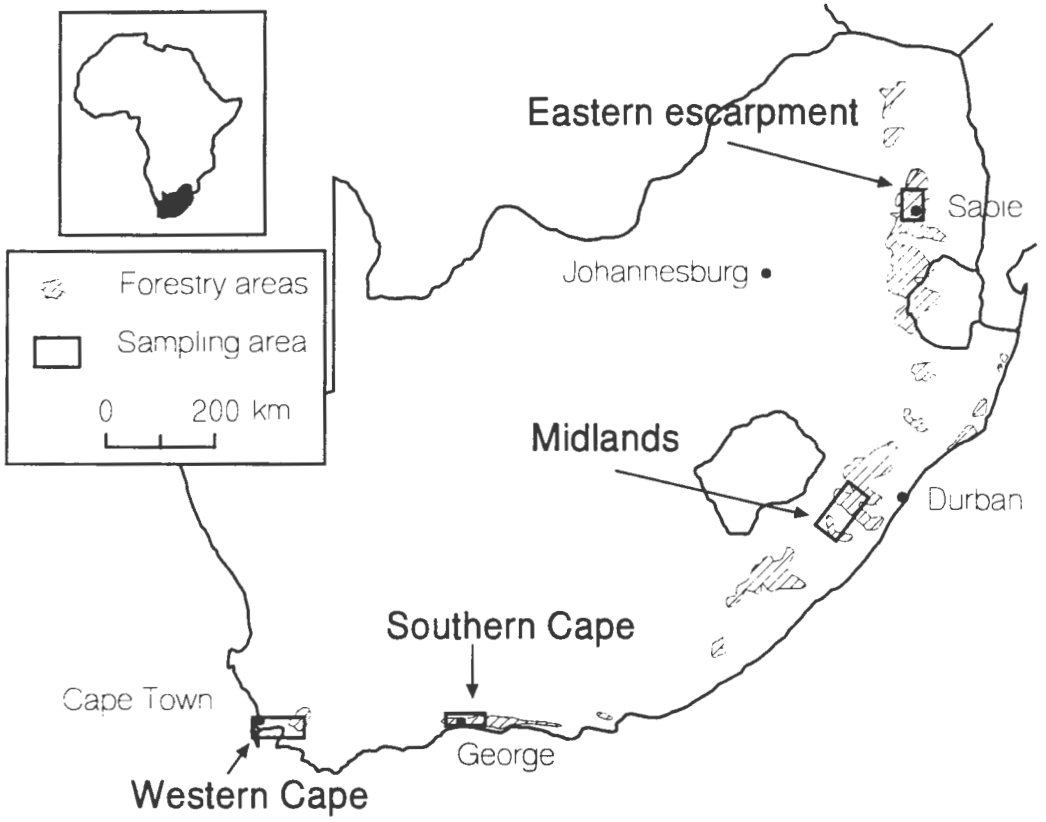

Figure 3.1: *Locality map showing the position of the four sampling areas and the distribution of commercial forests in South Africa*

Detailed maps showing the position of individual sampling sites in relation to major towns, roads and selected drainages are given in Appendix A and the characteristics of each region are summarised in Table 3.1. Site details are provided in Appendix A.

The four study regions are characterised by the presence of extensive pine (*Pinus)* plantations in mountainous areas with naturally acidic soils. The regions differ in terms of their climate, original vegetation type, dominant pine species and geology, as well as in their proximity to the ocean and to potential sources of atmospheric pollution.

Table 3.1: Summary information for the four sampling areas. Site details are given in Appendix A.

	Eastern escarpment	Midlands	Southern Cape	Western Cape
No. of soil sites	12*	14**	6	6
Stream sites	10	22	10	9
Sampling period	May 1995, May 1996	June 1995	July 1995	Nov. 1994, August 1995
Natural vegetation	grassland	grassland	fynbos	fynbos
Pinus species	*patula, elliottii, taeda*	*patula, elliottii, taeda*	*radiata, pinaster*	*radiata, pinaster*
Geology	quartzite, shale, dolerite (diabase), dolomite, granite	shale, dolerite, sandstone	quartzite	quartzite
Altitude range (m)	1300 - 1885	1080 - 1640	550 - 720	~300 - 630
Rainfall range (mm)	1050-1650	900-1100	600-1150	750-1200
Rainfall season	summer	summer	summer/winter	winter
Summer temperatures (°C)#	13.1 - 22.3 (17.7)	13.1 - 25.7 (19.4)	15.2 - 24.4 (19.8)	12.5 - 26.1 (19.3)
Winter temperatures (°C)#	4.2 - 16.8 (10.5)	2.4 - 20.3 (11.4)	7.4 - 18.6 (13)	3.2 - 16.1 (9.7)

* - Includes 4 sites sampled by DuToit (1993), ** - includes 12 sites sampled by DuToit (1993).
# - Temperature data are for the nearest weather station, all of which lie within the sampling areas. Values given are the average daily minimum, average daily maximum and average daily (in brackets) temperatures for the hottest (February) and coldest (July) months, respectively.

In the eastern escarpment and midlands regions, collectively referred to as the eastern seaboard, forests are developed on land previously covered by montane grasslands (White, 1978). The grassland adjacent to the pine plantations is regularly (annually or biennially) burnt in order to maintain fire breaks. This burning frequency is similar to that prevailing in unforested areas (Tainton and Mentis, 1984) and, in view of the low ratio of above- to below-ground biomass in these ecosystems, the burning of fire breaks is not expected to notably alter the composition of the soil relative to that in "pristine" areas. In the southern and western Cape, the forests replace mountain fynbos ecosystems composed of macchia type vegetation that is characterised by an abundance of sclerophyllous shrubs and by the presence of very few trees. The ecology of the fynbos biome is described by Cowling (1992). The dominant *Pinus* species grown in the eastern seaboard areas are *P. patula, P. elliottii* and *P. taeda*, whereas in the Cape regions *P. radiata* and *P. pinaster* are prevalent. Plantations of all of these species have been sampled.

The climate of southern Africa and its relationship to biogeography is reviewed by Schulze and McGee (1978). The study areas in the eastern seaboard lie within the afro-temperate climatic zone where rain falls predominantly in summer. Ocean-derived fogs regularly blanket these regions. The western Cape has a mediterranean climate and most rainfall is associated with cyclonic cold fronts which influence the region during winter (May to August). The southern Cape has a similar climate to that of the western Cape but rainfall occurs throughout the year. Mean annual precipitation (MAP) levels vary considerably within each of the regions and range from ~ 600 to 1650 mm. The highest MAP levels occur at high elevation sites in the eastern escarpment and the lowest levels occur in the relatively low-lying maritime sites of the southern and western Cape. However, all regions contain several sites with MAP levels in excess of 1000 mm. Temperatures do not vary considerably between the four regions (Table 3.1) with average daily temperature for the hottest month (February) ranging from approximately 17 to 20 °C and average daily temperature for the coldest month (July) varying from 10 to 13 °C.

A wide variety of parent materials are present in the eastern escarpment region and sites were selected in order to cover a range of underlying lithologies. These include quartzite, siltstone, shale and dolomite of the Transvaal Supergroup (SACS, 1980), as well as dolerite (diabase) intrusions and Archaean granite. Soil sampling sites in the midlands region all occur on either shale (Karoo Supergroup) or dolerite parent materials, whereas the forested soils in the Cape regions are developed almost exclusively on quartz arenites (generally referred to as quartzite) of the Cape Supergroup. Although other lithologies with higher clay-forming potential (e.g. granite and shale) are present in the Cape regions, no suitable forested sites could be found on these parent materials (they generally form fertile areas of subdued topography which are typically used for agricultural purposes). The geology of South Africa is reviewed by Truswell (1977).

Although the sites all occur in mountainous regions, care was taken to avoid sites with steep slopes and colluvial soils. Thus, the textural characteristics of the investigated soils strongly reflects the nature of the underlying bedrock. Sites in the midlands region and those in the eastern escarpment which are developed on non-quartzitic parent materials are characterised by loam and clay-loam soils, whereas all of the Cape soils and eastern escarpment soils formed above quartzite are very sandy.

Atmospheric pollution in South Africa is to large extent concentrated in the highly industrialised central and eastern highveld region encompassing the provinces of Gauteng and Mpumalanga. Thus, of the areas investigated for this study, it is only the eastern escarpment region which is likely to be markedly influenced by atmospheric pollution inputs. Olbrich and du Toit (1993) report total acid deposition (i.e. $[SO_4^{2-} + NO_3^-]$ - total base cations in forest throughfall) levels in this region of approximately 0.5 $kmol_c\ ha^{-1}\ yr^{-1}$, which are in the lower end of the range for polluted areas in northern Europe and North America. Although data for the midlands and Cape regions are limited, they are not located close to any major pollution sources and atmospheric deposition of pollutants is therefore likely to be negligible. These areas are, however, strongly influenced by the deposition of marine salts. This is particularly prevalent at sites in the maritime Cape regions, but is also evident in the midlands region, parts of which are regularly influenced by ocean-derived fogs. Even the eastern escarpment region, which is approximately 200 km from the nearest coastline, is affected by ocean-derived fogs which would be expected to impart a maritime signature to precipitation composition. Rainfall chemistry data indicate that, due to the strong marine influence, total solute deposition levels (i.e. wet and dry deposition) are likely to be significantly higher in the unpolluted Cape regions than in areas affected by atmospheric pollution (Table 3.2). In addition, inputs of oceanic SO_4^{2-} at maritime sites may in some cases exceed anthropogenic SO_4^{2-} inputs in the allegedly polluted eastern escarpment region.

Table 3.2: *Rainfall composition data for sites close to or within study areas. Sample types are: MAP - mean annual precipitation (values in brackets are estimates). Bd - bulk deposition; Wd - wet deposition only. * - These sulphate values are for forest throughfall and provide maximum estimates of bulk deposition concentrations in open areas.*

Region	Site	MAP (mm)	Type	pH	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Source
							$\mu mol_c\ L^{-1}$						
EE	Frankfort	1254	Bd	4.94		24	51*		6	11	92	13	1
EE	Long Tom	1853	Bd	4.60		19	52*		5	6	44	6	1
EE	Frankfort	1254	Wd	4.68		15	19		5	9	14	7	1
EE	Long Tom	1254	Wd	4.90		11	20		4	8	11	8	1
EE	Misty Mountain	(1200)	Wd	4.71	10	9	18	16	4	6	10	7	2
EE	Cairns (Nelspruit)	(800)	Wd	4.85	11	14	27	19	4	19	21	8	2
MI	Ladysmith	796	Wd	4.32	8	18	37	8	4	23	15	4	3
MI	Winterton		Bd	4.80	70	5	61	47	12	27	69	30	4
WC	Jakkalsrivier	(1000)	Bd	4.65	170	1	110	179	19	8	30	36	4
WC	Jonkershoek	(1500)	Bd	4.85	112	1	70	112	13	3	38	24	4

Data sources: 1 - Olbrich and du Toit (1993); 2 - Turner and de Beer (1993); 3 - Turner (1993); 4 - van Wyk and Stock (unpublished data).

3.2. SAMPLING METHODS

Soil sampling was carried out at suitable sites where the edge of a pine plantation adjoins undisturbed grassland or fynbos vegetation and where no change in parent material, slope or aspect occurs across the forest-virgin boundary (detailed site information is provided in Appendix A). Thirty-nine sites were originally selected but one of these (site EE1) was judged unsuitable at an early stage due to obvious differences in clay content between the forest and grassland soils. Twenty three of the sites were sampled during the current study. The remaining sixteen sites were sampled by du Toit (1993) and samples were kindly made available for further analysis.

Only topsoils were sampled for this study. Afforestation impacts are likely to be most prominent in the upper soil horizons. Data obtained from topsoil samples are, therefore, believed to provide an indication of the maximum possible impact of forests on soil and water chemistry. In addition, because this is a comparative study, it was important to sample a horizon that could be directly compared for all forest and virgin soil pairs. This was not possible with the organic horizon as it was usually absent from the grassland and fynbos soils, and was highly variable within the forest sites. Samples were taken from the upper mineral soil horizon between the depths of 0 and 15 cm below the base of the organic horizon. In order to obtain a representative sample of both the forest and grassland soils, ten samples were taken of each. These were taken at regular intervals (~ 20 m) in two rows (of 5 samples) laid out parallel to and at different distances (~ 10 and ~ 30 m, respectively) from the forest-grassland boundary. Samples were obtained by removing surface litter and the organic horizon and excavating a 15 cm deep, 25 by 25 cm hole into the upper A horizon. The excavated soil was placed on a plastic sheet and split on site (by the cone and quarter method) to obtain a final sample mass of approximately 500 g. All samples were air-dried and passed through a 2mm sieve prior to storage and analysis. The individual samples from each site were combined in equal proportions to form two composites representing the forest and grassland soil, respectively. With the exception of the "edge effect" study reported in Chapter 6, all of the analytical work reported in this thesis was carried out on these composite samples. Duplicate samples were taken from four sites in the eastern escarpment and two in the western Cape in order to assess sampling variability. The results of this are reported in Appendix E. Duplication of sampling at all sites was precluded due to practical considerations.

Spot sampling of stream waters draining pine plantations and natural grassland or fynbos catchments was undertaken in conjunction with the soil sampling. The main characteristics of these streams and the sampling methods that were employed are discussed in Chapter 7.

3.3. STATISTICAL TREATMENT

The impact of afforestation on virgin grassland and fynbos soils was evaluated statistically using the non-parametric Wilcoxon matched pairs test. This method is applicable to paired data and is particularly useful in cases where the effect being evaluated, in this case the effect of afforestation, is obscured or overshadowed by variations *between* the subjects (in this case by variation between sites). The Wilcoxon matched pairs test eliminates the variance resulting from initial differences between subjects (i.e. sites) by working only with the differences between the two values obtained for each subject. Test statistics are calculated for these difference values to assess whether they deviate significantly from zero. Because of the elimination of between-subject variance, tests for dependent samples are more sensitive than those for independent samples (StatSoft Inc., 1995). The Wilcoxon matched pairs test was chosen in preference to the parametric t-test for dependent samples as, for most variables, the data are not normally distributed, and because the non-parametric approach is more suitable for the relatively small sample sizes being evaluated. Statistical significance is assessed using p-values which indicate the likelihood of making an error in accepting the test result. A result is generally considered to be statistically significant if it can be accepted at the 95 % confidence level (i.e. if $p \leq 0.05$).

All statistical test results obtained for *inter-region comparisons* of forest and/or virgin soil properties were obtained using the Kruskal-Wallis ANOVA by ranks (StatSoft Inc., 1995). This is the non-parametric equivalent of an analysis of variance (ANOVA) for evaluating differences between the means of two or more groups. Statistical significance is assessed in the same manner as for the Wilcoxon matched pairs test.

Comparisons between different regions and between forest and virgin soils within each region are illustrated graphically using box and whisker diagrams. These diagrams summarise the data for each region in terms of a median value, an interquartile range (shown as a box), maximum and minimum values (represented by lines or "whiskers"), outliers and extremes (shown as markers). Outliers are defined as values which satisfy the following conditions:

> [75th percentile + 1.5 (inter-quartile range)], or

< [25th percentile - 1.5 (inter-quartile range)].

Extreme values are defined as follows:

> [75th percentile + 2 (inter-quartile range)], or

< [25th percentile - 2 (inter-quartile range)].

All statistical calculations and graphics, including the calculation of summary statistics and frequency distributions, were carried out using the STATISTICA (version 5) computer programme (StatSoft Inc., 1995).

4. CHARACTERISATION OF THE SOIL SOLID PHASE

4.1. INTRODUCTION

This chapter presents the results of textural, mineralogical and chemical analyses of the soil solid phase. With the exception of organic carbon concentrations and possibly the total concentrations of more mobile elements (e.g. the alkali and alkaline-earth elements), the data obtained from these analyses relate to soil properties which would not be expected to be influenced by the relatively recent afforestation of virgin grassland and fynbos soils. Thus, these data provide a means of confirming the pre-afforestation similarity of paired forest-virgin soils. In addition, the nature of the soil solid phase, particularly the soil mineralogy and clay concentration, is likely to have a significant bearing on how other soil properties are influenced by afforestation. Therefore, the data presented in this chapter provide an important basis for the interpretation of afforestation impacts on other soil properties described in the chapters which follow.

4.2. MATERIALS AND METHODS

4.2.1. Clay content and bulk composition

Clay concentrations for the 18 sites sampled by du Toit (1993) were determined qualitatively in the field and therefore only provide rough estimates of the true soil clay content. The clay concentration data for the remainder of the samples (22 sites, 44 samples) were obtained by the Lowy pipette method (Gee and Bauder, 1986; determinations carried out at the Institute for Soil Climate and Water, Pretoria). Organic carbon was removed by oxidation prior to the determination of clay content. These data can be qualitatively evaluated by comparison with quantitative bulk composition data which were obtained by XRF-spectrometry (Appendix B). Recalculation of the chemical composition of the clay fraction, based on the assumption that the sand and silt fraction is made up entirely of quartz, yields very low or negative SiO_2 values which are obviously erroneous. This indicates that the clay concentrations determined by the pipette method significantly underestimate the true soil clay content, resulting in an overestimation of the proportion of sand and silt. This effect is believed to result from incomplete dispersion of the clay fraction during the analytical procedure, possibly as a result of high soil organic matter contents (see section 4.3.3 below) and an associated high degree

of clay aggregation (Gee and Bauder, 1986). Because of these apparent analytical problems, the clay concentration data can only be regarded as qualitative, or semi-quantitative at best, and detailed interpretation based on these data is not feasible. However, broad variations in clay content between sites and, to some extent, differences between paired forest and virgin soils can be evaluated in a qualitative manner.

4.2.2. Soil mineralogy

X-ray diffraction (XRD) analysis was carried out on clay fractions from ten forest and five virgin composite soil samples. These were chosen such that sandy and clay-rich soils from each of the four regions are represented. The aim of this analysis was to identify the dominant minerals present in the soils of this study and, for selected sites, to evaluate mineralogical similarities and differences between the forest and virgin soils.

The clay fractions for XRD analysis were obtained by repeated dispersion (in a pH 10 Na_2CO_3 solution) and removal of the supernatant following settling of the > 2 μm fraction. The < 2 μm clay fraction contained in this supernatant was concentrated by flocculation (pH reduced to below 7 and NaCl added) and removal of the clear supernatant, and was dialysed for 48 to 62 hours (using tap water followed by de-ionised water) to remove excess salts. Organic matter was removed from all of the clay suspensions by treatment with H_2O_2 and heating to approximately 75 °C in a water bath. The clay fractions obtained in this way were sedimented onto glass slides and dried at room temperature to provide orientated samples. These were analysed with a Phillips PW1390 X-ray diffractometer using CuKα radiation (λ = 1.542 Å).

4.2.3. Organic carbon

The concentration of organic carbon was determined for all samples using the Walkley-Black dichromate oxidation method (Nelson and Sommers, 1982).

With the exception of the XRD data, which are presented graphically below, all analytical results are given in Appendix C.

4.3. RESULTS AND DISCUSSION

4.3.1. Soil texture and bulk composition

4.3.1.1 Comparison of paired forest and virgin soils

Clay concentration and bulk SiO_2, Al_2O_3 and Fe_2O_3 data for *individual* forest/virgin soil pairs (Figure 4.1 and 4.2.a to c; data given in Appendix C) indicate that, although differences are evident, these are in most cases relatively small in relation to inter-site variations. In the case of clay concentration, the differences in absolute terms are in all cases less than 4.5 % (Figure 4.1) and may, to a large extent, reflect analytical variance. This is particularly likely in the case of the sandy soils for which very low clay contents and, in some cases, relatively high concentrations of organic matter are likely to cause substantial analytical error.

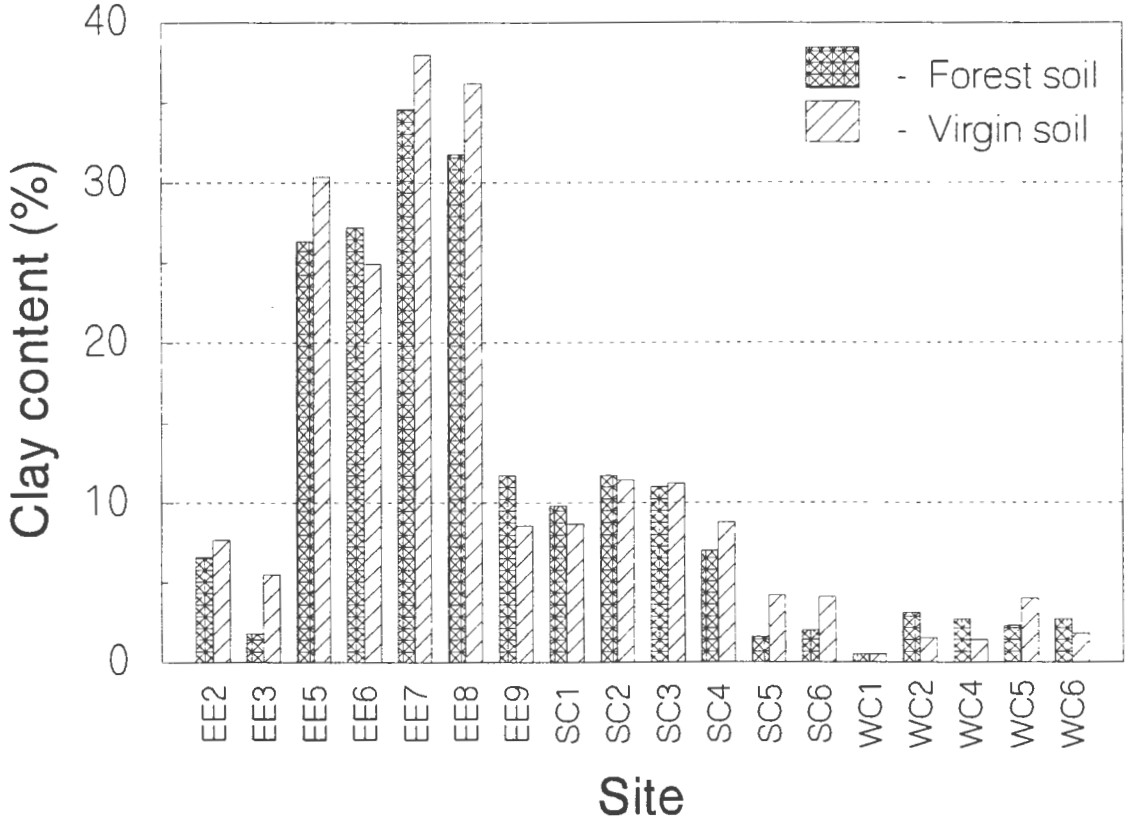

Figure 4.1: *Clay concentrations for forest-virgin soil pairs. Only clay contents obtained by the pipette method are shown.*

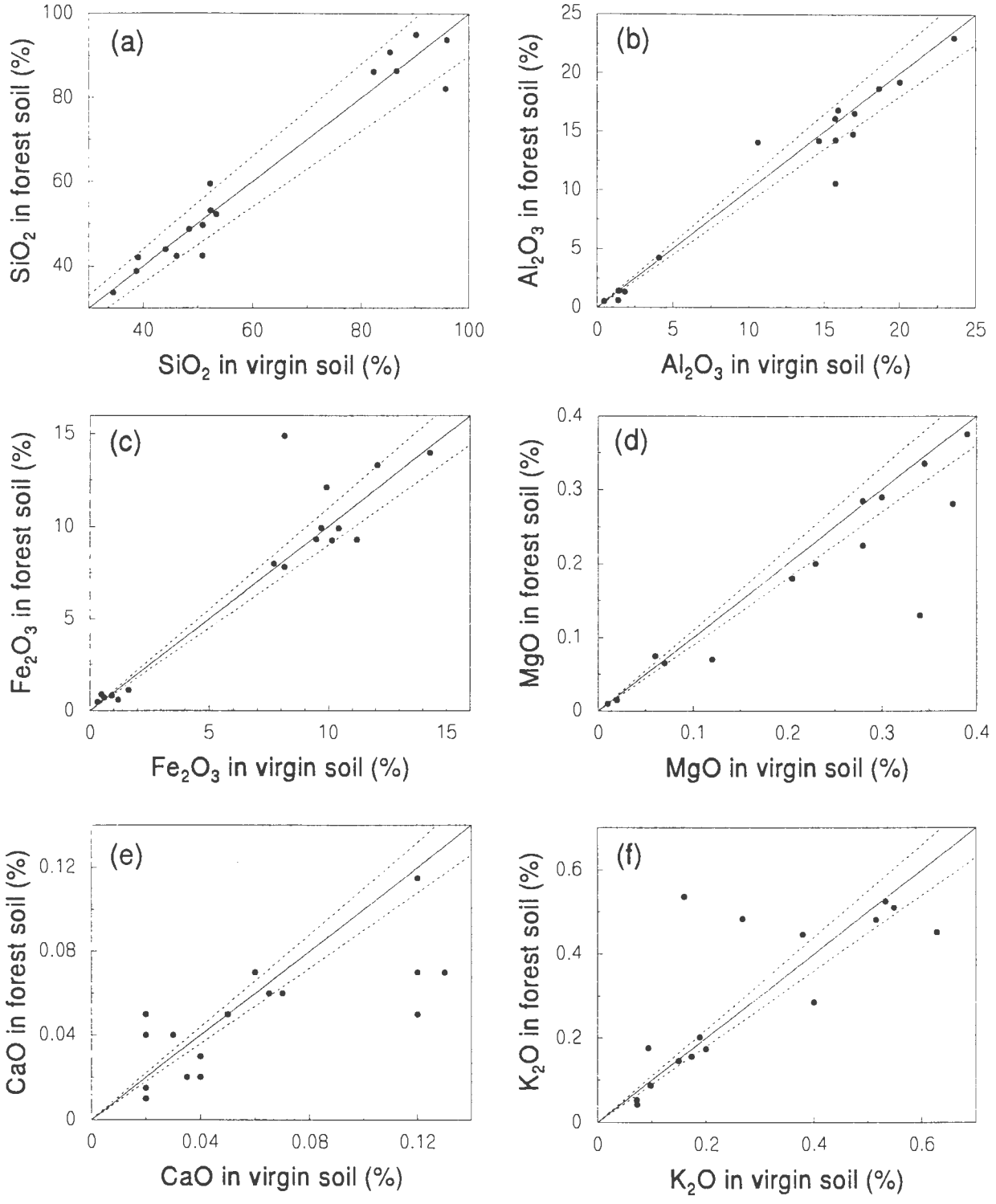

Figure 4.2: *Comparison of bulk concentrations of selected elements (expressed as oxides) in forest and virgin soils. Each point on the graphs represents a forest-virgin soil pair with the concentration value for the virgin soil plotted on the horizontal axis and that of the forest soil on the vertical axis. The solid line represents a 1:1 correlation (i.e. no difference between forest and virgin soil) and the dashed lines represent a 10 % deviation from equality on either side of this line.*

The bulk SiO_2, Al_2O_3 and Fe_2O_3 data confirm the compositional similarity of forest-virgin soil pairs, with only a small number of sites showing differences in excess of 10 % (Figure 4.2.a to c). These differences may reflect minor mineralogical variations in the original (pre-afforestation) soils, but in absolute terms they do not represent major compositional differences and are unlikely to significantly influence the soil properties being used to assess afforestation impacts. Nonetheless, it is possible that in a small number of cases, true afforestation impacts may be obscured or over-printed by differences which are inherited from the original soils. As a result of this, it may not be possible in some cases to directly equate forest-virgin differences *for individual sites* to afforestation impacts. Therefore, quantitative assessment of afforestation impacts should only be made in a statistical manner for the entire site population or for appropriate subsets. Statistical analysis confirms that, with the exception of bulk MgO concentration, there is no significant *overall* difference (at the 10 % significance level) in clay content or bulk elemental composition between the paired forest and virgin sites (Table 4.1).

Table 4.1: *Statistical test results and summary statistics for clay content and bulk composition data. Data for forest and virgin soil pairs were analysed using the Wilcoxon matched pairs test (Test results). bld - below limit of detection.*

	Test results		**Bulk composition summary statistics (%)**						
	n	p		Clay-rich soils (n = 22)			Sandy soils (n = 12)		
Clay	36	0.152		Min.	Mean	Max.	Min.	Mean	Max.
SiO_2	17	0.786	SiO_2	33.7	46.2	59.5	82.2	89.0	95.85
TiO_2	17	0.863	TiO_2	0.79	1.16	1.72	0.23	0.45	0.85
Al_2O_3	17	0.304	Al_2O_3	10.6	16.5	23.6	0.47	1.85	4.25
Fe_2O_3	17	0.442	Fe_2O_3	7.70	10.4	14.9	0.32	0.83	1.62
MgO	17	0.073	MgO	0.07	0.24	0.39	bld	0.01	0.10
CaO	17	0.379	CaO	0.02	0.10	0.66	0.01	0.04	0.10
Na_2O	17	0.556	Na_2O	0.04	0.73	3.30	0.05	0.11	0.23
K_2O	17	0.269	K_2O	0.15	0.41	1.22	0.04	0.18	0.53
P_2O_5	17	0.550	P_2O_5	0.09	0.13	0.19	0.01	0.03	0.07
H_2O	17	0.844	H_2O	3.06	5.12	7.63	0.23	1.14	2.21
LOI	17	0.740	LOI	13.3	19.0	28.0	1.73	6.18	12.27
Mn	17	0.434	Mn (mg L^{-1})	105	505	1594	8	51	96.77

The results presented in Table 4.1 and Figure 4.2.d suggest that there is a consistent reduction in total MgO concentration under forest relative to adjacent virgin soils. Possible causes of this depletion include the enhanced uptake of magnesium by the pine forests relative to the original grassland or fynbos vegetation and enhanced leaching under pine forests. The relative importance of these two processes with respect to base cation loss will depend on factors such as forest productivity and evapotranspiration rates. These are discussed in more detail in Chapter 5. The bulk CaO and K_2O concentration data show a high degree of variability (Figure 4.2.e and f) which, to a large extent, is likely to be a reflection of analytical uncertainty at the low concentration levels being determined. However, the data do suggest a tendency (not statistically significant) for lower calcium and possibly higher potassium in forest soils relative to their virgin equivalents.

4.3.1.2. Clay content and parent materials

The soil samples can be subdivided on the basis of clay content into two broad groups (Figure 4.3). Those developed on quartzitic parent materials have clay contents ranging from 0.5 to approximately 10 %. The lowest clay contents (≤ 4 %) occur in soils developed on pure quartzite in the western Cape region. Higher clay contents (5 - 10 %) in sandy soils of the eastern escarpment and southern Cape presumably reflect slightly more arkosic or argillaceous parent materials. The second group of sites have clay contents which range from 25 to 55 %. These soils occur on a wide range of parent materials including shale, dolerite, dolomite, granite and alluvium. Within this group there is no consistent relationship between clay content and parent material lithology, possibly due to the large analytical error associated with the clay determinations.

A lack of lithological variability in the afforested regions of the western and southern Cape, as well as those of the midlands, precluded the selection of sites of widely varying clay content within each of these regions. Thus all of the soils from the southern and western Cape are sandy (clay < ~ 10 %) whereas those from the midlands, all of which are developed on shale or dolerite, are clay rich (> ~ 25 % clay). It is only in the eastern escarpment region that both sandy and clay-rich soils could be sampled without extending into areas of significantly different climate and/or physiography. Three of the sites sampled in this region comprise sandy soils (4 to 10 % clay). Despite a wide variety of parent material lithologies, the clay-

rich soils of the eastern escarpment appear to display a relatively narrow range of clay contents, with values ranging from 25 to approximately 35 %. Qualitative estimation of clay content in these samples, as well as the bulk compositional constraints discussed above (section 4.2.1), indicate that these values significantly underestimate the true soil clay content and should therefore be regarded as minima.

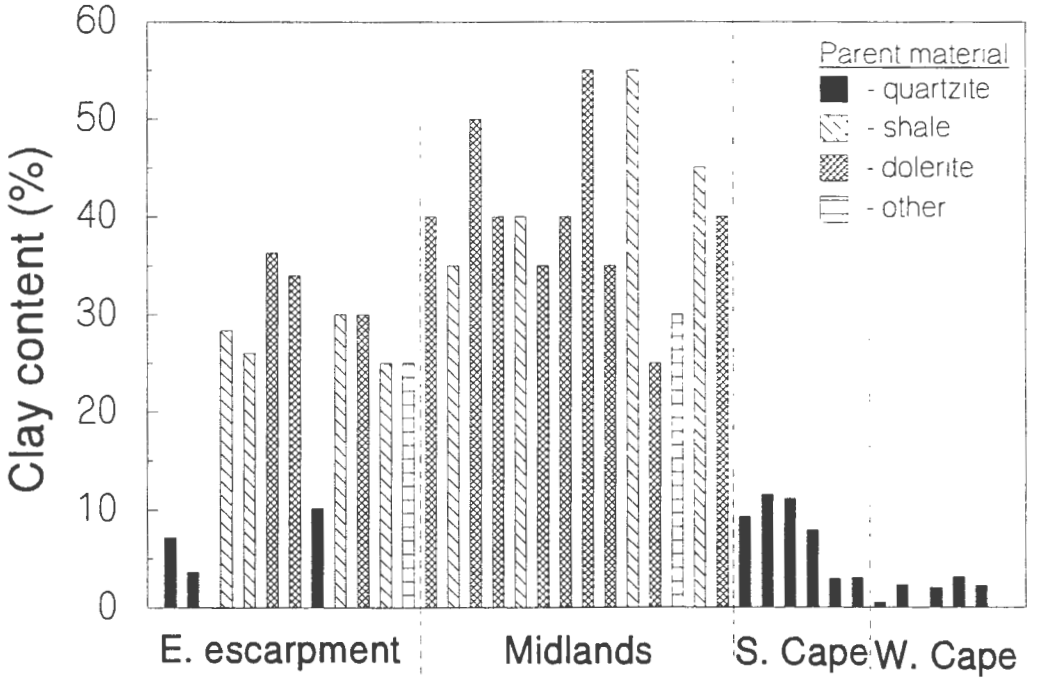

Figure 4.3: *Clay concentrations and parent material lithology. Each bar represents one site and clay contents are the averages of forest-virgin soil pairs. No data is available for the third eastern escarpment and the third western Cape sites. "Other" parent materials include alluvium (midlands) and granite (eastern escarpment).*

4.3.1.3. Bulk composition and degree of weathering

The summary statistics for both clay-rich and sandy soils (Table 4.1) indicate that the soils consist almost entirely of silica, sesquioxides and organic matter (as reflected by the high loss on ignition values), and confirm the highly weathered and leached nature of the soils investigated in this study. Titanium concentrations similar to or higher than those which would be expected for their associated parent materials (i.e. 0.8 to 1 % for dolerite and shale; less than 0.5 % for sandstone and quartzite; Marsh and Eales, 1984; Geological Survey, 1964) provide further evidence in support of a high degree of leaching, which has resulted in the preferential concentration of this highly immobile element. Calculation of recognised indices

based on the ratio of silica to sesquioxides in the clay fraction is precluded by a lack of quantitative data on soil clay concentrations (see section 4.2.1). However, it is possible to calculate chemical index of alteration values (CIA; Nesbitt and Young, 1984) from the bulk soil data based on the formula:

$$CIA = 100 \times [Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)]_{molar\ ratio}$$

where CaO^* represents Ca in silicate phase only (i.e. Ca in carbonate and phosphate minerals is excluded).

CIA values for the clay rich soils generally range from 95 to 98 indicating extreme weathering (Appendix C, Table C2). Although values for the sandy soils are generally significantly lower, ranging from approximately 68 to 89, these may not reflect reduced degrees of weathering. This is particularly true for the eastern escarpment sites where sandy soils occur in close proximity to clay-rich soils with very high CIA values. The lower values in sandy soils may reflect significant dilution of the CIA components by quartz, resulting in CaO, Na_2O and K_2O levels which are close to detection limits and therefore which may not be reliably determined. In addition, the quantity of calcium, potassium and to some extent sodium, in these quartz-dominated soils is likely to be significantly influenced by soil surface properties and, in particular, by interactions with soil organic matter, which are not accounted for in the formulation of the CIA. Thus the CIA may not be a reliable indicator of weathering or leaching intensity in very quartz-rich soils.

4.3.2. Clay mineralogy

The XRD results are presented in Figures 4.4 to 4.6 and are summarised in Table 4.2. For the purposes of the following discussion the samples have been grouped into clay-rich and sandy types.

4.3.2.1. Clay-rich soils

All of the clay-rich soils investigated (Figures 4.4 and 4.5.a) contain abundant kaolinite, undifferentiated 2:1 layer silicate and gibbsite. The dominant goethite XRD peak at ~ 4.16 Å is well developed in the EE4 samples, but occurs as a low intensity and rather diffuse peak in most of the other clay-rich samples investigated. While this may suggest relatively low goethite concentrations in these samples, it may also result from a low degree of goethite

crystallinity, and/or a relative enhancement of layer silicate peak intensities due to the preferred orientation of the sample. Thus, little quantitative significance can be attached to these data. The undifferentiated 2:1 layer silicate is prominent in all of the clay-rich samples investigated and is characterised by a well defined relatively narrow peak at 14.26 Å. This corresponds with the d-spacing of vermiculite, smectite and their hydroxy-interlayered equivalents (Barnhisel and Bertsch, 1989). It is not possible to distinguish between these minerals without further treatment which is beyond the scope of this preliminary investigation. However, the highly weathered nature of the soils (as supported by the presence of gibbsite) and data from previous studies of similar soils in South Africa (le Roux, 1973; Bühmann, 1986), suggests that the XRD peak probably represents hydroxy-interlayered vermiculite or smectite, often described as pedogenic chlorite. Other phases present in the clay fraction of the clay-rich soils include quartz, possible hematite (in EE7F only) and small amounts of probable mica in the samples from site MI1. Although too few samples were analysed to adequately evaluate the relationship between the clay mineralogy and parent material lithology, no obvious trends are evident.

Table 4.2: *Summary of clay mineralogical and other relevant data for samples analysed by XRD. Abbreviations: Q - quartz; K - kaolinite; Ch - pedogenic chlorite; Gi - gibbsite; Go - goethite; Ha - hematite; Mi - mica; Is - interstratified 2:1 layer silicates. Brackets denote minor phases and question marks indicate that the mineral identification is not certain.*

Site	Sample	Vegetation	Clay%	Parent material	Clay mineralogy (XRD)
EE2	EE2F	forest	6.6	quartzite	Q, Ch, K
EE4	EE4F	forest	30	shale	K, Ch, Gi, Go
	EE4N	grassland	30	shale	K, Ch, Gi, Go
EE7	EE7F	forest	35	dolerite	Gi, Ch, K, (H?), (Go)
	EE7F	grassland	38	dolerite	K, Ch, Gi, Go
EE8	EE8F	forest	32	dolorite	Ch, Gi, K, Q, (Go)
MI1	MI1F	forest	40	dolerite	Q, Ch, K, Gi, Go, (Mi?)
	MI1N	grassland	40	dolerite	Ch, K, Q, Gi, Go, (Mi)
MI2	MI2F	forest	35	dolerite	Ch, Gi, Q, K, (Go)
SC3	SC3F	forest	11	quartzite	Q, K, Is, Mi
	SC3N	fynbos	11	quartzite	Q, K, Ch, Is, Mi
SC4	SC4F	forest	7.0	quartzite	Q, Is, Mi, K
WC2	WC2F	forest	2.7	quartzite	K, Q, Gi?, Is, (Mi)
WC3	WC3F	forest	2.3	quartzite	K, Ch, Q, Gi, Is, Mi, (Go)
	WC3N	fynbos	4.0	quartzite	K, Q, Gi, Ch, Is, Mi

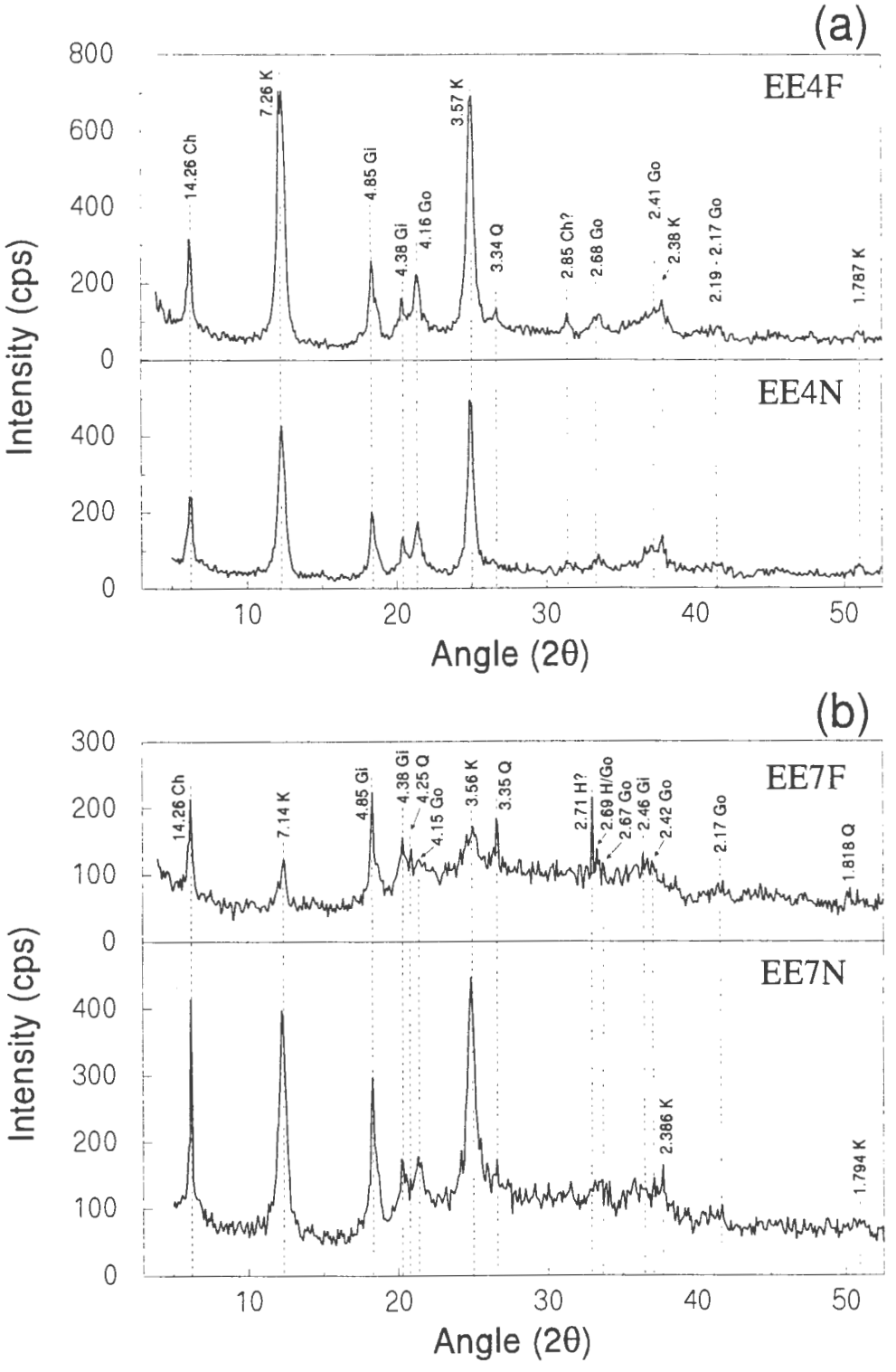

Figure 4.4: *Paired XRD scans of oriented clay fractions from clay-rich soil samples. Sample numbers are given in the upper right hand corner of each scan (F - forest; N- grassland). Peaks are annotated with their corresponding d-spacings (in Å) and the mineral or minerals to which they have been assigned. Abbreviations: Ch - chlorite; K - kaolinite; Gi - gibbsite; Go - goethite; Q - quartz; H - hematite; Mi - mica.*

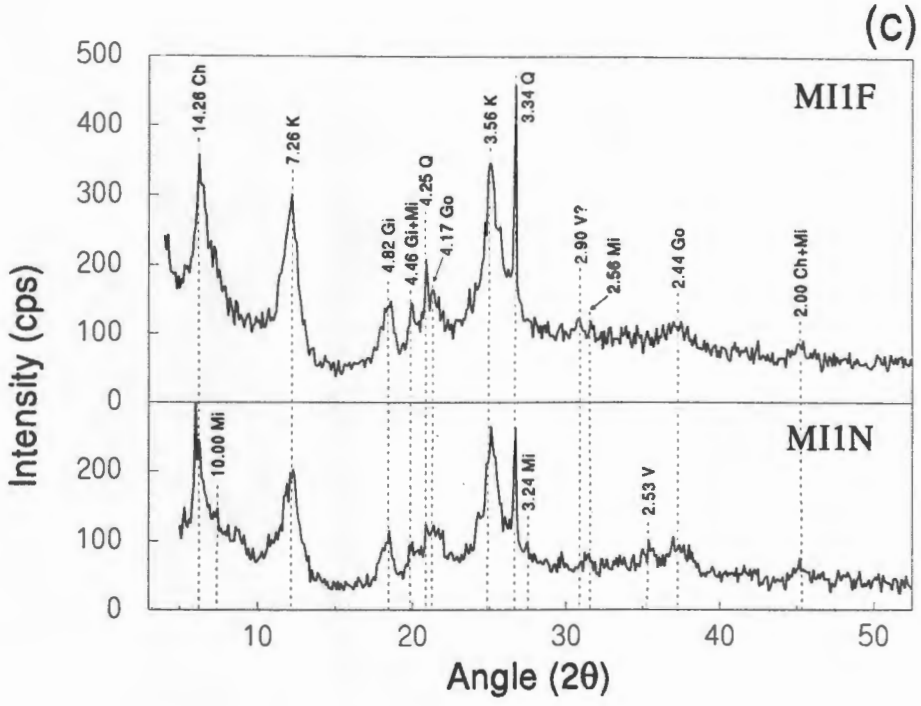

Figure 4.4: *Continued.*

4.3.2.2. Sandy soils

In contrast to the above, the sandy soils investigated (Figure 4.5.b and 4.6) are mostly devoid of gibbsite and goethite, reflecting their siliceous, aluminium-, iron- and magnesium-poor parent materials. Gibbsite occurs only in very minor amounts in the WC3 soils (Figure 4.6) and may be present in poorly-crystalline form in sample WC2F (Figure 4.5.b). The presence of poorly crystalline gibbsite in this sample is suggested by the well developed but rather broad peak at 4.85 Å and the absence of an associated peak at 4.35 Å (i.e. the gibbsite (110) reflection; Hsu, 1989). The clay fraction of the sandy soils is dominated by quartz, kaolinite and undifferentiated 2:1 layer silicates. In contrast to the well defined narrow 14.26 Å peak evident in the eastern escarpment soils, XRD scans for the soils from the southern and western Cape generally display a broad band of peaks from ~ 14 to ~ 10 Å suggesting the presence of interstratified mica and 2:1 clay minerals (i.e. chlorite, vermiculite and/or smectite). A strong 14.26 Å peak in samples SC3N, WC3F and WC3N may indicate the presence of pedogenic chlorite similar to that evident in EE2F and the clay-rich samples. Unidentified peaks at 2.24 Å and 2.14 Å in sample SC4F (Figure 4.5.b) may indicate the presence, in relatively minor amounts, of an additional mineral. The peaks could not be readily matched with d-spacings of common soil minerals and more detailed analysis (including pre-treatments) is beyond the scope of this preliminary investigation.

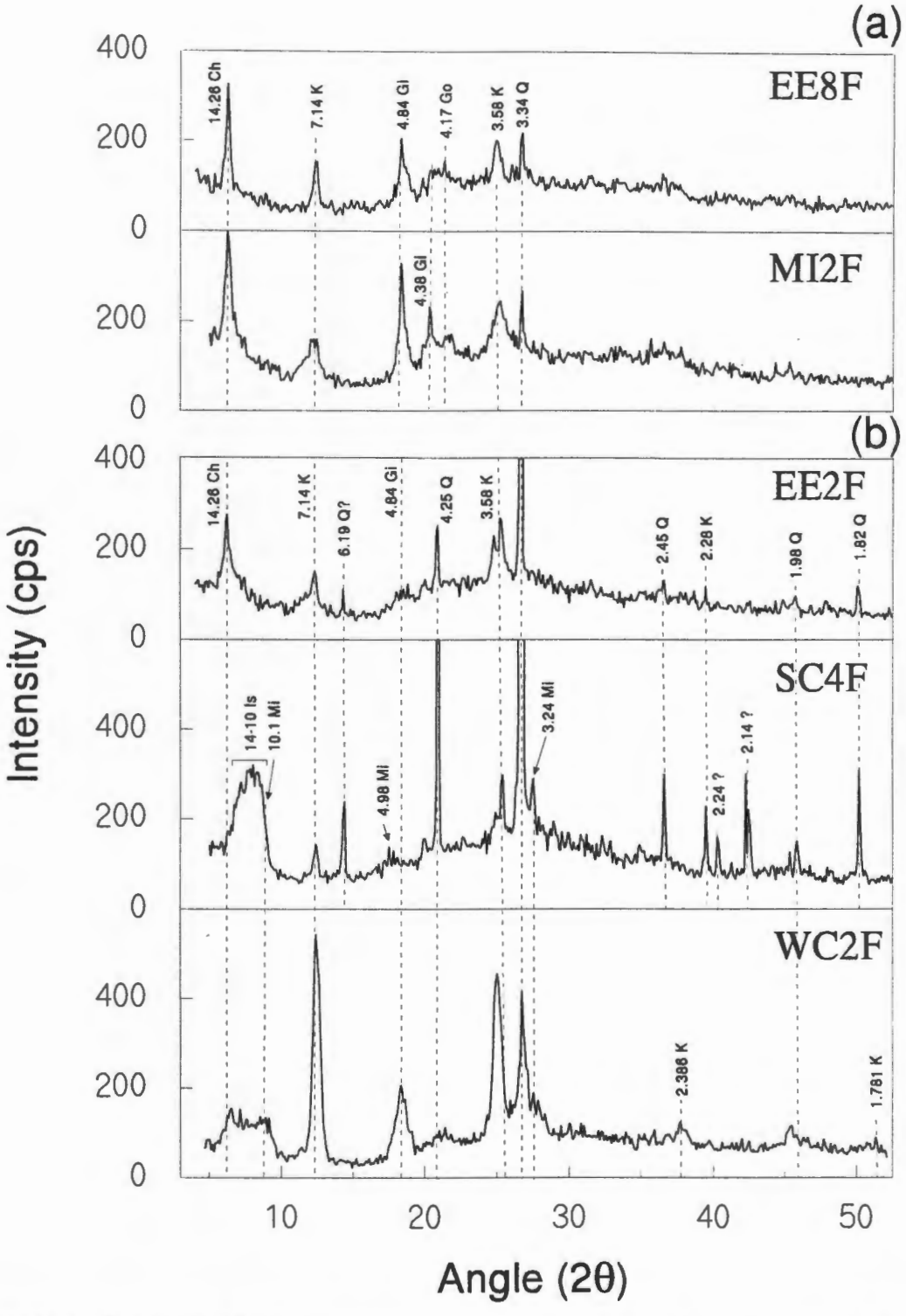

Figure 4.5: *XRD scans of oriented clay fractions from clay-rich (a) and sandy (b) forest soils. Sample numbers are given in the upper right hand corner of each scan. Peaks are annotated with their corresponding d-spacings (in Å) and the mineral or minerals to which they have been assigned. Abbreviations: Is - interstratified 2:1 layer silicate; Ch - chlorite; K - kaolinite; Gi - gibbsite; Go - goethite; Q - quartz; H - hematite; Mi - mica; V - vermiculite.*

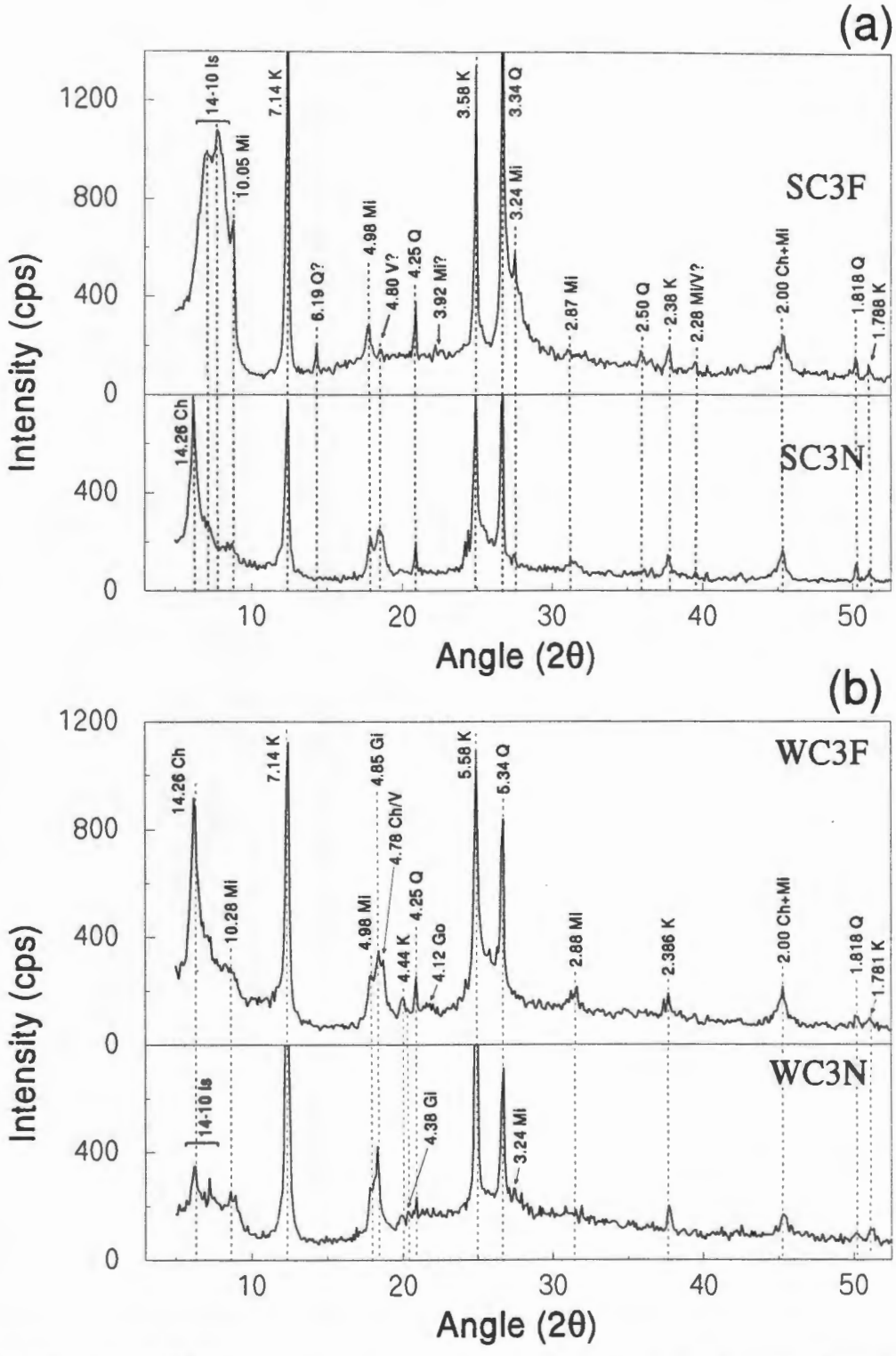

***Figure 4.6**: Paired XRD scans of oriented clay fractions from sandy soils. Sample numbers are given in the upper right hand corner of each scan (F - forest; N - fynbos). Peaks are annotated with their corresponding d-spacings (in Å) and the mineral or minerals to which they have been assigned. Abbreviations: Is - interstratified 2:1 layer silicate; Ch - chlorite; K - kaolinite; Gi - gibbsite; Go - goethite; Q - quartz; H - hematite; Mi - mica; V - vermiculite.*

The presence of interstratified 2:1 layer silicates and the persistence of mica in the Cape sites may indicate a less intense weathering regime in these regions compared to that of the eastern escarpment and the midlands. An alternative explanation is that the observed differences in the 2:1 layer silicate assemblage reflect the presence of different precursor minerals in the soil parent material. The persistence of mica and the *apparent* lack of extensive clay-mineral weathering in the Cape sites may result from the likely predominance of muscovite (as opposed to less stable primary minerals such as pyroxenes, feldspars and biotite) as a precursor for 2:1 layer silicates in the soil.

4.3.2.3. Mineralogical comparison of forest-virgin soil pairs

The XRD scans for paired forest-virgin soil samples (Figure 4.4 and 4.6) indicate that mineralogical differences between forest and virgin soils at each of the sites are limited to minor variations in the relative proportions of minerals present. Site SC3 shows the most prominent apparent differences between forest and virgin soils. The scans for this site suggest a greater proportion of interstratified 2:1 layer silicates in SC3F (forest soil) than in SC3N (fynbos soil), whereas the latter sample displays a well developed 14.26 Å peak which is not evident in the scan of the forest soil. While these differences in 2:1 layer silicate mineralogy may result from differences in parent material mineralogy and/or other soil forming factors (e.g. drainage), it is equally possible that they reflect minor differences in particle size, degree of crystallinity and/or degree of preferred orientation introduced during sample preparation.

As for the bulk composition data discussed above, the XRD data suggest minimal pre-afforestation variability in soil mineralogy. The observed minor variations in mineral proportions for certain sites may be artifacts of the sample preparation procedure. However, even if they do reflect real differences between samples, these would be minor and would not be expected to have a major influence on other soil properties (e.g. soil pH, exchangeable cation composition and soil solution composition).

4.3.3. Organic carbon

The soils of this study generally contain relatively high concentrations of organic carbon, although distinct regional differences are evident (Figure 4.7). Soils of the Cape regions contain significantly (Kruskal-Wallis $p < 0.001$) lower concentrations of organic carbon (0.2 to 3 %, average - 1.9 %) than those of the eastern escarpment and midlands (4.6 to 12 %, average - 5.6 %), with values in the western Cape generally being slightly lower than those in the southern Cape. These regional differences probably stem from a combination of soil textural, climatological and biological factors. Multiple regression analysis indicates that clay content and, to a lesser extent mean annual rainfall and altitude, can explain a significant proportion of the organic matter variability in both forest and virgin soils, but relatively low R^2 values (0.47 and 0.38 respectively) indicate that there are clearly other factors involved. High levels of organic carbon are evident in the soils of grassland ecosystems in the summer rainfall regions of the eastern escarpment and midlands. In the southern and western Cape, the very low soil clay content, which limits the ability of soils to bind and retain organic matter, as well as low rates of organic matter turnover in the fynbos ecosystem are likely to be the most important factors limiting the concentration of organic carbon in soils. The very high relative concentration of organic carbon at one of the southern Cape sites (SC4; extreme value on Figure 4.7.a and maximum value in Figure 4.7.b) is believed to be due to the cold and damp conditions prevailing at this site which occurs on a relatively steep, south-facing slope.

Changes in organic carbon are likely to be strongly influenced by site history. In view of this, it could be argued that a regional investigation of the impact of afforestation is of limited value and the data should be assessed on a site for site basis. Statistical analysis indicates, however, that despite some variability, the concentration of organic carbon is significantly ($p = 0.030$) reduced under forests relative to their virgin equivalents (Table 4.3; Figure 4.7.c). Stratification of the data on the basis of region and clay content indicates that this afforestation-induced reduction in the organic carbon concentration of the topsoil mineral horizon is primarily a feature of the eastern escarpment region, as forest-virgin differences in other regions are not statistically significant at the 95% confidence limit. This is particularly true if the samples from site EE9, sandy soils which displays anomalous large increases in organic carbon under forest, are excluded. Data for the naturally organic carbon-poor western Cape sites, suggests that, if anything, afforestation has resulted in minor increases in the amount of organic matter (not statistically significant, $p = 0.753$). This suggests that changes tend to be greater for soils which are naturally rich in organic carbon. There is no consistent relationship, however, between the original concentration of organic carbon and the reduction associated with afforestation (Figure 4.8).

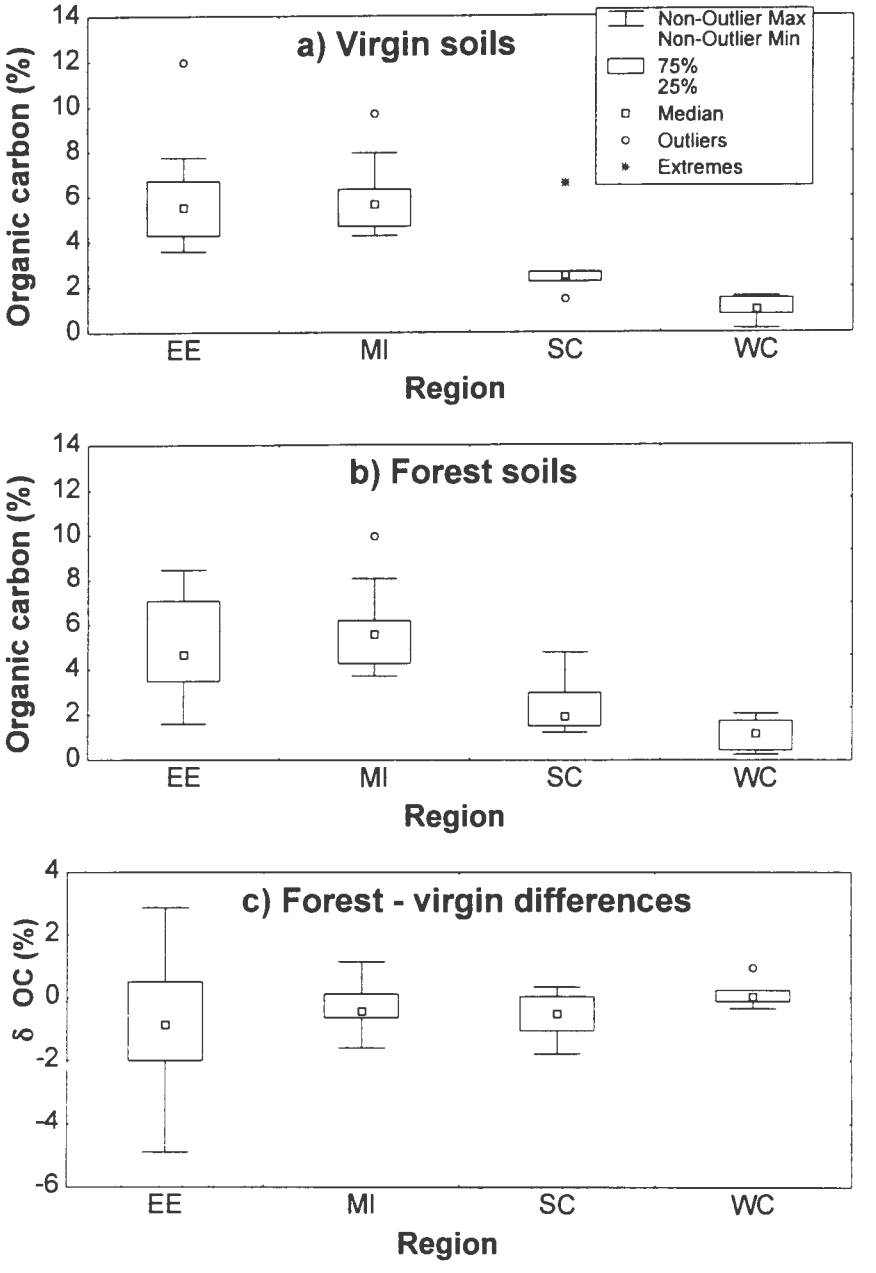

Figure 4.7: *Box and whisker plots summarising soil organic carbon concentration data for individual regions. a) Virgin soils, b) Forest soils, c) Forest-virgin differences ($\delta OC = OC_{forest}$ minus OC_{virgin}). EE - eastern escarpment, MI - midlands, SC - southern Cape; WC -western Cape. See section 3.3 for definitions of outliers and extreme values.*

Table 4.3: *Results of statistical analysis of forest-virgin differences in organic carbon concentration using the Wilcoxon matched pairs test. Results are given for the entire data set (i.e. all regions) as well as for subsets based on region and clay content. Clay-rich - > 20 % clay; Sandy - < 15 % clay. n - number of forest/virgin pairs analysed; p - statistical significance level; p^1 - statistical significance level when site EE9 is excluded. Underlined p value indicates a positive difference (i.e.overall increase in organic carbon concentrations under forest).* * - significant at the 95 % confidence level.*

Dataset	n	p	p^1
All regions	38	0.030*	0.012*
Eastern escarpment	13	0.152	0.041*
Midlands	13	0.173	-
Southern Cape	6	0.173	-
Western Cape	6	<u>0.753</u>	-
Clay-rich	23	0.048*	-
Sandy	15	0.363	0.140

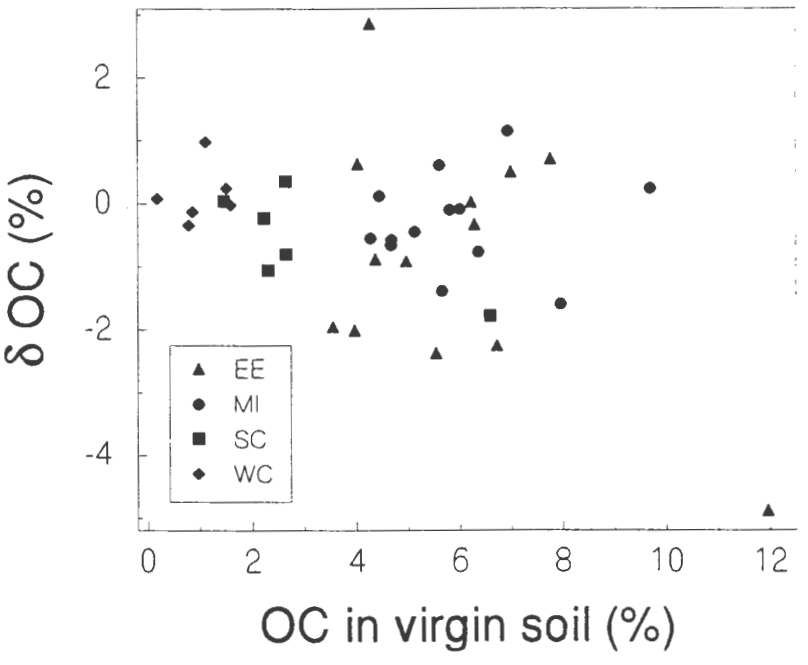

Figure 4.8: *Changes in soil organic carbon concentration ($\delta OC = OC_{forest}$ minus OC_{virgin}) in relation to the organic carbon concentration in the virgin soil (OC_{virgin}). EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

Afforestation-induced reduction of the organic carbon concentration in the upper portions of mineral soil horizons is well documented (e.g. Turner and Lambert, 1988; Almendinger, 1990) and is believed to result primarily from the observed accumulation and partial immobilisation of organic matter in thick organic horizons (Wardenaar and Sevink, 1992; Billet *et al.*, 1993; Morris, 1995). This reflects a situation where the rate of accumulation of organic matter exceeds its rate of decomposition, a phenonenon that is at least partly due to the nutrient-poor, polyphenol-rich and relatively acidic nature of pine litter that significantly retards microbial decomposition and bioturbation. Other factors which are likely to contribute significantly to reduced mineral-soil humus concentrations are reduced input, under forest, of organic matter from decaying roots, and the possible significant enhancement of humus mineralization, particularly mineralization of remnant grassland humus, in the mineral A horizon, under the drier, more oxidised conditions prevailing under forest. In general, one would expect the reduction of organic carbon concentration to be less prominent when the forest replaces fynbos than when grassland is replaced. The main reason for this is the lower organic carbon concentration in virgin fynbos soils relative to those of grasslands. This in turn is partly due to the refractory nature of fynbos litter which displays similar properties to those of pines.

4.4. SUMMARY AND CONCLUSIONS

The soils investigated for this study are made up almost entirely of quartz and sesquioxides, and their clay fractions are dominated by kaolinite and, to a lesser extent gibbsite and goethite. These features are indicative of a high degree of weathering and leaching, and reflect the combination of high rainfall and, in many cases, long periods of soil formation to which the soils have been subjected. The persistence of interstratified 2:1 layer silicates in soils of the southern and western Cape may reflect a somewhat less intense weathering and leaching regime than that prevalent in the eastern seaboard regions.

Soils in the different regions are developed on a variety of parent materials, but can be clearly subdivided into two main groups, i.e. sandy (less than ~ 12 % clay) and clay-rich (greater than ~ 25 % clay). The soils within each of these groups display broadly similar bulk properties and one would expect them to respond to afforestation in similar ways.

An additional characteristic feature of the soils is their high organic carbon contents. This is particularly true of the grassland soils of the summer rainfall regions (i.e. the eastern escarpment and midlands), in which organic carbon concentrations lower than 4 % are rarely encountered. Statistical and graphical evaluation indicates that afforestation has caused a decrease in organic carbon concentration in the upper mineral-soil horizon, particularly in the eastern escarpment region. This probably occurs as a result of changes in litter quantity, chemistry and decomposition rates, combined with reduced input from decaying roots and enhanced degradation of residual organic matter in the drier, more oxidising environment prevailing in the forest topsoil. The net effect of these processes is a depletion of organic carbon in the upper mineral soil and its accumulation, together with other nutrients, in thick pine litter layers.

Evaluation of bulk soil properties which are unlikely to have been influenced by afforestation, i.e. soil mineralogy and bulk SiO_2, Al_2O_3 and Fe_2O_3 concentrations, confirms that differences between forest and virgin soils are minimal. To a large extent this validates the assumption that any observed forest-virgin differences in other soil properties (e.g. soil pH, exchangeable cation composition and soil solution composition) are likely to reflect the impact of afforestation. The impact of minor mineralogical and bulk compositional differences observed for a small number of forest-virgin soil pairs is unlikely to be significant, but the possibility that they may obscure afforestation impacts on other soil properties cannot be totally precluded. Thus differences in the properties of forest and virgin soils for *individual sites* can not be rigorously interpreted with respect to the effect afforestation, and quantitative assessment of afforestation impacts should only be carried out statistically at the population level.

5. SOIL ACIDIFICATION

5.1. INTRODUCTION

Soil acidification is one of the most prominent and well-studied impacts of afforestation. It generally takes the form of reductions in soil pH, exchangeable bases and acid neutralising capacity (ANC), and enhancement of exchangeable acidity levels and base neutralising capacity (BNC). As discussed in section 2.5, these effects have been documented for a wide variety of forest species in a range of environments. In southern Africa, the potential influence of short rotation plantations on soil fertility and acidity has been recognised for some time (Keet, 1966), but it is only relatively recently that this has been demonstrated quantitatively for pine, eucalyptus and wattle (*Acacia mearnsii*) plantations in the eastern seaboard region of the subcontinent (Morris, 1984; Musto, 1992; du Toit, 1993). Acidification has also been documented for soils under plantations of loblolly pine *(Pinus taeda)* which replace indigenous forest in the southern Cape (Clough, 1991).

In this chapter, soil pH, and exchangeable cation data are presented for topsoil samples from paired forest-virgin sites in all four regions being investigated. The aim is to extend the evaluation of afforestation-induced acidification to the winter rainfall regions of the southern and western Cape, to provide a basis for the interpretation of data obtained for soil solutions and stream-waters and to evaluate acidification rates in relation to those reported from other local and international studies, and in relation to expected rates of base cation uptake by the pine plantations.

5.2. MATERIALS AND METHODS

The effect of afforestation on soil acidity was evaluated by comparing data for paired composite topsoil samples taken from pine plantations and adjacent virgin ecosystems (grassland or fynbos). Sampling was undertaken in such a way as to ensure that observed chemical differences between the forest and virgin soil samples are likely to reflect the effect of afforestation only (see Chapter 3). The validity of this assumption was, to a large extent, confirmed by the textural, compositional and mineralogical data presented in Chapter 4.

Soil pH and the concentration of exchangeable base cations and acidity were determined for composite forest and virgin soils from the 38 sites described in Chapter 3. The samples were air-dried and passed through a 2 mm sieve. Soil pH was determined in H_2O and 1M KCl at a soil:solution ratio of 1:2.5 using a Metrohm 691 pH meter and combination electrode. Soil suspensions were stirred and allowed to equilibrate for 1 hour prior to pH measurement. Extracts for exchangeable acidity analyses were obtained by shaking 2.5 g of soil in 25 ml of unbuffered 1M KCl for 30 minutes at 180 oscillations per minute, followed immediately by high-speed centrifugation and filtration through 0.45 µm membrane filters. Acidity was determined in the KCl extracts by titrating a 5 to 10 ml aliquot with 0.01M NaOH to pH 8.3 using a Radiometer TTT85 automatic titrator and ABU80 autoburrette. Exchangeable Ca, Mg, K and Na were determined in 1M ammonium acetate (pH 7) extracts using the same soil:solution ratio and extraction procedure as that used for exchangeable acidity. The elements were determined by atomic absorption spectroscopy. The ammonium acetate extractions and element analyses were carried out by the Institute for Soil Climate and Water in Pretoria. The concentration data are reported on a mass/volume ($mmol_c\ L^{-1}$) basis and were obtained by multiplying the original concentration values (in $mmol_c\ kg^{-1}$) by soil bulk density (Table C1, Appendix C) determined gravimetrically for air-dried samples in the laboratory.

The results of the above analyses are reported in Appendix C and are presented graphically in Figures 5.1 to 5.14. The data were evaluated statistically using the methods described in Chapter 3. The Wilcoxon matched pairs test was used to assess the significance of afforestation impacts and test results are summarised in Table 5.1.

5.3. RESULTS AND DISCUSSION

5.3.1. Soil pH

All of the soils sampled for this study are naturally acidic. Virgin soil pH values measured in water (pH_{aq}) and 1M KCl (pH_{KCl}) range from 4.3 to 5.7 and 3.1 to 4.5, respectively (Figure 5.1.a and b). The soils are probably buffered to a large extent by cation exchange processes and dissociation of weak organic acids (Ulrich, 1986; Reuss and Walthall, 1989). Kruskal-Wallis test results indicate that pH values in the different regions are not significantly

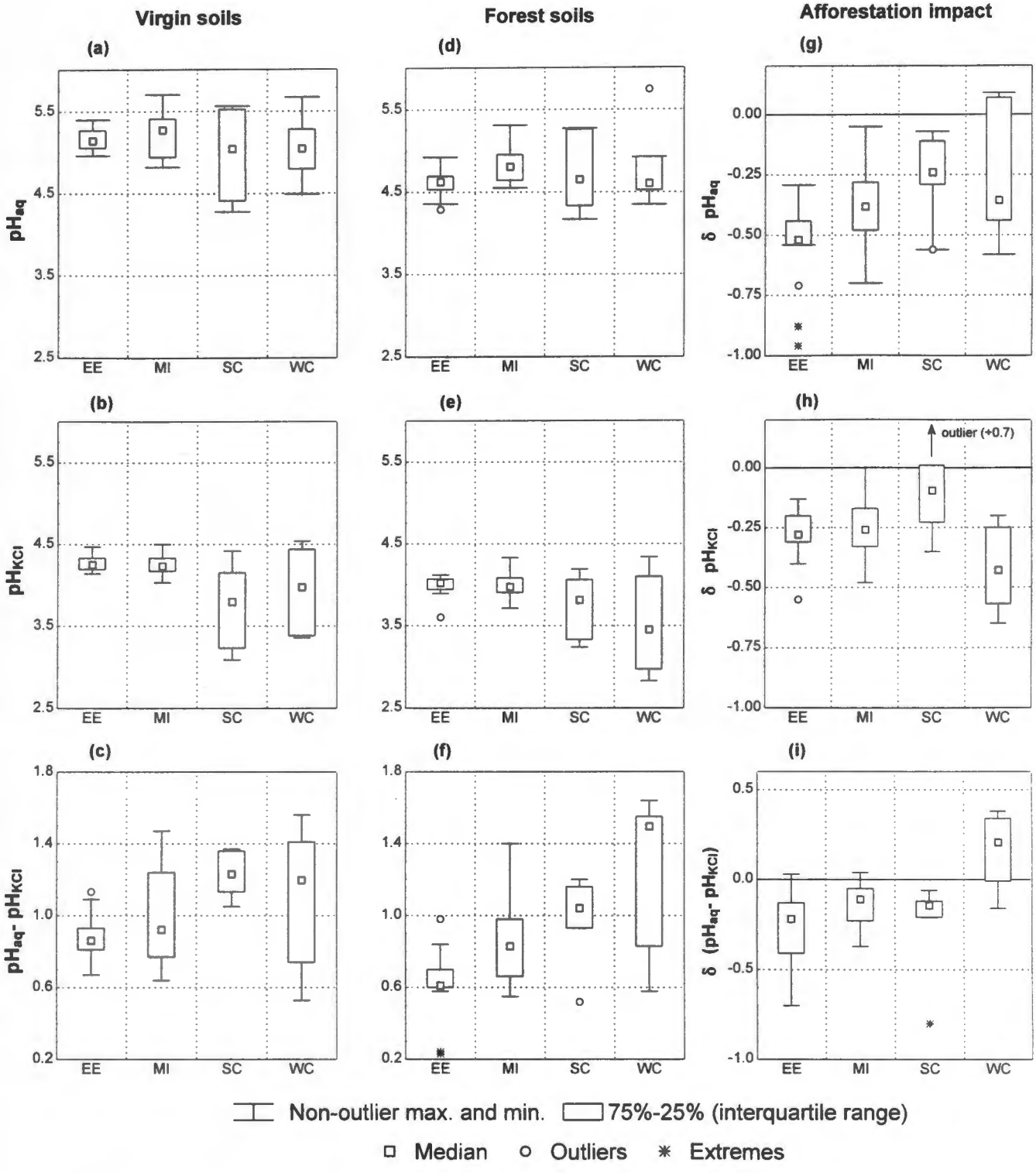

Figure 5.1: *Box and whisker plots summarising the pH data for forest and virgin soils in different regions. Results are presented for pH measured in water (pH_{aq} - a, d, g) and in 1M KCl (pH_{KCl} - b, e, h), as well as the difference between these two parameters (pH_{aq} - pH_{KCl}; c, f, i). Afforestation impacts are represented by δpH values which reflect pH differences for forest/virgin soil pairs ($\delta pH = pH_{forest} - pH_{virgin}$). For the definition of outliers and extremes see section 3.3.*

different with respect to their population means, but it is clear that pH variability (particularly for pH_{KCl}) is significantly greater in the Cape regions than in those of the eastern seaboard (Figure 5.1.b and e). This may reflect a higher degree of pH buffering in the generally more clay-rich eastern seaboard soils, as well as the possibly greater influence of variable humic and fulvic acid concentrations in the sandy soils of the southern and western Cape. In all cases pH_{aq} is significantly greater than pH_{KCl} (Figure 5.1.c). Differences range up to 1.56 pH units and generally exceed 0.7, suggesting a significant quantity of cation exchange capacity in most of the soils.

Afforestation has resulted in highly significant ($p < 0.001$) decreases in pH determined both in water and in 1M KCl (Table 5.1). Reductions of up to 0.7 pH units are evident (excluding outliers and extreme values), but in most cases pH decreases range from 0.2 to 0.5 pH units (Figure 5.1.g and h) and fall within the range of pH reduction values obtained from local and international studies of afforestation impacts (Table 2.2). Afforestation-induced reductions in soil pH appear to be less severe in the southern Cape soils than in soils of the other regions. Kruskal-Wallis test results ($p = 0.024$ and 0.046 for pH_{aq} and pH_{KCl}, respectively) confirm that this difference is statistically significant. The majority of forest soils have pH_{KCl} values below 4.2 suggesting that they fall within the pH range in which Al dissociation contributes strongly to buffering (Ulrich, 1986) and hence, that significant concentrations of Al^{3+} should be present in solution. With the exception of the western Cape sites, pH_{aq} is more strongly influenced by afforestation than is pH_{KCl} resulting in a reduction in the difference between these two parameters under forest (Figure 5.1.i). While this may reflect reductions in cation exchange capacity under forest, it is likely that it is caused, to some extent, by afforestation-induced enhancement of soluble salt concentrations (i.e. an enhanced salt effect; see Chapter 6).

In most of the soils investigated, pH_{KCl} is well correlated with exchangeable acidity and the samples define a shallow sloping trend on a plot of pH_{KCl} against exchangeable acidity (Figure 5.2). The pH_{KCl} values in very sandy soils (clay < 5 %), however, show no consistent relationship to exchangeable acidity, and most of these soils lie on a broad, steeply-sloping trend (Figure 5.2.b). These relationships reflect the greater degree of pH buffering exhibited by clay-bearing soils with relatively high CEC. Because of their low CEC and limited buffering capacity, the amount of additional acidity required to reduce the pH of sandy soils is less than that required for an equivalent pH reduction in soils with significant clay

concentrations. In soils with very low clay concentrations, the CEC and buffering capacity is governed, to a large extent, by organic matter. This is reflected by a negative correlation ($R^2 = 0.613$) between pH_{KCl} and organic carbon concentration in soils with less than 5 % clay (Figure 5.3).

*Table 5.1: P values (statistical significance levels) for forest-virgin differences in soil pH and exchangeable cation parameters. Significance levels were obtained using the non-parametric Wilcoxon matched pairs test. Underlined values reflect positive differences (i.e. increased values under forest), whereas all other p values reflect the significance of reductions under forest. EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape; * - differences significant at the 95% confidence level; ** - differences significant at the 99% confidence level.*

	Region				
	All	**EE**	**MI**	**SC**	**WC**
No. of soil pairs	38	13	13	6	6
pH_{aq}	<0.001**	0.001**	0.001**	0.027*	0.116
pH_{KCl}	<0.001**	0.001**	0.002**	0.463	0.028*
pH_{aq}-pH_{KCl}	<0.001**	0.002**	0.004**	0.028*	0.173
Base cations	0.011*	0.020*	0.114	0.028*	0.116
Acidity	0.001**	0.002**	0.001**	0.046*	0.753
Base saturation	<0.001**	0.005**	0.005**	0.028*	0.345
ECEC	0.001**	0.007**	0241	0.345	0.028*

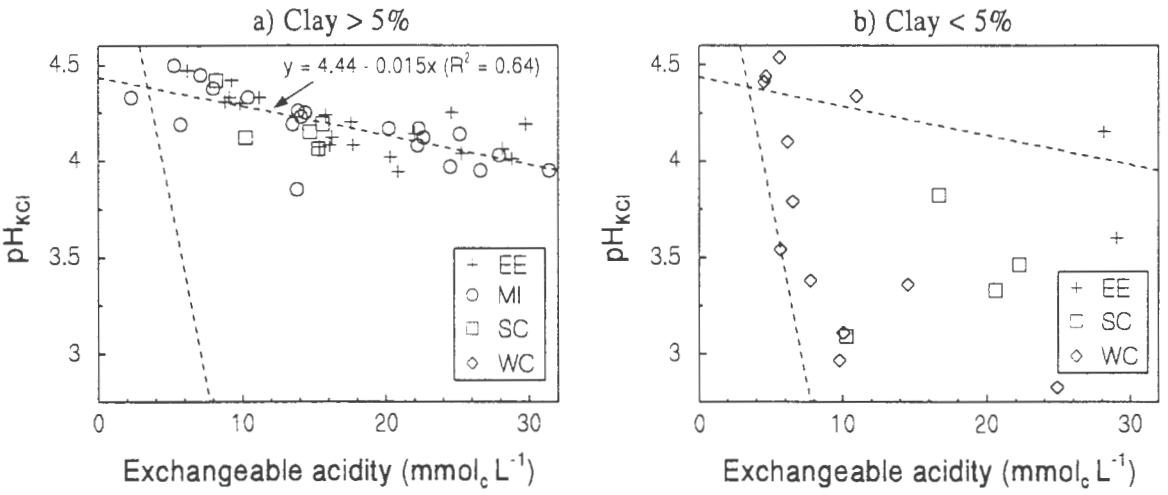

Figure 5.2: The relationship between pH_{KCl} and KCl-extractable acidity in clay-bearing (clay > 5%) and very sandy (clay < 5%) forest and virgin soils. EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape. The shallow-sloping dashed line is the regression line calculated for soils with > 5 % clay. The steeply-sloping dashed line is included for reference purposes to highlight the approximate maximum slope defined by very sandy soils (< 5 % clay).

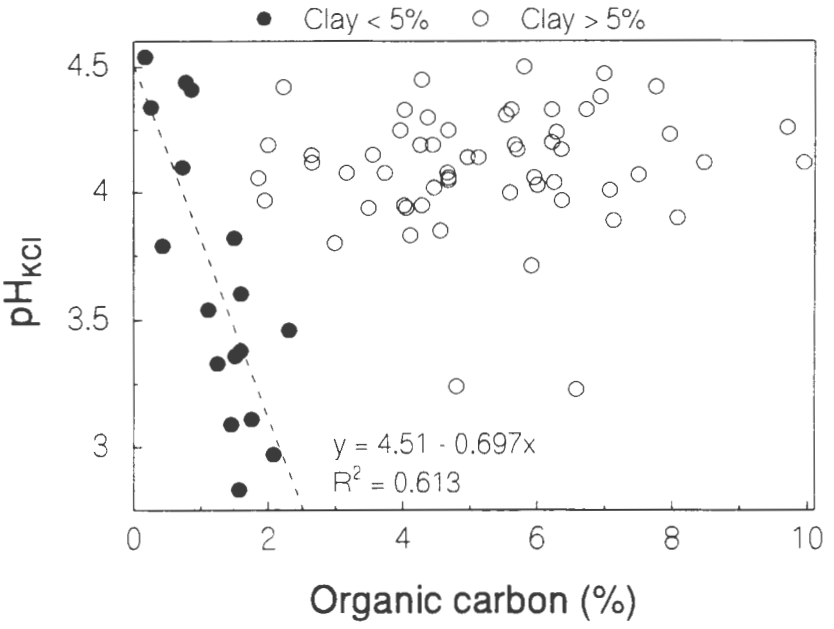

Figure 5.3: *The relationship between pH_{KCl} and soil organic carbon concentration in clay-bearing (clay > 5%) and very sandy (clay < 5%) forest and virgin soils.*

5.3.2. Exchangeable base cations

Exchangeable cation concentration data for paired forest and virgin soil samples are illustrated in Figure 5.4. In most of the soils investigated the exchangeable base cation suite is dominated by Ca and Mg. The concentration of exchangeable Ca ranges from approximately 1 to 38 $mmol_c\ L^{-1}$ and is well correlated with exchangeable Mg levels (Figure 5.5). The Mg/Ca ratio is ~ 0.6 and does not display any consistent variation between regions. Although some forest soils show increased exchangeable Ca and Mg concentrations relative to their virgin equivalents, the majority of sites display decreased levels under forest. The range of exchangeable K and Na concentrations is considerably smaller than that observed for Ca and Mg (Figure 5.4). Potassium concentrations in excess of 3 to 4 $mmol_c\ L^{-1}$ (up to 7 $mmol_c\ L^{-1}$) occur only in the midlands and certain eastern escarpment soils and generally reflect increased levels under forest. However, in most cases the effect of afforestation on exchangeable K concentrations is small and inconsistent. Concentrations of exchangeable Na do not exceed approximately 2.5 $mmol_c\ L^{-1}$. Although they are generally slightly higher in soils of the maritime Cape regions than those of the eastern seaboard, these differences are minor in absolute terms. Most sites show increased exchangeable Na concentrations under forest, with changes ranging up to 1 $mmol_c\ L^{-1}$.

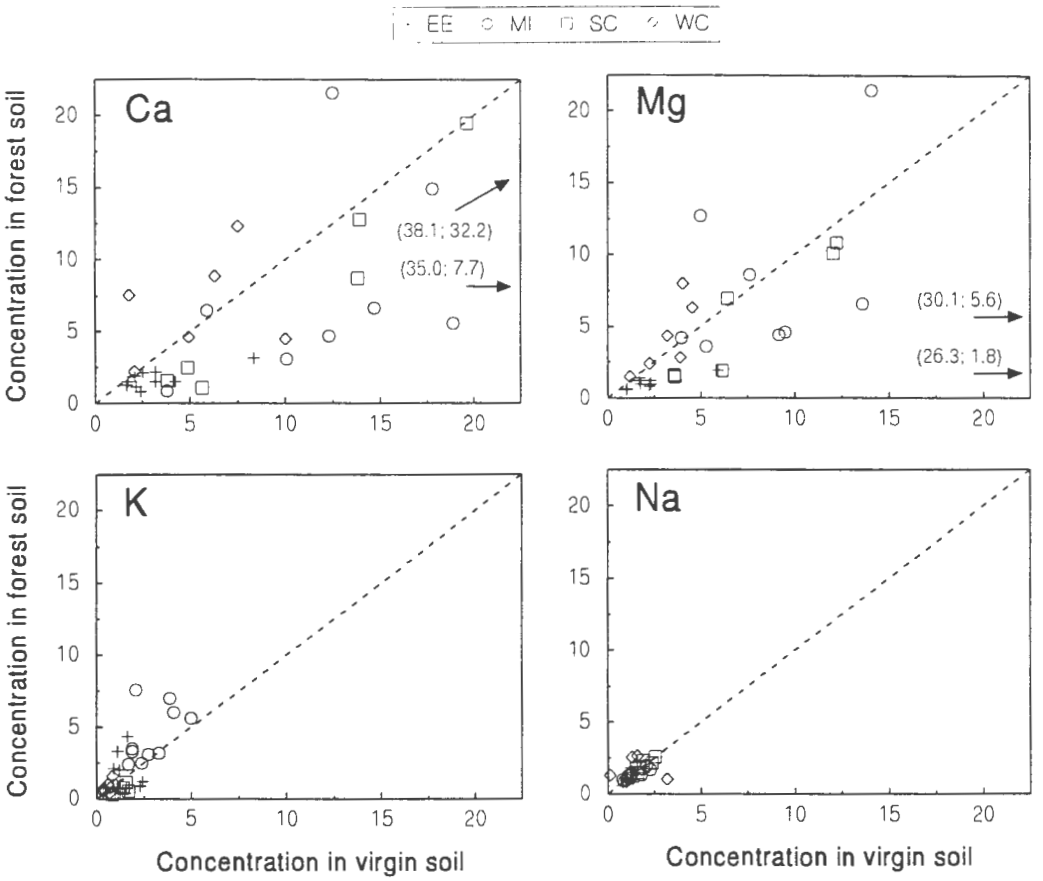

Figure 5.4: *Exchangeable Ca, Mg, K and Na concentrations ($mmol_c L^{-1}$) for paired forest and virgin soils. Each marker represents a sampling site. The value plotted on the horizontal axis is the concentration in the virgin soil and the value on the vertical axis is the concentration in its forest equivalent. The dashed lines represent a 1:1 correlation. Arrows and text in parentheses indicate outliers (the first value in parentheses denotes the concentration in the virgin soil). EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

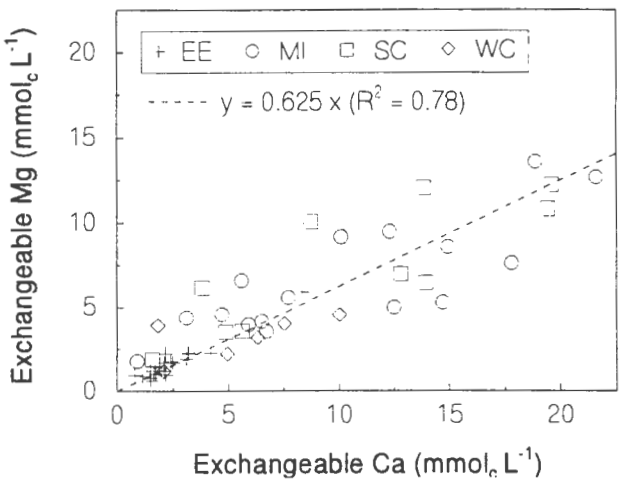

Figure 5.5: *The relationship between exchangeable Ca and Mg concentrations in forest and virgin soils. The regression includes two outliers which plot at elevated Ca and Mg values (see Figure 5.4). EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

Total exchangeable base cation concentrations range from approximately 5 to 68 $mmol_c L^{-1}$ in the virgin soils and from approximately 2 to 30 $mmol_c L^{-1}$ in their forest equivalents (Figure 5.6.a). Virgin soils from the eastern escarpment have the lowest concentrations of exchangeable bases (mostly < 10 $mmol_c L^{-1}$), suggesting that they are particularly highly leached. The values for midlands and southern Cape soils are highly variable but the majority show exchangeable base cation concentrations exceeding 20 $mmol_c L^{-1}$. The very sandy western Cape soils have intermediate concentrations, most of which range from 9 to 17 $mmol_c L^{-1}$.

Inter-region differences in exchangeable base cation concentrations are reduced in the forest soils. Afforestation has resulted in statistically significant reductions in exchangeable bases in the eastern seaboard and southern Cape sites (Figure 5.6.c; Table 5.1). Base cation depletion is strongest in regions (midlands and southern Cape) which have the greatest natural (i.e. pre-afforestation) endowment of base cations. Reductions in the eastern escarpment are small ($\delta BC < 5$ $mmol_c L^{-1}$) and are only significant at the 10% probability level (Table 5.1). In the western Cape, most soils show enhanced base cation concentrations under forest and the overall effect of afforestation is clearly not significant. In this region the forest edges at sites showing base cation enhancement all face into the strong prevailing summer winds (from the south-east). The relatively high concentration of exchangeable bases in these forest soils may therefore result from enhanced interception of marine salt aerosols and possibly wind-borne dust. Due to the high concentration of Mg (~ 100 $mmol_c L^{-1}$) relative to Ca (~ 20 $mmol_c L^{-1}$) in sea water, one would expect an increased marine salt input to be reflected in lower Ca/Mg ratios under forest relative to adjacent virgin soils. A plot of the afforestation-induced change in Ca/Mg ratio against distance from the nearest coastline indicates that most of the Cape and midlands soils show lower Ca/Mg ratio under forest, whereas the eastern escarpment sites, which are located considerably further inland, generally display increased Ca/Mg ratios in forest soils (Figure 5.7). Although this suggests an enhancement of marine salt inputs under forest in the more maritime sites, there is not a clear relationship between Ca/Mg ratio and distance from the coast and the Cape sites do not display lower Ca/Mg ratios than those of the midlands (Figure 5.5). Thus it is difficult to fully account for the increased base cation levels under forest in the western Cape in terms of increased marine salt inputs and other factors, such as reduced biomass uptake (see section 5.3.5) or dust input, may play a role.

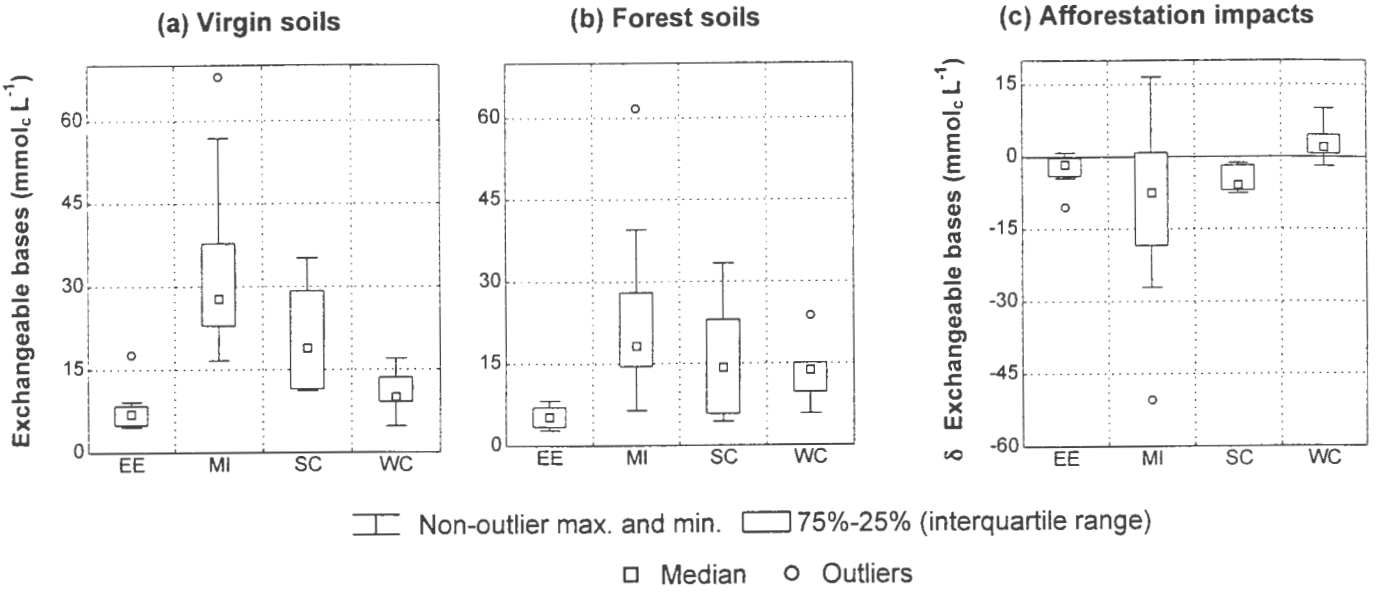

Figure 5.6: *Box and whisker plots summarising total exchangeable base cation (i.e. exchangeable Ca + Mg + K + Na) data for different regions. Data are given for virgin (a) and forest (b) soils. Afforestation impacts (c) are represented by δBC values which reflect differences in total exchangeable base cations for forest/virgin soil pairs (δBC = BC_{forest} - BC_{virgin}). For the definition of outliers and extremes see section 3.3.*

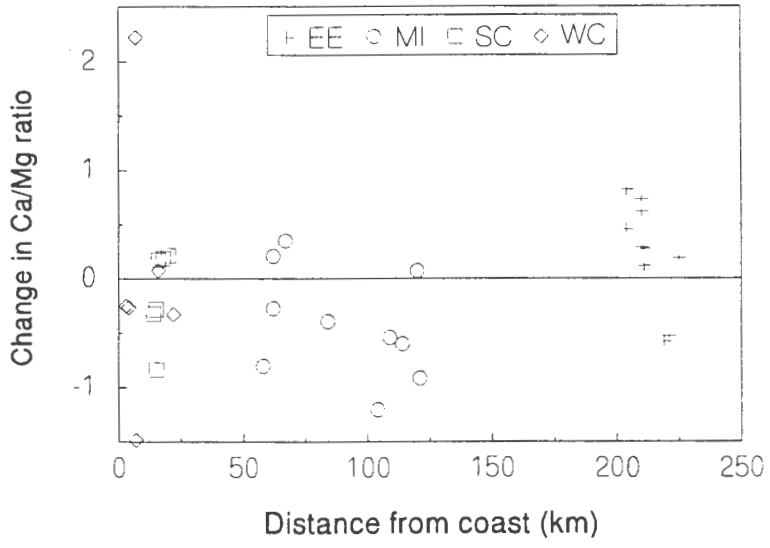

Figure 5.7: *The relationship between the change in the molar Ca/Mg ratio and distance from the nearest coastline. The change in Ca/Mg ratio is the difference between that in the forest soil and its virgin equivalent. Positive values indicate an increase in the Ca/Mg ratio under forest. EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

There is a broad inverse relationship, particularly evident in the virgin soils, between the concentration of exchangeable bases and mean annual precipitation (Figure 5.8). This largely reflects regional differences in parent material, clay content and rainfall. However, it is significant that none of the high rainfall (> ~ 1200 mm yr^{-1}) eastern escarpment or midlands sites have high exchangeable base cation levels, despite a wide range of clay contents and parent materials, while the lower-rainfall (< ~ 1100 mm yr^{-1}) sites in the Cape regions all have somewhat elevated base cation concentrations, despite their relatively base-poor quartzitic parent materials. Thus, the above-described regional variations in initial (virgin-soil) exchangeable base cation concentration appear to be related to variations in mean annual precipitation. This is in agreement with the findings of Donkin and Fey (1993) which indicate a negative correlation between mean annual precipitation and the levels of exchangeable base cations (R^2 = 0.79) in a suite of soils from southern KwaZulu-Natal.

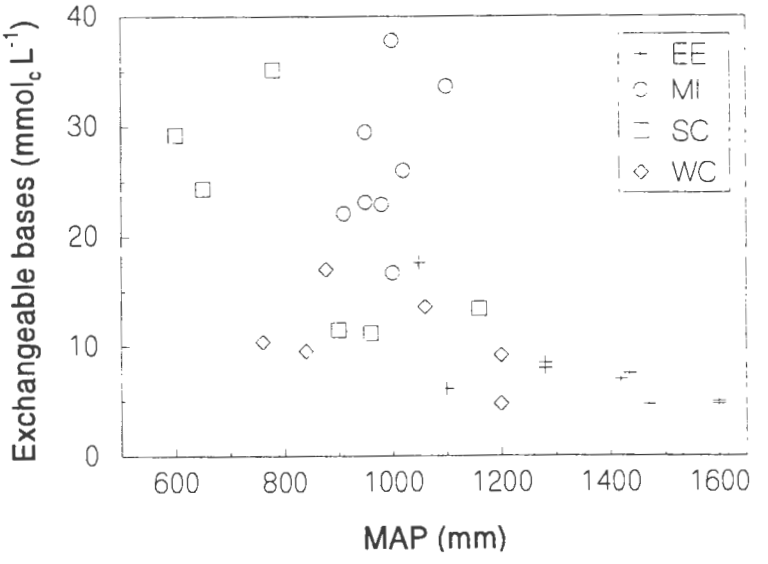

Figure 5.8: *The relationship between total exchangeable base cation (Ca + Mg + K + Na) concentrations in virgin soils and mean annual precipitation (MAP). EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape. Note: two outlying midlands samples plot beyond the vertical axis range (at 56.9 mmol$_c$ L^{-1} - MAP = 950 mm; and 67.9 mmol$_c$ L^{-1} - MAP = 1030 mm).*

5.3.3. Exchangeable acidity

Concentrations of exchangeable acidity (i.e. exchangeable Al^{3+} and H^{+}) in virgin soils range from less than 5 to greater than 40 $mmol_c\ L^{-1}$ and, with the exception of the western Cape, in which acidity values are uniformly very low (mostly < 5 $mmol_c\ L^{-1}$), regional trends are not evident (Figure 5.9.a). The highest natural level of exchangeable acidity occurs in the wet organic rich soil of site SC4 in the southern Cape (see section 4.3.3) and correlates with the very low pH values obtained for this soil. The ubiquitously low exchangeable acidity in the virgin soils of the western Cape is probably due, in part, to low cation exchange capacities resulting from low clay and organic matter contents. Differences in initial (virgin-soil) exchangeable acidity concentrations between the western Cape soils and similar sandy, low-ECEC soils in the eastern escarpment may stem from a lower degree of leaching in the western Cape, as mean annual precipitation levels in this region are 250 to 400 mm less than those at the sandy sites of the eastern escarpment (Table 3.1; Appendix A). An additional factor which may contribute to the low exchangeable acidity values in the western Cape is a greater influence of soil humic substances (i.e. fulvic and humic acids) which form strong complexes with aluminium (Schnitzer and Skinner, 1963), thus limiting its exchangeability in salt solutions (Hargrove and Thomas, 1982). The high exchangeable acidity concentrations in fynbos soils of the southern Cape relative to those of the western Cape sites probably stem from the generally higher clay contents of the former. Clay would be expected to reduce the influence of humic substances on exchangeable acidity due to the formation of clay humus complexes, which limit the ability of the organic matter to complex Al, and due to an enhancement of CEC and consequently an increased capacity for reversible adsorption of acid cations.

With few exceptions, the concentration of exchangeable acidity in the forest soils is considerably enhanced relative to adjacent virgin soils (Figure 5.9.c), with values generally exceeding 10 $mmol_c\ L^{-1}$ and ranging up to 56 $mmol_c\ L^{-1}$. The enhancement of acidity levels in forest soils appears to be least severe in the very sandy soils of the western and to some extent southern Cape (Figure 5.9.c; Table 5.1), even at sites where the natural acidity levels are relatively high (e.g. most of the southern Cape sites). This effect is not evident in the sandy soils of the eastern escarpment (2 out of the three sandy eastern escarpment soils show acidity increases under forest which exceed 10 $mmol_c\ L^{-1}$). Thus the limited enhancement of

exchangeable acidity in all of the western Cape and some of the southern Cape soils cannot be entirely attributed to their sandy nature and low ECEC, and may indicate lower rates of acidification in these regions. This is discussed further in section 5.3.5.

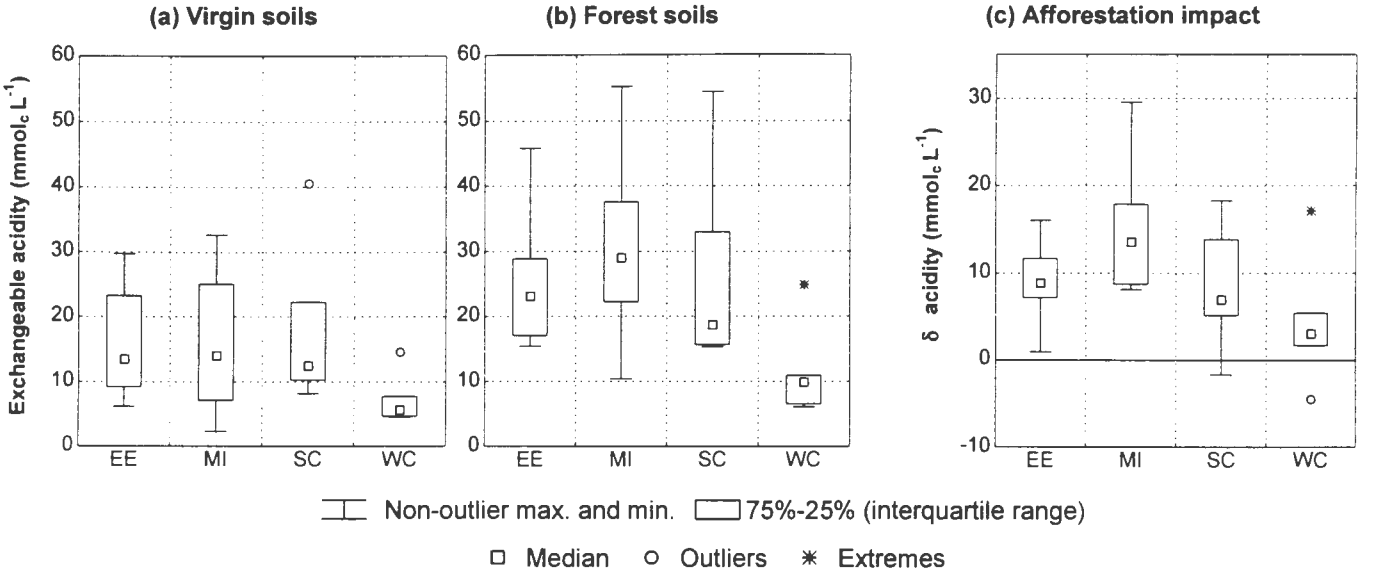

Figure 5.9: *Box and whisker plots summarising exchangeable acidity data for different regions. Data are given for virgin (a) and forest (b) soils. Afforestation impacts (c) are represented by δAcidity values which reflect exchangeable acidity differences for forest/virgin soil pairs (δAcidity = Acidity$_{forest}$ - Acidity$_{virgin}$). For the definition of outliers and extremes see section 3.3.*

5.3.4. Base saturation and effective cation exchange capacity

The base saturation levels of the virgin soils are highly variable and range from 15 to 90 %. Soils in the midlands and Cape regions generally display base saturation levels exceeding 40 % (Figure 5.10) indicating that, despite high degrees of leaching and low soil pH values, they are not strongly acidified. Base saturation in the eastern escarpment virgin soils appears to be lower than that of the other regions, with the majority of soils displaying values of less than 40 %. These values probably reflect the generally higher rainfall levels and consequently a greater degree of leaching, in this region (Donkin and Fey, 1993).

The decreases in exchangeable bases and enhancement of exchangeable acidity described in previous sections indicate that afforestation has caused substantial reductions in base saturation in the majority of soils sampled (Figure 5.10.c). Statistical analysis indicates that, with the exception of the western Cape, these reductions are significant at the 5 % probability level (i.e. $p < 0.05$; Table 5.1). Despite the lack of significant forest-fynbos differences for the western Cape region as a whole, only one site (WC4), characterised by anomalously high exchangeable Ca and Mg concentrations in its forest soil, displays a marked increase in base saturation under forest. Reductions in base saturation are highly variable, ranging from zero to greater than 50 %. No consistent regional trends are evident (Figure 5.10.c; Table 5.1) and the decline in base saturation does not correlate with soil properties, or with factors such as pine species, rainfall, regional climate or plantation age. This suggests that reductions in base saturation are probably related to localised effects, such as variable site productivity, forest management practices and localised changes in climatological and geomorphological factors.

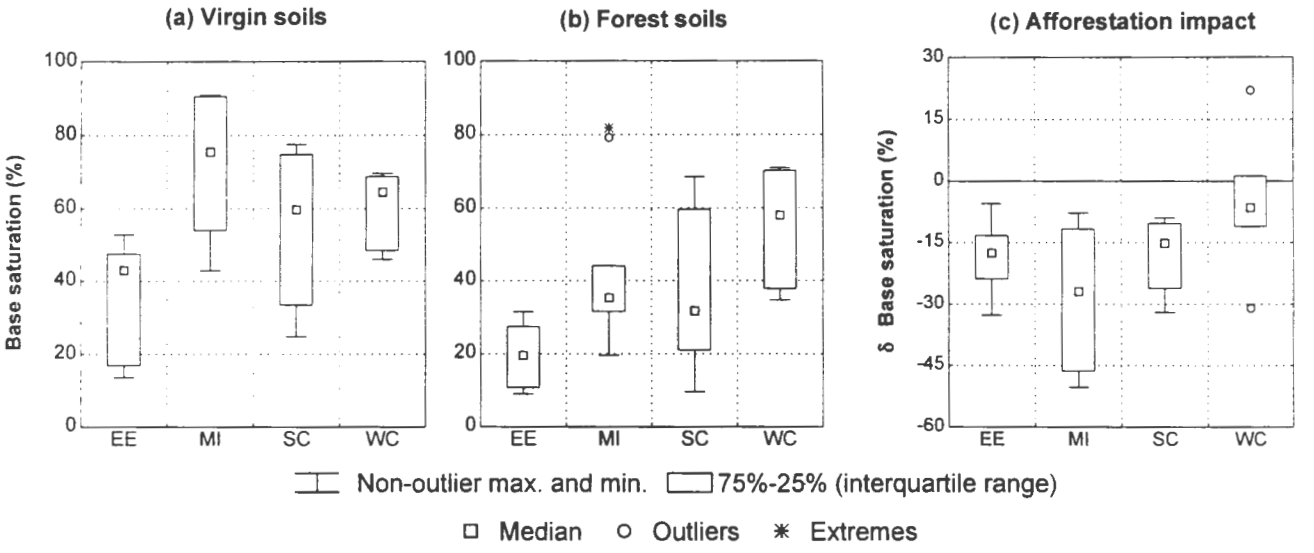

Figure 5.10: *Box and whisker plots summarising base saturation data for different regions. Afforestation impacts (c) are represented by δBS values which reflect the difference in base saturation for forest-virgin soil pairs ($\delta BS = BS_{forest} - BS_{virgin}$). For the definition of outliers and extremes see section 3.3.*

Effective cation exchange capacity (ECEC = exchangeable bases + acidity) values in the forest soils of the eastern seaboard are significantly higher than those of their grassland equivalents (Figure 5.11; Table 5.1). This contradicts findings based on differences between pH_{aq} and pH_{KCl} (section 5.3.1) and is anomalous in that acidification is generally expected to reduce cation exchange capacity due to reductions in pH-dependent negative surface charge

and blockage of exchange sites by relatively non-exchangeable aluminium oxy-hydroxides (Thomas and Hargrove, 1984; Ulrich, 1986; Sparks, 1995). Given the above-described base cation and acidity variations, an enhancement of ECEC implies that afforestation-induced increases in exchangeable acidity exceed base cation losses (by biomass uptake and leaching). This effect has been documented for *Pinus contorta* plantations developed on peat bogs in Great Britain (Williams *et al.*, 1978 - cited in Binkley and Richter, 1987). These authors attributed the increased CEC to enhanced production of humic and fulvic acids resulting from higher evapotranspiration rates and consequently improved aeration under the pines. This process may contribute to some extent towards the observed ECEC enhancement under many of the South African pine plantations sampled for this study. However, in view of the observed reductions in soil organic carbon concentrations at many of the sites investigated, increased production of humic substances is unlikely to be an important factor. A more feasible explanation is that the apparent enhancement of ECEC reflects the fact that only Ca, Mg, K and Na have been accounted for and that some of the acid input to forest soils may be associated with NH_4^+ uptake. Afforestation-induced ECEC enhancement has been documented in the eastern seaboard region by du Toit (1993), who noted that this effect appears to be peculiar to pine plantations. (Eucalyptus and wattle plantations generally showed reduced ECEC relative to adjacent grassland). Exchangeable NH_4^+ was not determined in du Toit's study, lending further support to the suggestion that the apparent increases in ECEC under pine plantations may reflect the fact that acidity inputs associated with afforestation are to some extent balanced by removal of NH_4^+.

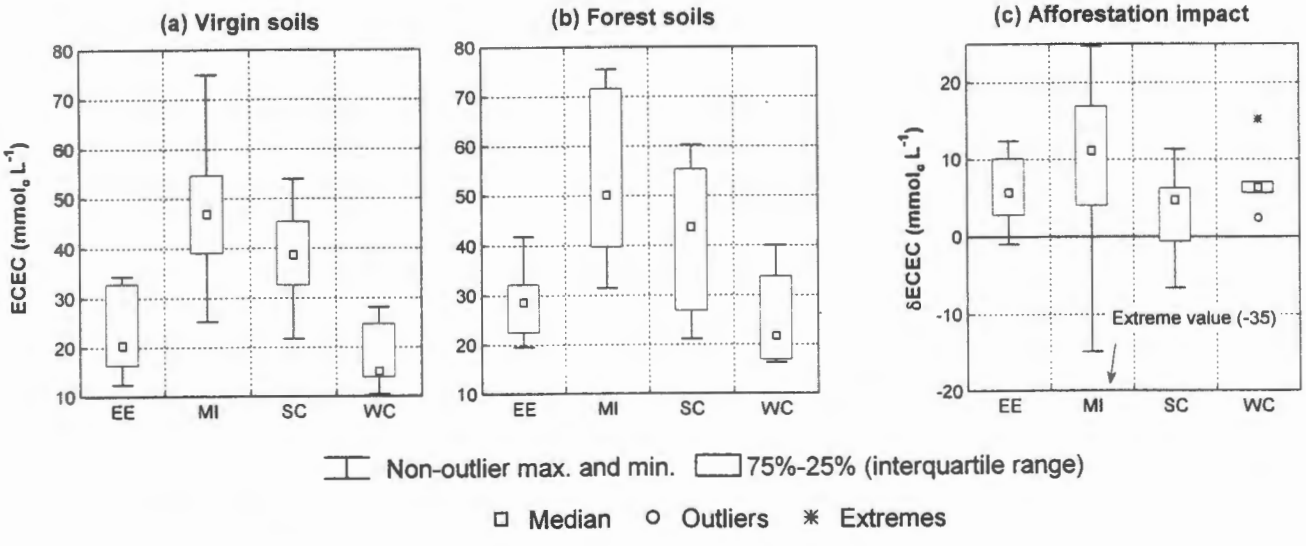

Figure 5.11: *Box and whisker plots summarising effective cation exchange capacity (ECEC = exchangeable bases + acidity) data and afforestation impacts (c) for the different regions.*

5.3.5. Acidification rates

5.3.5.1. Introduction

Afforestation-induced changes in the quantities of exchangeable bases (Ca + Mg) and acidity have been calculated for the top 20 cm of mineral soil, based on the above-described concentration differences. Average rates of input and/or output were estimated for each site by dividing these quantities by total plantation age, thus providing an indication of acidification rates under forest. These estimates do not incorporate changes taking place in the litter layer or in the subsoil and therefore do not provide a complete picture of acidification processes. Although afforestation-induced changes in exchangeable bases and acidity in the subsoil (i.e. below ~ 20 cm) are generally considerably smaller than those occurring in the topsoil, they do occur. In some cases, changes taking place between 20 and 100 cm can be equivalent to those occurring in the upper 20 cm (Morris, 1984; Richter *et al.*, 1994). Thus, calculations based on compositional changes occurring in the topsoil are likely to underestimate the total extent of acidification taking place in the mineral soil under forest. The magnitude of this underestimation will depend on a number of factors, including rooting depth, the initial base cation concentration of the subsoil, soil depth and site productivity. A further limitation of the calculated acidification rates is that the uptake of ammonium N is not explicitly accounted for. Thus acidification rates based on the change in exchangeable base cation content may underestimate the true rate of acidification. This is discussed further below.

A significant proportion of the base cations removed from the mineral soil can be translocated to accumulating litter layers (Alban, 1982; Gholz and Fisher, 1982; Gholz *et al.*, 1985; Billet *et al.*, 1993; Morris, 1995; see section 4.3.3). In this situation, depletion of bases in the mineral soil is likely to be accompanied by their accumulation in the forest floor and, with increasing acidification, the pine trees may become more reliant on tight nutrient cycling between living biomass and the forest floor (Miller, 1984). This, as well as declining biomass accumulation rates, results in reduced base cation uptake rates from the mineral soil with increasing plantation age (Madgwick *et al.*, 1977; Gholz *et al.*, 1985). Average estimates of base cation removal from the mineral soil over the entire period of afforestation, will encompass translocation to the living biomass and forest floor, as well as inputs of bases from

decomposing litter. Thus, base cation depletion rates for the mineral soil primarily reflect losses arising from permanent removal in harvestable biomass and leaching.

Average acidification rates are misleading to some extent, as they do not provide any indication of short term fluctuations in acidification processes. Acidification is likely to be most intense during initial establishment of a pine plantation, when biomass accumulation rates are highest (Ford, 1984; Morris, 1992). After canopy closure, rates of base cation uptake are slowed and accelerated mineralisation of forest litter following clearfelling may, notwithstanding the effect of nitrate leaching (see section 2.5), increase base saturation levels in the uppermost mineral soil underlying the forest floor. Similarly, seasonal variations in base cation uptake, litterfall and decomposition rates may cause short term variations in base cation concentrations in the A horizon (Haines and Cleveland, 1981; Johnson *et al.*, 1988b), although these are likely to be less significant for conifer plantations than for deciduous tree species.

5.3.5.2. Base cation uptake

Estimated average rates of base cation loss are given in Table 5.2 and are illustrated in Figure 5.12.a. With the exception of the Midlands region, base cation depletion rates generally do not exceed 0.3 $kmol_c\ ha^{-1}\ yr^{-1}$ and several sites in the eastern escarpment, midlands and western Cape show base cation additions to the mineral topsoil under forest. The high rate of base cation depletion (0.68 $kmol_c\ ha^{-1}\ yr^{-1}$) at site number 7 in the eastern escarpment is believed to reflect intensive nitrate leaching following recent clearfelling (~1 year prior to sampling; see section 6.3.1). In the midlands region, a large number of sites (5 out of 10) show base cation depletion rates which are in excess of 0.3 $kmol_c\ ha^{-1}\ yr^{-1}$ and which range up to ~1.5 $kmol_c\ ha^{-1}\ yr^{-1}$ (± 75 kg $CaCO_3\ ha^{-1}\ yr^{-1}$). These elevated depletion rates are associated with relatively high initial levels of exchangeable base cations (Table 5.2; Figure 5.13). Conversely, base cation depletion rates in soils with low initial base cation concentrations are invariably low, suggesting that in these soils the pine plantations may rely more heavily on tight cycling of nutrients via throughfall, litterfall and decomposition (Cole and Rapp, 1981; Miller, 1984; Versveld and Donald, 1991). Alternatively, a greater proportion of base cations may be supplied from the deeper portions of these soils. Low base cation depletion rates do occur in certain soils with high initial base cation levels, probably as a result of factors such as lower site productivity, input of bases from atmospheric sources, or faster litter decomposition.

Table 5.2: *Calculated rates of change in pH_{KCl}, and exchangeable calcium, magnesium, total base cations and acidity. Age - total plantation age; Rot. - rotation number; pH_i - virgin soil pH measured in KCl; BC_i - exchangeable Ca + Mg + K + Na in virgin soil; $\sum$ - rate of change of Ca + Mg + K + Na. Quantities and rates of change are calculated for a 20cm soil depth. Positive rates indicate inputs and negative rates indicate removal.*

Region	Site	Species	Age	Rot.	pH_i	BC_i	Rates of change				
						$kmol_c\ ha^{-1}$	pH per 10 yrs	Ca	Mg	$\sum$	Acidity
							$kmol_c\ ha^{-1}\ yr^{-1}$				
Eastern	2	*elliotii/taeda*	50	2	4.25	19.8	-0.06	-0.01	-0.02	-0.04	0.56
escarpment	3	*elliotii/taeda*	32	2	4.15	18.8	-0.17	-0.02	-0.03	-0.12	0.06
	4	*elliotii/taeda*	45	2	4.30	33.8	-0.08	-0.04	-0.06	-0.01	0.49
	5	*elliotii/taeda*	45	2	4.31	31.6	-0.05	-0.08	-0.06	-0.20	0.32
	6	*patula*	36	2	4.14	30.0	-0.04	-0.09	-0.05	-0.22	0.38
	7	*patula*	31	2	4.24	70.4	-0.06	-0.34	-0.26	-0.68	0.80
	8	*elliotii/taeda*	45	2	4.42	29.8	-0.07	-0.05	-0.06	-0.14	0.31
	9	*elliotii/taeda*	45	2	4.19	-	-0.07	-	-	-	0.71
	11	*patula*	22	1	4.47	24.8	-0.18	-0.02	-0.03	0.08	0.84
	12	*patula*	26	2	4.33	24.4	-0.10	-0.03	-0.04	0.03	0.66
	13	*patula*	28	1	4.33	36.8	-0.11	-0.19	-0.08	-0.11	0.65
	14	*patula*	35	1	4.20	-	-0.05	-	-	-	0.44
Midlands	1	*patula*	30	2	4.14	118	-0.07	-0.19	0.06	-0.10	1.2
	2	*patula*	40	1	4.14	-	-0.02	-	-	-	0.41
	11	*patula*	28	1	4.50	88.4	-0.12	-0.50	-0.34	-0.78	1.1
	12	*patula*	30	2	4.03	92.4	-0.11	-0.53	-0.11	-0.28	1.8
	13	*patula*	36	1	4.05	-	-0.06	-	-	-	0.93
	14	*patula*	40	1	4.17	66.8	-0.04	-0.03	0.01	0.04	0.52
	15	*patula*	65	2	4.25	134	-0.05	-0.09	-0.75	-0.83	0.38
	16	*patula*	65	2	4.45	272	-0.06	-0.84	-0.75	-1.55	0.46
	21	*elliotii/taeda*	16	1	4.23	-	-0.16	-	-	-	1.30
	22	*elliotii/taeda*	27	1	4.19	228	-0.13	-0.44	0.55	0.36	0.60
	23	*elliotii/taeda*	30	2	4.38	151	-0.16	-0.89	-0.47	-1.23	1.97
	24	*elliotii/taeda*	32	1	4.26	-	-0.04	-	-	-	0.54
	25	*elliotii/taeda*	50	2	4.19	114	-0.05	-0.30	-0.20	-0.46	0.72
	26	*elliotii/taeda*	60	2	4.33	71.6	0.00	0.30	0.26	0.55	0.27
Southern	1	*radiata*	15	1	4.42	97.4	-0.15	-0.15	0.07	-0.17	0.99
Cape	2	*pinaster*	60	2	4.15	117	-0.06	-0.17	-0.07	-0.23	0.61
	3	*radiata*	60	2	4.12	141	-0.01	-0.01	-0.05	-0.06	0.17
	4	*pinaster*	45	2	3.23	53.4	0.00	-0.10	-0.19	-0.34	0.62
	5	*pinaster*	60	2	3.09	46.0	0.12	-0.15	-0.07	-0.24	0.21
	6	*pinaster*	60	2	3.46	44.8	-0.02	-0.08	-0.07	-0.17	-0.06
Western	1	*radiata*	30	1	4.44	36.6	-0.22	-0.02	0.01	0.04	0.12
Cape	2	*radiata*	30	1	4.54	19.1	-0.07	0.01	0.02	0.07	0.36
	3	*pinaster*	42	1	3.54	38.2	-0.14	0.27	0.05	0.07	0.20
	4	*pinaster*	63	2	3.36	54.4	-0.04	0.15	0.13	0.32	-0.14
	5	*pinaster*	45	2	4.41	41.6	-0.07	0.11	0.05	0.21	0.07
	6	*pinaster*	43	1	3.38	68.2	-0.13	-0.26	0.08	-0.09	0.80

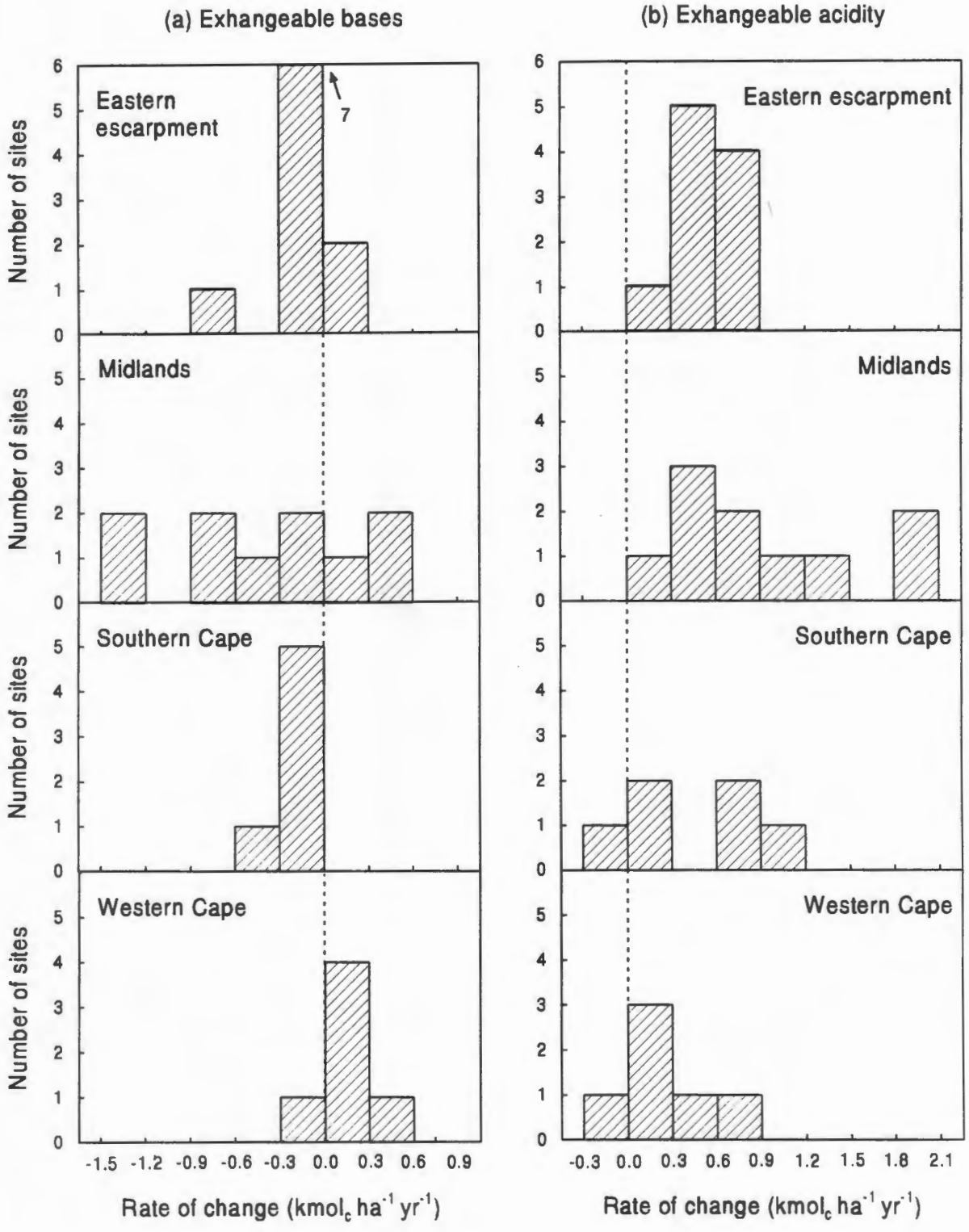

Figure 5.12: *Histograms illustrating the rates of change in exchangeable base cations (Ca + Mg + K + Na - a) and acidity (b) for afforested sites in the four study regions. Rates of change were calculated by dividing forest-virgin differences in the quantity (per hectare) of exchangeable base cations/acidity by total plantation age. Total base cation quantities per hectare were calculated from concentration data, for a soil depth of 20 cm. The dashed line represents a zero rate of change. Positive rates reflect inputs under forest, whereas negative changes reflect outputs.*

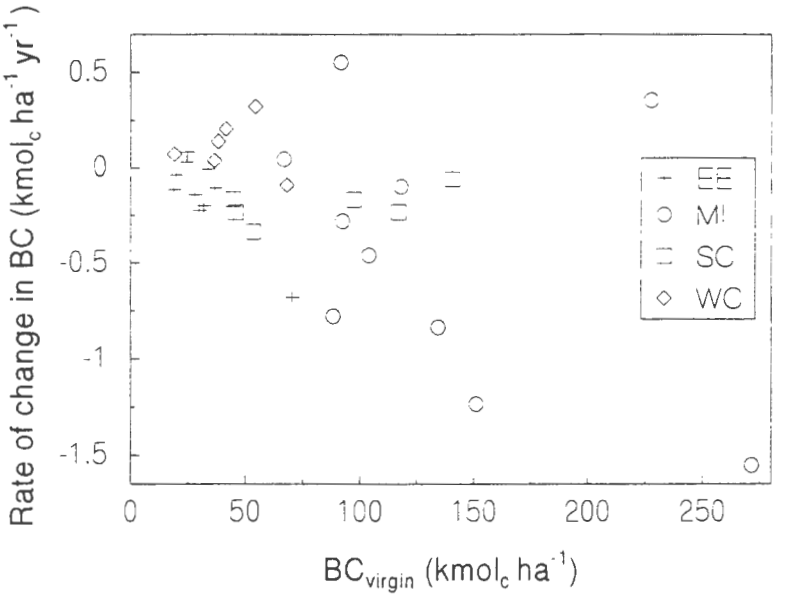

Figure 5.13: *The relationship between the rate of base cation (BC = Ca + Mg + K + Na) loss and the quantity of exhangeable base cations in the virgin soil. Rates of change were calculated by dividing forest-virgin differences in the quantity (per hectare) of exchangeable base cations by total plantation age. Total base cation quantities per hectare were calculated from concentration data, for a soil depth of 20 cm. The virgin soil data is assumed to represent the original base cation concentration of the forest soil. EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

With the exception of several midlands sites, base cation depletion rates observed for the sites investigated in this study generally lie within the range documented for topsoils in other forest ecosystems, including some which are subjected to significant acid deposition inputs (Table 5.3). High rates of base cation depletion (> 0.5 mmol$_c$ ha^{-1} yr^{-1}) have been observed in a study of spruce forests in southern Sweden (Hallbäcken, 1992) and in first rotation *Pinus patula* plantations in Swaziland (Morris, 1984). Hallbäcken (1992) ascribed approximately 50 % of the acidification in the southern Swedish forests to acid deposition, whereas in the unpolluted Swaziland sites base cation removal is entirely due to very rapid biomass accumulation (Morris, 1984; Morris, 1992). Gholz *et al.* (1985) document low rates of base cation depletion (0.08 kmol$_c$ ha^{-1} yr^{-1}) for *Pinus elliottii* forests developed on sandy soils in northern Florida. In terms of texture, mineralogy, CEC and original base status, these soils are very similar to the sandy soils of this study and, in both cases, the low base cation depletion rates reflect the original nutrient-poor nature of the soils.

Table 5.3: *Exchangeable base cation depletion rates for forest topsoils. Data are based on measured changes in concentration over a given depth range (depth) and time period (years). Hor. - soil horizon sampled; pH_i - initial pH; BC_i - initial total exchangeable base cation quantity; $\sum$ - Ca + Mg + K depletion rate. References: 1 - Halbäcken, 1992; 2 - Billett et al., 1990; 3 - Anderson, 1988 (cited in Johnson et al., 1991); 4 - Gholz et al., 1985; 5 - Morris, 1984.*

Region	Species	Time	Hor.	Depth	pH_i	BC_i	Rates of change				Ref.
							Ca	Mg	K	$\sum$	
				cm		$kmol_c\ ha^{-1}$	$kmol_c\ ha^{-1}\ yr^{-1}$				
S. Sweden*	*Picea* spp.	52	E	20	4.72[+]	37.3	-	-	-	0.54	1
Scotland*	*Pinus sylvestris*	37	A_h	20	3.5[#]	36.4	0.06	0.22	0.10	0.38	2
Scotland	*Pinus sylvestris*	37	A+E	25	3.4[#]	22.3	0.07	0.01	0.10	0.18	2
Scotland	*Pinus sylvestris*	37	B_{s1+s2}	20	4.2[#]	22.5	0.28	0.07	0.08	0.43	2
NE USA*	Mixed	-	-	-	-	-	0.38	-	-	-	3
SE USA*[?]	*Pinus elliottii*	32	A_{h1+h2}	28	4.0[+]	8.9	0.03	0.04	0.01	0.08	4
Swaziland	*Pinus patula*	17[(1)]	A	20	3.94[#]	41.5	0.31	0.16	0.05	0.52	5
Swaziland	*Pinus patula*	30[(2)]	A	20	3.94[#]	41.5	0.19	0.12	0.04	0.35	5

* - Sites impacted by acid deposition (? - uncertain).
[+] - pH measured in H_2O
[#] - pH measured in KCl or $CaCl_2$
[(1)] - First rotation
[(2)] - Second rotation

Base cation depletion rates obtained for the southern Cape sites appear to be significantly lower than values obtained for *Pinus elliottii* plantations replacing indigenous forest on similar soil types in the same region (~ 0.6 $kmol_c\ ha^{-1}\ yr^{-1}$ - assuming a bulk density of 1; Clough, 1991). The reason for this difference in depletion rates is not certain, but a possible explanation is that it reflects differences in the chemical nature of organic matter derived from the different original vegetation types (i.e. indigenous forest and fynbos). As discussed in section 4.3.3, pine litter is likely to be chemically similar to that of fynbos. Thus, changes in exchangeable bases associated with pine afforestation of fynbos may be less severe than those occurring when indigenous forest is replaced. The indigenous forest includes broadleaved tree species which are likely to produce litter with a considerably higher ash alkalinity than that of pine species (Noble and Randall, 1996). Thus, phytocycling in these forests would be expected to maintain base cation concentrations in the topsoil at higher levels than those prevailing under pine plantations or fynbos.

Estimates of the average rate of Ca and Mg uptake for pine plantations in the regions investigated in this study range from 0.07 $kmol_c\ ha^{-1}\ yr^{-1}$ in the *Pinus pinaster* plantations of the western Cape, to 0.28 $kmol_c\ ha^{-1}\ yr^{-1}$ in *Pinus taeda* plantations of the eastern escarpment (Table 5.4). The estimates presented in Table 5.4 suggest that biomass uptake can, to a large extent, account for the observed base cation depletion in the eastern escarpment, southern Cape and western Cape. Base cation loss in many of the midlands sites greatly exceeds estimated biomass uptake rates suggesting that leaching may contribute substantially to acidification in this region. Base cation depletion in the highly productive eastern escarpment area is not markedly greater than that in the southern and western Cape where forest productivity levels are considerably lower (Table 5.4). This and the very low initial base cation concentrations, suggests that tight cycling of nutrients between the forest floor and living forest biomass is an important process in the eastern escarpment region.

Table 5.4: *Rates of base cation (calcium and magnesium) retention in forest biomass for different pine species in the four regions under investigation. These values are rough estimates obtained by extrapolation of measured uptake rates for 30 year old Pinus patula in the Usutu forest, Swaziland (Morris, 1992), to other species and regions, based on relative productivity estimates (obtained from H. Kassier, of the South African Forestry Company, Pretoria). Estimates are given for base cation (Ca + Mg) accumulation (uptake) rates in the total biomass, and in harvestable biomass (stemwood and bark only). Productivity ratio - the ratio of forest productivity for a particular species in a particular region to that of Pinus patula in the Usutu forest, Swaziland.*

Region	Species	Productivity (stemwood only)	Productivity ratio	Total biomass uptake	Harvestable biomass uptake
		$m^3\ ha^{-1}\ yr^{-1}$		$kmol_c\ ha^{-1}\ yr^{-1}$	
Usutu	*patula*	25	1	0.35	0.28
Eastern escarpment	*patula*	19	0.76	0.27	0.21
	taeda	20	0.80	0.28	0.22
	elliottii	17	0.68	0.24	0.19
Midlands	*patula*	17	0.68	0.24	0.19
	taeda	18	0.72	0.25	0.20
	elliottii	14	0.56	0.20	0.16
Southern Cape	*radiata*	14	0.56	0.20	0.16
	pinaster	7	0.28	0.10	0.08
Western Cape	*radiata*	12	0.48	0.17	0.13
	pinaster	5	0.20	0.07	0.06

5.3.5.3 Exchangeable acidity

Rates of exchangeable acidity enhancement are higher in the eastern escarpment and midlands regions than in the western and to a lesser extent southern Cape (Table 5.2; Figure 5.12.b). Estimated input rates for the majority of sites in the eastern seaboard regions range from 0.3 to 0.9 $kmol_c\ ha^{-1}\ yr^{-1}$ and two midlands sites show rates exceeding 1.8 $kmol_c\ ha^{-1}\ yr^{-1}$. With the exception of these strongly acidified midlands sites, rates of acidity input for the eastern seaboard region lie at the lower end of the range of internal proton production rates obtained from proton budget studies of forest ecosystems in the northern hemisphere (Table 2.3). Biomass accumulation in the productive eastern seaboard region is unlikely to be significantly lower than that of most other forest ecosystems, particularly those in temperate climates, and the apparent modest rates of acidification are probably partly due to the fact that only the upper 20 cm has been considered in this study. The inherently-acidic nature of soils in this region may also limit the extent of further acidification impacts (see section 2.3). In contrast to base cation depletion, rates of acidity enhancement in the southern Cape sites are comparable to those obtained by Clough (1991) for *Pinus elliottii* plantations replacing indigenous forest in the same region.

The rate of acidity enhancement shows a broad correlation with base cation depletion, confirming the expected relationship between acid input and base cation loss (Figure 5.14). However, acidity enhancement generally exceeds base cation depletion, suggesting that some of the acid input is associated with loss, either by leaching or biomass uptake, of NH_4^+. In view of du Toit's (1993) findings on afforestation-induced changes in ECEC (see section 5.3.4), as well as evidence indicating preferential uptake of ammonium nitrogen by pines (Keltjens and van Loenen, 1989; Arnold, 1992), it is tentatively suggested that unmeasured NH_4^+ loss (uptake) may be the most important factor accounting for this apparent discrepancy.

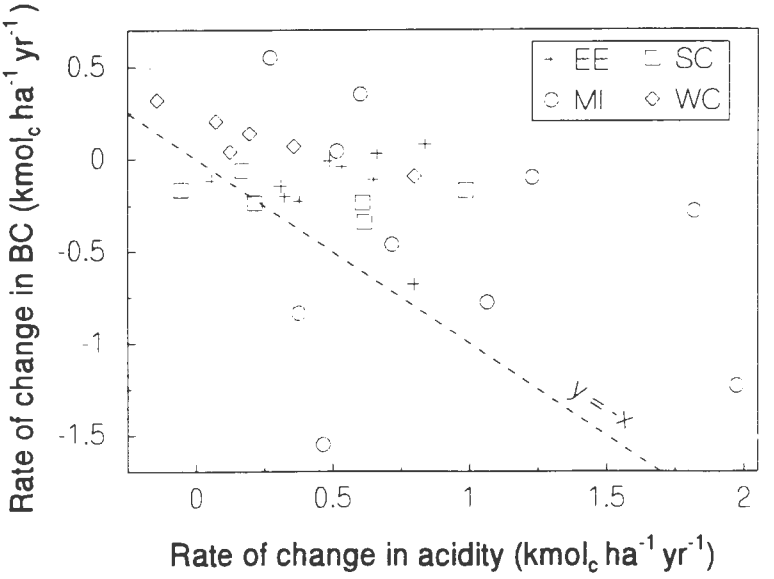

Figure 5.14: *The relationship between the rate of exchangeable base cation (BC = Ca + Mg + K + Na) loss and acidity enhancement. Rates of change were calculated by dividing forest/virgin differences in the quantity (per hectare) of exchangeable base cations/acidity by total plantation age. Total quantities per hectare were calculated from concentration data, for a soil depth of 20 cm. EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

5.4. SUMMARY AND CONCLUSIONS

Soil pH and exchangeable cation data confirm the strong acidifying effect of pine afforestation in the eastern seaboard region of southern Africa. Acidification rates in this region, measured in terms of changes in topsoil exchangeable acidity, range from 0.3 to 0.9 kmol$_c$ ha^{-1} yr^{-1} and are similar to or slightly lower than internal proton production rates calculated for acidic forest soils in the northern hemisphere. For the majority of sites, base cation depletion rates range from zero to 0.3 kmol$_c$ ha^{-1} yr^{-1} and span a very similar range to that observed in other studies of afforestation impacts in a wide variety of environments. Rough estimates of biomass uptake rates range up to ~ 0.28 kmol$_c$ ha^{-1} yr^{-1} and thus can account for the observed depletion of base cations in the majority of sites investigated. However, high base cation depletion rates (> 0.6 kmol$_c$ ha^{-1} yr^{-1}) are evident in several of the midlands sites and in one eastern escarpment site, suggesting that in some cases enhanced leaching may have contributed substantially to soil acidification under forest. In contrast to this, the majority of eastern escarpment sites display base cation depletion rates which are significantly lower than estimated rates of biomass uptake, possibly reflecting tight cycling of nutrients between living biomass and the forest floor.

Base cation depletion rates are generally lower than observed rates of acidity enhancement. This discrepancy may reflect the fact that the uptake of NH_4^+ by biomass has not been accounted for in this study (exchangeable NH_4^+ was not determined). Indirect evidence from other studies suggests that NH_4^+ uptake could contribute substantially to acidification under pine plantations.

The acidifying effect of afforestation is less prominent in the western and southern Cape where the pine plantations replace fynbos vegetation. Nonetheless, forest soils in these regions show significantly reduced pH values. In the western Cape, increases in exchangeable acidity are not statistically significant and most sites show afforestation-induced *enhancement* of exchangeable base cation concentrations. Input of marine salts is likely to contribute towards this base cation enrichment. However, this effect is not prominent and other processes, such as inputs of wind-blown dust and low biomass uptake rates, may be more important. Rates of acidification in the Cape regions and particularly those in the western Cape, are generally lower than those observed in the eastern seaboard forests and are believed to primarily reflect lower rates of biomass accumulation. Forest productivity is particularly low in the western Cape region, probably on account of low mean annual precipitation (relative to other forestry areas), summer drought and very nutrient-poor quartzitic parent materials.

6. THE COMPOSITION OF SOIL SOLUTIONS

6.1. INTRODUCTION

The data presented in previous chapters clearly demonstrate that pine afforestation has, in most cases, had a considerable impact on the chemistry, and in particular on the acidity, of soils previously under grassland and fynbos vegetation. As discussed in section 2.6, the extent to which soil acidity is transferred into soil solutions is critically dependent on the supply and mobility of the strong acid anions Cl^-, NO_3^- and SO_4^{2-}. In acid soils, HCO_3^- and organic anions which predominate in "natural" ecosystems are, to a large extent, protonated and, due to charge balance considerations, the displacement and leaching of acidity (primarily in the form of Al^{3+} and H^+ cations) is only possible if sufficient quantities of strong acid anions are present. It has been argued that, in view of the limited availability of strong acid anions in "natural" forest ecosystems, the extent to which soil acidification can lead to acidification of soil solutions and drainage waters is restricted (Ulrich, 1986; Reuss *et al.*, 1987). However, few studies have directly investigated the impact of afforestation on the composition of soil solutions in areas which are not influenced by acid deposition. In particular, the extent to which processes such as enhanced interception of natural atmospheric salts, evaporative concentration and disruption of nutrient cycles can enhance the concentration of strong acid anions, thereby facilitating the acidification of drainage waters, has not been thoroughly addressed. Nonetheless, studies of the effects of forest clearfelling (Bormann and Likens, 1979; Martin *et al.*, 1984; Mitchell *et al.*, 1989) and investigations of salt events in maritime forest ecosystems (Hindar *et al.*, 1994; Pedersen and Bille-Hansen, 1995) indicate that, under certain conditions, forests can have a dramatic impact on the composition of soil solutions and surface waters.

In this chapter, the impact of pine plantations on the composition of soil solutions is investigated for a range of environments in South Africa. Emphasis is placed on evaluating the effect of afforestation on the concentration of strong acid anions in solution and on the processes which control the solubility of Al, an element which is of critical importance with respect to the environmental impact of soil acidification.

6.2. MATERIALS AND METHODS

The impact of afforestation on the composition of soil solutions was studied using the same set of soil samples that was used to assess soil acidity changes. This includes forest-virgin sample pairs for 22 sites sampled during this study and 16 sites sampled for a previous study by du Toit (1993). Methods of sampling are discussed in section 3.2.

6.2.1. Saturated paste extraction

Estimates of soil solution composition were obtained by analysis of saturated paste extracts, the composition of which is believed to provide an indication of the "average" equilibrium composition of the soil solution (Sposito, 1989). Because they are extracted from relatively large and homogeneous volumes of soil, saturated paste extracts are not subject to the temporal and spatial variability which one would expect for small solution volumes obtained by *in situ* sampling (e.g. using tension lysimeters). Saturated paste extracts are therefore particularly useful for elucidating relative changes in composition resulting from afforestation, as well as other anthropogenic or natural influences.

Saturated paste extracts were prepared by wetting approximately 300 g of air-dried and sieved (< 2 mm) soil to saturation point with deionised water and allowing the samples to equilibrate for 24 hours before extracting solutions under vacuum using a plastic Buchner funnel. The amount of water required to reach saturation point was found to be highly reproducible (to better than ± 5 %) in repeated soil extracts from splits of the same sample.

Drying and rewetting of soil samples is known to influence the composition of aqueous extracts, and has a particularly strong influence on soil pH and soluble organic matter concentrations (Bartlett and James, 1980). This is not considered to be a major hindrance to this study as all of the soils investigated dry out annually for relatively long periods (several months) in their natural environment. By drying all of the samples prior to saturated paste extraction, they are all brought to an equivalent state which does not differ significantly from that likely to pertain for dry *in situ* soils. Thus more meaningful comparisons can be made between samples than if the samples were retained in their field moist states which span a wide range of soil moisture contents. However, long term storage of the samples was found

to have a considerable impact on the concentrations of dissolved organic carbon (DOC) in saturated paste extracts, and may result in an overestimation of this parameter in soils stored for long time periods (i.e. greater than 1 to 2 months; see section 6.2.2).

Because the saturated paste extracts are prepared with deionised water, the influence of forest litter on the composition of soil solutions in underlying horizons is not accounted for. As demonstrated by James and Riha (1989), solutions percolating through forest litter are enriched in DOC. Thus, saturated paste extracts of the forest soil samples may contain lower concentrations of DOC than those of soil solutions occurring *in situ*. This effect is likely to be most significant for soils of the eastern escarpment where accumulation of thick litter layers occurs.

Initial studies were carried out to evaluate the possible effects of microbial activity and varying equilibration times on the composition of the extracts (Appendix D). This work indicated that effective equilibration of saturated paste extracts generally occurs within ten hours and increased saturation times does not have a significant effect on the composition of the extracts. Within this time frame (i.e. 24 hours) microbial activity did not appear to significantly influence extract composition.

Saturated paste extracts were centrifuged and passed through 0.45 μm membrane filters within half an hour of extraction. The pH and electrical conductivity (EC) of the extracted solution were determined immediately after extraction and again after filtration. Differences between these two measurements were found to be negligible. The solutions were stored under refrigerated conditions (~ 4 °C) prior to further analysis.

6.2.2. Analysis

Solution pH and EC, and the concentrations of major anions (Cl^-, NO_3^- and SO_4^{2-}), major cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}), manganese (Mn^{2+}) and dissolved organic carbon (DOC) were determined for saturated paste extracts of all samples. The solution pH was determined using a Metrohm 691 pH meter and combination electrode, and EC was measured using a Crison microCM 2201 conductivity meter. Major anion, major cation and Mn^{2+} concentrations were determined by ion chromatography using a Dionex DX300 suppressed IC system (analytical details are provided in Appendix B). Dissolved organic carbon was determined using an ANATOC organic carbon analyser (SGE Scientific). This method involves

photocatalytic oxidation (by UV radiation using TiO_2 as a catalyst) of organic carbon in pretreated samples, followed by determination of evolved CO_2 by measuring the associated change in solution EC in a high-sensitivity conductivity cell (Bennet and Richards, 1994). Sample pretreatment involves acidification to pH 4.5 with 0.1 M perchloric acid, and degassing of sample immediately prior to analysis in order to remove any dissolved CO_2.

Aluminium and silicon were determined for a second batch of extracts obtained from a subset of thirty samples (paired forest and virgin samples from 15 sites - see Table C5, Appendix C). The pH and major ion composition of these extracts were determined by the methods described above. This work was undertaken primarily to investigate the speciation and solubility of Al in soil solutions. Dissolved Al concentrations were obtained by colorimetry using the Cr-azurol S (CAS) method of Kennedy and Powell (1986) (Appendix B). This method determines monomeric Al in solution and has a lower limit of detection of ~ 0.075 mg L^{-1}. Kennedy and Powell report that addition of fulvic acid to a 0.5 mg L^{-1} Al solution did not influence absorbence readings, indicating that Al which is complexed to dissolved organic matter (DOM) is also determined by this method. Dissolved monomeric silica (H_4SiO_4) was determined colorimetrically using the blue silicomolybdic acid procedure of Weaver *et al.* (1968). A lower limit of detection of 0.08 mg L^{-1} was obtained for this method. The Al and Si analyses were carried out within one hour of saturated paste extraction.

Exchangeable SO_4^{2-} and Mn were determined on the same subset of 30 samples that were analysed for Al and Si. Exchangeable SO_4^{2-} was determined using a 0.01 M Ca-phosphate ($Ca(H_2PO_4)_2 \cdot H_2O$) extractant solution with 10 ml of Superfloc added per L. The extracts were prepared using a soil:solution ratio of 1:10. Suspensions were stirred for 30 minutes and filtered (Watman filter paper) before being analysed for SO_4^{2-} using the automated turbidimetric method of Wall *et al.* (1986). The analyses were undertaken by the Agricultural Research Council laboratories at Cedara, in KwaZulu-Natal. Exchangeable Mn was determined in 1M KCl extracts with a soil:solution ratio of 1:10. These were analysed for Mn using atomic absorption spectroscopy.

Twenty-two of the 30 samples used for the above-described investigation had been stored (air-dried) for a period of approximately one year prior to extraction. This resulted in DOC concentrations which were elevated relative to those in the original extracts obtained within

a few weeks of sampling. Assuming that the saturated paste extracts are likely to be in equilibrium with the least stable Al-bearing solid phase (see section 6.3.3.5), the activities and concentrations of Al^{3+} and other inorganic Al species should not be affected by DOC concentration. However, because of the strong complexation of Al by DOM, increased levels of the latter will result in enhanced *total concentrations* of soluble Al. Total Al activities and concentrations expected under equilibrium with the original, lower DOC concentrations, were estimated using the MINTEQA2 speciation programme (this procedure is described in more detail in section 6.3.3.3) and are believed to provide a more realistic indication of Al concentrations prevalent under field conditions.

6.2.3. Data reproducibility

Sampling, extraction and analytical reproducibility were evaluated by analysis of duplicate extracts, as well as of extracts from duplicate samples taken one year after original sampling (Appendix E). Data for twenty duplicate extracts carried out on the same samples and at the same time as the original extractions and analyses provide a basis for estimating extraction and analytical error. Although error estimates obtained from these data are relatively high (~ 4 to 38 %), inter-site variations, in terms of both absolute concentrations and forest/virgin differences, are well duplicated, suggesting that extraction and analytical error does not obscure real trends in soluble ion concentrations. Data obtained for extracts carried out a year after the original analytical work was done (Appendix E) confirmed the reproducibility of the methods used and indicated that the effect of long-term sample storage on solute concentration is minimal (with the exception of DOC).

Results obtained for duplicate *samples* (taken one year later) indicate that, with the exception of site EE7, temporal and spatial variability associated with sampling was relatively minor and, for most variables, did not obscure observed trends. However, DOC and Cl^- concentration data exhibited a high degree of variability, suggesting that, in the case of these two variables, caution needs to be exercised when interpreting differences between individual samples (Appendix E). Site EE7 differed from all of the other sites which were resampled in that it consistently showed large differences between solute concentration values obtained on 1996 samples and those obtained in 1995. As discussed in Appendix E and section 6.3.1.2 below, these differences are believed to reflect short term variations following clearfelling of the site one year prior to the original sampling.

6.2.4. Speciation calculations and mineral equilibria

Chemical speciation calculations were carried out for forest and virgin soil solutions using the MINTEQA2 mathematical model (Allison *et al.*, 1990) and the equilibrium constants given in Table 6.1. Calculations involve the simultaneous solution of a set of non-linear mass action expressions (i.e. the equilibrium relationship between reactants and products) and linear mass balance equations by an iterative procedure. The Davies equation option was selected for the calculation of activity coefficients.

Table 6.1: *Equilibrium constants for relevant aqueous reactions involving Al. Sources: 1 - Nordstrom and May, 1996; 2 - MINTEQA2 database (Allison et al., 1990). The default logK values used by MINTEQA2 are given in parentheses where they differ from the chosen values.*

Reaction	log*K*	Source
Al hydrolysis reactions		
$Al^{3+} + H_2O \Leftrightarrow Al(OH)^{2+} + H^+$	-5.00 (-4.99)	1
$Al^{3+} + 2H_2O \Leftrightarrow Al(OH)_2^+ + 2H^+$	-10.1	1
$Al^{3+} + 3H_2O \Leftrightarrow Al(OH)_3^\circ + 3H^+$	-16.8 (-16.0)	1
$Al^{3+} + 4H_2O \Leftrightarrow Al(OH)_4^- + 4H^+$	-22.99 (-23.0)	1
Al sulphate complexes		
$Al^{3+} + SO_4^{2-} \Leftrightarrow AlSO_4^+$	3.5 (3.02)	1
$Al^{3+} + 2SO_4^{2-} \Leftrightarrow Al(SO_4)_2^-$	5.0 (4.92)	1
Al fluoride complexes		
$Al^{3+} + F^- \Leftrightarrow AlF^{2+}$	7.0 (7.01)	1
$Al^{3+} + 2F^- \Leftrightarrow AlF_2^+$	12.7 (12.75)	1
$Al^{3+} + 3F^- \Leftrightarrow AlF_3^\circ$	16.8 (17.02)	1
Organic complexes		
Al^{3+} + DOM ⇔ Al-DOM	5.20	2
H^+ + DOM ⇔ H-DOM	3.87	2
Ca^{2+} + DOM ⇔ Ca-DOM	2.90	2
Mg^{2+} + DOM ⇔ Mg-DOM	1.90	2

Mineral equilibria were evaluated by means of saturation indices and log(Al^{3+}) - pH solubility diagrams (based on the reactions and log$K$ values given in Table 6.2). Saturation indices (SI) were calculated from ion activity products (IAP) by the equation:

$$SI = \log(IAP/K_{sp}) \quad \ldots . (1).$$

Thus, SI values greater than 0 indicate supersaturation with respect to the mineral being considered, whereas negative values indicate undersaturation. Saturation index values close to 0 suggest that the mineral is in equilibrium and is therefore likely to be controlling the activity of its constituent components in the saturated paste extracts. The use of SI values for the study of mineral solubility equilibria is well established (e.g. Nordstrom and Munoz, 1994) and log(Al^{3+}) - pH diagrams have been extensively used to illustrate equilibria pertaining to the solubility of Al in aqueous solutions (e.g. Bloom *et al.*, 1979; Lindsay, 1979; Lindsay and Walthall, 1989).

Table 6.2: *Equilibrium constants for dissolution reactions involving Al-bearing phases and silica. Sources: 1 - Lindsay, 1979; 2 - Manley et al., 1987; 3 - Farmer et al., 1979; 4 - Nordstrom, 1982; 5 - Adams and Rawajfih, 1977. Default equilibrium constants used by MINTEQA2 are shown in parentheses (dashes indicate that these reactions are not represented in the MINTEQA2 database). Am. = amorphous.*

Mineral/phase	Reaction	log$K$	Source
Al hydroxides			
Gibbsite	$Al(OH)_3 + 3H^+ \leftrightarrow Al^{3+} + 3H_2O$	8.04 (8.77)	1
"Soil" $Al(OH)_3$	$Al(OH)_3 + 3H^+ \leftrightarrow Al^{3+} + 3H_2O$	8.77 (-)	1
Am. $Al(OH)_3$	$Al(OH)_3 + 3H^+ \leftrightarrow Al^{3+} + 3H_2O$	9.66 (10.38)	1
Al silicates			
Kaolinite	$Al_2Si_2O_5(OH)_4 + 6H^+ \leftrightarrow 2Al^{3+} + 2H_4SiO_4 + H_2O$	5.45 (5.726)	1
Halloysite	$Al_2Si_2O_5(OH)_4 + 6H^+ \leftrightarrow 2Al^{3+} + 2H_4SiO_4 + H_2O$	8.72 (8.994)	1
Allophane	$Al_2O_3{\cdot}2SiO_2{\cdot}3H_2O + 6H^+ \leftrightarrow 2Al^{3+} + 2H_4SiO_4 + 2H_2O$	7.62 (-)	2
Imogolite	$Al_2O_3SiOH(OH)_3 + 6H^+ \leftrightarrow 2Al^{3+} + H_4SiO_4 + 3H_2O$	11.57 (-)	3
Silica			
Quartz	$SiO_2 + 2H_2O \leftrightarrow H_4SiO_4$	-4.00 (-4.006)	1
"Soil" silica	$SiO_2 + 2H_2O \leftrightarrow H_4SiO_4$	-3.10 (-3.911)	1
Al sulphates			
Jurbanite	$AlSO_4(OH){\cdot}5H_2O + H^+ \leftrightarrow Al^{3+} + SO_4^{2-} + 6H_2O$	-3.80 (-3.23)	4
Alunite	$KAl_3(SO_4)_2(OH)_6 + 6H^+ \leftrightarrow K^+ + 3Al^{3+} + 2SO_4 + 6H_2O$	-1.04 (-1.346)	5

6.3. RESULTS AND DISCUSSION

This section discusses the analytical results obtained for the saturated paste extracts, focusing primarily on the impact of afforestation and on regional variations. The compositional parameters that are covered are: strong acid anions; dissolved organic carbon (DOC); pH and Al; Mn; and basic cations. This is followed by an evaluation of the extent to which the "edge effect" has influenced the composition of soil solutions. All analytical data pertaining to the saturated paste extracts are given in Appendix C (Tables C4 and C5).

6.3.1. Afforestation impacts on strong acid anion concentrations

Due to the acidic nature of the soil solutions, the concentration of HCO_3^- is negligible. Thus the strong acid anions, Cl^-, NO_3^- and SO_4^{2-}, dominate the inorganic anion suite and the following discussion deals only with these components. As in the case of exchangeable cation data, regional variations and afforestation impacts are evaluated in a statistical manner using box and whisker plots (Figure 6.1) and the non-parametric Wilcoxon matched pairs test (Table 6.3).

6.3.1.1. Chloride

Chloride is the dominant soluble inorganic anion in the virgin soils of all four regions sampled (Figure 6.1). Concentrations range from 0.27 to 1.41 $mmol_c\,L^{-1}$, but few sites have concentrations lower than 0.5 $mmol_c\,L^{-1}$. The lack of any consistent regional differences in the soluble Cl^- concentrations of virgin soils is somewhat surprising in view of the dramatic differences between the Cl^- concentration of rainfall in the western Cape and that of other regions (Table 3.2). This may reflect the high degree of mobility of the Cl^- anion which is unlikely to accumulate to any extent in strongly leached soils.

Soluble Cl^- concentrations for forest soils of the southern and western Cape are significantly higher ($p < 0.05$) than those of their fynbos equivalents (Table 6.3; Figure 6.1), with increases ranging from approximately 0.1 to 2 $mmol_c\,L^{-1}$. This is consistent with the combination of elevated Cl^- levels in rainfall, enhanced interception of salt aerosols and considerable enhancement of evapotranspiration in the forests relative to fynbos ecosystems. Changes in

Cl^- concentrations under forests in the eastern escarpment and midlands regions are far more erratic and many sites, particularly those of the eastern escarpment, show reduced levels of soluble Cl^- in forest soils. Although the statistical tests results presented in Table 6.3 suggest that the reduction in soluble Cl^- levels in the eastern escarpment is significant, conflicting results obtained for several duplicate samples taken in 1996 (Appendix E) indicate that this effect may be a transient phenomenon.

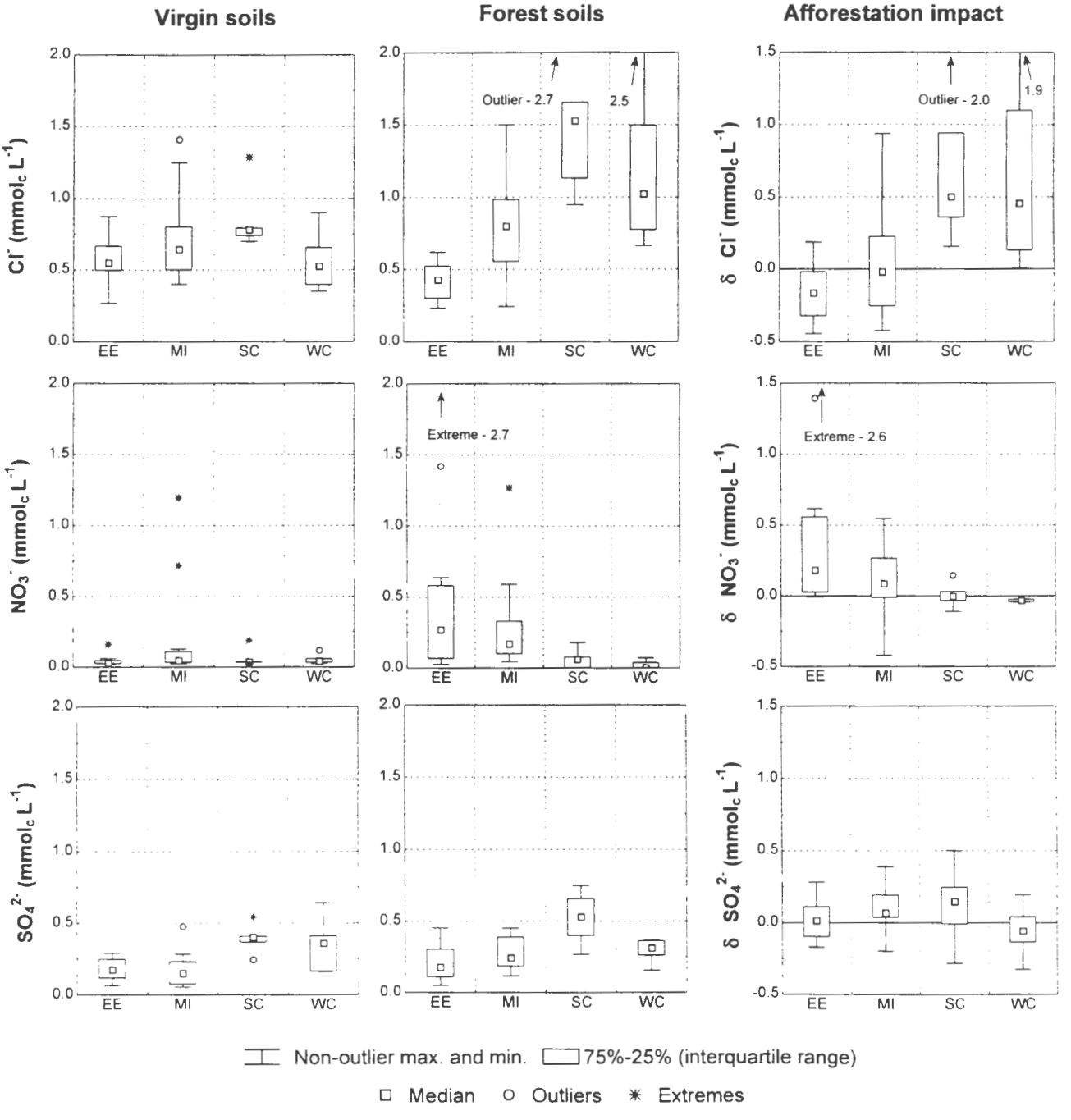

Figure 6.1: *Box and whisker plots illustrating regional variations in inorganic anion concentrations in saturated paste extracts from virgin and forest soils. δ Values represent the difference between the concentration in the forest extracts and those in their virgin equivalent (i.e. $\delta X = X_{forest} - X_{virgin}$, where $X = Cl^-$, NO_3^- or SO_4^{2-}). EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

Table 6.3: *P values (statistical significance levels) for forest-virgin differences in electrical conductivity and anion concentrations of saturated paste extracts. Significance levels were obtained using the non-parametric Wilcoxon matched pairs test. Underlined values indicate positive differences (i.e. increased concentrations under forest). ** - differences significant at the 99% confidence level; * - differences significant at the 95% confidence level.*

	All	**Eastern escarpment**	**Midlands**	**Southern Cape**	**Western Cape**
No. of soil pairs	38	12	14	6	6
EC	0.000**	0.028*	0.272	0.075	0.028*
Cl^-	0.180	0.023*	0.975	0.028*	0.028*
NO_3^-	0.008**	0.004**	0.041*	0.917	0.028*
SO_4^{2-}	0.081	0.638	0.019*	0.345	0.463
Inorganic anions	0.000**	0.182	0.041*	0.046*	0.116
DOC	0.080	0.308	0.005**	1.000	0.028*
All anions	0.094	0.209	0.433	0.345	0.028*

Concentration data for strong acid anions in soil solutions have been compiled from studies of forest ecosystems in North America and Northern Europe and are presented in Table 6.4. The majority of these data are average concentrations determined for soil solutions sampled over extended time periods (6 months to 7 years) using tension lysimeters. Because of the different methods used, these data are not directly comparable to those obtained for saturated paste extracts. However, they do provide a qualitative basis for comparison with the data of this study. The Cl^- concentrations in solutions from most of the Northern Hemisphere forest ecosystems represented in Table 6.4 are considerably lower than those reported here for both forest and virgin soils. Only soil solutions from maritime sites in north America and northern Europe which are strongly impacted by marine salt deposition have Cl^- concentrations of a similar magnitude to those observed for both the forest and the virgin soils of this study. The ubiquitously high Cl^- levels in the South African forest soils may result from high rates of evaporative concentration, reflecting higher temperatures and possibly lower precipitation levels than those prevailing at most of the sites represented in Table 6.4. Alternatively, high Cl^- levels may stem from a maritime influence at all sites, with the eastern seaboard soils receiving salt inputs from frequent fogs which regularly reach the escarpment area in both the midlands and the eastern escarpment.

Table 6.4: *Anion concentrations in soil solutions from forest topsoils in North America and northern Europe. With the exception of the data for Camels Hump, the data represent average values for solutions sampled over extended time periods (6 months to 7 years) using tension lysimeters. The Camels Hump solutions were obtained from individual soil samples by the pressure syringe method. Acid dep. - qualitative indication of the extent of acid deposition. Sea salt - qualitative indication of the extent of marine salt inputs (base primarily on proximity to the ocean). Sources: 1 - Cronan and Aiken, 1985; 2 - Rustad et al., 1996; 3 - Johnson et al., 1985; 4 - Bockheim and Langley-Turnbaugh, 1997; 5 - Binkley et al., 1982; 6 - Homann et al., 1994; 7 - LaZert and Scott, 1996; 8 - Farrel et al., 1994; 9 - Marschner et al., 1992.*

Site	Genus	Acid dep.	Sea salt	Cl^-	NO_3^-	SO_4^{2-}	Sum	Ref.
				$mmol_c\ L^{-1}$				
North America - acid deposition impacted								
Adirondack Park, New York	mixed	moderate	moderate	0.032	0.085	0.210	0.327	1
Bear Brook,Maine, USA	mixed	moderate	moderate	0.039	0.004	0.074	0.117	2
Bear Brook,Maine, USA	mixed	severe	moderate	0.044	0.220	0.337	0.601	2
Walker Branch, Tennessee	*Quercus*	moderate	v.minor	0.039	0.000	0.330	0.369	3
Walker Branch, Tennessee	*Liriodendron*	moderate	v.minor	0.036	0.001	0.348	0.385	3
North America - Sea salt impacted								
Cape Blanco, Oregon	*Picea*	v.minor	v.severe	5.830	0.003	0.936	6.769	4
Pioneer terrace, Oregon	*Picea*	v.minor	v.severe	4.130	0.002	0.831	4.963	4
Silver Butte, Oregon	*Picea*	v.minor	severe	1.210	0.003	0.205	1.418	4
Indian Creek, Oregon	conifer	v.minor	severe	0.047	0.002	0.045	0.094	4
Poverty Ridge, Oregon	conifer	v.minor	severe	0.503	0.002	0.281	0.786	4
UBC Research forest., B.C.	conifer	v.minor	moderate	0.035	0.136	0.064	0.235	5
UBC Research forest., B.C.	conifer	v.minor	moderate	0.031	0.022	0.053	0.106	5
Cedar River, Washington	*Pseudotsuga*	minor	moderate		0.002			6
Cedar River, Washington	*Alnus*	minor	moderate		0.255			6
North America - minimal acid or salt impacts								
Harp Lake, Ontario, Canada	*Pinus*	v.minor	v.minor	0.016	0.000	0.098	0.113	7
Harp Lake, Ontario, Canada	*Pinus*	v.minor	v.minor	0.014	0.001	0.074	0.089	7
Europe - acid deposition impacted								
Kootwijk, Holland	*Pinus*	severe	minor	1.002	0.962	1.047	3.011	8
Hardewijk, Holland	*Pinus*	severe	minor	0.681	0.026	0.480	1.187	8
Högwald, Germany	*Picea*	severe	minor	0.150	2.030	1.356	3.536	8
Solling, Germany	*Picea*	severe	minor	0.130	0.680	0.747	1.557	8
Grunewald, Berlin, Germany	*Pinus*	severe	v.minor		0.726	0.469	1.195	9
Grunewald, Berlin, Germany	*Pinus*	severe	v.minor		0.081	0.052	0.133	9
Europe - marine salt impacted								
Klosterheide, Denmark	*Picea*	minor	severe	2.886	0.062	0.669	3.617	8
Ballyhooly, Ireland	*Picea*	v.minor	severe	0.999	0.091	0.164	1.254	8

6.3.1.2. Nitrate

With the exception of two midlands sites, the concentrations of soluble NO_3^- in the virgin soils are extremely low and generally do not exceed 0.1 $mmol_c\ L^{-1}$ (Figure 6.1). At most of the eastern escarpment and many of the midlands sites afforestation appears to have dramatically enhanced these NO_3^- concentrations to the extent that in some of these sites it is the dominant soluble anion. These high NO_3^- levels are similar to those observed in forest sites of northern Europe which have been severely impacted by anthropogenic nitrogen deposition (Table 6.4). In contrast to this, NO_3^- levels in forest soil solutions of the southern and western Cape are, if anything, slightly lower than in their fynbos counterparts.

The degree of NO_3^- enhancement in the eastern escarpment and midlands sites is highly variable, with increases ranging from approximately 0.2 to 2.6 $mmol_c\ L^{-1}$ (Figure 6.1; Appendix C). The largest NO_3^- increase occurs at a site (EE7) which had been clearfelled approximately one year prior to sampling, suggesting that the extreme NO_3^- concentrations are probably generated by rapid oxidation of forest litter following harvesting (Vitousek *et al.*, 1979; Mitchell *et al.*, 1989). The temporary nature of this extreme NO_3^- enhancement under forest was confirmed by data obtained for a bulk sample taken one year later at the same site. The NO_3^- concentration of the saturated paste extract obtained from this sample was reduced to 0.89 $mmol_c\ L^{-1}$, from an original value of 2.65 $mmol_c\ L^{-1}$. Apart from EE3, however, which was clearfelled approximately four years prior to sampling, the other sites with enhanced NO_3^- concentrations are mature plantations (>15 years old, see Appendix C) and, therefore, an alternative mechanism needs to be invoked to account for the high NO_3^- levels.

A possible explanation for elevated NO_3^- concentrations in the saturated paste extracts is that they result from mineralisation and nitrification processes taking place during drying and/or storage of the soil samples (Bartlett and James, 1980). These processes may well occur during natural drying and wetting cycles prevailing in the forest. In the case of the saturated paste extracts, however, the NO_3^- produced by microbially mediated oxidation processes cannot be removed by plant uptake. This could account for the elevated NO_3^- levels, but the following questions still remain: 1) why do the forest soils have higher soluble NO_3^- levels than their grassland equivalents? and 2) why are elevated NO_3^- levels prevalent in the eastern seaboard

but not in the Cape regions? Due to the uncertainties regarding the effect of sample processing on N dynamics, it is not possible to answer these questions conclusively based on the data generated in this study (an in-depth PhD study of the N dynamics in pine plantations of the Eastern Escarpment is currently uderway [S.Jacobs supervised by Dr W. Stock] and should help to answer some of the questions generated by the current work). Nonetheless, it is worthwhile considering some of the factors that are likely to play a role in determining the N dynamics in the soils of this study.

The data on rainfall chemistry presented in Chapter 3 (Table 3.2) indicate significantly elevated levels of NO_3^- in precipitation at sites in the eastern escarpment relative to precipitation in the western Cape. Although no rainfall data is available for the midlands study region, data from other parts of KwaZulu-Natal suggest that some areas may be subject to elevated NO_3^- deposition in rainfall (Table 3.2). Thus it is possible that the elevated NO_3^- concentrations in forest soil solutions in these regions results from enhanced interception and evaporative concentration of atmospheric NO_3^-. The high degree of variability in NO_3^- enhancement within the eastern escarpment and midlands regions is, however, difficult to reconcile with an atmospheric NO_3^- source which is unlikely to vary substantially between sites. In addition, nitrogen inputs (< 1 $kmol_c\ ha^{-1}\ yr^{-1}$ in the eastern escarpment; Olbrich and du Toit, 1993) are small in relation to the total soil nitrogen pool. Thus, modifications of the nitrogen cycle can potentially have a far greater influence on soluble N levels than variations in atmospheric inputs. The processes involved in the nitrogen cycle have been discussed in Chapter 2 and include variations in NO_3^- uptake by trees, litter accumulation on the forest floor, rates of oxidation of this forest litter and rates of immobilisation, nitrification and denitrification by soil microbes (Johnson, 1992). The presence of elevated NO_3^- concentrations in the soil solution implies that NO_3^- inputs, primarily from atmospheric deposition and litter decomposition, exceed plant and soil microbial requirements. This contrasts with the situation in most northern hemisphere forest ecosystems which, in most cases, are significantly undersaturated with respect to nitrogen, to the extent that elevated soluble NO_3^- levels and NO_3^- leaching generally only occur when very large amounts of nitrogen are added to the soil (e.g. Johnson *et al.*, 1986; Ring, 1995; Stuanes *et al.*, 1995).

Microbially mediated N cycling processes are likely to play a critical role in determining the concentrations of soluble NO_3^-. The availability of NO_3^- depends on the relative rates of

ammonification of organic N, N uptake by heterotrophic organisms, nitrification, and denitrification. The activity of soil heterotrophs, which are strong competitors for NH_4^+, as well as that of denitrifying organisms, requires an adequate supply of labile organic C (Riha *et al.*, 1986; Johnson, 1992). Thus, reductions in the availability of mineralisable organic matter can inhibit NH_4^+ uptake and denitrification and, in an oxidising environment, can lead to increased soluble NO_3^- levels. This may account for the enhanced levels of NO_3^- in soil solutions of the eastern seaboard forests, as most of these soils have lower organic carbon contents than their grassland equivalents. In addition, increased inputs of N via atmospheric deposition may, over time, lead to a general enrichment of N in the forest ecosystem and is likely to be an important factor contributing to enhanced concentrations of NO_3^- in soil solutions under forest in the eastern seaboard. Conversely, apparent low levels of N deposition (Table 3.2) may account for the ubiquitously low NO_3^- concentrations in soil solutions from both forest and fynbos sites of the southern and western Cape.

An additional factor which is likely to influence the concentration of soluble NO_3^- is the reduced pH levels observed under forest. Although several studies have suggested that nitrification processes are sensitive to soil pH and are therefore limited in acid soils (Robertson, 1982; Roseberg *et al.*, 1986; Binkley and Richter, 1987), the extent of this effect is uncertain (Johnson, 1992). Increased NO_3^- concentrations in soil solutions from the eastern seaboard forests suggest that, if anything, processes leading to NO_3^- removal (i.e. uptake and denitrification) are more sensitive to acidification than are those which lead to NO_3^- generation (i.e. ammonification and nitrification). It is also possible that the negative effect of acidification on nitrification rates is offset by the drier more oxidising conditions under forest compared to those prevailing under grassland.

The factors controlling the concentration of NO_3^- in the soil solutions investigated for this study are not well understood and further work is required to resolve the issues discussed above. However, it would appear that, in the eastern seaboard region, afforestation has at least led to an increased *potential* for the generation and consequently the leaching of NO_3^-. This effect is not evident in the southern and western Cape.

6.3.1.3. Sulphate

Sulphate concentrations in extracts from virgin soils are intermediate between those of Cl^- and NO_3^-, and range from approximately 0.1 to 0.5 $mmol_c\ L^{-1}$ (Figure 6.1). In general, soluble SO_4^{2-} levels are slightly elevated in the virgin soils of the southern and western Cape relative to most sites in the eastern escarpment and midlands regions. These trends correlate with rainfall chemistry data reported in Table 3.2 which indicate higher levels of SO_4^{2-} deposition in the western Cape than in the eastern escarpment or midlands. High SO_4^{2-} inputs may result from a stronger marine influence in the Cape region which is likely to introduce large amounts of sulphur. However, molar SO_4^{2-}:Cl^- ratios for precipitation in the western Cape are considerably higher than those of average sea water (~ 1:10). Possible causes of these high ratios include atmospheric pollution, elevated production of H_2S and dimethyl sulphide (DMS) by marine organisms (Dodds, 1995), or an analytical overestimation of SO_4^{2-} concentrations. An anthropogenic source of sulphur is considered unlikely, particularly in the southern Cape region which is situated very far from any industrialised area (> 400 km).

Soluble SO_4^{2-} concentrations in the virgin soils display a broad inverse relationship to clay content (Figure 6.2), suggesting that the more clay-rich soils generally have higher SO_4^{2-} sorption capacity and therefore subtend lower SO_4^{2-} concentrations in soil solution than soils with lower clay contents. This is reflected in the relationship between soluble and exchangeable SO_4^{2-} for both forest and virgin soils (Figure 6.3.a). Soluble SO_4^{2-} concentrations in the clay-rich soils of the eastern escarpment and, to some extent, of the midlands region, are generally very low, despite very high concentrations of exchangeable SO_4^{2-}. In contrast to this, the virgin soils of the Cape region (as well as a sandy eastern escarpment soil - site EE2) have very low exchangeable SO_4^{2-} concentrations, but generally display relatively high soluble SO_4^{2-} levels. The degree of SO_4^{2-} sorption would be expected to correlate with clay content, since the soils are highly weathered and sesquioxides, with a high anion retention capacity, are likely to constitute an important component of the clay fraction (as indicated in section 4.3.2).

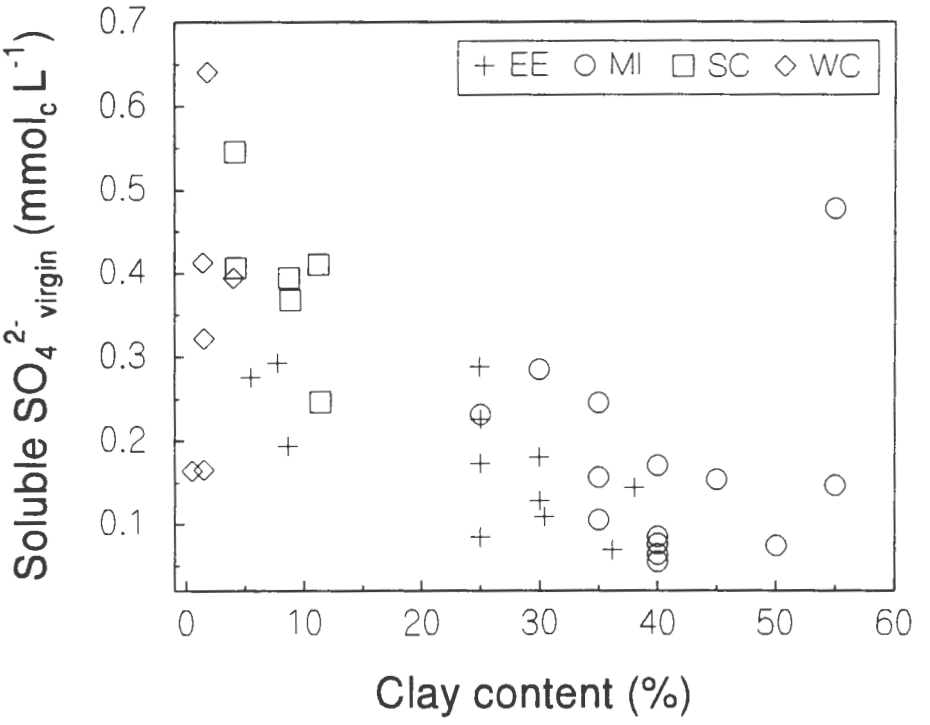

Figure 6.2: *Plot illustrating the relationship between the concentration of soluble SO_4^{2-} in virgin soils and the soil clay content. Soluble SO_4^{2-} concentrations are based on the composition of saturated paste extracts. EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

The relationship between exchangeable SO_4^{2-} concentration and clay content is illustrated in Figure 6.3.b. This clearly demonstrates the association of high exchangeable SO_4^{2-} concentrations with soils of high clay content, but indicates a significantly higher degree of SO_4^{2-} enrichment in clay-rich forest soils compared to those of associated grasslands. The dramatic enhancement of exchangeable SO_4^{2-} concentration in the clay-rich forest soils of the eastern escarpment and midlands is more clearly evident in Figure 6.3.c in which the concentration in forest soils is directly compared to that of their grassland or fynbos equivalents. This also illustrates the negligible effect of afforestation on exchangeable SO_4^{2-} concentrations in the majority of sandy soils. Due to the pH dependence of SO_4^{2-} sorption capacity, the observed acidification of forest soils is likely to be a major factor contributing to the enhancement of exchangeable sulphate concentration in clay-rich soils. A plot of exchangeable SO_4^{2-} against soil pH confirms that there is a significant relationship ($R^2 = 0.72$) between pH and SO_4^{2-} retention (Figure 6.4). However, no clear relationship was found between the *change* in pH and the change in exchangeable SO_4^{2-} under forest. It is likely that other factors, such as variations in sesquioxide content and atmospheric inputs of SO_4^{2-}, substantially influence the degree to which SO_4^{2-} retention is enhanced by afforestation.

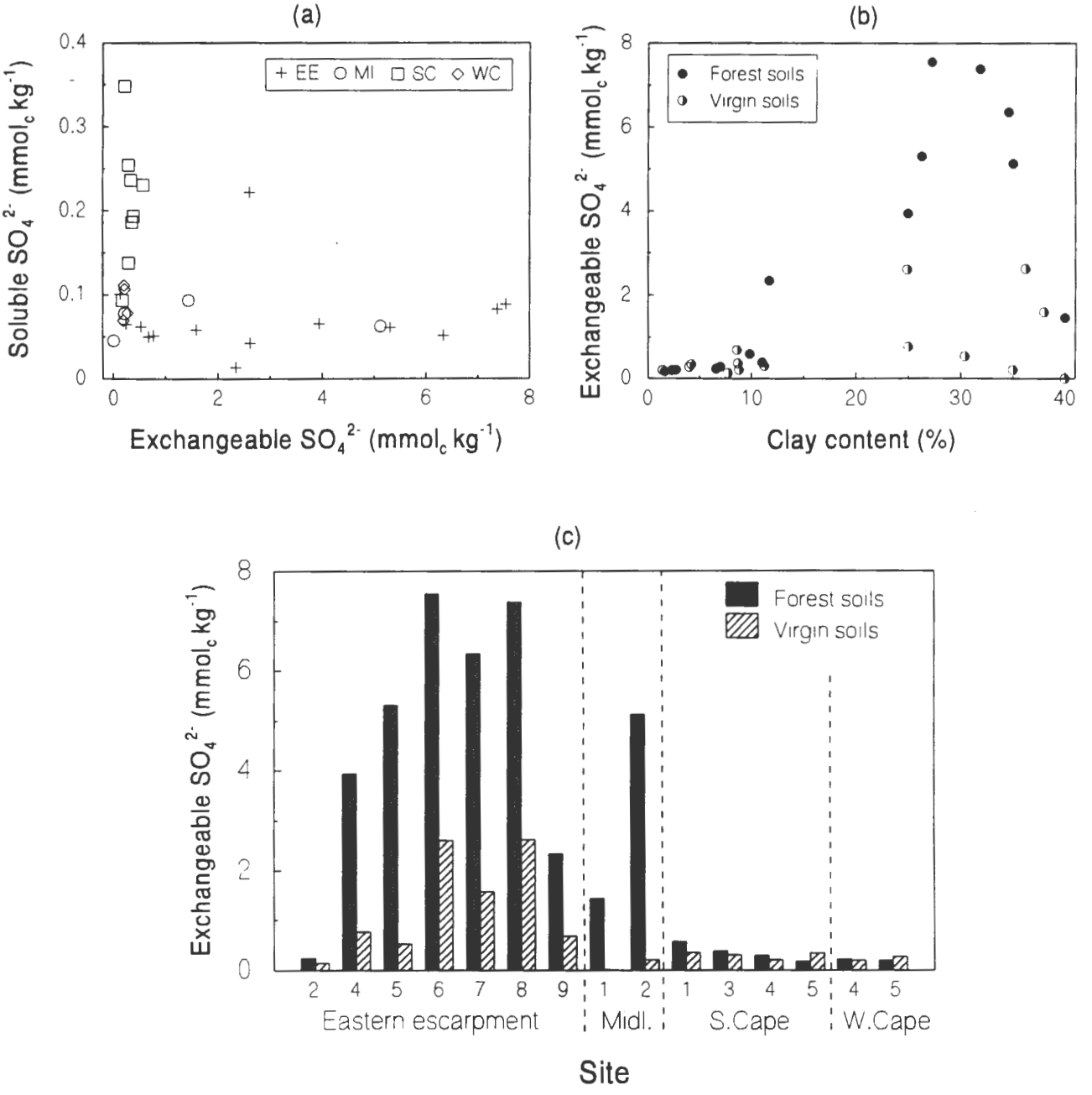

Figure 6.3: *Soluble and exchangeable sulphate relationships. a) The relationships between water soluble SO_4^{2-} (saturated paste extracts) and exchangeable (Ca-phosphate extractable) SO_4^{2-}. b) The relationship between exchangeable SO_4^{2-} and clay content. c) Exchangeable SO_4^{2-} concentrations for forest-virgin soil pairs. EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

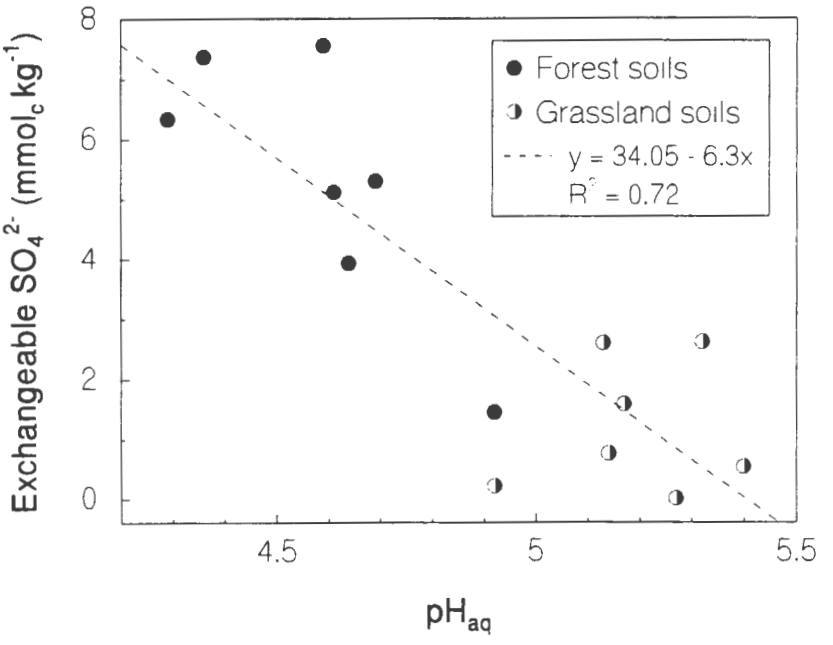

Figure 6.4: *The relationship between phosphate-extractable SO_4^{2-} and soil pH (measured in water) in clay-rich (clay > 15 %) forest and grassland soils from the eastern escarpment and midlands regions (no suitable clay-rich soils could be sampled in the Cape regions - see Chapter 3).*

The effect of afforestation on the concentration of SO_4^{2-} in soil solution is variable and significantly less dramatic than effects on exchangeable SO_4^{2-} (Figure 6.1). Only the midlands sites display statistically significant enhancement of soluble SO_4^{2-} concentrations under forest (Table 6.3). The data suggest that a large proportion of the sandy (< ~ 12 % clay) sites show afforestation-induced reductions in soluble SO_4^{2-} levels, whereas most clay-rich forest soils show minor or positive changes relative to their virgin equivalents. This may reflect the higher SO_4^{2-} sorption capacity of the latter which buffers the concentration of SO_4^{2-} in soil solutions against losses by leaching and biomass uptake.

Soluble SO_4^{2-} concentrations in both forest and virgin soils are comparable to those observed in soil solutions from the northern hemisphere forests represented in Table 6.4, including those impacted by moderate to high levels of acid deposition. As was the case for Cl^- concentrations, these high levels of SO_4^{2-} are believed to reflect higher rates of evaporative concentration and/or a maritime influence at the South African sites.

6.3.1.4. Total strong acid anion concentration

The total concentration of strong acid anions in the virgin soil solutions does not vary dramatically between or within regions (Figure 6.5), with values ranging from approximately 0.5 to 1.8 $mmol_c L^{-1}$. Afforestation introduces a greater degree of variability and, in the majority of sites, results in considerable enhancement of total strong acid anion concentrations. Concentration increases are as high as 2.16 $mmol_c L^{-1}$ and at most sites exceed 0.2 $mmol_c L^{-1}$. Percentage changes range from -55 % to 262 %, with the majority of sites showing increases in strong acid anion concentration of more than 30 %. Wilcoxon matched pairs test results indicate that the enhancement of soluble strong acid anion concentrations under forest is highly significant when all sites are considered ($p < 0.001$). However, because of the high degree of variability within regions, when regions are considered separately only the midlands and southern Cape sites show statistically significant strong acid anion enhancement at the 5 % probability level (i.e. $p \leq 0.05$)(Table 6.3).

6.3.2. Dissolved organic carbon

The saturated paste extracts from soils of this study all contain relatively high concentrations of dissolved organic carbon (DOC) (Figure 6.5). Values ranged from 95 to 1070 $mg L^{-1}$ and for the most part considerably exceed the concentrations reported in other studies of forest soil solutions ($< \sim 100$ $mg L^{-1}$) (Cronan and Aiken, 1985; LaZert and Scott, 1996; Bokheim and Langley-Turnbach, 1997). It is possible that the high values reflect oxidation of organic matter during sample drying and storage. While this may lead to elevated DOC levels in saturated paste extracts, it is also likely to occur under field conditions as the soils dry out naturally for several months every year. This implies that the DOC concentrations obtained from saturated paste extracts of dried soil samples represent the maximum values which are likely to occur in the field. DOC concentrations are not correlated with the colour of the extracts. Extracts from the midlands samples were all colourless despite DOC concentrations which ranged from 105 to 1070 mg L^{-1}. Coloured extracts (yellow to dark orange brown) were only obtained from the western and southern Cape soils, many of which have DOC concentrations which are lower than colourless extracts from the midlands and eastern escarpment regions.

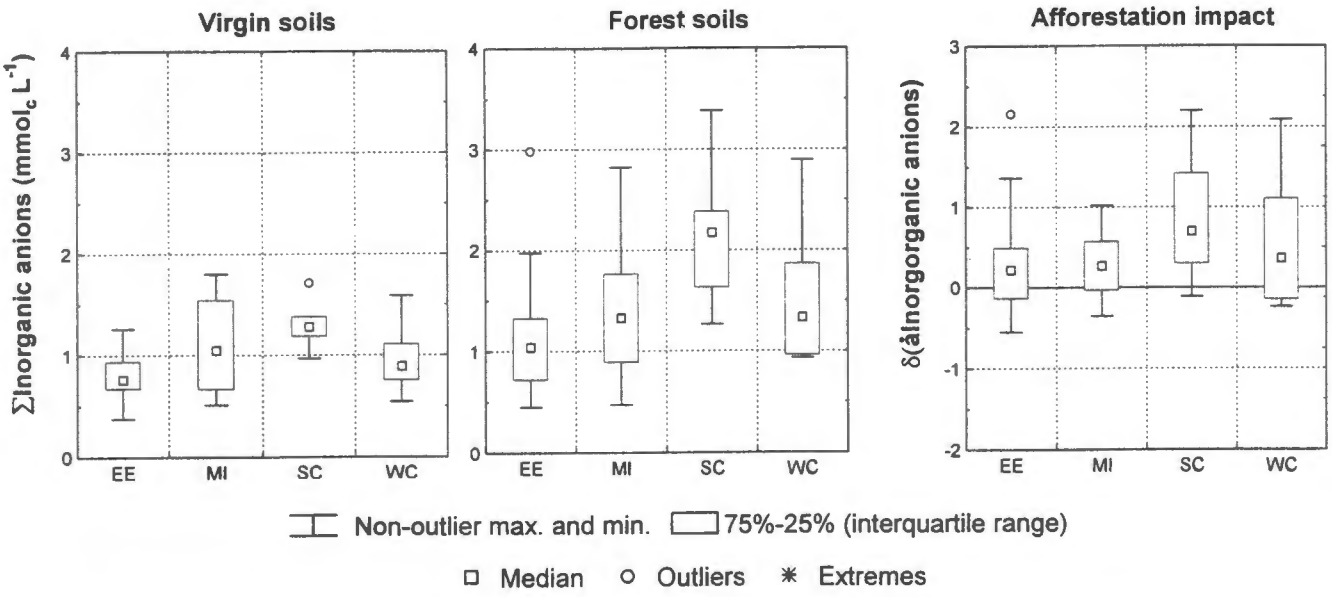

Figure 6.5: *Box and whisker plots illustrating regional variations in total inorganic anion concentration (ΣInorganic anions) in saturated paste extracts from virgin and forest soils. δ Values represent the difference between total inorganic anion concentration in the forest extracts and that in their virgin equivalent. EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

A broad correlation (R^2 = 0.52; n = 76) exists between DOC and excess positive charge, calculated as the balance of major inorganic cations[1] and anions in solution (Figure 6.6). This indicates that the DOC is anionic and allows the calculation of an approximate average negative charge per gram of organic carbon. The DOC-charge relationship is not affected in any consistent manner by afforestation (Figure 6.6.a), but different regions appear to display markedly different charge/DOC ratiós (Figure 6.6.b). Distinguishing between regions improves the correlation between DOC and excess positive charge (particularly for the eastern seaboard region), and reduces intercept values considerably. The largest differences in the DOC-charge relationship occur between the Cape sites and those of the eastern seaboard. Differences within each of these broad regions are considerably smaller. The variations in the DOC-charge relationship may reflect broad differences in the chemical nature of soluble organic matter. In particular, DOC from the southern and western Cape soils appears to have a significantly higher average charge per gram of organic carbon (5.1 ± 2.2 $\mu mol_c\ mg^{-1}$ C) than does that of the midlands and eastern escarpment soils (2.3 ± 0.6 $\mu mol_c\ mg^{-1}$ C). Assuming that most of

[1]Al and Mn were not included in the calculation because concentration data were not available for the full sample set. However, inclusion of these cations for a more limited set of samples did not modify the DOC-charge relationship substantially.

that most of the dissolved organic matter is made up of humic substances, a high charge density in the southern and western Cape DOC would be consistent with a more oxidised, acidic character, or a higher proportion of fulvic acid relative to humic acid (Stevenson, 1985). This may also account for the observed difference in extract colour between these and the other two regions. Cronan and Aiken (1985) report a strong correlation (R^2 = 0.69 to 0.90) between DOC and anionic charge deficit for solutions from podzolic forest soils of north-eastern U.S.A. On the basis of this relationship, they obtained average charge densities between 3.8 and 4.1 $\mu mol_c\, mg^{-1}$ C which are in good agreement with the range observed for the South African soils.

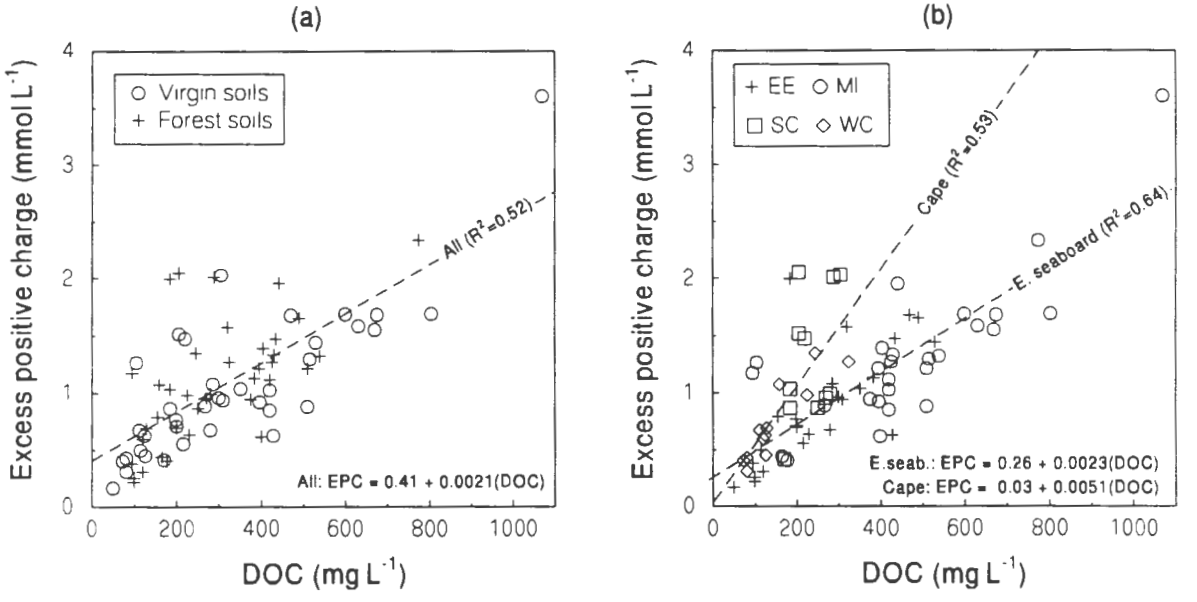

Figure 6.6: *The relationship between dissolved organic carbon concentration (DOC) and excess positive charge. The latter is calculated as the difference between the total concentration of major inorganic anions and cations(Al and Mn were not included in the calculation because concentration data were not available for the full sample set). a) Data classified according to vegetation type, regression for all data. b) Data classified according to region, regressions carried out for the eastern seaboard (EE and MI) and Cape (SC and WC) regions, respectively. EE - eastern escarpment; MI - midlands; SC -southern Cape; WC - western Cape.*

The approximate charge associated with organic anions has been calculated on the basis of the DOC-charge relationships established for the eastern seaboard and Cape soils, respectively, and is plotted in Figure 6.7. It is clear that DOC constitutes a major component of the anion suite in the majority of soils sampled (concentrations range from ~ 0.3 to 3.5 $mmol_c L^{-1}$) and at certain sites is the dominant anion in solution.

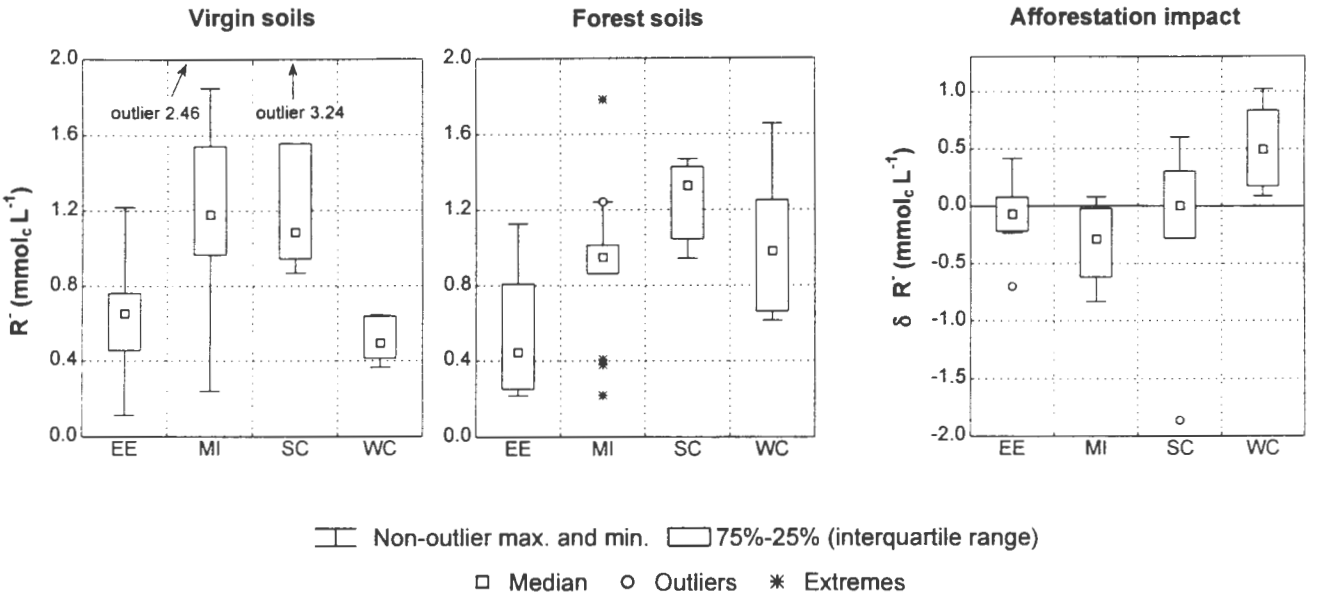

Figure 6.7: Box and whisker plots illustrating regional variations in estimated organic anion concentration (R^-) in saturated paste extracts from virgin and forest soils. Concentrations are calculated from dissolved organic carbon levels (DOC) on the basis of the DOC/charge relationships illustrated in Figure 6.6.b. δ Values represent the difference between organic anion concentration in the forest extracts and that in their virgin equivalent ($\delta R^- = R^-_{forest} - R^-_{virgin}$). EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.

Afforestation-induced changes in organic anion concentration are highly variable but appear to be regionally controlled to some extent. All of the western Cape forest soils have enhanced organic anion concentrations relative to their fynbos equivalents. In contrast, the majority of midlands and eastern escarpment forest soils display reduced concentrations. In the southern Cape, changes in organic anion concentration are highly erratic, although only one site (SC4) shows a significant reduction under forest. The afforestation-induced change in organic anion concentration for all regions shows a negative correlation (R^2 = 0.59) with the original

concentration in grassland or fynbos soils (Figure 6.8). In particular, soil solutions from the western Cape fynbos soils have relatively low organic anion concentrations which tend to be enhanced by afforestation, whereas the relatively high concentrations in soil solutions under grassland in the midlands region are in most cases significantly reduced under forest. A further factor which may have a bearing on the effect of afforestation on organic anion concentration is the relative strength of the organic acids involved. Weak acids may be protonated due to reductions in pH under forest, thereby reducing the negative charge associated with DOC. However, this effect is not believed to be significant in the soils of this study, since the DOC-charge relationships illustrated in Figure 6.6.a provide no evidence for a consistent difference in charge/DOC ratio between forest and virgin soils.

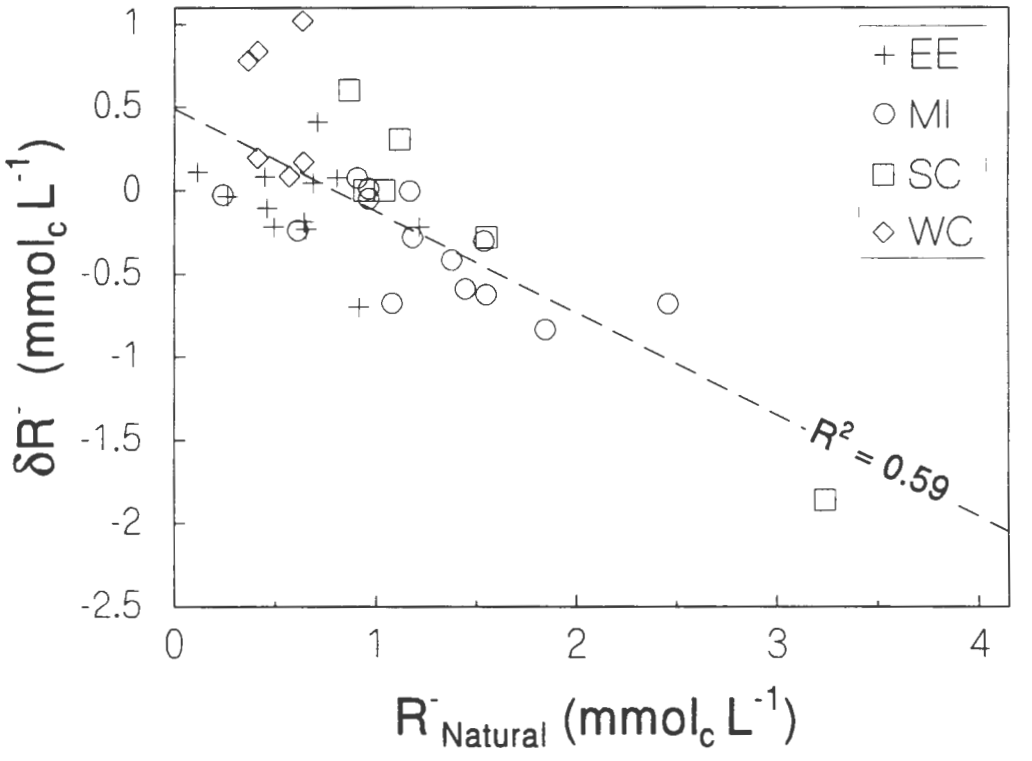

Figure 6.8: *The relationship between the change in organic anion concentration ($\delta R^- = R^-_{forest} - R^-_{virgin}$) and the original organic anion concentration (R^-_{virgin}). EE - eastern escarpment; MI -midlands; SC -southern Cape; WC - western Cape.*

6.3.3. Soil solution pH and aluminium chemistry

6.3.3.1. Impact of afforestation on the pH of soil solutions

The pH values of soil solutions are naturally low, ranging from 3.92 to 5.88 in the grassland and fynbos soils (Figure 6.9). At almost all of the sites sampled, the pH of forest soil solutions is significantly lower than that of the virgin equivalent. Reductions in pH range from 0.1 to just under 1.2, with an average change of approximately 0.4 pH units. This is particularly critical in the naturally acidic soils of this study because it shifts them from conditions under which Al is sparingly or marginally soluble (i.e. at pH values close to or above 5), to those under which significant Al dissolution is likely.

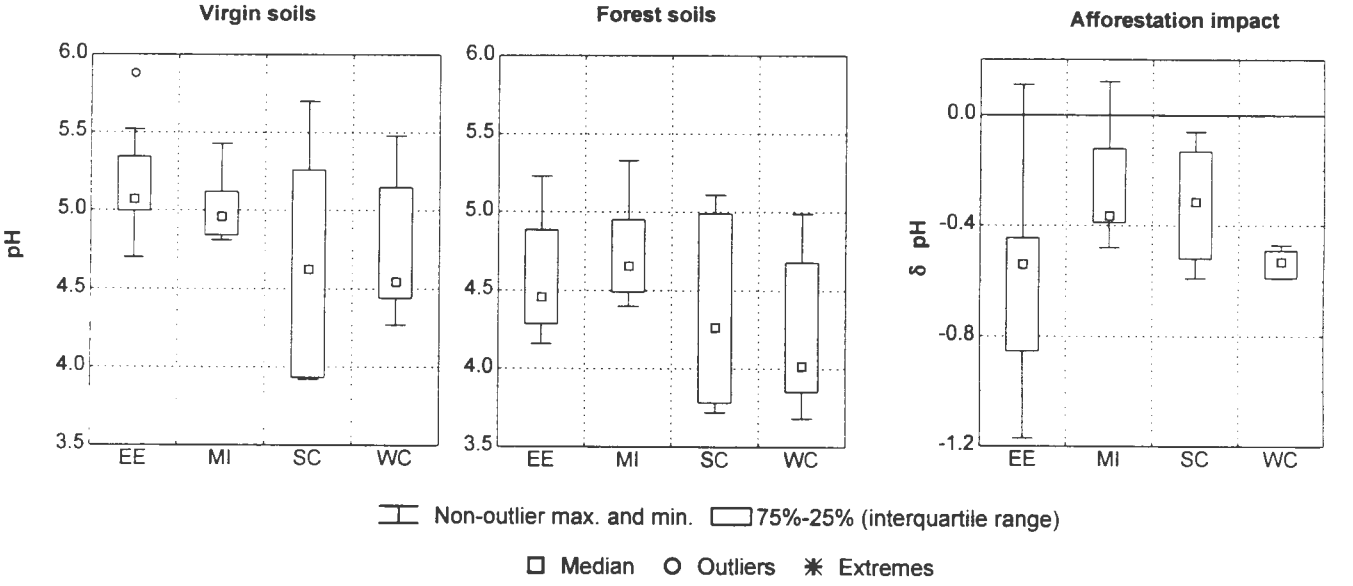

Figure 6.9: Box and whisker plots illustrating regional variations in soil solution pH. δ Values represent the pH difference between forest extracts and their virgin equivalent. EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.

These changes in the pH of soil solutions would be expected due to the combined effect of increased acid saturation of the exchange complex (Chapter 5) and increased total solute concentrations in most of the soils (section 6.3.1). No clear correlations are evident, however, between these variables and soil solution pH. This probably reflects the poorly buffered nature of most of the soils of this study, as indicated by their low ECEC. Because of this, soil solution pH is likely to be sensitively controlled by a complex interplay of numerous factors which include inputs of organic and possibly mineral acids, variations in total solute concentration and variations in the composition of the ion exchange complex.

6.3.3.2. Aluminium: regional variations and afforestation impacts

Total Al concentrations in the soil solutions are highly variable. Values in solutions from forest soils range from 0.014 to approximately 1 $mmol_c L^{-1}$ and in all cases are significantly enhanced (usually by factors of more than 100 %) relative to those of their equivalent virgin soils (Figure 6.10). Although there are no consistent regional trends, soluble Al concentrations of both forest and virgin soils are generally higher in the Cape regions than in those of the eastern seaboard. In some cases the elevated Al levels stem from the highly acidic nature of the solutions (pH values down to 3.68). Even in the less acidic solutions of the southern and western Cape (i.e. SC1; SC3; WC5), however, concentrations of Al are higher than in solutions of similar pH from eastern seaboard soils, suggesting different controls on Al solubility. The particularly dramatic enhancement of total Al concentrations in forest soil solutions for sites SC4 and SC5 are somewhat anomalous, since the pH differences between forest and virgin soils are relatively small (less than 0.2 pH units). In addition, these large increases in Al concentration are not associated with similar changes in exchangeable acidity concentrations, base saturation or total solute concentrations. A possible explanation for the Al increases in these soils is that they result from a major afforestation-induced change in the chemical nature of DOM (see section 6.3.3.5).

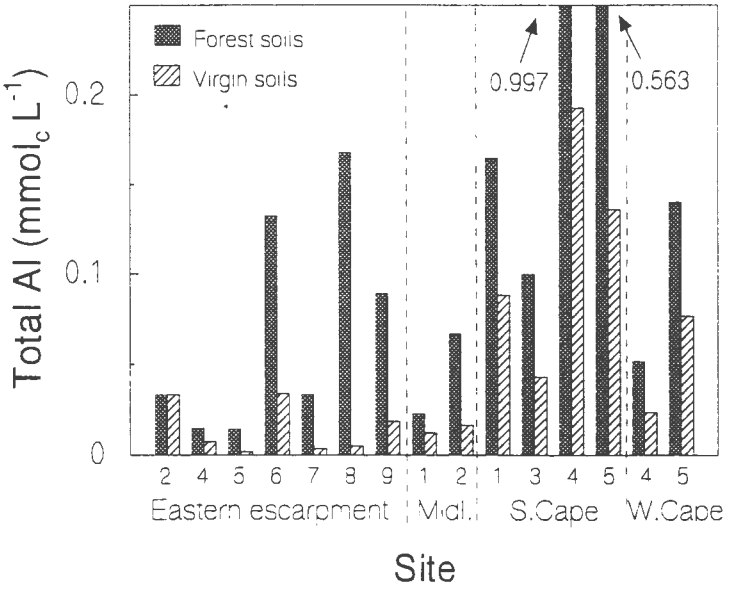

Figure 6.10: *Concentration of total monomeric Al in saturated paste extracts from paired forest and virgin soils. Total Al concentrations was recalculated for original DOC values (i.e. those obtained for extracts taken soon after sampling) assuming that the activities of inorganic Al species are "fixed" by equilibrium with Al-bearing solid phases (see section 6.3.3.3. for details - page 105).*

Total Al concentration values obtained from a review of studies undertaken on acidic forest topsoils in North America and northern Europe are presented in Table 6.5. As for the anion data presented in Table 6.4, quantitative comparison of these data with those obtained from saturated paste extracts is not possible. Nonetheless, they do provide a means of qualitatively assessing the relative magnitude of Al concentrations observed in this study. The highest Al concentrations (mostly greater than 0.5 $mmol_c\ L^{-1}$ and ranging up to 2.2 $mmol_c\ L^{-1}$) were documented for sites in northern Europe that have been severely impacted by acid deposition. In contrast, the North American sites listed in Table 6.5 have low soluble Al concentrations which, in most cases, do not exceed 0.04 $mmol_c\ L^{-1}$, even at sites which are purportedly influenced by moderate levels of acid deposition. European sites which have not been subjected to severe acid deposition but which have received considerable atmospheric inputs of marine salts, show soluble Al levels which are intermediate between these two extremes.

The concentrations of soluble Al in forest soils of this study show a similar range to that observed for the northern hemisphere sites. Although some of the eastern seaboard forest soils have Al levels similar to those of the unpolluted sites in North America, the majority of local sites have elevated concentrations which, in certain cases, are comparable to those observed in sites influenced by severe acid deposition (Table 6.5). It is important to note, however, that many of the *virgin* soils display Al concentrations which are elevated relative to the North American and several of the European forest soils.

6.3.3.3. Modelling interactions between Al and dissolved organic matter

Thermodynamic data for reactions involving inorganic species only (Table 6.1) are relatively well constrained (Schecher and Driscoll, 1987). A major source of uncertainty in the determination of Al species in solution, however, is the influence of dissolved organic matter (DOM). It is well known that DOM has a strong tendency to complex Al (Schnitzer and Skinner, 1963) and, in addition to its considerable effect on Al speciation, can significantly increase the total concentration of Al in solution (Stevenson, 1985; Driscoll, 1989). A large proportion of the DOM in soil solutions and other natural waters is made up of poorly-defined, heterogeneous molecules of high molecular weight (generally referred to collectively as humic substances).

Table 6.5: *Soil solution pH values and Al concentrations ($mmol_c L^{-1}$) for forest topsoils in North America and northern Europe. With the exception of the data for Camels Hump, the data represent average values for solutions sampled over extended time periods (6 months to 7 years) using tension lysimeters. The Camels Hump solutions were obtained from individual soil samples by the pressure syringe method. Acid dep. - indication of the extent of acid deposition. Sea salt - indication of the extent of marine salt inputs. Sources: 1 - Rustad et al., 1996; 2 - LaZert and Scott, 1996; 3 - Ross and Bartlett, 1996; 4 - Farrel et al., 1994; 5 - Marschner et al., 1992; 6 - Pedersen and Bille-Hansen, 1995.*

Site	Species	Acid dep.	Sea salt	pH	Al	Ref.
North America - acid deposition impacted						
Bear Brook, Maine, USA	mixed	moderate	moderate	4.9	0.021	1
Bear Brook, Maine, USA	mixed	severe	moderate	4.6	0.034	1
North America - minimal acid or salt impact						
Harp Lake, Ontario, Canada	*Pinus strobus*	v.minor	v.minor	5.2	0.013	2
Harp Lake, Ontario, Canada	*Pinus strobus*	v.minor	v.minor	4.9	0.020	2
Camels Hump, Vermont	mixed conifer	uncertain	uncertain	4.0	0.032	3
Camels Hump, Vermont	mixed conifer	uncertain	uncertain	3.5	0.042	3
Europe - acid depostiion impacted						
Kootwijk, Holland	*Pinus sylvstris*	severe	minor	3.5	1.495	4
Hardewijk, Holland	*Pinus sylvstris*	severe	minor	4.1	0.735	4
Högwald, Germany	*Picea abies*	severe	minor	4.0	2.214	4
Solling, Germany	*Picea abies*	severe	minor	3.5	1.042	4
Grunewald, Berlin, Germany	*Pinus sylvstris*	severe	v.minor	3.9	0.297	5
Grunewald, Berlin, Germany	*Pinus sylvstris*	severe	v.minor	3.9	0.056	5
Europe - acid deposition impacted						
Klosterheide, Denmark	*Picea abies*	minor	severe	3.8	0.519	4
Ballyhooly, Ireland	*Picea abies*	v.minor	severe	4.2	0.14	4
Ulborg, Denmark	*Picea abies*	moderate	v.severe	5.1	0.156	6
Ulborg, Denmark	*Picea abies*	moderate	v.severe	4.4	0.019	6
Lindet, Denmark	*Picea abies*	moderate	v.severe	5.0	0.378	6
Lindet, Denmark	*Picea abies*	moderate	v.severe	4.2	0.056	6

These constitute a complex mixture of a number of different ligand types with varying affinity for Al (Driscoll, 1989). Electrostatic interactions between binding sites on the same molecule and varying geometric configurations, both of which are dependent on solution pH and ionic strength (Ritchie and Posner, 1982; Perdue, 1989), further complicate Al-DOM interactions. As a result, complexation reactions involving DOM are very poorly constrained.

A number of models have been developed to describe and predict complexation of Al and other cations by humic substances. These have recently been reviewed by Woolard (1994) and can be grouped into 3 main types: 1) discrete ligand models; 2) continuous distribution models: and 3) electrostatic models. Discrete ligand models assume that binding of cations

takes place at a small number of discrete sites (Perdue and Lytle, 1983; Dzombak *et al.*, 1986; Turner *et al.*, 1986). Dissolved organic matter is characterised in terms of metal binding constants and binding site densities - parameters which are determined experimentally using graphical and numerical optimisation procedures. Continuous distribution models assume a continuum of binding sites that can be described by a particular distribution (Perdue *et al.*, 1984; Dzombak *et al.*, 1986). The electrostatic approach (e.g. Tipping *et al.*, 1988; Bartschat *et al.*, 1992; Tipping and Hurley, 1992) involves modelling humic substances as impermeable spheres with an evenly-spread charge resulting from surface ionisation, and assumes that binding of cations to one site affects other sites by electrostatic interactions only (Woolard, 1994).

A general problem with the above-described models is that they require information about binding site concentrations and stability constants which is only obtainable by optimising the models to fit experimental data. Thus application of the models beyond the range of experimental conditions under which they are calibrated is limited. A variant of the discrete ligand approach, whereby dissolved humic substances are modelled as mixtures of relatively simple, well-characterised ligands with known stability constants, has been developed by Murray (1982; see also Linder and Murray, 1987). This model, known as RANDOM, has the advantage of being applicable over a wide range of conditions and it can be readily incorporated into computer speciation programmes. However, the model requires detailed information regarding the chemical nature of the humic substances being modelled, including data on the concentrations of important functional groups. Its application is therefore limited to studies involving well-characterised DOM.

The DOM model incorporated into MINTEQA2 has been used to estimate the effect of dissolved organic matter on Al speciation. This is a continuous distribution model in which DOM is treated as a complex material consisting of many different monoprotic acid sites, the concentration of which is taken to be normally distributed with respect to their binding constants ($\log K$ values) for protons and metals (US EPA, 1991). For each cation, the binding site distribution is characterised by a mean $\log K$ and standard deviation value based on data obtained for Suwannee River fulvic acid. Binding site concentrations (L) are estimated using the relationship:

$$L \text{ (moles of sites)} = (DOC \times 2)(5 \times 10^{-4}) \quad \ldots . (2).$$

The dissolved organic carbon concentration (in mg L^{-1}) is multiplied by 2 to obtain a DOM value which is related to binding site concentration by a constant term based on site densities obtained for Suwannee River fulvic acid. Although this model is empirically based, recent work has indicated that for acidic solutions (pH < ~5) it produces results which are comparable to those obtained using the more complex RANDOM model in conjunction with MINTEQA2 (Woolard, 1997). The DOC-charge relationships discussed in section 6.3.2 strongly suggest that DOM in soil solutions of the eastern seaboard soils has a significantly lower charge density than that derived from the Cape soils, and application of the same DOM model to all of these solutions is not believed to be appropriate. Thus, the MINTEQA2 model has been modified slightly to accommodate the apparent chemical differences between DOM derived from the different regions. Because the model is based on experiments using Suwannee River fulvic acid, it was assumed that it is most appropriate for the coloured soil solutions and surface waters of the Cape regions. In the case of the eastern seaboard soil solutions, the ligand concentration obtained using equation 2 was reduced in proportion with the difference in the charge/DOC ratio obtained for the different regions. Thus the formula used for these solutions is:

$$L\ (M) = (DOC \times 2)(5 \times 10^{-4}) \times 0.45 \quad \ldots . (3),$$

where 0.45 represents the ratio of charge density (charge/DOC) for the eastern seaboard soils (2.3 $\mu mol_c\ mg^{-1}$ C) to that of the Cape soils (5.1 $\mu mol_c\ mg^{-1}$ C)(see section 6.3.2).

Estimates of total Al concentrations in equilibrium with original DOM levels (i.e. those in extracts taken soon after sampling) were obtained by fixing the activities of the inorganic components in solution (based on speciation calculations incorporating the measured DOC values) and repeating the speciation calculations using the original DOC values as input. Thus the total Al concentrations discussed below are estimates based on the following assumptions: 1) the colorimetric method used to determine Al measures inorganic monomeric Al and that which is complexed by dissolved organic matter; 2) calculated concentrations for inorganic Al species reflect equilibrium with an Al-bearing solid phase and are therefore independent of DOC concentration (see section 6.3.3.5); 3) the original DOC values are a more realistic estimate of likely concentrations in soil solutions than those obtained approximately one year later; and 4) the modelling by MINTEQA2 of interactions between dissolved Al and organic matter is valid and produces meaningful results.

Due to the high degree of uncertainty associated with the modelling of Al-DOM interactions, as well as uncertainty with respect to the relevance of DOC concentrations obtained from saturated paste extracts of stored soil samples, one cannot expect to be able to accurately model Al speciation in a quantitative manner. Nonetheless, comparison of results obtained using the MINTEQA2 DOM model with those obtained when DOM is excluded from the calculations, provides a qualitative indication of the influence of DOM on Al speciation and solubility.

6.3.3.4. Aluminium speciation

The relative proportions of the dominant inorganic Al species are illustrated in Figure 6.11.a. The ratio of Al^{3+} to hydrolysed Al species ($AlOH^{2+}$ and $Al(OH)_2^+$) is highly variable and, as expected, is primarily related to solution pH values. The relative concentration of Al^{3+} is, therefore, higher in forest soil solutions than in their virgin equivalents, and is particularly high (up to 78 %) in the very acidic soil solutions of sites SC4, SC5 and WC4 in the southern and western Cape. Soluble $AlSO_4^+$ occurs in significant concentrations in most of the solutions investigated. The proportion of $AlSO_4^+$ relative to other inorganic Al species is generally substantially higher (up to 34 %) in soils of the Cape regions than those of the eastern seaboard and reflects the observed variations in soluble SO_4^{2-} concentrations. Speciation calculations incorporating DOM suggest that organically-bound Al is an important species in all of the soil solutions (Figure 6.11.b). Relative abundances range from 20 to 88 % and in many solutions Al-DOM is the dominant form of Al. This high degree of complexation of Al by DOM is in agreement with that observed in a studies of acidic surface waters in the Adirondack region of the United States (Driscoll and Bisgoni, 1984; reported in Driscoll, 1989), Canada (Campbell *et al.*, 1983) and Sweden (Lee, 1985). In these studies, the percentage of Al that was organically bound was found to vary from 0 to > 50 % and appeared to be inversely related to pH (Driscoll, 1989).

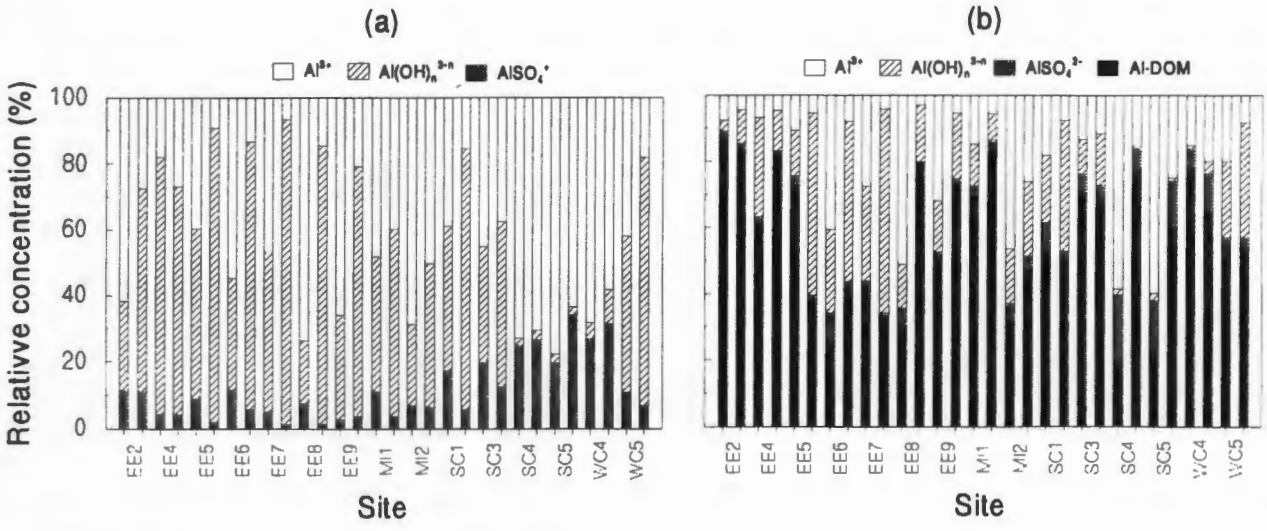

Figure 6.11: *Relative concentrations of Al species in saturated paste extracts calculated using the MINTEQA2 computer speciation programme. (a) Inorganic species. (b) Inorganic species and Al-organic matter (Al-DOM) complexes. Concentrations of Al-DOM have been recalculated using original DOC values (i.e. those obtained for extracts taken soon after sampling; see text for details). For each site, the first bar represents the forest soil and the second bar represents its virgin equivalent.*

The most prominent effect of afforestation is to enhance the concentration of Al^{3+} relative to other Al species in solution (Figure 6.12.a). This results primarily from the effect of reduced pH on Al hydrolysis equilibria, which increases the concentration of Al^{3+} at the expense of hydrolysed Al species ($Al(OH)_n^{3-n}$). When normalised with respect to DOM binding site concentrations, the concentrations of Al-DOM relative to other Al species are in almost all cases lower in forest soil solutions than in their virgin equivalents (Figure 6.12.b). Thus, if DOM binding site concentrations are kept constant, afforestation and associated reductions in pH appear to enhance the concentration of inorganic species relative to organically complexed Al. In certain soils, notably those of many eastern seaboard sites, this effect is exacerbated by reductions in DOM concentrations under forest, whereas in others, enhancement of DOM levels under forest (e.g. in soils of the western Cape) may substantially offset the afforestation-induced reduction in the proportion of Al that is bound to DOM.

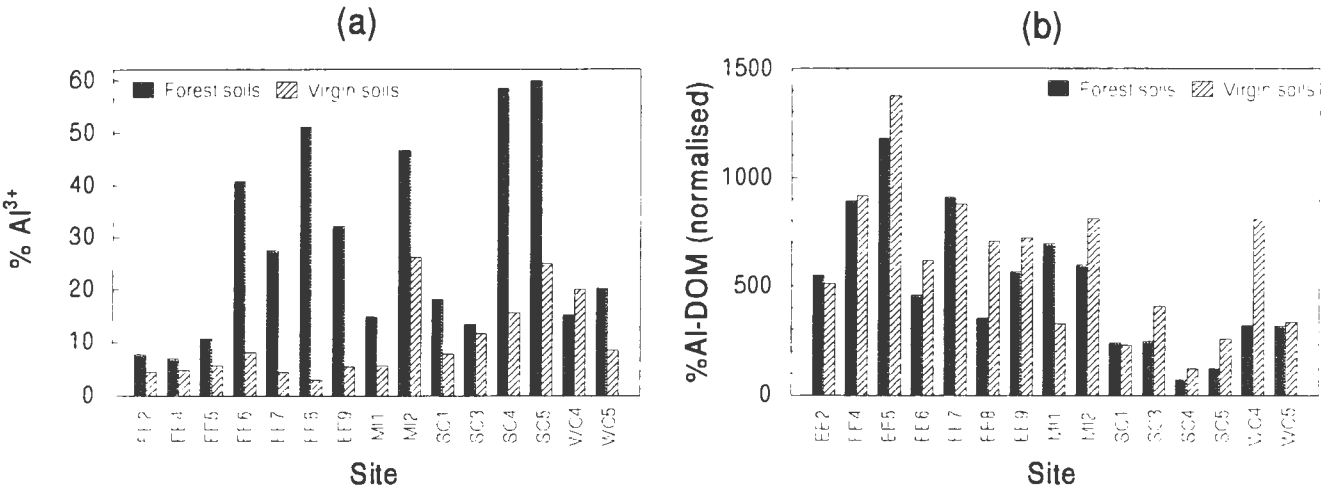

Figure 6.12: *Relative concentrations of Al^{3+} and Al-DOM in saturated paste extracts. a) Amounts of Al^{3+} as a percentage of total Al. b) DOM-normalised percentage of organic Al relative to total Al concentration (i.e. %Al-DOM values were divided by the DOM binding site concentrations determined from DOC values using equations 2 and 3, section 6.2.4). The concentration of Al-DOM was calculated using original DOC values (i.e. those obtained for extracts taken soon after sampling) assuming that the activities of inorganic Al species were "fixed" by equilibrium with Al-bearing solids (see text for details).*

6.3.3.5. Aluminium solubility relationships

There is a broad correlation between the concentration of soluble Al and pH (Figure 6.13). However, the nature of the Al-pH relationship was found to vary quite widely between sites and between regions, suggesting that Al solubility may be controlled by a number of different processes.

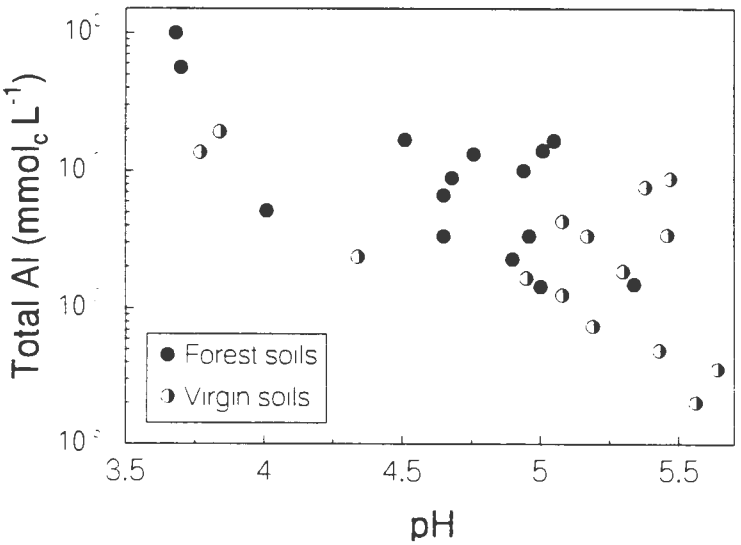

Figure 6.13: *The relationship between total aluminium concentration (recalculated on the basis of original DOC levels - see text for details) and pH in soil solutions from forest and virgin soils of all regions.*

In order to evaluate solubility relationships, data for the saturated paste extracts have been plotted on graphs of log(Al^{3+} activity) versus pH, together with the stability fields and lines for possible solubility-controlling phases (Figure 6.14). The activity of Al^{3+} was calculated from total solute concentrations using MINTEQA2. Because of the uncertainty associated with speciation calculations involving dissolved organic matter (DOM), as well as uncertainty regarding the determination of appropriate DOC concentrations, the activity of Al^{3+} used to evaluate Al solubility was calculated both on a DOM-free basis and using the modified MINTEQA2 DOM model described in section 6.3.3.3. The $Al(OH)_3$ field plotted on the stability diagrams is constrained by the solubility of the "soil" $Al(OH)_3$ phase (log$K$ = 8.77) of Lindsay (1979) and by that of amorphous $Al(OH)_3$ (log$K$ = 9.66). In plotting the stability fields for alunite, jurbanite and kaolinite, activity values or ranges for relevant components other than Al^{3+} and H^+ (i.e. SO_4^{2-}, K^+ and H_4SiO_4) have been fixed on the basis of values observed for the saturated paste extracts. This gives an instructive indication of the ranges of Al^{3+} and H^+ activities over which these minerals are potentially stable. However, it does not necessarily indicate that solution compositions which plot within a particular stability field, or on a stability line, are in equilibrium with the mineral concerned, since this is also dependent on the activities of SO_4^{2-}, K^+ or H_4SiO_4 in the solution in question. Thus, saturation indices (Table 6.6) have been used in conjunction with the solubility diagrams to clarify solubility relationships as far as possible. The above-mentioned Al-hydroxide, -sulphate and -silicate minerals are generally considered, together with Al-organic matter complexes, to be the most important phases controlling the solubility of Al in acid soils (Lindsay and Walthall, 1989), and their precipitation/dissolution equilibria are well constrained (e.g. May *et al.*, 1979; Nordstrom, 1982; May *et al.*, 1986). Mineralogical studies indicate that aluminous chlorite ("pedogenic chlorite") constitutes an important component of most soils investigated in this study (section 4.3.2) and it is possible that this mineral plays a role in controlling the concentration of Al in solution. However, due to a lack of quantitative thermodynamic data on Al-chlorite, it has not been considered in the following discussion. Because of this, as well as the uncertainty associated with the determination of Al in solution and the calculation of activity values for Al^{3+} (section 6.3.3.3), interpretations and conclusions based on the log(Al^{3+})/pH relationships should be regarded as tentative.

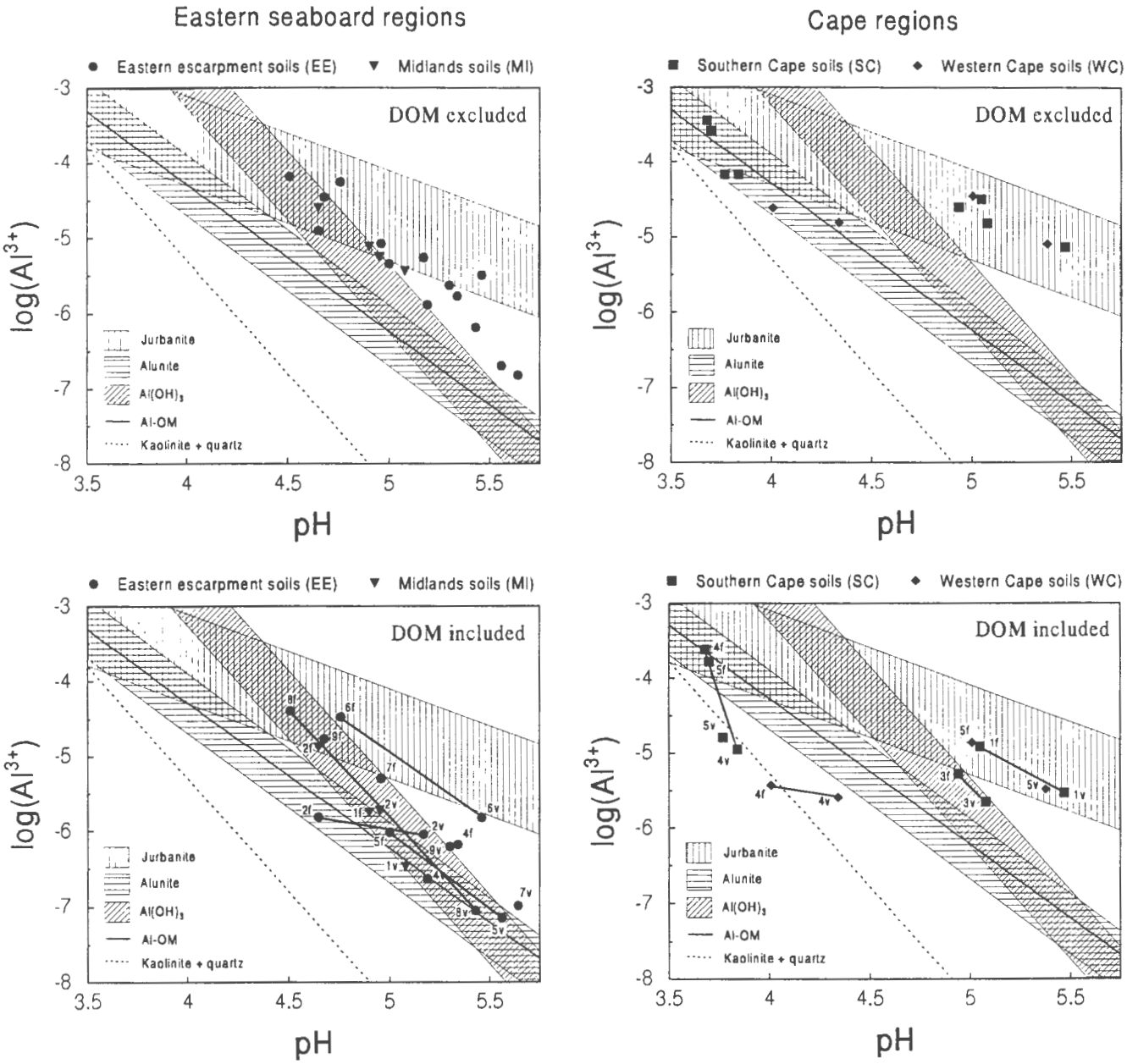

Figure 6.14: *Plots of $log(Al^{3+})$ versus pH showing the position of soil solutions in relation to the stability of possible solubility-controlling solid phases. The $Al(OH)_3$ field is defined by the solubility of amorphous and "soil" $Al(OH)_3$. Stability fields for jurbanite and alunite are based on the range in SO_4^{2-} activity values observed in the soil solutions (i.e. $10^{-3.5}$ to $10^{-4.7}$ M) and the activity of K^+ has been fixed at 10^{-4} M which is close to the average value for the solutions. The Al-OM line represents Al equilibrium with organically complexed Al and is based on the relationship established by Bloom et al. (1979) for a Mardin soil ($log(Al^{3+}) = 3.53 - 1.95pH$). The kaolinite stability line is based on a silica activity subtended by equilibrium with quartz ($H_4SiO_4 = 10^{-4}$ M). Bold lines join selected forest-virgin soil pairs.*

Table 6.6: *Mineral saturation indices for saturated paste extracts. Values in section A are based on calculations which exclude DOM. Calculations for section B incorporate the slightly modified MINTEQA2 DOM model (see text for details). f - forest soils; v - virgin soils. Positive SI values (i.e. indicative of supersaturation) are shaded.*

A) SI values calculated on a DOM-free basis

Site	$Al(OH)_3$ (soil)		$Al(OH)_3$ (am.)		Jurbanite		Alunite		Halloysite		Kaolinite		Quartz		SiO_2 (soil)	
	f	v	f	v	f	v	f	v	f	v	f	v	f	v	f	v
EE2	0.28	1.49	-0.61	0.60	-0.49	0.02	2.46	5.37	1.62	4.28	4.89	7.55	0.13	0.25	-0.86	-0.74
EE4	1.48	0.92	0.59	0.03	-0.59	-1.03	3.64	2.38	4.67	1.46	7.94	4.73	0.45	-0.60	-0.54	-1.58
EE5	0.90	1.22	0.01	0.33	-0.50	-1.35	3.73	2.45	3.17	3.45	6.44	6.72	0.28	0.10	-0.70	-0.89
EE6	1.26	2.12	0.37	1.23	0.29	0.14	4.60	6.36	3.81	5.21	7.08	8.48	0.24	0.08	-0.75	-0.91
EE7	1.04	1.33	0.15	0.44	-0.55	-1.44	3.24	2.38	3.90	3.84	7.17	7.11	0.51	0.18	-0.48	-0.81
EE8	0.58	1.34	-0.31	0.45	-0.09	-1.25	3.28	2.63	2.83	3.38	6.10	6.65	0.43	-0.05	-0.56	-1.04
EE9	0.82	1.51	-0.07	0.62	-0.66	-0.57	2.54	4.31	3.01	3.91	6.28	7.18	0.28	0.05	-0.70	-0.94
MI1	0.81	1.04	-0.08	0.15	-0.31	-0.81	3.71	2.85	3.53	3.71	6.80	6.98	0.55	0.41	-0.44	-0.58
MI2	0.58	0.83	-0.31	-0.06	-0.32	-0.56	3.61	3.76	2.96	3.24	6.23	6.51	0.49	0.38	-0.49	-0.61
SC1	1.89	2.50	1.00	1.61	0.84	0.53		7.72	5.14	5.96	8.41	9.23	0.28	0.08	-0.71	-0.91
SC3	1.45	1.65	0.56	0.76	0.63	0.39	5.69	5.86	4.76	4.81	8.03	8.08	0.53	0.35	-0.46	-0.64
SC4	-1.18	-1.44	-2.07	-2.30		-0.10	1.42	0.92	-1.31	-2.01	1.96	1.26	0.12	0.01	-0.87	-0.98
SC5	-1.25	-1.63	-2.14	-2.52		-0.12	0.79	0.41	-2.16	-2.86	1.11	0.41	-0.23	-0.21	-1.22	-1.19
WC4	-1.34	-0.55	-2.24	-1.44	-0.42	-0.21	0.11	1.84	-2.25	-1.03	1.02	2.24	-0.18	-0.36	-1.17	-1.35
WC5	1.81	2.28	0.92	1.39	0.52	0.43	6.21	7.03	4.41	5.36	7.68	8.63	-0.01	0.00	-1.00	-0.99

B) Calculations incorporating DOM

	$Al(OH)_3$ (soil)		$Al(OH)_3$ (am.)		Jurbanite		Alunite		Halloysite		Kaolinite		Quartz		SiO_2 (soil)	
	f	v	f	v	f	v	f	v	f	v	f	v	f	v	f	v
EE2	-0.64	0.70	-1.53	-0.19	-1.40	-0.77	-0.28	2.99	-0.21	2.70	3.06	5.97	0.13	0.25	-0.86	-0.74
EE4	1.07	0.17	0.18	-0.72	-1.00	-1.79	2.41	0.12	3.85	-0.05	7.12	3.22	0.45	-0.60	-0.54	-1.58
EE5	0.21	0.77	-0.68	-0.12	-1.18	-1.81	1.69	1.07	1.80	2.53	5.07	5.80	0.28	0.10	-0.70	-0.89
EE6	1.04	1.79	0.15	0.90	0.09	-0.20	3.98	5.36	3.37	4.55	6.64	7.82	0.24	0.08	-0.75	-0.91
EE7	0.81	1.17	-0.08	0.28	-0.78	-1.60	2.55	1.87	3.44	3.50	6.71	6.77	0.51	0.18	-0.48	-0.81
EE8	0.37	0.48	-0.52	-0.41	-0.27	-2.12	2.69	0.03	2.41	1.65	5.68	4.92	0.43	-0.05	-0.56	-1.04
EE9	0.51	0.93	-0.38	0.04	-0.96	-1.15	1.64	2.57	2.39	2.75	5.66	6.02	0.28	0.05	-0.70	-0.94
MI1	0.18	0.00	-0.71	-0.89	-0.94	-1.84	1.82	-0.26	2.26	1.64	5.53	4.91	0.55	0.41	-0.44	-0.58
MI2	0.31	0.35	-0.59	-0.54	-0.59	-1.04	2.80	2.32	2.41	2.28	5.68	5.55	0.49	0.38	-0.49	-0.61
SC1	1.46	2.11	0.57	1.21	0.43	0.14		6.54	4.29	5.17	7.56	8.44	0.28	0.08	-0.71	-0.91
SC3	0.77	0.82	-0.12	-0.07	-0.03	-0.43	3.67	3.38	3.39	3.14	6.66	6.41	0.53	0.35	-0.46	-0.64
SC4	-1.34	-2.20	-2.23	-3.09	0.24	-0.85		-1.37	-1.64	-3.58	1.63	-0.31	0.12	0.01	-0.87	-0.98
SC5	-1.45	-2.25	-2.34	-3.14	-0.10	-0.70		-1.38	-2.54	-4.11	0.73	-0.84	-0.23	-0.21	-1.22	-1.19
WC4	-2.18	-1.34	-3.07	-2.23	-1.24	-0.98	-2.35	-0.50	-3.91	-2.60	-0.64	0.67	-0.18	-0.36	-1.17	-1.35
WC5	1.40	1.88	0.51	0.99	0.13	0.04	5.02	5.86	3.59	4.58	6.86	7.85	-0.01	0.00	-1.00	-0.99

The eastern seaboard and Cape soils display distinctly different log(Al^{3+})/pH relationships, each of which shows a higher degree of consistency when data calculated on a DOM-free basis are plotted (Figure 6.14). Solutions from the eastern seaboard samples show a well defined trend with a slope which parallels that defined by equilibrium with tribasic Al-bearing phases. However, the majority of soil solutions are supersaturated with respect to amorphous $Al(OH)_3$ (log$K$ = 9.66) suggesting that the activity of Al^{3+} may be overestimated when DOM is not accounted for. Inclusion of DOM in the speciation calculations for the eastern seaboard soils results in a more diffuse log(Al^{3+})/pH trend, a feature which may, in part, be due to the inadequacy of the simple DOM model employed. However, Al^{3+} activities are reduced to levels which, in most cases, are suggestive of equilibrium with a soil $Al(OH)_3$ phase with a solubility between 8.77 and 9.66. In addition, lines drawn through forest-virgin soil pairs from the same site have slopes which, in most cases, are close to 3, providing a further indication of Al solubility control by tribasic Al-hydroxide phases. This is also consistent with the relatively high gibbsite concentrations indicated by X-ray diffraction analysis of several eastern seaboard soils (section 4.3.2).

The only soil solution from the eastern seaboard sites which is undersaturated with respect to $Al(OH)_3$ is that obtained from the very sandy forest soil of site EE2. In this soil the pH and Al^{3+} activity obtained by calculation including DOM suggest equilibrium with alunite, and an SI value close to 0 (-0.28) indicates that SO_4^{2-} or K^+ activities are consistent with this possibility. However, the shallow slope defined by this sample and its grassland equivalent (i.e. EE2v) suggests that Al solubility may be controlled by complexation with solid organic matter. This possibility is discussed in more detail below (page 114).

The solution from the grassland soil of site EE6 is considerably supersaturated with respect to amorphous $Al(OH)_3$, even when DOM is accounted for. The concentration of soluble SO_4^{2-} in this soil is considerably higher than that observed for any of the other eastern seaboard samples, suggesting that Al solubility may be controlled by jurbanite. A somewhat shallower log(Al^{3+})/pH slope (defined by the forest-grassland soil pair for this site) and jurbanite saturation index values close to zero (Table 6.6) support this possibility. Saturation indices also suggest that solutions from the forest soils of sites EE6 (SI = 0.09), EE8 (SI = -0.27) and, to a lesser extent, MI2 (SI = -0.59) may also be in equilibrium with jurbanite. These solutions plot at the intersection of the stability fields for jurbanite and $Al(OH)_3$ indicating

that, depending on the activity of SO_4^{2-}, both phases may coexist in these samples at equilibrium. However, the solution compositions for forest-grassland soil pairs from sites EE8 and MI2 define $\log(Al^{3+})$/pH slopes which are very close to 3 and, therefore, suggest Al solubility control by an $Al(OH)_3$ phase. Similarly, despite the evidence given above suggesting equilibrium with jurbanite, the soil solutions for the forest and virgin soil at site EE6 define a slope suggesting solubility control by a dibasic Al-bearing phase. While the solutions are clearly supersaturated with respect to crystalline alunite, it is possible that they are in equilibrium with a more soluble, possibly amorphous, equivalent or with dibasic Al-DOM (see below). Although soil solutions for site EE5 both lie within the area of overlap between $Al(OH)_3$ and alunite, they define a slope of approximately 2 suggesting that the latter mineral may control Al solubility at this site. Soils from site EE4 are anomalous in that the forest soil solution has a substantially higher Al solubility ($\log Al^{3+}$ + 3pH) than that of its grassland equivalent, suggesting that in these two samples, Al solubility is controlled by different phases or by phases with differing crystallinity. This could possibly reflect pre-afforestation differences in mineralogy between the forest and grassland soils.

The activities of Al^{3+} and H^+ in solutions from the sandy soils of the Cape regions show a considerably wider scatter than those of the eastern seaboard solutions, regardless of whether or not DOM is accounted for. They clearly do not conform to a trend indicative of equilibrium with an $Al(OH)_3$ phase. When DOM is excluded from the calculations, all of the less acidic Cape soil solutions (pH > ~5) lie within the jurbanite stability field. However, somewhat elevated jurbanite SI values for these solutions suggest supersaturation with respect to this mineral and may indicate a slight overestimation of Al^{3+} activity when DOM is not accounted for. Inclusion of DOM introduces more scatter and shifts two of the solutions (SC3f and SC3v) out of the jurbanite solubility "window" to Al^{3+} activities indicative of equilibrium with a soluble $Al(OH)_3$ phase. Possible control of Al solubility by such a phase is supported by the $\log(Al^{3+})$/pH slope defined by this soil pair. Jurbanite SI values for the other solutions are, in most cases, reduced to values close to 0. However, as for site EE6, forest-fynbos soil pairs subtend $\log(Al^{3+})$/pH slopes which are very close to 2 suggesting equilibrium with a relatively soluble dibasic Al-bearing phase such as an amorphous alunite-like mineral or Al-DOM. In a similar way to that described above for the eastern seaboard solutions, the incorporation of a DOM model in to the speciation calculations produces results which are more compatible with likely solid-phase control of Al solubility than those obtained on a DOM-free basis.

The more acidic Cape soils (pH ≤ ~ 4) show distinctly different Al solubility relationships to those described above. The acidic solutions from the very sandy WC4 soils define a shallow log(Al^{3+})/pH trend at low Al solubility levels. This is effectively identical to the trend observed for site EE2 and is suggestive of Al solubility control by Al-organic matter complexes (Al-OM)(Figure 6.15). The equilibrium between Al^{3+} in solution and that complexed to organic solids can be described (in log form) by the equation:

$$\log(Al^{3+}) + x\text{pH} = \log K + \log(AlR)/(H_xR) \quad \ldots . (4),$$

where R represents an organic binding site and x is the slope of the log(Al^{3+})/pH relationship (Bergren and Mulder, 1995). While Bloom *et al.* (1979) obtained a value for x of approximately 2 ($\log K \approx 3.53$) for an A-horizon Mardin silt loam, these and several other authors (Cronan *et al.*, 1986; Walker *et al.*, 1990) have clearly demonstrated that a reduction of the proportion of organic binding sites that are occupied by Al (i.e. the bound Al ratio), results in a significant reduction in Al solubility and in the slope of the pH/log(Al^{3+}) relationship. The soils from EE2 and WC4 define a trend with a slope of 0.6 and an intercept of -3.0 (i.e. log(Al^{3+}) + 0.6pH = -3.0). Very similar solubility relationships for Al-OM equilibria have been reported by Cronan *et al.* (1986) and Franken *et al.* (1995). These are shown in Figure 6.15. In particular, the slope obtained by Cronan *et al.* (1986) for organic matter with a bound Al ratio (BAR) of 0.2 to 0.3 is identical to that described above. Thus it would appear that, in the soils with very low clay contents (< 3% clay) and with moderate concentrations of organic carbon (> 1.5 %), the solubility of Al may be controlled by Al-OM with a very low basicity.

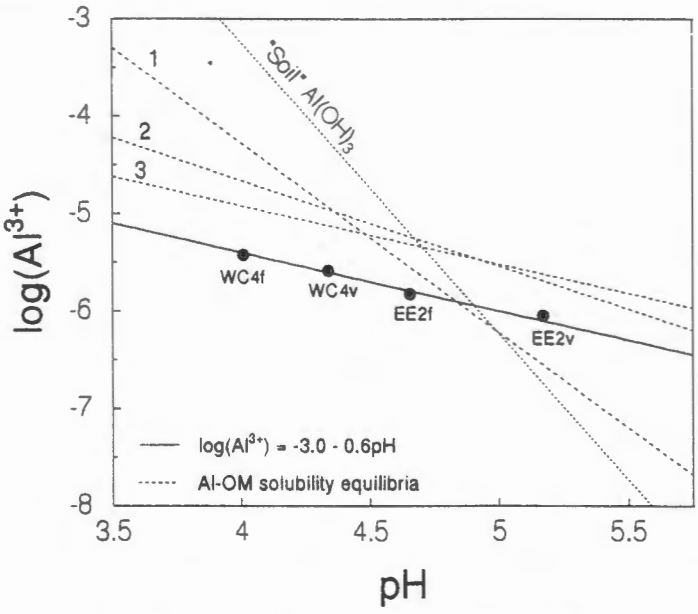

Figure 6.15: *Plot illustrating the log(Al^{3+})/pH relationship defined by soil solutions for sites EE2 and WC4 in relation to solubility equilibria for organically complexed Al. Solubility lines: 1) log(Al^{3+}) = 3.53 - 1.95pH (Bloom et al., 1979); 2) log(Al^{3+}) = -1.53 - 0.88pH (Franken et al.., 1995); 3) log(Al^{3+}) = -2.52 - 0.6pH (Cronan et al., 1986). The "soil" $Al(OH)_3$ solubility line (logK = 8.77) is shown for reference purposes.*

Solutions from the two highly acidic (pH = 3.68 and 3.70, respectively) forest soils of sites SC4 and SC5 lie at the intersection of the stability fields for jurbanite, alunite and organically bound Al (Al-OM) and their position is essentially unaffected by incorporation of DOM into the speciation calculations (Figure 6.14). This may suggest the stable coexistence of these phases, although SI values indicate that alunite equilibrium is unlikely, particularly in the SC4 forest soil. The slope defined by forest-virgin soil pairs for both sites indicates an excessively high pH dependence for Al solubility, which is not consistent with control by known Al-bearing solids. This suggests that Al solubility in the forest soils is controlled, at significantly higher levels, by processes which are different to those prevailing in their fynbos equivalents. In the latter, Al solubility appears to be controlled by kaolinite, whereas in the forest soils Al-OM or jurbanite are the most likely equilibrium phases. An alternative explanation is that Al concentrations in both forest and fynbos soils are controlled by Al-OM complexes. The dramatically enhanced solubility in the forest soils may stem from a significantly greater degree of Al-saturation of organic matter. As discussed above, this would result in a steeper $\log(Al^{3+})$/pH slope (i.e. an increased basicity), as well as significantly enhanced Al solubility (Cronan *et al.*, 1986; Walker *et al.*, 1990).

Calculated activities of dissolved silica (H_4SiO_4) range from $10^{-4.6}$ to $10^{-3.5}$ and, for the most part, are consistent with control by equilibrium with quartz or a slightly more soluble "soil" silica phase ($\log K$ < -3.1). At these relatively high H_4SiO_4 activities, the most stable assemblage is kaolinite + quartz. It is clear from the preceding discussion that equilibrium with kaolinite is in most cases precluded by high Al solubility (i.e. high $\log(Al^{3+}) + 3pH$ values) which is more consistent with $Al(OH)_3$, Al-sulphate or Al-DOM equilibrium. Thus the apparent equilibrium between these phases and quartz represents a metastable state, which probably results from the relatively slow precipitation/dissolution kinetics of kaolinite (Rai and Kittrick, 1989). Silica activities are consistently higher in forest soil solutions than in those of their virgin equivalents. This may reflect higher rates of evapotranspiration and consequently a lower degree of leaching under forest plantations relative to that under grassland or fynbos vegetation.

6.3.4. Manganese

Enhancement of soluble Mn^{2+} concentration under forest is less frequently encountered than is the case for Al^{3+}. At most sites, solution concentrations of Mn^{2+} are lower than 0.2 $mmol_c\ L^{-1}$ in both virgin and forest soils (Figure 6.16.a). However, certain forest soils, particularly those in the eastern escarpment region, show significantly elevated Mn^{2+} levels, with values ranging up to 0.89 $mmol_c\ L^{-1}$. The highest Mn^{2+} concentrations occur in soils which appear to have had relatively high soluble Mn^{2+} levels prior to afforestation (i.e. their virgin equivalents have soluble Mn^{2+} concentrations between 0.15 and 0.26 $mmol_c\ L^{-1}$), but Mn^{2+} enhancement also occurs in several soils with original concentrations below 0.1 $mmol_c\ L^{-1}$.

Although all of the soil solutions with elevated Mn^{2+} concentrations have pH values less than 5, the extent of Mn^{2+} enrichment is not correlated with pH differences, either between sites or between forest soils and their virgin equivalents. For example, no significant enhancement of soluble Mn^{2+} concentration occurs in forest soils from some of the midlands sites (MI12, 13 and 15), despite solution pH values less than 4.5 and soluble Mn^{2+} concentrations in their virgin equivalents which range from approximately 0.07 to 0.1 $mmol_c\ L^{-1}$. Total anion concentrations in these midlands forest soils are not significantly enhanced relative to their grassland equivalents. In contrast to this, a significantly elevated soluble Mn^{2+} concentration occurs in the forest soil at site SC3, despite a relatively high solution pH (4.99) which is only marginally lower than that of its fynbos equivalent (5.05). The elevated Mn^{2+} concentrations in this soil are believed to result from the observed considerable enhancement of total solute concentrations, combined with moderately high original Mn^{2+} solubility levels (as reflected in the fynbos soil solution Mn^{2+} concentration of 0.03 $mmol_c\ L^{-1}$). The data suggest therefore, that in these naturally acidic soils, afforestation-induced reduction in pH *per se* is not an important factor governing enhanced solubilisation of Mn^{2+}.

Enhancement of Mn^{2+} appears to be broadly related to changes in total electrolyte load, as represented by total anion concentrations (Figure 6.16.b). Elevated Mn^{2+} concentrations occur only in forest soils with an increased total anion concentration in solution relative to their virgin equivalent. However, increased anion levels are generally only associated with elevated Mn^{2+} concentrations when the soluble Mn^{2+} concentration in the virgin soil is greater than approximately 0.02 $mmol_c\ L^{-1}$. This is supported by KCl extract data for 15 forest-virgin soil

pairs which suggests that elevated concentrations of Mn^{2+} in solution only occur if soils originally had high levels of exchangeable Mn^{2+} (Figure 6.16.c).

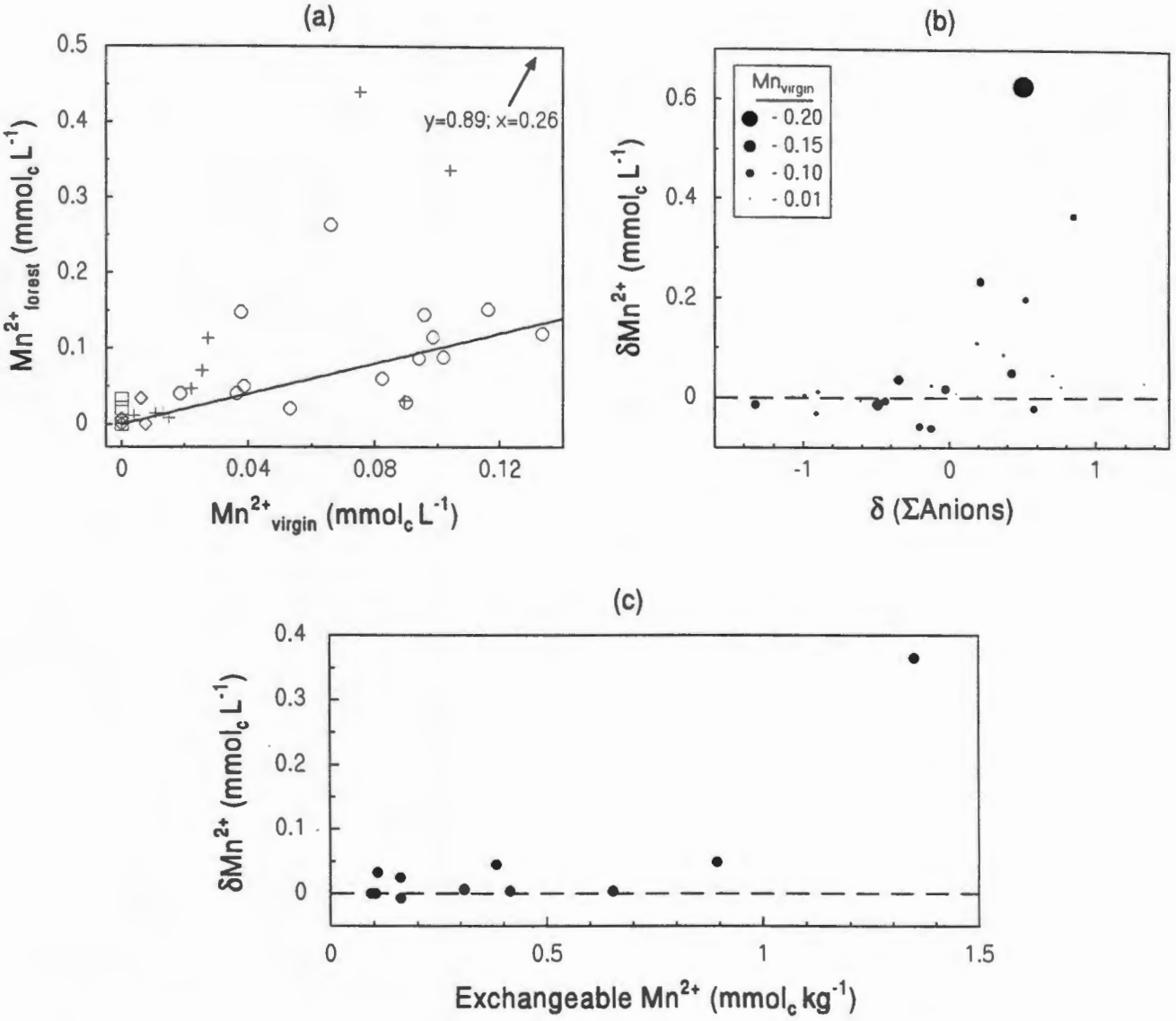

Figure 6.16: *Soluble and exchangeable Mn^{2+} relationships. a) The relationship between soluble (i.e. saturated paste extract) Mn^{2+} concentrations in forest soils and those in their equivalent virgin soil (solid line represents a 1:1 correlation). b) The relationship between the change in Mn^{2+} concentration ($\delta Mn^{2+} = Mn^{2+}_{forest} - Mn^{2+}_{virgin}$), the change in total anion concentration ($\delta(\Sigma Anions) = \Sigma Anions_{forest} - \Sigma Anions_{virgin}$) and the concentration of soluble Mn^{2+} in the virgin soil (Mn^{2+}_{virgin}). c) The relationship between the change in soluble Mn^{2+} concentration under forest and the exchangeable Mn^{2+} concentration of the virgin soil (exchangeable Mn^{2+} data only available for 15 forest-virgin soil pairs). EE -eastern escarpment; MI - midlands; SC -southern Cape; WC - western Cape.*

The solubility of Mn^{2+} is known to be strongly influenced by redox status (McBride, 1994), and the drier soil conditions prevailing under forest would be expected to cause an increased redox potential and, therefore, a reduced potential for Mn^{2+} solubilisation. However, manganese concentrations were determined on aqueous extracts obtained after equilibration for 24 hours under saturated conditions. Thus, it is possible that the enhanced concentrations of soluble Mn^{2+} in certain forest soils stem from higher concentrations of readily oxidisable organic matter compared to those in their virgin counterparts. Under saturated conditions, higher concentrations of oxidisable organic matter would be expected to result in lower redox potentials and, therefore, could lead to enhanced concentrations of soluble Mn^{2+}.

6.3.5. Base cations

To a large extent, variations in the concentrations of Ca^{2+} and Mg^{2+} in soil solutions reflect those observed for the exchange complex (section 5.3.2). Concentrations are highest for the midlands and southern Cape soils (Ca^{2+} and Mg^{2+} mostly > 0.4 $mmol_c\ L^{-1}$; forest and virgin soils) and are particularly low (< 0.2 $mmol_c\ L^{-1}$) for some of the highly leached soils of the eastern escarpment. With the exception of several sites in the midlands and southern Cape regions, soil solution concentrations of Ca^{2+} and Mg^{2+} are generally greater in forest soils than in their virgin equivalents (Figure 6.17), despite the reductions in exchangeable Ca^{2+} and Mg^{2+} levels and enhancement of exchangeable acidity documented in section 5.3. Elevated levels of soluble Ca^{2+} and Mg^{2+} in forest soil solutions reflect the overall increases in total solute concentrations under forest at most sites, combined with probable preferential displacement from the exchange complex of divalent cations by Al^{3+}. Afforestation-induced reductions in soluble $Ca^{2+}$and Mg^{2+} are evident for some midlands and southern Cape sites. To a large extent these simply reflect reduced total solute concentrations in the forest soils in question relative to their virgin equivalents (see section 6.3.1.4), but they may also stem from the particularly large reductions in exchangeable bases observed for many of the forest sites (section 5.3.2). The above-described variations are reflected in the statistical test results presented in Table 6.7. These indicate significant overall increases in Ca^{2+} and Mg^{2+} concentration under forest in the eastern escarpment and western Cape, but no statistically significant effects in the Midlands and southern Cape regions.

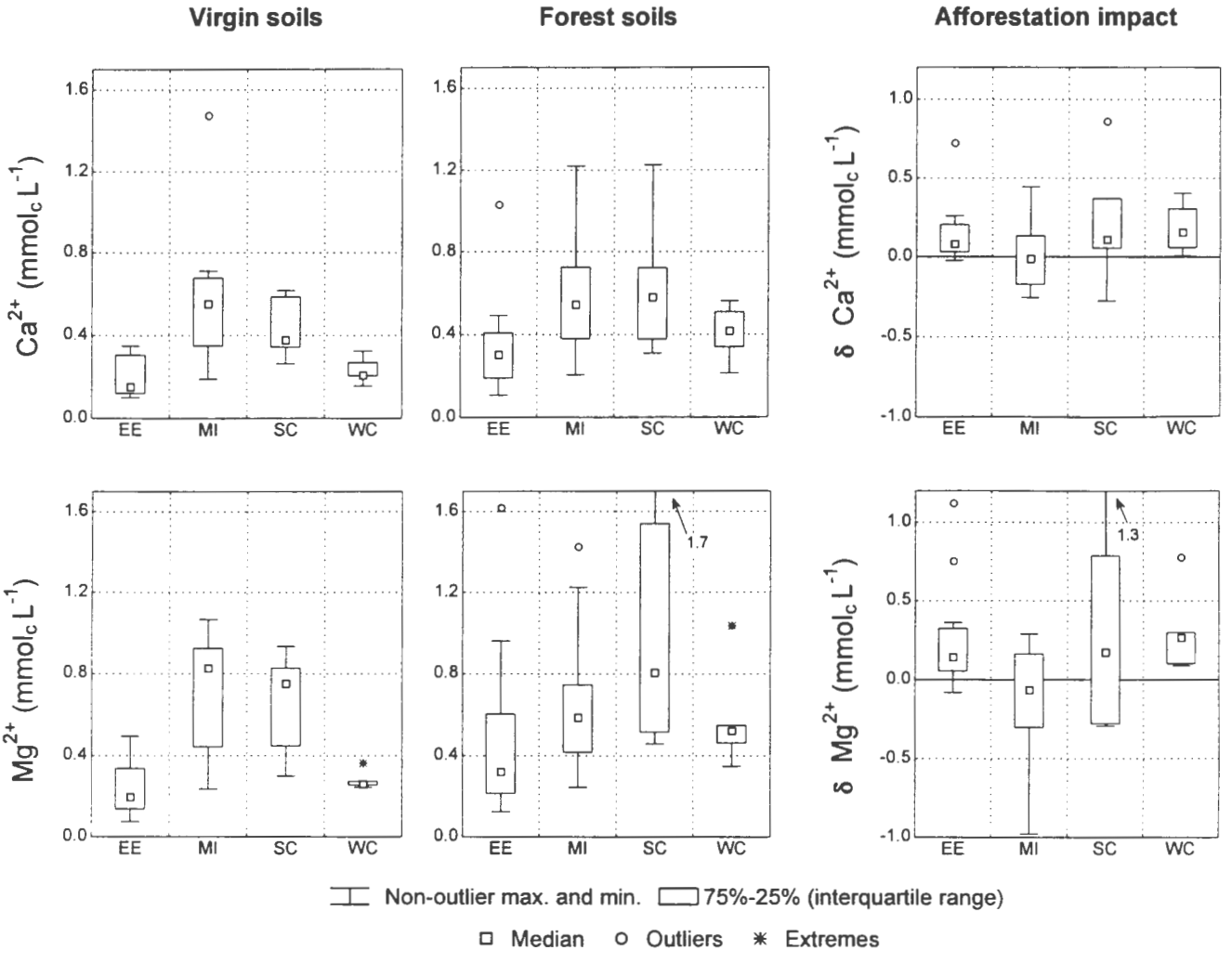

Figure 6.17: *Box and whisker plots illustrating regional variations in the concentration of Ca^{2+} and Mg^{2+} in saturated paste extracts from virgin and forest soils. δ Values represent the difference between concentrations in the forest extracts and those in their virgin equivalent. EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

Table 6.7: *P values (statistical significance levels) for forest-virgin differences in the concentration of base cations in saturated paste extracts. Significance levels were obtained using the non-parametric Wilcoxon matched pairs test. Underlined values indicate positive differences (i.e. increased concentrations under forest). ** - differences significant at the 99% confidence level; * - differences significant at the 95% confidence level.*

	All	Eastern escarpment	Midlands	Southern Cape	Western Cape
No. of soil pairs	38	12	14	6	6
Ca^{2+}	0.007**	0.005**	0.925	0.173	0.028*
Mg^{2+}	0.071	0.019*	0.300	0.463	0.028*
Na^{+}	<0.001**	0.023*	0.009**	0.116	0.028*
K^{+}	0.007**	0.050*	0.096	0.345	0.917
NH_4^{+}	0.153	0.308	0.683	0.173	0.046*

Calcium and magnesium concentrations are closely correlated in both forest and virgin soil solutions (Figure 6.18), suggesting a similar origin as well as similar cation exchange properties for these elements. The Mg/Ca ratio (~ 1) is high compared to that observed in other studies of forest ecosystems (Table 6.8) and appears to increase with increasing total concentration of Ca and Mg. Sea water has a high ratio of Mg^{2+} to Ca^{2+} (~ 5), thus elevated Mg/Ca ratios may suggest a marine influence in all of the regions investigated. There is, however, no correlation between the Mg/Ca ratio and the concentration of soluble Na^+ (Figure 6.18). Thus, for some of the sites, other factors such as relatively Mg-enriched parent materials, may contribute towards the high concentrations of Mg^{2+} relative to Ca^{2+}.

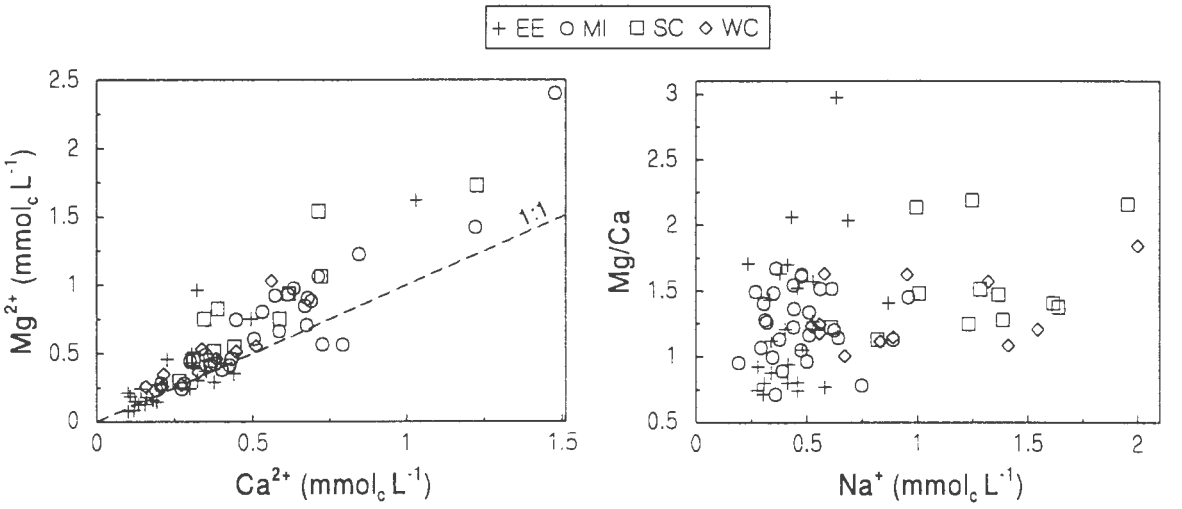

Figure 6.18: *The relationship between the concentration of Mg^{2+} and Ca^{2+} and that between the Mg/Ca ratio and the concentration of Na^+ in saturated paste extracts from forest and virgin soils. EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

Concentrations of soluble Na^+ are considerably higher in the forest and virgin soils of the Cape regions (generally > 0.8 $mmol_c\ L^{-1}$ up to 2 $mmol_c\ L^{-1}$) than in those of the eastern seaboard (generally < 0.8 $mmol_c\ L^{-1}$)(Figure 6.19) and confirm the influence of marine salt deposition, as inferred from the Cl^- data (section 6.3.1). These variations in soluble Na^+ are not reflected in exchangeable Na^+ levels, presumably due to the low cation exchange capacity of the sandy Cape soils and the inability of Na^+ to compete for exchange sites with divalent and trivalent cations. Afforestation has resulted in increased concentrations of soluble Na^+ in all of the regions investigated (Figure 6.19), presumably due to enhanced interception and/or evaporative concentration of atmospheric salts. This effect is particularly dramatic in the maritime Cape sites (increases of up to 1.4 $mmol_c\ L^{-1}$) where a significant component of salt input is likely to be in the form of wind blown aerosols. The statistical test results presented in Table 6.7 suggest that the effect of afforestation on the concentration of soluble Na^+ is

highly significant ($p < 0.001$) for all sites combined and, with the exception of the southern Cape, is significant at the 5% probability level for individual regions as well.

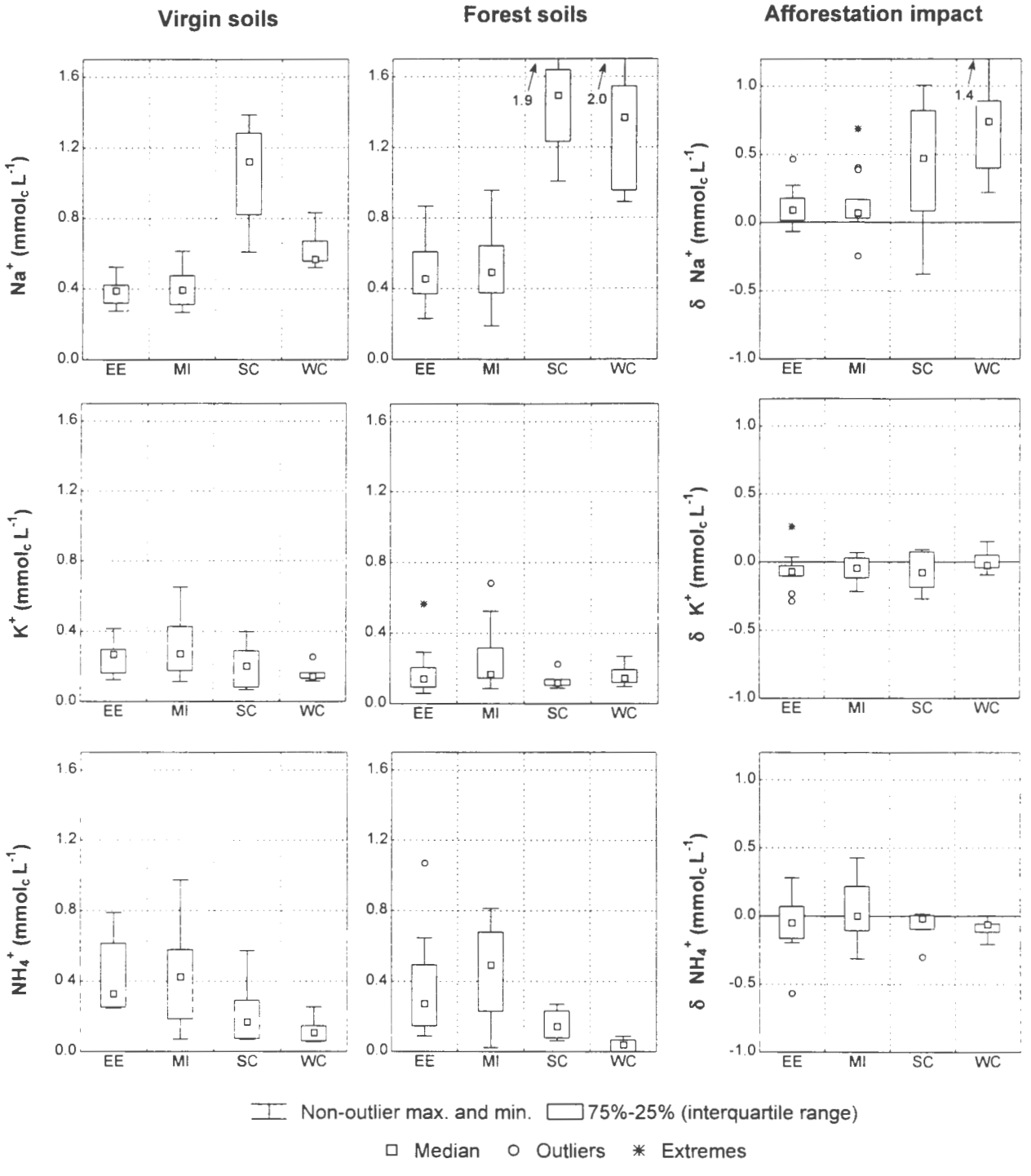

Figure 6.19: *Box and whisker plots illustrating regional variations in the concentration of monovalent base cations in saturated paste extracts from virgin and forest soils. δ Values represent the difference between the concentration in the forest extracts and those in their virgin equivalent (i.e. $\delta X = X_{forest} - X_{virgin}$, where $X = Na^+$, K^+ or NH_4^+). EE - eastern escarpment; MI - midlands; SC - southern Cape; WC - western Cape.*

The concentrations of soluble Ca^{2+} and Mg^{2+} in both forest and virgin soils are high compared to those reported in studies of forest ecosystems in the Northern Hemisphere (Table 6.8). Only two of the sites listed in Table 6.8 show soluble Ca^{2+} and Mg^{2+} levels greater than 0.4 $mmol_c\ L^{-1}$. These sites are severely impacted by marine salt deposition and, as a result, have elevated Mg^{2+} concentrations (approaching 1 $mmol_c\ L^{-1}$) and very high concentrations of Na^+ (4.19 and 6.61 $mmol_c\ L^{-1}$, respectively). The high Ca^{2+} and Mg^{2+} concentrations in the soil solutions of this study are in keeping with higher total solute concentrations. As discussed in section 6.3.1, it is possible that the increased solute levels result from a greater degree of evaporative concentration and/or a greater maritime influence at the South African sites. With the exception of sites impacted by severe salt deposition, the concentrations of soluble Na^+ observed in the north American and European forest soils represented in Table 6.8 are considerably lower than those observed in this study. While this supports the suggestion of a maritime influence, it does not rule out the possibility that the enhanced solute concentrations in solutions from the South African soils are caused by high levels of evapotranspiration compared to their Northern Hemisphere counterparts. Soil solutions from the Cape regions show a similar range in Na^+ concentration to that of Northern Hemisphere sites that have been severely impacted by marine salt deposition. However, the very high Na^+ concentration values (> 3 $mmol_c\ L^{-1}$) observed at some of these sites, are not evident in any of the South African soils.

Soluble K^+ concentrations are generally very low (mostly < 0.4 $mmol_c\ L^{-1}$; Figure 6.19) and display broadly similar variations to those observed for exchangeable K^+ (section 5.3.2). The majority of forest sites show slightly lower levels of soluble K^+ than their virgin equivalents. Reduced concentrations of soluble K^+ under forest may reflect increased rates of biomass uptake, combined with preferential adsorption or fixation of K^+ by clay minerals which limits the extent to which the soil solution can be replenished by ion exchange. Alternatively, in some soils the reduction in pH associated with afforestation may stabilise alunite, leading to a reduction in the solubility of K^+. This mechanism has been suggested as a possible explanation for K^+ fixation in certain acid, kaolinitic soils which do not contain vermiculite (Sumner *et al.*, 1991).

Table 6.8: *Cation concentrations in soil solutions from forest topsoils in North America and northern Europe (full site names are given in Table 6.5). With the exception of the data for Camels Hump, the data represent average values for solutions sampled over extended time periods (6 months to 7 years) using tension lysimeters. The Camels Hump solutions were obtained from individual soil samples by the pressure syringe method. Acid dep. - indication of the extent of acid deposition. Sea salt - indication of the extent of marine salt inputs. Sources: 1 - Cronan and Aiken, 1985; 2 - Rustad et al., 1996; 3 - Johnson et al., 1985; 4 - Bockheim and Langley-Turnbaugh, 1997; 5 - Binkley et al., 1982; 6 - Homann et al., 1994; 7 - LaZert and Scott, 1996; 8 - Farrel et al., 1994; 9 - Marschner et al., 1992.*

Site	Genus	Acid dep.	Sea salt	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	$NH4^{+}$	Ref
						$mmol_c\ L^{-1}$			
North America - Acid deposition impacted									
Adirondack	mixed	moderate	moderate	0.124	0.036	0.020	0.028	0.002	1
Bear Brook	mixed	moderate	moderate	0.048	0.027	0.061	0.01	0.001	2
Bear Brook	mixed	severe	moderate	0.279	0.087	0.094	0.012	0.003	2
Walker Branch	*Quercus*	moderate	v.minor	0.149	0.078	0.038	0.051	0.001	3
Walker Branch	*Liriodendron*	moderate	v.minor	0.23	0.09	0.022	0.033	0.002	3
North America - Sea salt impacted									
Cape Blanco	*Picea*	v.minor	v.severe	0.25	0.826	6.61	0.239		4
Pioneer terrace	*Picea*	v.minor	v.severe	0.367	0.965	4.19	0.108		4
Silver Butte	*Picea*	v.minor	severe	0.156	0.339	1.23	0.095		4
Indian Creek	conifer	v.minor	severe	0.137	0.21	0.712	0.076		4
Poverty Ridge	conifer	v.minor	severe	0.06	0.091	0.755	0.061		4
UBC Res. for.	conifer	v.minor	moderate	0.16	0.079		0.035	0.001	5
UBC Res. for.	conifer	v.minor	moderate	0.071	0.038		0.007	0.0001	5
Cedar River	*Pseudotsuga*	minor	moderate	0.055	0.024	0.047	0.023		6
Cedar River	*Alnus*	minor	moderate	0.183	0.072	0.044	0.055		6
North America - Minimal acid or salt impacted									
Harp Lake	*Pinus*	v.minor	v.minor	0.060	0.023	0.031	0.008	0.000	7
Harp Lake	*Pinus*	v.minor	v.minor	0.092	0.031	0.015	0.023	0.001	7
Europe - Acid deposition impacted									
Kootwijk	*Pinus*	severe	minor	0.196	0.231	0.65	0.015	0.304	8
Hardewijk	*Pinus*	severe	minor	0.034	0.131	0.766	0.014	0.001	8
Högwald	*Picea*	severe	minor	0.268	0.505	0.158	0.027	0.022	8
Solling	*Picea*	severe	minor	0.196	0.087	0.096	0.025	0.021	8
Grunewald	*Pinus*	severe	v.minor	0.750			0.205	1.444	9
Grunewald	*Pinus*	severe	v.minor	0.125			0.051	0.139	9
Europe - Acid deposition impacted									
Klosterheide	*Picea*	minor	severe	0.438	0.66	2.374	0.13	0.007	8
Ballyhooly	*Picea*	v.minor	severe	0.072	0.143	0.738	0.015	0.009	8

Ammonium concentrations are highly variable but tend to be significantly higher in soils of the eastern escarpment and midlands regions than those of the southern and western Cape (Figure 6.19). In most cases, the effect of afforestation in the latter regions is to reduce NH_4^+ levels in the soil solution. This is probably due to the combined effect of increased biomass uptake and the inability of the soil to retain NH_4^+ either in the litter layer (litter layers are generally poorly developed in the Cape sites) or on the soil exchange complex. Thick litter layers (in some cases exceeding 50 cm) are commonly developed under pine plantations in the eastern seaboard region (Schutz *et al.*, 1983; Morris, 1995) and, together with high clay contents are likely to provide large pools of mineralisable and exchangeable NH_4^+ in most of the forest soils of this region. However, the effect of afforestation is extremely variable and no consistent trends or relationships are evident. This may reflect the complexity of processes mediating soluble NH_4^+ levels, but sample storage effects (e.g. oxidation) and a large analytical error (Appendix E) is likely to contribute significantly to the uncertainty associated with the NH_4^+ data.

With the exception of a few sites in Europe that are strongly influenced by acid deposition, K^+ and NH_4^+ concentrations reported for North American and European forest ecosystems generally do not exceed 0.1 $mmol_c\ L^{-1}$ and are, therefore, considerably lower than the values obtained in this study. Once again, this reflects the generally higher solute concentrations observed in the South African soils.

6.3.6. Ratios of acidic and basic cations in solution

Despite the observed increase in soluble base cations in most of the forest soils, reductions in soil solution pH and large increases in soluble Al concentrations have caused decreases in the percentage of base cations in solution. However, in most cases this reduction is small (< 5 %) and base cation proportions generally remain above 90 %. Because of the strong preferential adsorption of Al^{3+} relative to divalent and monovalent base cations, it is only in soils with very low base saturation (i.e. < ~ 20 % exchangeable base cations) that the enhancement of solute concentrations under forest causes significant reductions in the percentage of soluble base cations (Figure 6.20). Nonetheless, a base saturation value below 20% does not *necessarily* result in significantly reduced proportions of soluble base cations and clearly other factors, such as the degree of solute concentration enhancement, solid-phase control of Al solubility and possibly the involvement of soluble organic acids, must play a role.

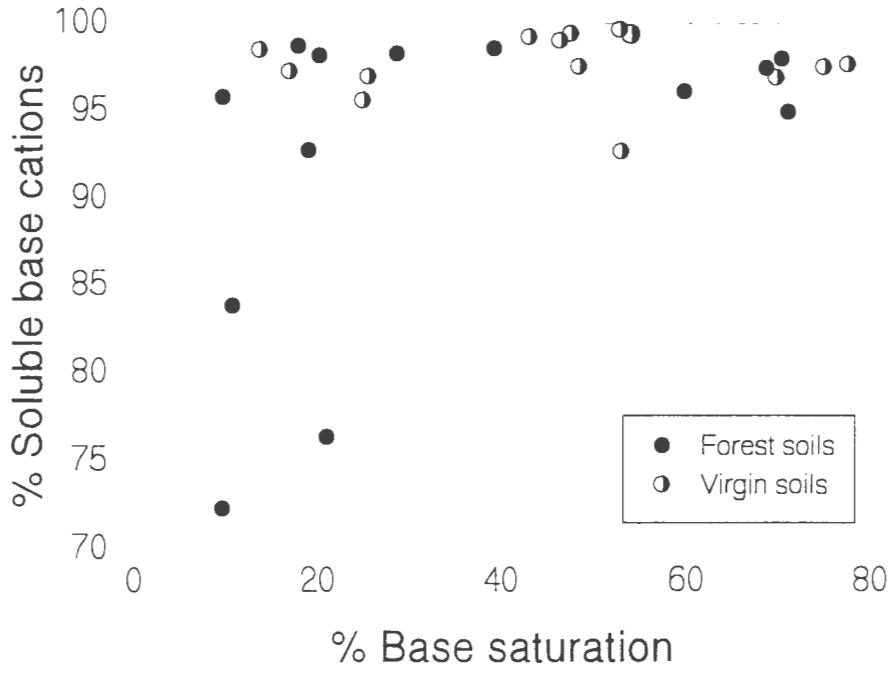

Figure 6.20: *The relationship between percent soluble base cations and base saturation of the exchange complex. Soluble base cation percentages are calculated from saturated paste concentration dataas follows: % Sol. BC = [100 × $(Na^+ + K^+ + NH_4^+ + Ca^{2+} + Mg^{2+})$/ $(Na^+ + K^+ + NH_4^+ + Ca^{2+} + Mg^{2+} + H^+ + Al_i)$], where Al_i = the total concentration of monomeric Al and all concentrations are in $mmol_c L^{-1}$.*

Calcium/aluminium ratios of the soil solution are of particular interest as they have been used extensively as indicators of stress in forest ecosystems (Sverdrup *et al.*, 1993; Cronan and Grigal, 1995). Cronan and Grigal (1995) have recently reviewed the literature on Al stress on forest species and other plants. Fifty percent of the reviewed studies indicate detrimental impacts on growth or tissue nutrient content at Ca/Al concentration ratios of 1 or less. The calcium/aluminium ratios of saturated paste extracts are illustrated in Figure 6.21. Although in almost all cases Ca/Al ratios of forest soil solutions are considerably lower than their virgin equivalents, only two of the sites investigated (SC4f and SC5f) showed ratios lower than the threshold value of 1. This suggests that, despite severe acidification, afforestation has not yet led to conditions of Al stress at the majority of sites.If the current rates of acidification continue, however, Ca/Al ratios at several sites are likely to be reduced to critical levels in the near future. Rates of change in the Ca/Al ratio range from 0.03 to 2.1 per year (based on the total age of the plantations; Figure 6.21) and suggest that certain plantations may experience Al toxicity problems within the next thirty-year rotation.

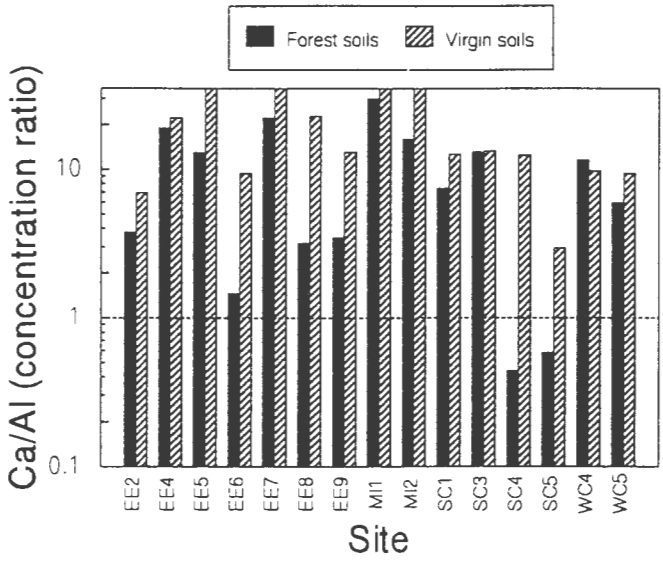

Figure 6.21: Calcium/aluminium ratios for saturated paste extracts from paired forest and virgin soils. The Ca/Al values represent ratios of total Ca^{2+} over total monomeric Al (both in mmol L^{-1}). The dashed line represents a Ca/Al "threshold" value of 1. See text for details.

6.3.7. Assessment of the "edge effect " at forest margins

The enhancement of solute inputs at forest margins is well documented (e.g. Draaijers *et al.*, 1988; Lindberg and Owens, 1993) and recent work has demonstrated the influence of the "edge effect" on unsaturated zone pore-water chemistry (Kinniburgh and Trafford, 1996). Because the soil solutions obtained for this study were derived from soil samples taken within 10 to 25 m of the forest edge, it is possible that they have been influenced by this effect. In view of this, a study was carried out to assess whether the composition of the soil solutions are representative of the entire plantation or, whether they reflect processes which are restricted to or significantly modified at the forest margin.

Sampling traverses were carried out at 4 eastern escarpment and 3 western Cape sites. Each sample in the traverse is a composite of 3 subsamples (each ~ 1 kg) taken at the same distance from the forest margin but spaced 10 m apart from each other. Four such bulk samples were taken for each traverse. These include: a virgin soil sample taken between 20 and 30 m away from the forest margin; a forest edge sample taken at approximately 10 to 20 m into the plantation (this corresponds to the position of the first subsamples taken for the original bulk forest soil sample); and two samples taken at increasing distances (45 to 90 m) away from

the forest margin in the interior of the plantation. Saturated paste extracts were obtained for each of the bulk samples using the methods described in section 6.2.1 and the EC, pH major anion concentration and total monomeric Al concentration of these extracts were determined by the analytical methods described in section 6.2.3.

6.3.7.1. Eastern escarpment

Data obtained for saturated paste extracts of the original forest-grassland soil pairs from the eastern escarpment indicate a consistent enhancement of soluble NO_3^- concentration under forest but variable effects on the concentration of soluble Cl^- and SO_4^{2-}. This is reflected in the data obtained for the traverse samples which indicate that Cl^- and SO_4^{2-} concentrations are in some cases increased and in other cases decreased at the forest edges. With the exception of site EE2, the largest differences are between forest and virgin samples and variations within the forest are relatively minor (Table 6.9; Figure 6.22). This, and the fact that in most cases Cl^- is reduced at the forest edge relative to the grassland, suggests that the soil solutions have not been significantly influenced by an edge effect. With the possible exception of site EE7, this conclusion is supported by the NO_3^- data, which indicate consistent increases from grassland to forest and relatively minor variations within the forest. The traverse for site EE2 is somewhat anomalous as the third forest sample was taken in a younger portion of the plantation and, therefore, strictly speaking this sample cannot be compared to the first and second samples in the traverse. If this sample is excluded, however, the data suggest that relatively high Cl^- and SO_4^{2-} concentrations in the grassland and at the forest edge drop off with increasing distances into the forest. The cause of these variations is uncertain, but they probably reflect spatial variability in soil properties which are not related to the type of vegetation cover. This variability is unlikely to substantially influence the bulk samples used to evaluate afforestation impacts as these are composites of ten samples taken within 20 to 30 m of the forest margin (as supported by duplicate sampling - see Appendix E).

The solution pH and Al concentration data indicate that, where forest-virgin differences are evident, these are generally maintained or enhanced with increasing distances into the forest interior (Figure 6.23). The only exception to this is the relative enhancement of pH and reduction of Al concentration in the younger portion of the plantation at site EE2 where one would expect the forest to have had less of an impact.

Table 6.9: *Electrical conductivity (EC), anion concentrations , pH and total Al concentrations for saturated paste extracts of soil samples taken on traverses from virgin vegetation into the forest. EE - eastern escarpment; WC - western Cape. Distances are measured from the forest-virgin boundary. Negative distance values indicate samples taken in the virgin vegetation (i.e. grassland and fynbos for the eastern escarpment and western Cape samples, respectively).*

Site	Distance	EC	Cl^-	NO_3^-	SO_4^{2-}	pH	Al_t
		$\mu S\ cm^{-1}$	———	$mmol_c\ L^{-1}$	———		$mmol_c\ L^{-1}$
EE2	-45	141	0.517	0.221	0.264	5.17	0.031
	15	184	0.549	0.439	0.242	4.65	0.097
	60	166	0.355	0.448	0.100	4.18	0.177
	90	103	0.359	0.239	0.069	4.91	0.041
EE4	-20	102	0.439	0.013	0.090	5.19	0.008
	20	95	0.285	0.281	0.139	5.34	0.015
	55	104	0.230	0.408	0.084	4.86	0.036
	80	90	0.247	0.312	0.100	5.22	0.012
EE7	-20	85	0.403	0.005	0.111	5.64	0.003
	20	182	0.199	0.897	0.087	4.96	0.032
	50	134	0.179	0.548	0.078	5.09	0.013
	65	139	0.237	0.529	0.126	5.05	0.028
EE9	-20	117	0.548	0.004	0.117	5.30	0.018
	20	137	0.225	0.352	0.031	4.68	0.084
	45	95	0.195	0.386	0.031	4.73	0.085
	70	97	0.143	0.467	0.029	4.41	0.130
WC3	-20	88	0.353	0.033	0.129	4.83	0.361
	20	234	1.134	0.021	0.265	3.84	0.261
	45	170	0.800	0.017	0.191	4.07	0.174
	80	158	0.675	0.015	0.199	3.91	0.147
WC5	-25	162	0.754	0.031	0.270	5.59	0.609
	15	167	0.683	0.019	0.197	5.17	1.525
	40	130	0.436	0.019	0.141	5.68	1.482
	65	131	0.419	0.018	0.188	5.17	1.565
WC6	-20	159	0.568	0.018	0.377	4.34	0.206
	20	215	0.774	0.019	0.203	4.08	0.777
	45	167	0.598	0.012	0.156	4.00	0.495
	70	130	0.558	0.017	0.153	4.17	0.305

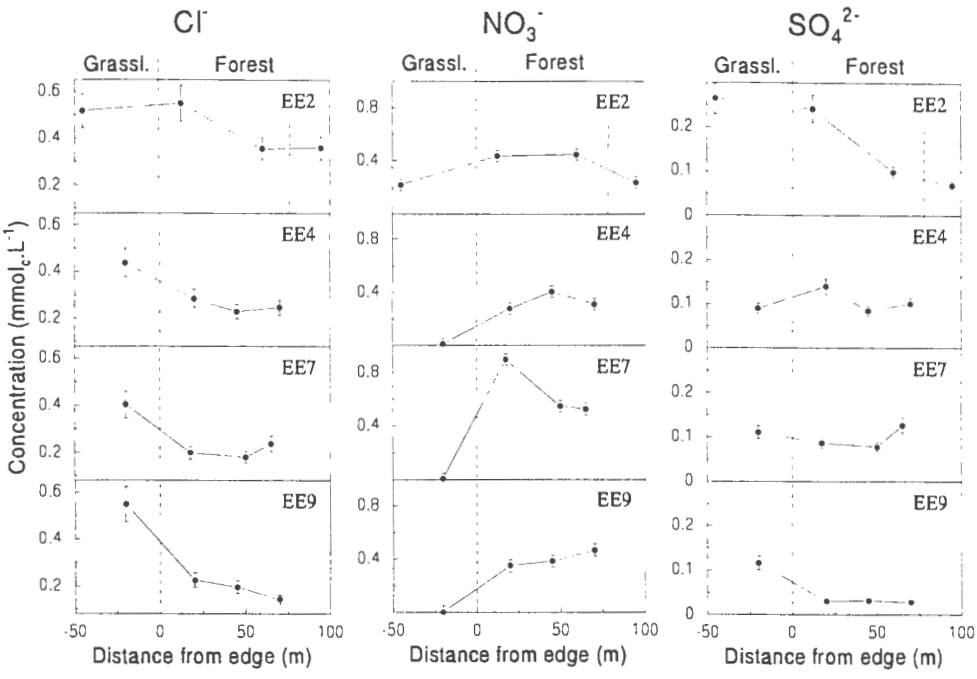

Figure 6.22: *Anion concentrations in saturated paste extracts of traverse samples from eastern escarpment sites. The dashed line at distance 0 represents the forest margin. The dashed line between the second and third forest sample at site EE2 represents the boundary between an older (left) and younger (right) portion of the plantation. Error bars are estimates of analytical error based on duplicate extracts (see Appendix E).*

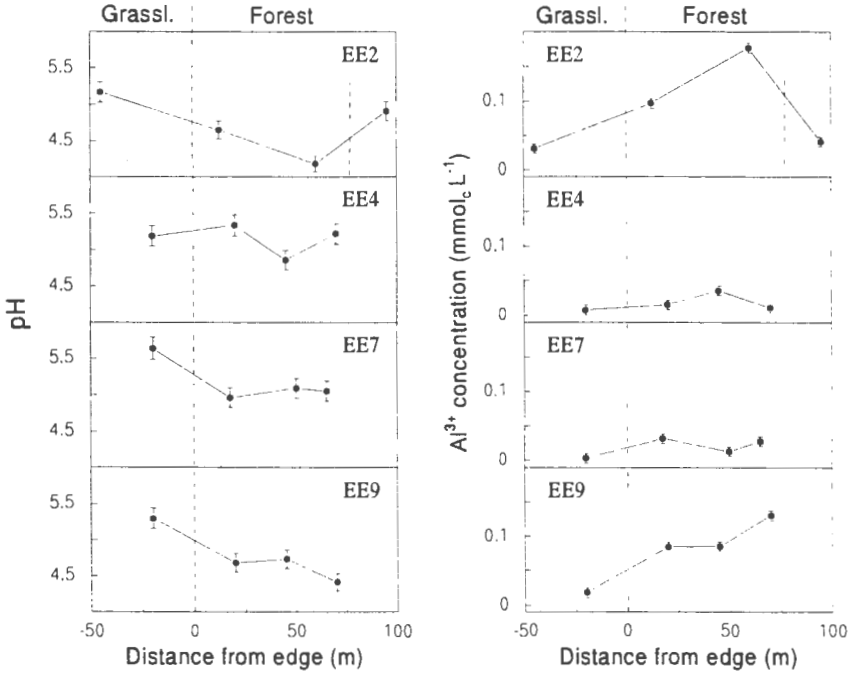

Figure 6.23: *Solution pH and total monomeric Al concentrations in saturated paste extracts of traverse samples. The dashed line at distance 0 represents the forest margin. The dashed line between the second and third forest sample at site EE2 represents the boundary between an older (left) and younger (right) portion of the plantation. Error bars are estimates of analytical error based on duplicate extracts (see Appendix E).*

6.3.7.2. Western Cape

Two of the western Cape sites investigated (WC3 and WC6) show evidence of an edge effect which manifests itself in significantly enhanced Cl^- (and in one case SO_4^{2-}) concentrations (Figure 6.24). The most dramatic enhancement occurs at site WC3 where Cl^- and SO_4^{2-} concentrations are considerably elevated in the forest edge sample relative to those taken at greater distances into the forest. Despite the drop in concentration away from the forest margin, however, the soluble Cl^- and SO_4^{2-} levels are elevated in all of the forest samples relative to that of the fynbos soil. Of the three western Cape sites investigated, WC3 is the closest to the sea (~ 5 km). The edge of the forest at this site faces into strong south-easterly winds which prevail during the dry summer period and which blow directly off the ocean. Thus the edge effect at this site probably stems from enhanced interception by the forest of marine salt aerosols, an effect which is likely to be particularly pronounced at the forest margin. Site WC6 faces into the north-westerly winds which prevail during winter. Most of the rainfall in the western Cape is associated with these winds. Thus, the fact that only modest increases in soluble Cl^- levels are observed at the margin of site WC6, suggests that increased interception of precipitation is not a major factor contributing to the enhancement of anion concentrations under forests in the western Cape region.

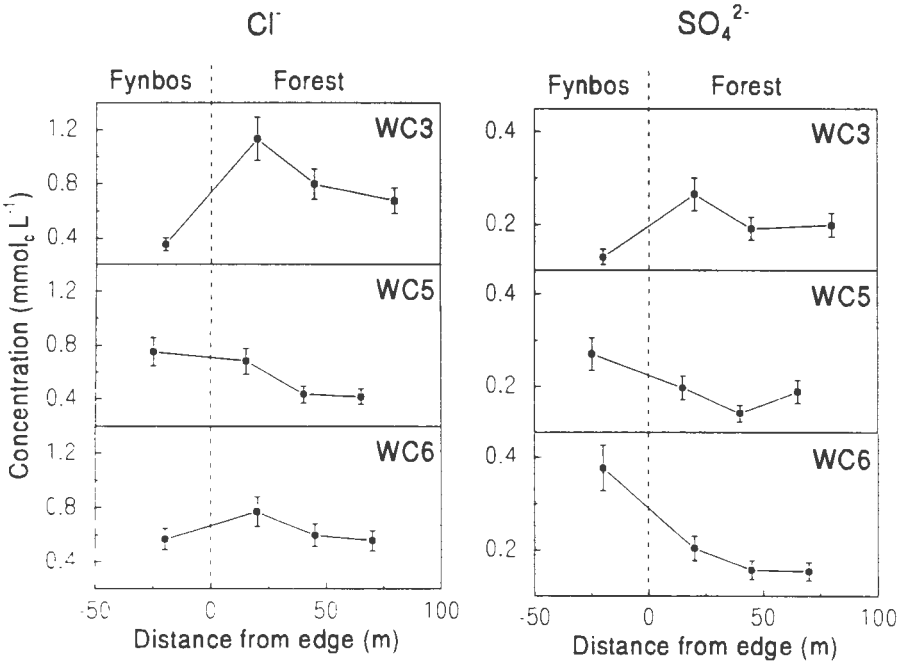

Figure 6.24: *Chloride and sulphate concentrations in saturated paste extracts of traverse samples from western Cape sites. Error bars are estimates of analytical error based on duplicate extracts (see Appendix E).*

The reduced concentrations of SO_4^{2-} in the forest samples of the WC5 and WC6 traverses is in agreement with the data obtained for the original composite samples (Appendix C) and is possibly suggestive of increased uptake by the forest (see section 6.3.1.3). Similarly, the original samples for site WC5 did not show a significant change in the concentration of soluble Cl^- between the grassland and fynbos soils.

As was the case for the eastern escarpment samples, the pH and Al data do not show any consistent trends away from the forest margin (Table 6.9; Figure 6.25). With the exception of one sample at site WC5, pH decreases observed at the forest edges are maintained with increased distance into the forest.

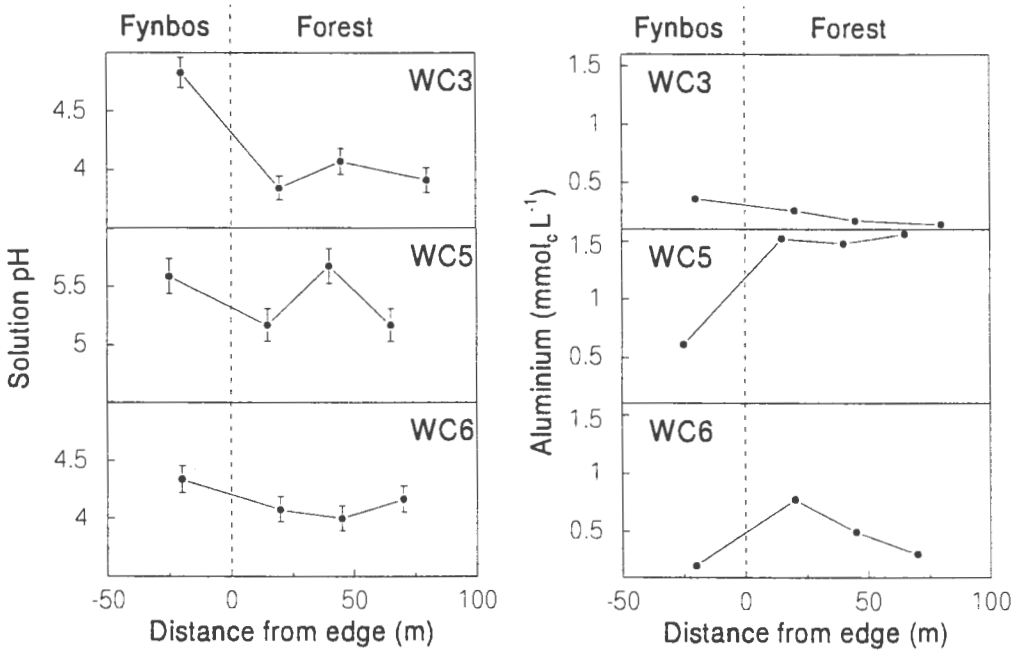

Figure 6.25: *Solution pH and total monomeric Al concentrations in saturated paste extracts of traverse samples from western Cape sites. Error bars are estimates of analytical error based on duplicate extracts (see Appendix E).*

6.3.7.3. Conclusions of the edge effect study

The data presented above suggest that preferentially enhanced interception of atmospheric solutes at forest edges is not a major factor influencing soil solution compositions at the majority of sites investigated. Where large differences in solute concentrations occur at forest

edges, these are usually maintained with increasing distance into the forest. Although at some sites there is a slight decline in concentration away from the forest margin, levels significantly higher than those of the virgin soils are generally maintained. This indicates that the variations in solute concentrations observed in bulk samples taken within 30 m of the forest edge, reflect processes which take place throughout the plantation. Nonetheless, at some sites and particularly at those which are influenced by marine aerosol deposition, an intensification of these processes may occur at the forest edge. Thus, while the differences in solute concentrations observed for forest-virgin soil pairs are believed to be meaningful, they should be regarded as estimates of the maximum possible effect of afforestation.

In contrast to the above, the observed impact of afforestation on solution pH and on the concentration of soluble Al does not appear to be in any way related to proximity to the forest edge and can be assumed to be representative of processes taking place throughout the plantation.

6.4. SUMMARY AND CONCLUSIONS

The effect of afforestation on the concentration of soluble Cl^-, NO_3^- and SO_4^{2-} is highly variable and is strongly influenced by regional factors. Chloride concentrations are considerably enhanced in most forest soil solutions of the western and southern Cape regions, whereas the majority of eastern escarpment and midlands forest soils show increased nitrate levels relative to their grassland equivalents. In the case of both of these anions, afforestation-induced changes appear to be related to regional differences in rainfall chemistry. In the Cape regions, high chloride concentrations in rainfall and dry deposition of marine aerosols have been magnified under forest due to enhanced interception and evaporative concentration processes. Elevated nitrate concentrations in rainfall in the eastern escarpment and possibly also the midlands region may play a role in the enhancement of soil-solution nitrate levels in the forest soils of these regions. However, this effect is probably significantly influenced by biological processes and much of the nitrate may be generated indirectly by oxidation of accumulated pine litter. It is likely that drying and storage of soil samples has a significant effect on the concentration of soluble nitrate, and the enhancement of NO_3^- in the eastern seaboard soils may, therefore, be an artifact of the sample preparation and saturated paste

extraction procedures. Nonetheless, consistent forest-grassland differences indicate that the pine plantations do have a considerable impact on nitrogen dynamics which could potentially lead to NO_3^- leaching.

Variations in the concentration of phosphate-extractable and, to a lesser extent, water-soluble sulphate appear to be related to soil texture and probably reflect differences in sulphate sorption capacity. Afforestation dramatically enhances exchangeable sulphate concentrations in the clay-rich soils of the eastern escarpment and midlands, but does not significantly influence exchangeable sulphate concentrations in the majority of sandy soils, and has only a minor and somewhat inconsistent effect on soluble sulphate levels. The enhancement of exchangeable sulphate in clay-rich forest soils of the eastern seaboard is thought to result from a combination of increased interception and evaporative concentration of atmospheric SO_4^{2-} and acidification-induced reduction of soil pH with associated enhancement of anion adsorption capacity. In these soils, however, soluble sulphate levels are maintained at low levels or are reduced under forest. This may reflect SO_4^{2-} retention by adsorption on clay minerals and/or precipitation of Al-sulphate minerals. Further work is required in order to determine the SO_4^{2-} sorption capacity of the soils, the degree to which this has been saturated and the extent to which Al-sulphate minerals control SO_4^{2-} concentrations in soil solutions. A recent study by Alewell *et al.* (1997) has highlighted the link between SO_4^{2-} leaching dynamics and soil acidification and recovery. This emphasises the fact that an understanding of the factors controlling SO_4^{2-} mobility and storage is necessary in order to assess the potential for future leaching of SO_4^{2-} and acidity.

The concentration of dissolved organic carbon (DOC) in both forest and natural soil solutions is high compared to that reported in other studies of forest soils. Organic anion concentrations, calculated on the basis of observed correlations with excess positive charge, indicate that DOC constitutes a major component of the anion suite in soil solutions. Afforestation-induced changes in organic anion concentration appear to be related to the concentration in the original grassland or fynbos soils. The grassland soils tend to have high DOC concentrations which are generally reduced under forest, whereas fynbos soil solutions usually contain relatively low DOC concentrations which are generally enhanced by afforestation. Differences in colour and the DOC-charge relationship in different regions probably reflect variations in the chemical nature of the DOC. No such differences were observed between forest soil solutions and their natural equivalents.

The total concentration of strong acid anions is in most cases significantly enhanced by afforestation, in some cases by as much as double the natural levels. However, at some of the sites investigated, and particularly those of the midlands region, significant reductions in organic anion concentration may offset this enhancement, and in certain sites could result in an overall reduction in total anion concentration.

In absolute terms, the concentration of inorganic and organic anions in all of the soil solutions is high relative to those observed for similar forest ecosystems in the northern hemisphere and is thought to reflect higher rates of evaporative concentration and/or a greater maritime influence in the regions investigated. Thus, there is clearly potential for significant leaching of anions and acidity from most of the soils investigated and in most cases this potential is enhanced by afforestation. The effect of these enhanced solute concentrations on the quality of associated surface waters will, however, depend on the volumes of solutions being leached from topsoils, as well as on the extent of interaction with less acidic subsoils or saprolite. Because of the increased rates of evapotranspiration from forests relative to the virgin vegetation, the long term impact of acidification and enhanced solute concentrations will probably be offset, to a large extent, by reduced leaching from the forest soils. A build-up of solutes during dry periods, however, may result in major acidity "flushes" following the first major rains when a high percentage of water will flow through the upper soil horizons. Because of the increased acidity and solute concentrations, this effect is likely to be significantly enhanced in pine plantations relative to undisturbed land.

Saturated paste extracts of forest soils have consistently lower pH values (by 0.2 to 1.2 pH units) than those from their virgin equivalents. Because of the naturally acidic nature of the soils, these changes in pH have resulted in considerably enhanced concentrations of soluble monomeric Al, which ranges from 0.014 $mmol_c L^{-1}$ (0.13 $mg L^{-1}$) to ~ 1 $mmol_c L^{-1}$ (9 $mg L^{-1}$). In addition, afforestation appears to have enhanced the concentration of inorganic Al species (and that of Al^{3+} in particular) relative to organically complexed Al (Al-DOM). Despite this reduction in the *relative* concentration of organically complexed Al, however, speciation calculations indicate that Al-DOM is the dominant Al species in most of the soil solutions investigated.

There is much uncertainty regarding the incorporation of aqueous Al-organic matter interactions into Al speciation calculations and into the calculation of Al^{3+} activities in particular. As a result, interpretations based on the relationship between pH and Al^{3+} activity and, to a lesser extent, on the activity of SO_4^{2-}, K^+ and H_4SiO_4, can only be regarded as tentative. Nonetheless, calculations incorporating the simple DOM model of MINTEQA2 yield results which are more compatible with likely solid-phase control of Al solubility than those obtained on a DOM-free basis. The resultant $\log(Al^{3+})$/pH relationships suggest that Al-hydroxide phases probably control the solubility of Al in the majority of eastern seaboard soils and in the soils of one southern Cape site. This is consistent with the relatively high concentrations of gibbsite determined in several of these soils by X-ray diffractometry (section 4.3.2). The $\log(Al^{3+})$/pH relationships displayed by soil solutions for two of the eastern escarpment sites, indicate possible equilibrium with dibasic Al-bearing phases. While alunite equilibrium is possible in the one of the sites, high Al activities preclude this for the other site and suggest solubility control by either a more soluble possibly amorphous equivalent of alunite, or by dibasic Al-DOM. Aluminium-hydroxides do not appear to play a significant role in controlling Al-solubility in most of the sandy soils of the Cape regions. Solutions with pH values exceeding ~ 5 are generally oversaturated with respect to amorphous $Al(OH)_3$ and appear to be in equilibrium with a dibasic Al-bearing phase such as Al-DOM or an amorphous equivalent of alunite. In contrast to this, the more acidic solutions (pH < ~ 4.5) are strongly undersaturated with respect to gibbsite and show evidence for control of Al solubility by Al-organic matter complexes (Al-OM). In particular, the data suggest that Al-OM with a very low basicity may control Al solubility in soils with very low clay contents (< 3 % clay) and with moderate concentrations of organic carbon (> 1.5 %).

The most stable Al-bearing mineral assemblage for the pH values and the ranges of SO_4^{2-}, K^+ and H_4SiO_4 activity prevailing in the soil solutions, is kaolinite + quartz. Thus, the apparent solubility control by $Al(OH)_3$, Al-sulphates and Al-OM reflect metastable conditions under which Al solubility is maintained at considerably higher levels than those subtended by equilibrium with kaolinite. This suggests that metastable phases have a controlling influence on Al solubility in saturated paste extracts. Nonetheless, the observed solubility relationships may provide an indication of the processes which operate under the dynamic conditions prevailing in the field. During dry periods with limited leaching, the activity of H_4SiO_4 may be raised to high levels such as those observed in the saturate paste extracts. Under these

conditions kaolinite is stabilised, but kinetic factors may limit the extent to which this mineral influences the solubility of Al. Thus, depending on the pH, the activity of SO_4^{2-} and/or K^+ and the concentration of organic matter, metastable phases such as $Al(OH)_3$, jurbanite, alunite and Al-OM, are likely to control the activity of Al^{3+} in solution. Due to the relatively high mobility of silica, concentrations of H_4SiO_4 may be considerably reduced by leaching during wet periods. A preferential reduction of H_4SiO_4 activity would result in conditions under which kaolinite is destabilised and precipitation of $Al(OH)_3$, or possibly an Al-sulphate mineral is favoured.

Several of the soils show considerable enhancement of soluble Mn^{2+} concentrations relative to their virgin equivalents. The data suggest that this results from the combination of afforestation-induced enhancement of total solute concentrations with moderately elevated inherent concentrations of soluble Mn^{2+} in certain soils. Relatively high levels of Mn solubility are presumably related to the low pH values of both forest and natural soils. Afforestation-induced reductions in pH do not, however, appear to influence the degree of Mn enrichment in forest soil solutions. The extent to which changes in redox potential contribute towards enhancing the concentrations of Mn^{2+} in forest soil solutions requires further investigation.

Despite the major reductions in exchangeable Ca^{2+} and Mg^{2+} reported in the previous chapter, the concentration of these cations is enhanced in the majority of forest soil solutions from the eastern escarpment, southern Cape and western Cape. This probably occurs as a result of the combined effect of increased total solute concentrations under forest and preferential displacement of divalent cations by exchangeable Al. Many of the midlands forest sites show reductions in soluble Ca^{2+} and Mg^{2+} concentrations which are believed to primarily reflect the reduced total solute concentrations observed for these soils. Variations in soluble Na^+ are not significantly influenced by cation exchange processes and afforestation has led to increased concentrations in almost all of the soil solutions investigated. This effect is particularly prominent in the Cape regions and is thought to result from enhanced interception and evaporative concentration of atmospheric salts. Base cation concentrations in solutions from both forest and virgin soils are high compared to those observed in studies of forest ecosystems in North America and Europe. This may reflect increased levels of evapotranspiration caused by the warm South African climate, but high Mg/Ca ratios and

considerably elevated Na^+ concentrations observed in the saturated paste extracts, suggest that marine salt inputs could contribute substantially to the elevated solute concentrations in all of the regions investigated. Concentrations of soluble K^+ and NH_4^+ are in most cases lower than those of Ca^{2+}, Mg^{2+} and Na^+ and, although the effect of afforestation on these cations is variable, their concentration is generally reduced in forest soil solutions. This may result from high rates of biomass uptake and, in some cases, from strong adsorption onto clay minerals. In certain soils, alunite precipitation could play a role in reducing the K^+ concentration in soil solutions.

Despite increased concentration of total soluble base cations under forest, afforestation - induced reduction of pH and major increases in Al concentration have reduced the proportion of base cations in the majority of soil solutions. However, for most soils this reduction is small and soluble base cation proportions generally remain above 90%. It is only in soils with very low exchangeable base saturation levels (i.e. < ~20% base saturation) that the enhancement of solute concentrations and the reduction in pH under forest cause significant reductions in the percentage of soluble base cations (to values of 70 to 80%). Calcium/aluminium ratios for most of the forest soil solutions are greater than one, suggesting that the majority of sites are unlikely to be influenced by Al stress in terms of criteria proposed by Cronan and Grigal (1995). Afforestation has, however, reduced Ca/Al ratios considerably over time periods ranging from 30 to 65 years, suggesting that continued silvicultural activities may lead to widespread conditions of Al stress.

7. THE COMPOSITION OF STREAM WATERS: REGIONAL VARIATION AND THE IMPACT OF AFFORESTATION

7.1. INTRODUCTION

In the past few decades, much attention has focused on the impact of acid deposition on the acidity of surface waters (Reuss and Johnson, 1986; Cresser and Edwards, 1987; Batterbee, 1990), many of which drain afforested catchments. Few studies, however, have focused directly on the effect of afforestation and associated soil acidification, as opposed to the effects resulting from the iteraction of forests with atmospheric pollution, on the composition of stream waters. Processes which may lead to acidification of stream waters draining afforested areas are discussed in Chapter 2. A key aspect is the extent to which the leaching of strong acid anions, with associated transfer of soil acidity to drainage waters, is enhanced by afforestation. The mechanisms by which this is most likely to occur are disruption of the nitrogen cycle with associated leaching of NO_3^- (Bormann and Likens, 1979; Vitousek *et al.*, 1979; Martin *et al.*, 1984) and enhanced interception and evaporative concentration of atmospheric salts, processes which are particularly important in maritime regions (Heath *et al.*, 1992; Pedersen and Bille-Hansen, 1995).

The data presented in the previous chapter demonstrate that afforestation has caused considerable changes in the composition of the soil solution and in particular has led to a reduction in solution pH, increased soluble Al concentration and in many cases an increased concentration of strong acid anions. This suggests that the large-scale introduction of pine plantations can *potentially* lead to a significant modification of the quality of associated surface waters. However, the soil solution data pertain only to the upper 20 cm of the soil profile and, therefore, provide an indication of the maximum possible impact of afforestation on drainage water composition. The extent to which surface waters are influenced by these changes taking place in the topsoil will be highly variable and will depend on numerous factors. The most important of these are likely to be:

1) the volume and flow path of drainage waters which, on the one hand, will determine the degree of dilution and on the other, will determine the extent to which percolating waters are able to interact with less acidic subsoils, saprolite and bedrock; and

2) the chemical and mineralogical nature of the subsoils and soil parent materials, which will determine their weathering potential and ability to neutralise the acidity of percolating solutions, as well as their potential to adsorb dissolved organic matter, SO_4^{2-} and other solutes.

A comprehensive evaluation of surface water quality and the extent to which it is influenced by afforestation would require long-term monitoring of carefully selected catchments and would need to take into account short-term fluctuations in the composition of stream water associated with variations in discharge. Such a study is beyond the scope of this investigation which focuses on the effect of afforestation on soil solution composition. However, in order to obtain some indication of whether the observed changes in soil solution composition are reflected in the quality of associated surface waters, spot samples of streams draining forested and nearby undisturbed catchments were taken in all four of the regions investigated. In this chapter, the analytical data pertaining to these samples are presented. Regional variations in stream water composition and the impact of afforestation thereon are discussed in relation to the trends and relationships observed for associated soil solutions.

7.2. MATERIALS AND METHODS

A total of 69 water samples were taken from streams draining comparable afforested and undisturbed grassland or fynbos catchments in all four of the regions under investigation. In some cases, comparative samples were taken from the same river upstream and downstream of afforested areas. The position of these samples in relation to forest cover, selected rivers and the position of soil sampling sites is illustrated in Appendix A. Some characteristics of the streams are provided in Table 7.1.a and b. The rivers are all relatively small (maximum width ~ 4 m), of a low order (mostly 1st to 3rd order) and drain small mountain catchments. The catchments are underlain by a range of different rock types including pure quartzites (eastern escarpment and Cape), sandstones (in some cases arkosic; midlands and possibly southern Cape), siltstones (eastern escarpment), shale (eastern escarpment and midlands), dolomite (eastern escarpment) and dolerite (midlands). The original samples were taken between May and August 1995 and follow-up sampling was undertaken in 1996 and 1997 in the eastern escarpment and midlands regions respectively (Table 7.1.a and b). The follow-up sampling was carried out at the same time of year that original samples were taken (i.e May

Table 7.1.a: *Site details for stream samples from the eastern escarpment, southern Cape and western Cape regions. Pos. - sample position. Type: f = forest; v = grassland (eastern escarpment) or fynbos (Cape). Size - qualitative indication of the width of the streams which ranges from < 50 cm to ~ 4 m: vs = very small; s = small; sm = small to medium; m = medium; ml = medium to large; l = large.*

Name	Date	Riv. No.	Pos.	Type	Size	Order	Catchment geology
Eastern escarpment							
Lisbon-F1	06/05/95	EER1	1	f	ml	3	quartzite (siltstone)
Lisbon-F1	22/05/96	EER1	1	f	l	3	quartzite (siltstone)
Lisbon-V1	06/05/95	EER1	2	v	m	1	quartzite (siltstone)
Heddle-V1	06/05/95	EER2	1	v	ml	3	quartzite (siltstone)
Heddle-V1	22/05/96	EER2	1	v	l	3	quartzite (siltstone)
Heddle-V2	06/05/95	EER2	2	v	m	2	quartzite (siltstone)
Heddle-V2	22/05/96	EER2	2	v	m	2	quartzite (siltstone)
Heddle-V3	06/05/95	EER2	3	v	m	2	quartzite (siltstone)
Blyde-F1	06/05/95	EER3	1	f	s	3	quartzite (siltstone)
Blyde-F1	24/05/96	EER3	1	f	s	3	quartzite (siltstone)
Mac-Mac-V1	12/05/95	EER4	1	v	sm	1	quartzite (siltstone)
Mac-Mac-V1	23/05/96	EER4	1	v	s	1	quartzite (siltstone)
Klipkraal-F1	12/05/95	EER5	1	f	m	2	quartzite (siltstone)
Klipkraal-F1	23/05/96	EER5	1	f	m	2	quartzite (siltstone)
Blyde-F2	24/05/96	EER6	1	f	m	1	quartzite (siltstone)
Klipkraal-F2	24/05/96	EER7	1	f	s	1	quartzite (siltstone)
Klipkraal-F3	24/05/96	EER8	1	f	s	1	dolomite (shale)
Sabie-F1	24/05/96	EER9	1	f	l	4	dolomite (shale)
Sabie-F2	24/05/96	EER9	2	f	l	4	dolomite (shale)
Sabie-F3	25/05/96	EER9	3	f	l	4	dolomite (shale)
Lone-Creek F1	24/05/96	EER10	1	f	l	4	dolomite (shale)
Southern Cape							
Bergplaas-V1	25/07/95	SCR1	1	v	s	2	quartzite/sandstone
Bergplaas-F1	25/07/95	SCR2	1	f	s	2	quartzite/sandstone
Bergplaas-V2	25/07/95	SCR3	1	v	s	2	quartzite/sandstone
Bergplaas-F2	25/07/95	SCR4	1	f	vs	2	quartzite/sandstone
Diep-V1	26/07/95	SCR5	1	v	ml	3	quartzite/sandstone
Bergplaas-F3	26/07/95	SCR6	1	f	ml	3	quartzite/sandstone
Diep-F1	26/07/95	SCR7	1	f	l	4	quartzite/sandstone
Touw-V1	26/07/95	SCR8	1	v	m	4	quartzite/sandstone
Karatara-V1	27/07/95	SCR9	1	v	ml	3	quartzite/sandstone
Plaat-F1	27/07/95	SCR10	1	f	ml	3	quartzite/sandstone
Western Cape							
Lebanon-F1	16/08/95	WCR1	1	f	sm	1	quartzite
Lebanon-F2	16/08/95	WCR2	1	f	ml	2	quartzite
Lebanon-V1	16/08/95	WCR3	1	v	m	3	quartzite
Highlands-V1	16/08/95	WCR4	1	v	s	2	quartzite
Highlands-F1	16/08/95	WCR5	1	f	m	3	quartzite
Highlands-V2	17/08/95	WCR6	1	v	vs	1	quartzite
Highlands-F2	17/08/95	WCR7	1	f	vs	1	quartzite
Highlands-V3	17/08/95	WCR8	1	v	ml	1	quartzite
Highlands-F3	17/08/95	WCR9	1	f	ml	2	quartzite

Table 7.1.b: *Site details for stream samples from the midlands region. Pos. - sample position. Type: f = forest; v = grassland. Size - qualitative indication of the width of the streams which ranges from < 50 cm to ~ 4 m: vs = very small; s = small; sm = small to medium; m = medium; ml = medium to large; l = large.*

Name	Date	Riv. No.	Pos	Type	Size	Order	Catchment geology
Dargle-F1	21/06/95	MIR1	1	f	vs	1	dolerite
Dargle-V1	21/06/95	MIR2	1	v	vs	1	dolerite
Pinewoods-F1	22/06/95	MIR3	1	f	m	2	dolerite/shale
Pinewoods-F2	22/06/95	MIR4	1	f	m	1	dolerite/shale
Pinewoods-V2	26/06/95	MIR4	2	v	sm	1	dolerite/shale
Pinewoods-V1	22/06/95	MIR5	1	v	ml	3	dolerite/shale
Mossbank-V1	23/06/95	MIR6	1	v	s	1	shale
Mossbank-V2	23/06/95	MIR7	1	v	s	1	dolerite/shale
Mossbank-F1	23/06/95	MIR8	1	f	m	2	sandstone/shale
Mossbank-F2	23/06/95	MIR9	1	f	m	1	sandstone/shale
Mossbank-V3	23/06/95	MIR10	1	v	m	2	sandstone/shale
Mossbank-V4	23/06/95	MIR11	1	v	m	2	sandstone/shale
Mossbank-F3	23/06/95	MIR12	1	f	vs	2	dolerite
Mossbank-F4	23/06/95	MIR13	1	f	vs	1	dolerite
Mossbank-F5	23/06/95	MIR14	1	f	vs	1	dolerite/shale
Clairmont-V1	24/06/95	MIR15	1	v	s	1	sandstone/shale
Clairmont-V1	20/06/97	MIR15	1	v	s	1	sandstone/shale
Clairmont-F1	24/06/95	MIR16	1	f	m	2	sandstone/shale
Clairmont-F2	24/06/95	MIR17	1	f	m	2	sandstone/shale
Clairmont-F3	24/06/95	MIR18	1	f	ml	3	sandstone/shale/dol.
Clairmont-F3	20/06/97	MIR18	1	f	ml	3	sandstone/shale/dol.
Clairmont-V2	24/06/95	MIR19	1	v	l	3	sandstone/shale
Clairmont-V2	20/07/97	MIR19	1	v	l	3	sandstone/shale
Clairmont-V3	20/07/97	MIR25	1	v	s	1	sandstone/shale
Cedara-F1	26/06/95	MIR20	1	f	s	2	shale
Vaalhoek-V1	26/06/95	MIR21	1	v	vs	1	dolerite (shale)
Vaalhoek-F1	26/06/95	MIR22	1	f	ml	3	dolerite/shale
Vaalhoek-F2	26/06/95	MIR23	1	v	s	2	dolerite/shale
Adamshurst-V1	27/06/95	MIR24	1	v	s	1	dolerite/shale

in the eastern escarpment and June in the midlands). Streams in the eastern escarpment and western Cape were sampled during the wet season immediately after (within 2 to 4 days of) a period of high rainfall. Sampling of the southern Cape streams was carried out during the wet season but did not correspond with a period of particularly high rainfall. The midlands streams were sampled in the middle of the dry season.

Despite careful selection, it was not possible to ensure unequivocally that the forest and grassland/fynbos catchments were identical in all respects excluding their vegetation cover. Nonetheless, it is felt that the catchments are sufficiently similar, particularly with respect to size, parent materials and climate, to be able to make a meaningful comparison of sampling and analytical results. Although many of the soil sampling sites lie within the catchment areas of streams that were sampled, the soil solutions cannot be regarded as representative of the entire catchment and, therefore, direct comparison with stream water composition is not possible. Nonetheless, comparison of stream and soil solution data on a *regional* basis provides a good indication of the extent to which observed trends in the composition of soil solutions are reflected in associated surface waters (for further discussion see section 7.3 - page 146).

The stream water samples were taken in plastic bottles which were soaked in ultra-deionised water (prepared using a Millipore Milli-RO4 purification system) for more than 48 hours and thoroughly rinsed with stream water prior to sampling. The bottles were completely filled to minimise interaction with air following sampling. The pH of stream waters was determined in the field using a CIBA-CORNING M90 field pH meter. This was found to be unreliable, however, presumably due to the highly dilute nature of the samples. Thus, pH values determined in the laboratory (within one week of sampling), using a Metrohm 691 pH meter and combination electrode, are reported here (Table 7.2.a). In view of the poorly-buffered nature of the stream waters and the likely short-term (daily and weekly) fluctuations in pH, the quantitative significance of these determinations is questionable. Comparison of pH values obtained for similar forest and grassland or fynbos streams, however, should provide an indication of whether gross pH differences occur. All other analytical work was carried out in the laboratory on filtered (0.45 µm millipore membrane filters) samples. This included the determination of electrical conductivity (EC), alkalinity (HCO_3^- concentration), the concentration of major anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}),

monomeric Al and monomeric Si. Concentrations of major ions were determined by ion chromatography (Appendix B) and those of Al and Si were determined colorimetrically using the methods described in section 6.2.2. Bicarbonate concentrations were determined by Gran titration (Gran, 1952; Appendix B) using a Radiometer ABU80 autoburette and TTT85 titrator (detection limit ~ 20 $\mu mol\ L^{-1}$).

Speciation calculations were undertaken for all stream waters with detectable concentrations of Al. This was carried out using the MINTEQA2 computer programme incorporating an empirical model to account for dissolved organic matter. A detailed description of the application of MINTEQA2 is provided in section 6.2.4 and 6.3.3.3.

A biological assessment of water quality was undertaken at five of the streams sampled in 1995. The work was carried out by H. Dallas from the Freshwater Research Institute at the University of Cape Town (Department of Zoology). The main aim of this was to determine the extent to which observed changes in water composition influence the aquatic ecosystems in these streams. The assessment was carried out using the SASS system developed by the Department of Water Affairs (Moore & McMillan, 1993). The system involves identifying families of invertebrates present in a net sample taken from the stream. Families are assigned a score based on their sensitivity to changes in water quality. Water quality evaluation is based on the sum of the family scores and on the average score per taxon (Appendix F).

7.3. RESULTS AND DISCUSSION

Charge balance calculations indicated that in many cases there was a large difference (> 10%) between the sum of anionic and cationic charge, suggesting considerable analytical error. This was expected to some extent due to the very low solute concentrations in many of the samples and for the purposes of this study, which primarily involves a qualitative evaluation of regional compositional variations and a broad comparison of the composition of forest and virgin streams, charge differences of less than 30 % were deemed acceptable. Analyses which satisfy this constraint are presented in Table 7.2 and only these data were used for interpretations involving the major ions.

Table 7.2.a: *Chemical data for stream samples from all regions. EC - electrical conductivity ($mS\,m^{-1}$). DOC - dissolved organic carbon ($mg\,L^{-1}$). Al - total monomeric Al ($mg\,L^{-1}$). Si - total monomeric Si ($mg\,L^{-1}$). bld - below limit of detection. Blank values - not determined.*

Name	pH	EC	DOC	Al	Si	Name	pH	EC	DOC	Al	Si
Eastern escarpment						*Southern Cape*					
Lisbon-F1	6.67	1.40				Bergplaas-F1	6.25	14.0	6.86	bld	0.032
Lisbon-F1	6.28	1.26	5.62	bld	0.021	Bergplaas-V2	6.00	15.2	6.24	bld	bld
Lisbon-V1	6.66	1.19				Diep-V1	6.15	12.1	10.84	bld	0.033
Heddle-V1	6.78	1.48				Bergplaas-F3	6.19	15.6	8.4	bld	0.033
Heddle-V1	6.85	1.32	3.29	bld	0.023	Touw-V1	5.42	15.1	9.6	0.080	0.031
Heddle-V2	6.42	0.75	9.42		0.014	Plaat-F1	4.45	9.94		0.245	0.029
Blyde-F1	5.88	1.80		bld	0.025	*Western Cape*					
Blyde-F1	5.46	1.92	3.53		0.022	Lebanon-F1	3.20	39.1	116.97	0.632	0.034
Mac-Mac-V1	6.47	1.08	1.45			Lebanon-F2	3.46	28.0	58.78	1.323	0.029
Mac-Mac-V1	6.59	1.04	2.2		0.020	Lebanon-V1	4.30	9.30	20.36	0.400	0.011
Klipkraal-F1	4.95	2.03	1.37			Highlands-V1	4.75	10.3	15.51	0.275	0.018
Klipkraal-F1	4.97	1.86	4.09	0.228	0.023	Highlands-F1	5.42	18.1	7.88	bld	0.022
Blyde-F2	4.88	1.97	4.15	0.317	0.020	Highlands-V2	6.02	10.4	6.28	bld	0.011
Sabie-F1	7.25	2.97	6.17	bld	0.051	Highlands-F2	5.57	10.9	10.37	bld	0.007
Sabie-F2	7.27	2.59	6.79	bld	0.049	Highlands-V3	4.73	9.30	14.97	0.375	0.015
Sabie-F3	7.17	2.42	8.57	bld	0.054	Highlands-F3	3.78	19.20	39.9	1.007	0.020
Lone-Creek F1	7.08	2.76	5.73	bld	0.045						
Midlands											
Dargle-F1	7.45	4.15		bld	0.066						
Dargle-V1	7.16	4.30		bld	0.051						
Pinewoods-V1	6.83	2.47	11.69	bld	0.013						
Pinewoods-V2	6.99	3.28	8.98	bld	0.018						
Pinewoods-V3	6.88	2.84	11.88	bld	bld						
Mossbank-V1	7.12	4.54	4.19	bld	0.106						
Mossbank-V2	7.29	5.16	6.69	bld							
Mossbank-F1	7.07	3.53	10.6	bld	0.058						
Mossbank-V3	7.27	3.49	7.03	bld	0.061						
Mossbank-F4	6.71	3.71	7.17	bld	0.041						
Mossbank-F5	6.52	3.16	10	0.084	0.008						
Clairmont-V1	6.94	3.82	9.75	bld	0.054						
Clairmont-F2	7.56	3.26	8.76	bld	0.064						
Cedara-F1	7.81	12.1		bld	0.090						
Vaalhoek-F2	7.52	9.83		bld	0.078						
Adamshurst-V	7.84	18.8		bld							

Table 7.2.b: *Major anion and cation data ($\mu mol_c L^{-1}$) for stream samples from all regions. Samples were excluded if the charge balance (CB% - percentage difference between total anions and cations) exceeded 30 %. bld - below limit of detection. Blank values - not determined*

Name	HCO_3^-	Cl^-	NO_3^-	SO_4^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	CB%
Eastern escarpment										
Lisbon-F1	20	45	18	6	54	bld	9	38	17	28
Lisbon-F1	43	49	20	5	53	4	13	34	25	9
Lisbon-V1	33	44	5	8	50	bld	3	38	18	20
Heddle-V1	83	37	7	10	39	bld	9	61	44	12
Heddle-V1	93	48	bld	8	41	2	18	51	34	-3
Heddle-V2	40	45	bld	3	35	2	8	17	13	-16
Blyde-F1	bld	58	35	16	58	bld	11	45	29	26
Blyde-F1	33	81	68	2	72	5	7	44	33	-14
Mac-Mac-V1	50	42	3	6	44	bld	9	31	22	5
Mac-Mac-V1	50	54	2	7	41	3	14	27	24	-3
Klipkraal-F1	bld	67	49	6	72	bld	12	37	18	14
Klipkraal-F1	bld	67	53	6	54	4	7	42	36	13
Blyde-F2	bld	61	65	6	66	13	6	19	13	-13
Sabie-F1	250	49	23	20	65	3	8	149	126	3
Sabie-F2	215	36	48	12	54	bld	9	96	77	-27
Sabie-F3	210	31	9	11	56	6	5	110	93	3
Lone-Creek F1	220	43	23	15	49	6	5	129	109	-2
Midlands										
Dargle-F1	670	36	11	7	155	bld	9	246	137	-28
Dargle-V1	550	64	24	25	179	bld	8	150	156	-30
Pinewoods-F2	158	92	22	16	85	bld	8	104	72	-7
Pinewoods-V2	297	56	6	10	77	bld	8	133	98	-15
Mossbank-V1	604	63	17	18						
Mossbank-V2	934	16	5	11	181	bld	17	284	249	-28
Mossbank-F1	380	61	9	30	114	bld	8	133	98	-30
Mossbank-V3	413	36	10	15	135	bld	8	121	168	-9
Mossbank-F4	257	80	26	87	120	bld	7	155	121	-11
Mossbank-F5	257	62	47	30	162	3	14	69	92	-13
Clairmont-V1	485	36	bld	28	176	bld	9	126	104	-28
Clairmont-V1		37	bld	15						
Clairmont-F2	505	29	6	13	101	bld	7	160	167	-24
Clairmont-F3		58	40	61						
Clairmont-V2		49	4	41						
Clairmont-V3		50	9	15						
Cedara-F1	1820	170	12	50	523	bld	20	698	433	-20
Vaalhoek-F2	1452	138	16	74	440	bld	37	467	459	-18
Adamshurst-V1	3040	166	7	84	674	bld	37	1380	962	-8
Southern Cape										
Bergplaas-F1	80	1142	bld	50	1021	bld	3	258	68	6
Bergplaas-V2	80	1038	bld	56	1189	bld	2	336	48	29
Diep-V1	75	851	bld	58	873	bld	6	260	63	20
Bergplaas-F3	90	1270	bld	71	1276	bld	1	365	40	16
Touw-V1	35	1171	bld	90	1172	bld	6	357	50	20
Plaat-F1	bld	668	14	74	605	bld	5	201	36	11
Western Cape										
Lebanon-F1	bld	1449	bld	244	1540	bld	2	438	53	18
Lebanon-F2	bld	1281	bld	165	1315	bld	4	417	44	21
Lebanon-V1	bld	590	3	78	528	bld	9	121	27	2
Highlands-V1	40				684	bld	17	194	102	
Highlands-F1	50	1217	13	139	1433	bld	20	322	50	25
Highlands-V2	100	657	bld	94						
Highlands-F2	80	697	17	143	710	bld	28	207	56	7
Highlands-V3	bld	679	bld	68	656	bld	10	194	71	26
Highlands-F3	bld	1119	bld	90	1052	bld	10	292	49	22

In view of the expected short term variability in stream water composition associated with variations in discharge, as well as with diurnal and seasonal effects, the information obtainable from single "spot" samples is limited. However, analysis of duplicate stream water samples taken one and two years apart in the eastern escarpment and midlands regions, respectively, suggests that, with the possible exception of DOC and HCO_3^- concentration , data obtained for individual samples are surprisingly reproducible, despite the very dilute nature of most of the waters (Table 7.3). Although compositional differences are observed, in most cases these are low compared to differences between streams and relative concentrations of the different ions are generally very similar. These similarities reflect the fact that the samples were taken at the same time of year and under roughly the same conditions of stream flow. Nonetheless, they do suggest that the data obtained for individual samples is representative of stream water compositions which prevail at the time of year that the samples were taken and that this does not appear to vary dramatically from year to year. This implies that comparison of stream water composition within regions and especially the comparison of data for forest and virgin streams is meaningful, since any major differences between streams are unlikely to be obscured by short term compositional variations. In comparing stream water data *between* regions, allowance has to be made for variations in the hydrological conditions prevailing at the time of sampling and quantitative comparison of analytical results is not possible. Nonetheless, by interpreting the data in conjunction with that from independent regional studies (i.e. Day and King, 1995), useful interpretations can be made regarding regional variations and the causes thereof.

Table 7.3.a: *Analytical results for duplicate stream samples. The eastern escarpment samples were taken in May 1995 (1) and May 1996 (2). The midlands samples were taken in June 1995 (1) and June 1997 (2). EC - electrical conductivity in* $mS\,m^{-1}$*. DOC - dissolved organic carbon in* $mg\,L^{-1}$*.* HCO_3^- *concentrations are in* $mmol_c\,L^{-1}$*.*

River	pH		EC		DOC		HCO_3^-	
	1	2	1	2	1	2	1	2
Lisbon-F1	6.67	6.28	1.40	1.26			20	43
Lisbon-V1	6.66	6.85	1.19	1.32			33	93
Heddle-V2	6.51	6.42	0.84	0.75			33	40
Blyde-F1	5.88	5.46	1.80	1.92			bld	33
Mac-Mac-V1	6.47	6.59	1.08	1.04	1.5	2.2	50	50
Klipkraal-F1	4.95	4.97	2.03	1.86	1.4	4.1	bld	bld
Clairmont-V1	6.94	7.34	3.82	3.90				
Clairmont-F3	7.38	7.39	4.51	3.70				
Clairmont-V2	7.36	7.41	3.15	5.2				

Table 7.3.b: Major inorganic ion concentrations ($\mu mol_c L^{-1}$) in duplicate stream samples. The eastern escarpment samples (EE) were taken in May 1995 (1) and May 1996 (2). The midlands samples (MI) were taken in June 1995 (1) and June 1997 (2).

Name	Region	Cl^-		NO_3^-		SO_4^{2-}		Na^+		Mg^{2+}		Ca^{2+}	
		1	2	1	2	1	2	1	2	1	2	1	2
Lisbon-F1	EE	45	49	18	20	6	5	54	53	38	34	17	25
Lisbon-V1	EE	44	48	5	0	8	8	50	41	38	51	18	34
Heddle-V2	EE	35	45	0	0	2	3	79	35	9	17	10	13
Blyde-F1	EE	58	81	35	68	16	2	58	72	45	44	29	33
Mac-Mac-V1	EE	42	54	3	2	6	7	44	41	31	27	22	24
Klipkraal-F1	EE	67	67	49	53	6	6	72	54	37	42	18	36
Clairmont-V1	MI	36	37	0	0	28	15						
Clairmont-F3	MI	46	58	45	40	60	61						
Clairmont-V2	MI	40	50	0	4	8	41						

Despite the above-described considerations, the results demonstrate consistent regional variations in stream-water composition which are believed to be related to differences in parent materials, flow rates and proximity to the ocean. In addition, the data suggest that under certain conditions, afforestation does have a significant effect on stream-water quality. These differences will be examined in more detail in the ensuing sections.

7.3.1. Regional variation in stream water composition

Total solute concentrations are in all cases very low. This is reflected in electrical conductivity (EC) values which generally do not exceed 15 mS m^{-1} (Table 7.2.a) and which are typical of rivers draining mountainous regions in South Africa (Day and King, 1995). Solute concentrations are particularly low in the eastern escarpment, where streams draining quartzite-dominated catchment areas have EC values of less than 2 mS m^{-1} and even in catchments underlain by dolomite and shale, EC values do not exceed 3 mS m^{-1}. The eastern escarpment samples were taken during a period of high discharge following recent heavy rains. Thus, in the case of the dolomite and shale dominated catchments, low solute concentrations probably stem from the dilution of base flow by rain water (due to increased water volume and a change in hydrological pathways). The highest concentrations of solutes occur in stream waters of the southern and western Cape regions. All of the streams in these regions have EC values in excess of 9 mS m^{-1} and high conductivity values ranging up to 64 mS m^{-1} were recorded for certain streams draining afforested catchments (Table 7.2.a). These relatively high solute concentrations reflect the strong influence of sea salt deposition in the maritime Cape regions. The midlands streams have intermediate EC values which generally

range from ~ 3 to ~ 10 mS m^{-1}. All of these streams are in excess of 100 km from the ocean and, therefore, are likely to be considerably less strongly influenced by marine salt inputs than the Cape streams. The streams were sampled towards the end of the dry season, however, and flow rates were generally very low, reflecting base flow conditions. Thus, waters draining into streams are likely to have undergone significant interaction with the readily weatherable and base-rich saprolite and/or bedrock (dolerite, shale and arkosic sandstone) which underlies all of the catchments investigated.

The above-described processes are reflected in the relative concentrations of different inorganic anions (Figure 7.1). The anion suite in the Cape streams is almost entirely dominated by Cl^-, whereas HCO_3^- is the dominant anion in the streams of the midlands region reflecting the alkalinity generated by interaction with base-rich materials.

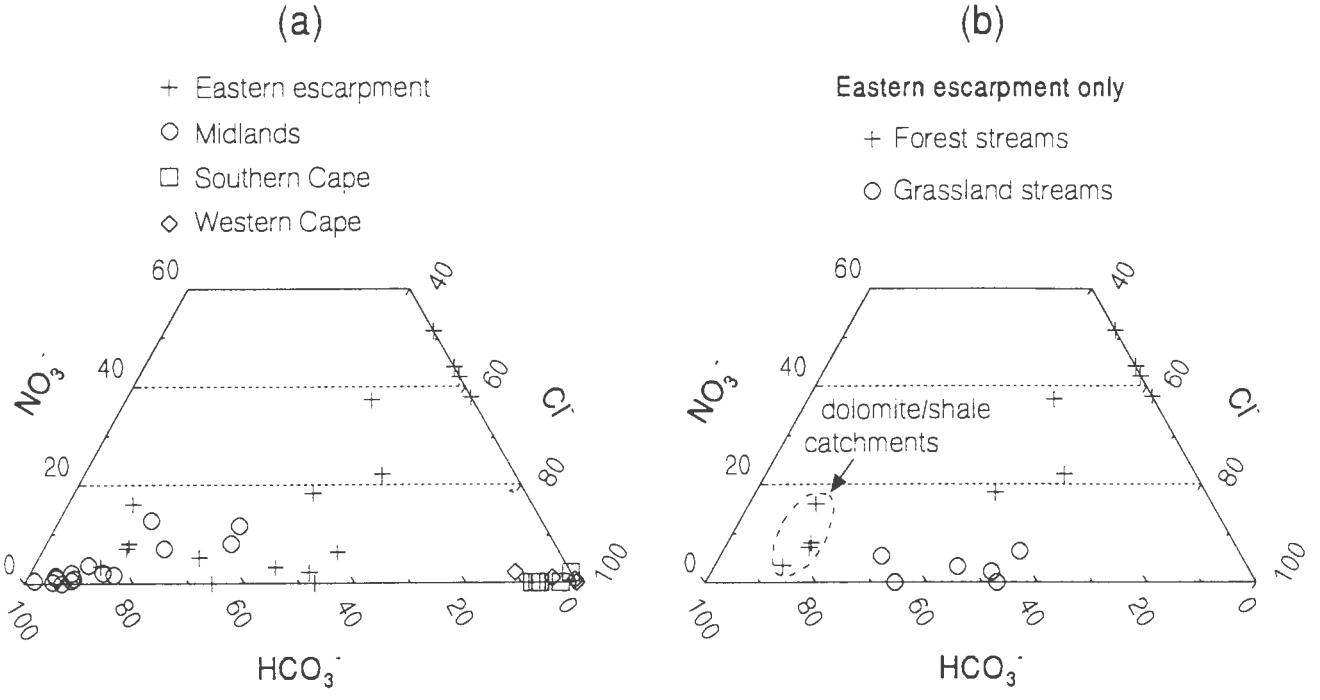

Figure 7.1: *Diagrams illustrating the relative concentrations of Cl^-, NO_3^- and HCO_3^- in stream waters. a) All regions. b) Illustrates differences between forest and grassland streams in the eastern escarpment only. Eastern escarpments streams draining catchments dominated by dolomite (± shale) are highlighted.*

The relative concentration of different anions in streams of the eastern escarpment is more variable and is dependent both on the nature of the bedrock and on the vegetation type (Figure 7.1.b). The relative concentration of HCO_3^- is high in the forest streams which drain catchments underlain by dolomite and shale. In grassland streams which drain catchments underlain by quartzite, HCO_3^- constitutes approximately 40 to 65 % of the inorganic anion

suite, but in streams which drain forested quartzitic catchments, alkalinity levels are considerably reduced and NO_3^- concentrations are enhanced roughly in proportion with the decline in the concentration of HCO_3^-. This suggests that NO_3^-, in the form of nitric acid, is being leached from forest soils resulting in reduced alkalinity and enhanced NO_3^- concentrations in poorly-buffered stream waters.

The concentration of SO_4^{2-} is lowest for streams of the eastern escarpment region ($\leq$ 20 $\mu mol_c\ L^{-1}$) and highest for certain streams of the western Cape (up to 244 $\mu mol_c\ L^{-1}$) (Figure 7.2). Stream waters from all four regions have SO_4^{2-}/Cl^- ratios greater than that of sea water (0.1). The high mobility of Cl^- relative to SO_4^{2-} should result in stream-water SO_4^{2-}/Cl^- ratios which are lower than those of atmospheric inputs. Thus SO_4^{2-}/Cl^- ratios greater than 0.1 may suggest considerable input of non-marine SO_4^{2-}. Despite low absolute SO_4^{2-} concentrations, the SO_4^{2-}/Cl^- ratio is particularly high in streams of the eastern escarpment (Figure 7.2) and is consistent with the very high SO_4^{2-}/Cl ratios observed for rainfall in this region (Table 3.2). In the streams of the southern and western Cape, elevated SO_4^{2-} concentrations are associated with high Cl^- levels and reflect the strong marine influence in these regions. However, some western Cape streams, particularly those draining afforested catchments, show SO_4^{2-}/Cl^- ratios which are considerably higher than that of sea water. As discussed in the previous chapter, an anthropogenic source of SO_4^{2-} is considered unlikely in this region and it is possible that the elevated SO_4^{2-}/Cl^- ratios in both rainfall and stream waters are the result of biogenic emission of S-containing gases from the ocean.

Variations in the concentration of Ca^{2+}, Mg^{2-} and Na^+ (Figure 7.3) are, to a large extent, consistent with the processes invoked to account for the above-described anion relationships. In streams of the southern and western Cape, the cation suite is dominated by Na^+ and the ratio of $Na^+/(Ca^{2+}+Mg^{2+})$ is remarkably constant throughout the Cape region ($Na^+/(Ca^{2+}+Mg^{2+}) = 3.03$; $R^2 = 0.98$). This, as well as the high concentrations of Mg^{2+} relative to Ca^{2+} (Table 7.2.b), reflects the strong marine influence on the composition of these stream waters. In the eastern seaboard regions, Ca^{2+} and Mg^{2+} are generally the dominant cations in stream waters and $Na^+/(Ca^{2+}+Mg^{2+})$ ratios are generally between 1 and 0.5 in the eastern escarpment and between 0.5 and 0.2 in the midlands. As for the Cape streams, there appears to be a broadly consistent relationship between Na^+ and $Ca^{2+} + Mg^{2+}$ within each of the eastern seaboard regions, suggesting that similar processes control the concentrations of these ions in eastern escarpment and midlands streams, respectively.

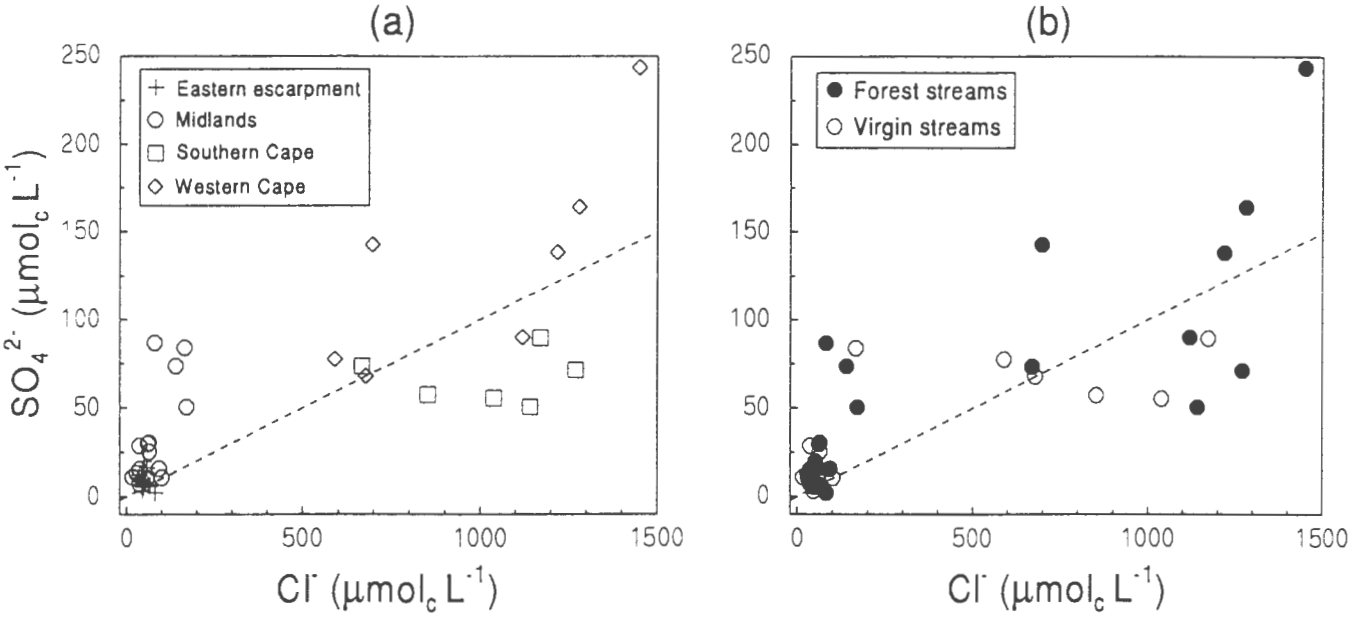

Figure 7.2: The relationship between Cl^- and SO_4^{2-} in stream waters classified according to region (a) and according to the presence or absence of forest plantations in their catchments (b). The dashed line in each plot represents the molar SO_4^{2-}/Cl^- ratio of sea water (~ 1/10).

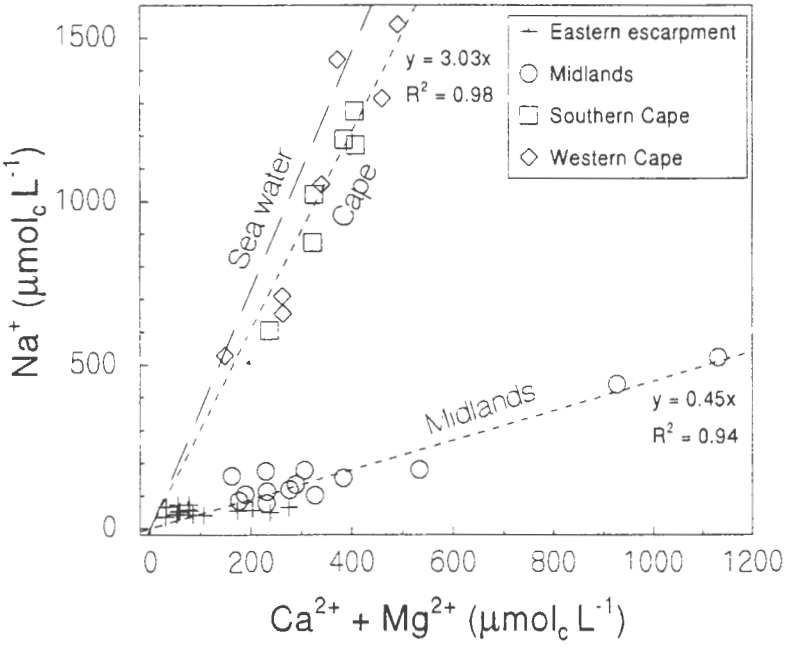

Figure 7.3: The relationship between $Ca^{2+}+Mg^{2+}$ and Na^+ in stream waters classified according to region. Regression lines are shown for the midlands and cape (southern and western Cape) regions, respectively (dotted lines). The $Na^+/(Ca^{2+} + Mg^{2+})$ ratio of sea water is also represented (dashed line). Although $Na^+/(Ca^{2+} + Mg^{2+})$ ratios are generally low (< 1) in the eastern escarpment stream waters, there is no consistent relationship between Na^+ and $Ca^{2+} + Mg^{2+}$ and, therefore, no regression line is shown.

7.3.2. Classification of stream waters on the basis of the relative concentrations of major ions

The regional variations described above correlate well with geographical patterns of major ion dominance observed by Day and King (1995) for South African rivers. Most of the streams can be classified into one of the four categories identified by these authors (Table 7.4; Figure 7.4). The NaCl-dominated streams of the southern and western Cape regions fall into category 4.1 indicating that they are precipitation-dominated with minimal supply of solutes from bedrock or associated saprolite. It is interesting to note that all of the Cape streams have total solute concentrations which are higher than would be expected for "typical" precipitation-dominated waters (Gibbs, 1970; Figure 7.5). This phenomenon has been noted by Day and King (1995) who ascribe it to evaporative concentration taking place primarily during the hot, and mostly dry, summers which prevail in most of the region.

Table 7.4: *Compositional characteristics and dominant geographical and lithological associations for the categories and subcategories of ionic dominance established by Day and King (1995) for South African rivers. The percentage values that define most of the categories and some of the subcategories reflect the concentration of the listed cations or anions relative to the total concentration of cations or anions, respectively .*

Category	Characteristic features	Subcategories	Association
1	$Ca^{2+}+Mg^{2+}$ > 75% HCO_3^- > 66%	1. $Mg^{2+}:Ca^{2+}$ = 0.86-1.14 2. $Mg^{2+}:Ca^{2+}$ < 0.85 3. $Mg^{2+}:Ca^{2+}$ > 1.15	Primarily associated with basaltic and carbonate lithologies in the central regions of S.A.
2	$Ca^{2+}+Mg^{2+}$ = 60-75% HCO_3^- > 66%	1. $Mg^{2+}:Ca^{2+}$ = 0.86-1.14 2. $Mg^{2+}:Ca^{2+}$ < 0.85 3. $Mg^{2+}:Ca^{2+}$ > 1.15	Encircles category 1, associated with sediments (shale and sandstone) and intrusive igneous rocks
3.1 and 3.2	Na^+ ≥ 25% of HCO_3^- $Ca^{2+}+Mg^{2+}$ = 25-40% HCO_3^- > Cl^- Na^+ = 30-70%	1. SO_4^{2-} = 16-35% 2. SO_4^{2-} < 15%	Widespread distribution, no strong lithological associations. Category 3.1 mostly confined to the west of S.A., 3.2 and 3.3 occur mostly in a belt along the eastern seaboard
3.3	Ca^{2+}, Mg^{2+}, Na^+: All = 25-40% HCO_3^- > Cl^- > SO_4^{2-}		
4.	Na^+ and Cl^- dominated	1. Na^+, Cl^- > 55% Others all < 30% 2. Na^+, Cl^- > 45-54% Others all < 30% 3. Na^+ > Ca^{2+} or Mg^{2+} Cl^- > HCO_3^- or SO_4^{2-}	Primarily confined to coastal regions but also prevalent in the interior of the western and southern Cape

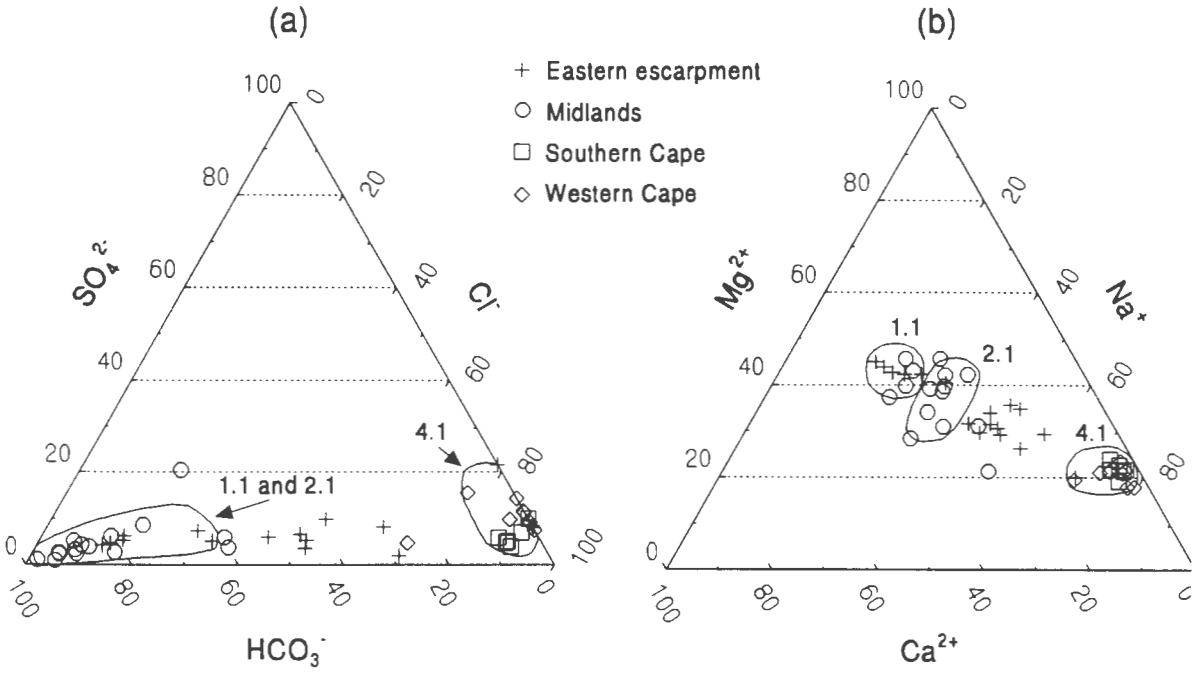

Figure 7.4: *Triangular plots illustrating the relative concentrations of the anions Cl^-, HCO_3^- and SO_4^{2-} (a) and the cations Na^+, Ca^{2+} and Mg^{2+} (b) in stream waters classified according to region. Compositional fields corresponding to the categories of Day and King (1995; Table 7.4) are shown.*

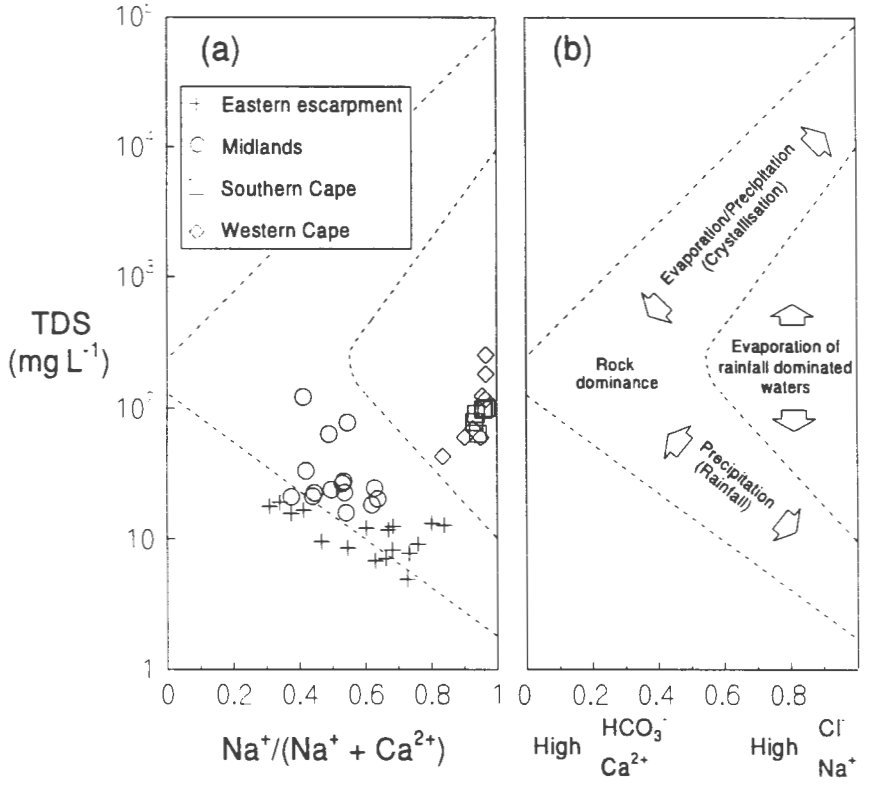

Figure 7.5: *The relationship between $Na^+/Na^+ + Ca^{2+}$ and the concentration of total dissolved solids (TDS) in stream waters classified according to region (a), and processes controlling ionic proportions in natural waters (b; modified from Gibbs, 1970). TDS was calculated on the basis of the empirical relationship: TDS = EC ($mS\,m^{-1}$) x 6.6, which was derived for South African waters by the Department of Water Affairs and Forestry.*

In contrast to the Cape streams, relatively high concentrations of HCO_3^- (> ~ 66 %), Ca^{2+} and Mg^{2+} in streams of the Midlands region and those draining dolomite and shale in the eastern escarpment (Figure 7.4), suggest that these waters are "rock-dominated". Alkalinity, Ca^{2+} and Mg^{2+} are supplied primarily by weathering of underlying bedrock and the degree of concentration depends on the extent to which these ions are diluted by relatively pure rainwater. Streams in which Ca^{2+} and Mg^{2+} jointly make up more than 75 % of the total cation suite (category 1, see Table 7.4) are typically associated with basaltic and carbonate lithologies (Day and King, 1995). In the case of the midlands streams these compositions probably reflect the dominant influence of dolerite (an intrusive equivalent of basalt), whereas in the eastern escarpment the Ca^{2+} and Mg^{2+} is likely to be derived primarily from dissolution of dolomitic (CaMg-carbonate) bedrock. Slightly lower relative concentrations of Ca^{2+} and Mg^{2+} (Ca^{2+} + Mg^{2+} between 60 and 65 % of the cation suite; i.e. category 2) may reflect interaction with shales which are prevalent in portions of the eastern escarpment region and in many of the midlands catchments that were sampled.

As one would intuitively expect, the relative concentrations of major ions are most variable in the very pure, unbuffered waters draining quartzite-dominated catchments of the eastern escarpment (Figure 7.1 and 7.4). Most of the grassland streams have moderately high relative concentrations of HCO_3^- (≥ 40 % of inorganic anions), Ca^{2+} and Mg^{2+} (Ca^{2+} + Mg^{2+} generally ≥ 40 % of cations), which suggest a small degree of buffering by minor shale and siltstone units interbedded with the quartzites. The composition of these streams appear to be intermediate between that of Day and King's categories 3.2 and 4.3. The concentrations of HCO_3^-, Ca^{2+} and Mg^{2+} are reduced in stream waters draining afforested catchments, resulting in a significant shift in ion dominance towards that of category 4.1 (i.e. strongly NaCl-dominated).

The good correlation between the results of this study and those of Day and King (1995) suggest that, provided a sufficient number of streams are sampled (~ 10 or more) and the conditions at the time of sampling are accounted for, sporadic spot sampling of streams can provide a useful indication of regional variations in the composition of stream waters, as well as the processes that influence these.

7.3.3. The impact of afforestation on stream water composition

In the eastern escarpment region, afforestation significantly enhances the concentration of NO_3^- in stream waters and, in the poorly-buffered waters draining quartzitic lithologies, this NO_3^- enhancement is accompanied by reductions in alkalinity and pH. In two forest streams where the pH has been reduced to values below 5, acidification is accompanied by elevated Al concentrations of 0.23 and 0.32 mg L^{-1}, respectively (Figure 7.6). These values are amongst the highest Al concentrations observed in streams and lakes of northern Europe and North America which have purportedly been severely impacted by acid deposition (e.g. Driscoll *et al.*, 1980; Brakke *et al.*, 1987).

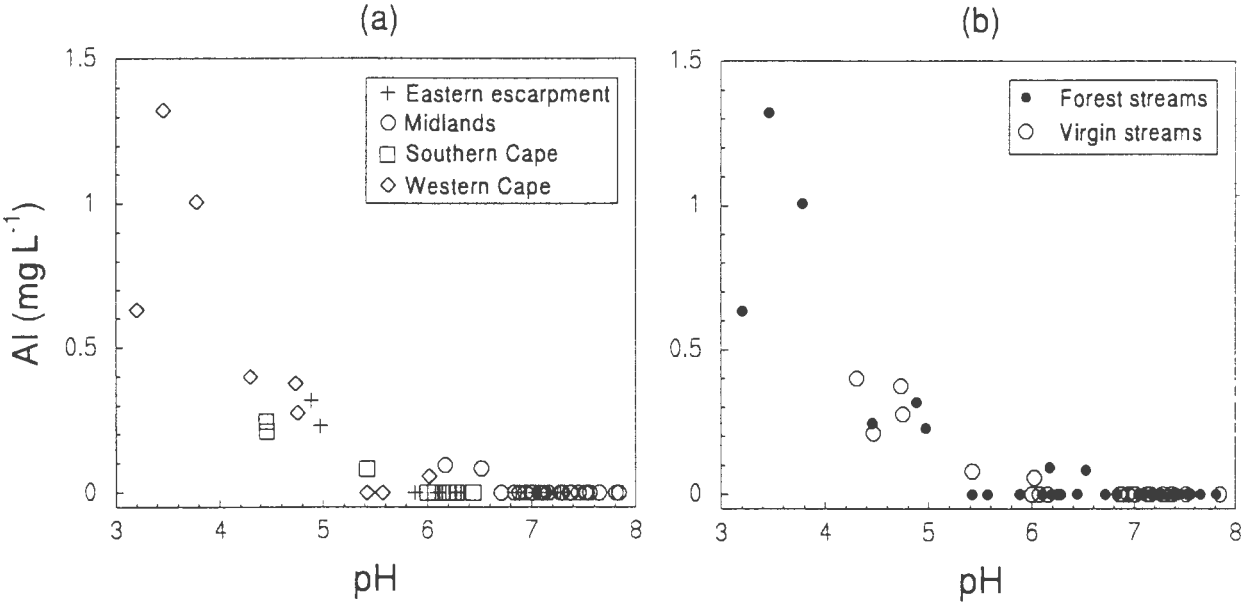

Figure 7.6: The relationship between pH and the total concentration of monomeric Al in stream waters classified according to region (a) and according to the presence or absence of forest plantations in their catchment.

Leaching of NO_3^- from forest soils with associated acidification of surface waters has been documented in several studies and is generally ascribed to the oxidation of forest litter following clearfelling of forest plantations (Bormann and Likens, 1977; Martin *et al.*, 1984; Mitchell *et al.*, 1989). A similar origin can be suggested for the NO_3^- draining into the eastern escarpment forest streams, as a portion of each forested catchment had been recently harvested at the time of sampling. The soil solution data described in Chapter 6, however, suggest that NO_3^- leaching may not be restricted to clearfelled plantations and may be a more widespread and chronic phenomenon associated with major disruption of the nitrogen cycle by afforestation. The mechanism by which high levels of NO_3^- are generated in soil solutions is not clear and further work is required in order to gain a better understanding of these processes which have a major impact on the composition of associated stream waters.

The biological (SASS) assessments carried out for this study (Appendix F) suggest that the overall quality of the eastern escarpment stream waters is good. A comparison of data for pairs of grassland and forest streams, however, indicates that there are significant differences in aquatic biota, and for one pair of streams a relative deterioration in water quality is evident in the stream draining forest. This is the stream (EER5) with the lowest pH, and highest NO_3^- and Al concentrations, suggesting that the observed biological changes may reflect changes in the composition of stream waters. Without more extensive biological monitoring, however, it is not possible to rule out other factors associated with afforestation (e.g. changes in the type of allochtonous material) as reasons for the observed biological changes.

Several of the western and southern Cape streams have pH values lower than 5, with associated elevated concentrations of Al ranging up to 1.3 mg L^{-1} (Figure 7.6). In the western Cape, proton activities (derived from pH measurements) are very closely correlated with dissolved organic carbon (DOC) levels (Figure 7.7) indicating that organic acids are the dominant factor controlling stream-water acidity in this region. Four of the five western Cape forest streams have DOC concentrations which are considerably higher than those of nearby streams draining fynbos catchments (Figure 7.8.a). The paired forest and fynbos streams were selected to ensure that the only major difference between their catchments was the type of vegetation cover. The data suggest, therefore, that in the western Cape, afforestation leads to increased leaching of organic acids with an associated reduction in pH and an increase in the concentration of Al. However, naturally-occurring acidic brown waters are common in mountain fynbos catchments of this region as well as of the southern Cape (Midgley and Schafer, 1992). Thus, afforestation-induced increases in DOC levels may not have a major detrimental effect on aquatic ecosystems.

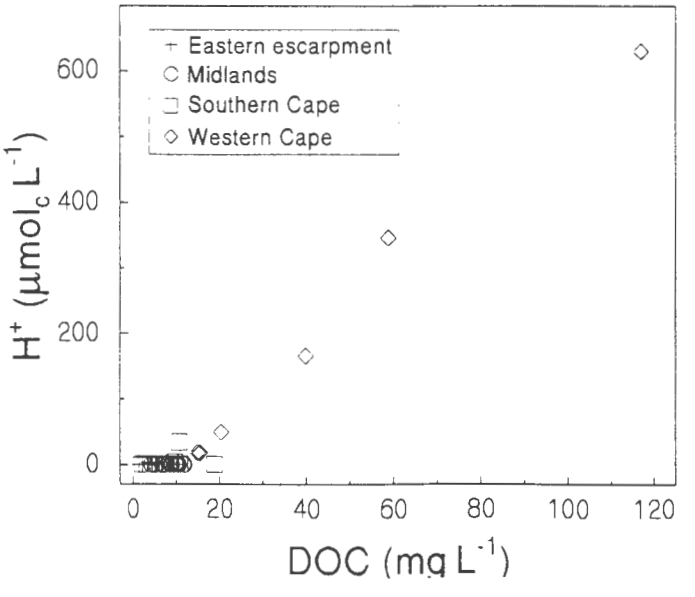

Figure 7.7: *The relationship between dissolved organic carbon (DOC) and free hydrogen ion (H^+) concentration (based on measured pH) in stream waters classified according to region.*

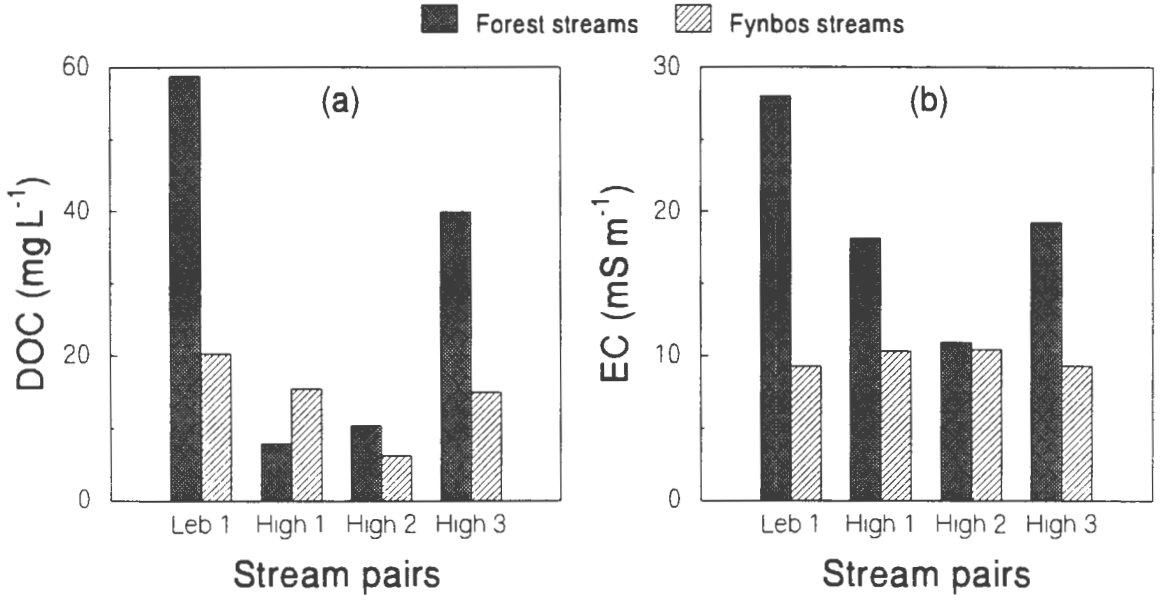

Figure 7.8: *Dissolved organic carbon (DOC; a) and electrical conductivity (EC; b) levels in paired forest and fynbos streams of the western Cape. Stream pairs: Leb 1 - Lebanon F2 and V1; High 1 - Highlands F1 and V1; High 2 - Highlands F2 and V2; High 3 - Highlands F3 and V3.*

In most cases, forest streams also show considerable increases in total solute concentrations to levels which are not observed in any of the fynbos streams (Figure 7.8.b). These changes primarily reflect increased concentrations of Cl^-, SO_4^{2-}, Na^+ and Mg^{2+} (Table 7.2.b) and correlate closely with changes in the composition of soil solutions observed under forests in the western Cape region. As discussed in the previous chapter, the enhancement of solute concentrations in association with afforestation probably reflects increased evaporative concentration, due to an increased rate of transpiration from forest plantations relative to that from the fynbos vegetation, as well as increased interception of marine aerosols by the forest canopy. It is not certain what effect these changes are likely to have on stream ecology. Natural variations in solute concentration (e.g. Britton, 1991) appear to be of the same order of magnitude as the changes observed under forest. Aquatic organisms are, therefore, likely to be well adapted to variable solute concentrations, suggesting, as for DOC, that the observed changes in stream water composition associated with afforestation are unlikely to have major ecological consequences. However, the stream water samples were taken towards the end of the wet season in the western Cape and it is likely that more extreme flushes of inorganic solutes and possibly of DOC, will occur earlier in the year due to the presence of accumulated salts and soluble organic matter. Under these conditions, the solute concentrations in forest streams may considerably exceed the highest concentrations observed in streams draining

undisturbed catchments. Further study, involving regular monitoring of suitable paired forest and fynbos catchments, is required in order to assess the extent to which this occurs, as well as the ecological impact thereof.

Although many of the streams draining afforested catchments in the midlands region show elevated NO_3^- concentrations (Table 7.2.b), total solute levels, alkalinity and pH values are not influenced in any consistent way. This reflects the strong buffering effect of the base-rich saprolite and bedrock (dolerite and shale) through which much of the surface water is likely to have drained. Thus the changes in soil solution composition observed in forest topsoils are overshadowed by processes (primarily ion exchange and mineral dissolution reactions) which occur as the water percolates through the underlying materials. The soil solution data suggest that, during periods of high discharge when interaction with subsoils, saprolite and bedrock is minimised, stream waters draining forested catchments may be acidified to some extent. Long term monitoring of stream water quality is required in order to confirm this.

No consistent effects of afforestation are evident in the southern Cape. The reason for this is not clear, but a possible explanation is that it reflects somewhat more arkosic sandstone parent materials with higher clay forming potential than those of the western Cape catchments that were investigated. This may also account for the lower DOC levels in the southern Cape streams relative to those of the western Cape, as clay content is a major factor influencing the mobility of DOC (Kononova, 1966) and is believed to be the prime determinant of the distribution of brown waters in the western and southern Cape (Midgley and Shafer, 1992).

7.3.4. Aluminium speciation and mineral saturation indices

One of the main concerns regarding the impact of surface water acidification is the associated increase in Al concentration which has been shown to have major detrimental effects on several aquatic organisms (Cronan and Schofield, 1979; Driscoll, *et al.*, 1980; Baker and Schofield, 1982, cited in Cronan *et al.*, 1986). Thus the above-described enhancement of the Al concentrations of certain stream waters as a result of afforestation is of some concern. It is well established that the bioavailability and hence the ecological impact of Al in stream waters is strongly dependent on the form in which it occurs (Driscoll, 1985). The presence

of natural dissolved organic substances (predominantly fulvic and humic acids) is particularly important in this regard as they have a strong tendency to complex Al, thereby rendering it biologically unavailable (Petersen *et al.*, 1986; Driscoll 1989; Kullberg *et al.*, 1993). Thus, in order to assess the ecological implications of the increased Al concentrations observed in certain forest streams, it is necessary to obtain an indication of the relative concentration of different Al species. Because of the large uncertainty associated with the modelling of chemical interactions involving dissolved organic matter (see detailed discussion in section 6.3.3.3), values obtained from speciation calculations can only be regarded as qualitative estimates. They do, however, provide some indication of the relative abundances of biologically available inorganic species and organically-bound Al, as well as the extent to which these are likely to be influenced by other changes in the composition of stream waters.

The results of speciation calculations suggest that between 15 and 54 % of the Al in the investigated stream waters is organically complexed (Table 7.5). In the eastern escarpment, DOC concentrations are relatively low and most Al occurs as free Al^{3+} and as Al-hydroxy complexes. Thus, the chemical modelling suggests that in this region, increased total concentrations of Al primarily reflect increases in inorganic species and therefore may lead to toxicity problems for some aquatic organisms.

Table 7.5: *The pH, dissolved organic carbon concentration (DOC), percentage distribution of different Al species and selected mineral saturation indices (SI values) for stream waters with detectable Al concentrations. Al-DOM = Al complexed to dissolved organic matter. Speciation calculations were carried out using the MINTEQA2 speciation programme (see text for details). SI values = log[(IAP)/K_{sp}], where IAP is the ion activity product and K_{sp} is the equilibrium constant for mineral dissolution (Table 6.2).*

Sample	pH	DOC	% Distribution of Al species					SI values		
		mg L^{-1}	Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	$AlSO_4^+$	Al-DOM	gibbsite	quartz	kaolinite
Klipkraal-F1	4.9	4.1	38	28	17	0	16	0.386	-0.642	3.288
Blyde-F2	4.8	4.2	45	27	13	0	15	0.315	-0.703	3.026
Lebanon-F1	3.2	117	40	0	0	9	51	-4.362	-0.469	-5.860
Lebanon-F2	3.4	59	37	1	0	8	54	-3.290	-0.525	-3.828
Lebanon-V1	4.3	20	42	8	1	4	45	-1.156	-0.968	-0.446
Highlands-V3	4.7	15	36	16	6	3	39	-0.052	-0.828	2.043
Highlands-F3	3.7	40	54	2	0	5	39	-2.482	-0.691	-2.545

The MINTEQA2 results suggest that in the very acidic brown waters of the western Cape, between 39 and 54 % of Al is organically complexed, despite very high DOC levels which range up to 117 mg L^{-1}. Thus approximately 50 % or more of the Al in the western Cape streams is likely to be inorganic, occurring mostly in the free cationic form (Al^{3+}). The data indicate that afforestation-induced increases in DOM concentrations do not lead to equivalent increases in the proportion of organically-complexed Al (Table 7.5). This suggests that the degree of Al complexation by DOM is reduced with decreasing pH, probably due to competition with protons for binding sites. This may have ecological implications as it suggests that afforestation could lead to considerable increases in the concentration of inorganic Al. Once again, a more comprehensive study covering an extended time period is required in order to quantify these processes and to obtain a better understanding of their possible ecological effects.

The mineral saturation indices (SI) given in Table 7.5 suggest that, at least in some cases, the concentrations of Al in stream waters may be controlled by equilibrium with certain Al-bearing minerals. The eastern escarpment streams have gibbsite SI values which are close to zero but are slightly positive. This is compatible with Al solubility control by an $Al(OH)_3$ phase which has a slightly higher solubility than that of crystalline gibbsite. The apparent equilibrium with a gibbsite-like phase, as well as the strong supersaturation of the eastern escarpment stream waters with respect to kaolinite, is in good agreement with relationships observed in most soil solutions of the region.

Most of the western Cape stream waters are slightly undersaturated with respect to gibbsite and strongly undersaturated with respect to kaolinite. This agrees to some extent with soil solution data for the same region which suggest undersaturation with respect to gibbsite but equilibrium or slight supersaturation with respect to kaolinite. An exception to this is the Highlands-V3 stream sample, which has a composition suggestive of equilibrium with gibbsite and supersaturation with respect to kaolinite. All streams in the eastern escarpment and western Cape are slightly undersaturated with respect to quartz.

7.4. SUMMARY AND CONCLUSIONS

Despite the superficial nature of the water sampling programme, analytical results for duplicate samples suggest that their composition is representative of the stream water composition at the time that the samples were taken. Total solute concentrations are generally low, as would be expected for streams draining small upland catchments. Particularly low solute concentrations in streams of the eastern escarpment are reflected in EC values which do not exceed 3 mS m^{-1}. Solute concentrations are considerably higher (EC up to 64 mS m^{-1}) in streams of the southern and western Cape regions and probably reflect a strong oceanic influence combined with high rates of evapotranspiration in these regions. In the midlands streams, intermediate solute concentrations were observed (EC ~ 3 to 10 mS m^{-1}). These are thought to reflect base flow conditions, interaction with moderately to highly weatherable bedrock (dolerite, shale and arkosic sandstone) and possibly a weak maritime influence.

Consistent regional variations in the relative concentrations of major ions are evident. In most cases, these correlate well with geographical patterns of ion dominance observed by Day and King (1995) and are related to differences in catchment geology, flow rate, input of oceanic salts and degree of evapotranspiration. Stream waters in the Cape regions are strongly dominated by NaCl, indicating that their compositions are primarily controlled by atmospheric inputs with minimal contribution from the weathering of bedrock. High Mg^{2+}/Ca^{2+} ratios provide further confirmation of the marine influence in these regions. Total solute concentrations are significantly higher than would be expected for "typical" precipitation-dominated waters and probably reflect a high degree of evaporative concentration associated with hot dry summers, as well as major inputs of marine aerosols. In contrast, the midlands streams and those draining dolomite-dominated catchments of the eastern escarpment, are dominated by HCO_3^-, Ca^{2+} and Mg^{2+}, indicating a considerable degree of interaction with underlying, relatively base-rich bedrock. Streams draining quartzite-dominated catchments in the eastern escarpment are very poorly buffered and consequently show a high degree of variability in relative ion concentrations. Those which drain grassland catchments are generally dominated by HCO_3^-, Ca^{2+} and Mg^{2+}, with slightly lower concentrations of Cl^- and Na^+. Bicarbonate concentrations are considerably reduced and the ratio of Na^+ to divalent cations is enhanced in stream waters draining afforested catchments.

The enhanced concentrations of NO_3^- observed in forest soil solutions of the eastern escarpment are reflected in the composition of all streams draining afforested catchments in this region. In poorly-buffered waters draining quartzitic catchments, enhanced NO_3^- concentrations are accompanied by reductions in alkalinity and pH, reflecting the displacement of soil acidity into drainage waters, primarily via the leaching of small amounts of nitric acid. Acidification of the stream waters has also resulted in elevated concentrations of monomeric Al (up to 0.32 mg L^{-1}), which reach levels observed in northern hemisphere streams that have been severely impacted by acid deposition. Speciation calculations suggest that more than 80% of the Al is in inorganic form. Although much of the NO_3^- draining into streams may be associated with clearfelling and associated rapid oxidation of forest litter, the soil solution data (Chapter 6) suggest that NO_3^- leaching may not be restricted to clearfelled plantations and may be a more widespread phenomenon associated with disruption of the nitrogen cycle by afforestation. Further work is required in order to obtain a better understanding of nitrogen dynamics of forest ecosystems in the eastern escarpment as these processes appear to have a major impact on the composition of poorly-buffered stream waters.

In the western Cape, afforestation has led to a considerable enhancement of naturally-high concentrations of DOC and total inorganic solutes (primarily Cl^-, SO_4^{2-}, Na^+ and Mg^{2+}) in stream waters. Dissolved organic carbon is very strongly correlated with pH and Al concentration. Thus, afforestation causes increased levels of acidity in streams which drain quartzitic catchments and Al concentrations are raised to very high values in certain cases (up to 1.3 mg L^{-1}). Because elevated Al concentrations are associated with high concentrations of dissolved organic substances, a large fraction (~ 40 to 50 %) of the Al is complexed with organic matter. However, increased DOC concentrations in forest streams do not appear to enhance the percentage of organically bound Al, presumably due to a parallel decrease in pH. Thus the reduced pH values and increased concentrations of total Al associated with afforestation are accompanied by considerable increases in the absolute concentrations of inorganic Al.

Elevated NO_3^- concentrations are evident in stream waters draining several of the afforested catchments in the midlands region. Other compositional parameters, however, do not appear to be influenced in any consistent manner by afforestation. This is believed to reflect the low discharge levels at the time of sampling and the fact that waters draining topsoils are likely

to have been significantly modified by interaction with base-rich saprolite and bedrock which underlies most of the sampled catchments. In the southern Cape, afforestation does not seem to have influenced the composition of stream waters in any consistent manner. The reason for this is not clear, but it may reflect sandstone bedrock which is more arkosic than the pure quartzites that prevail in the western Cape and eastern escarpment regions.

In conclusion, the data obtained for stream water samples suggest that, in certain cases, afforestation has caused significant changes in the composition of associated surface waters and that these changes are well correlated with the observed effects of forest plantations on the composition of soil solutions. The effect of afforestation is particularly prevalent in catchments underlain by materials with low buffering capacity and under conditions of high discharge. The ecological impact of these changes is uncertain, however, particularly in view of the high natural compositional variability observed in relatively unbuffered streams draining mountain catchments. A detailed chemical and biological study of carefully selected pairs of forest and virgin streams is recommended in order to better quantify natural and afforestation-induced compositional changes in stream water composition, as well as the possible ecological implications thereof.

8. GENERAL DISCUSSION AND CONCLUSIONS

This study has confirmed the acidifying impact of pine plantations on sensitive upland soils in South Africa, and indicates that, in general, acidification is accompanied by increased concentrations of strong acid anions and acidity in soil solutions. This implies that afforestation leads to an increased potential for leaching of solutes, including Al and protons, from the naturally acidic and poorly buffered soils on which forest plantations are typically established. Data obtained for stream waters indicates that under conditions of high discharge, the concentration of solutes is increased in streams draining acidified forest soils and, in catchments underlain by quartzitic parent material with low buffering capacity, these are accompanied by decreased pH levels and increased concentrations of Al.

The key findings of this thesis are given below and are broadly structured to address the key questions posed for this study. The first key question relates to the extent of soil acidification by pine plantations and is addressed in section 8.1. Section 8.2 deals with the effect of afforestation on the concentration of strong acid anions as well as that of acid and basic cations in soil solutions and stream waters. These aspects relate to the second and third key questions and constitute the most important findings of this thesis. An additional aspect of the third key question, i.e. the effect of afforestation on the concentration of Al and Mn in soil solutions and stream waters, is discussed in section 8.4. Conclusions regarding the effect of afforestation on the concentration of DOC (4th key question) are given in section 8.3. The chapter is concluded with a brief discussion on the implications of the key findings with respect to forest productivity and environmental impact, and with some recommendations regarding future work.

8.1. SOIL ACIDIFICATION

This study has shown that the acidifying effect of pine afforestation is prevalent in a range of environments within South Africa. The intense acidification associated with afforestation of grassland in the eastern seaboard region, as documented in previous studies, was confirmed. Similar effects were shown for the winter rainfall region in the southern and western Cape where pine forests replace fynbos (macchia) vegetation growing in naturally acidic, nutrient depleted sandy soils. Acidification is less intense in these areas, however, and, although reductions in pH are ubiquitous, in the western Cape afforestation-induced changes

in exchangeable acidity and base cation concentrations are not statistically significant. Calculations based on changes in exchangeable acidity and base cations indicate that the rate of acidification in the eastern seaboard region is similar to that observed in forest ecosystems in the northern hemisphere that are subject to moderate levels of acid deposition. For most of the South African sites, estimated rates of biomass uptake can account for the observed rates of acidification but, in some cases, particularly in certain midlands sites with high original base cation levels, leaching is likely to contribute substantially to acidification. Although there is some overlap, rates of acidification in the Cape regions are significantly lower than those observed in the eastern seaboard. The low acidification rates in the Cape are associated with low levels of forest productivity and probably stem from the naturally acidic, base cation-depleted nature of the soils in which the forests are developed. Further factors which may contribute towards reducing acidification rates in the western and, to a lesser extent, southern Cape include: 1) the fact that a large proportion of the rainfall in these regions occurs in winter, when the temperatures are not optimal for tree growth, and; 2) the input of bases to forests in the form of wind-borne marine aerosols and/or dust.

8.2. STRONG ACID ANIONS AND ACIDITY OF SOIL SOLUTIONS AND DRAINAGE WATERS

Comparison of data for paired forest and virgin soils indicates that pine afforestation generally leads to increased concentrations of strong acid anions in soil solutions and that this can occur in areas which are not impacted by atmospheric pollution.

In the western and southern Cape regions, afforestation has led to considerable increases in the concentration of Cl^- and Na^+ in soil solutions. This is probably caused by increased interception of marine aerosols by the forest canopy combined with higher rates of evapotranspiration in pine plantations relative to that in fynbos.

The most prominent impact of afforestation in the eastern escarpment and midlands regions is a dramatic increase in the concentration of NO_3^- in saturated paste extracts. While this may, to some extent, reflect processes associated with sample preparation and saturated paste extraction, it suggests that the pine plantations have a considerable impact on N dynamics that may lead to the leaching of NO_3^- from forest soils. It is likely that high NO_3^- concentrations

in saturated paste extracts are related to the high levels of N deposition observed in the eastern escarpment and in parts of KwaZulu-Natal, and the lack of this N source may account for the ubiquitously low NO_3^- concentrations in soils of the southern and western Cape. Atmospheric inputs of NO_3^- and NH_4^+ are low in relation to the total N pool, however, and the most prominent effect of afforestation probably stems from an associated modification of N cycling processes. The fact that enhanced concentrations of soluble NO_3^- were observed in most midlands forest soils suggests that atmospheric inputs of N from industrial sources or automobile emissions is unlikely to be a prerequisite for increased levels of NO_3^- under forest.

The concentration of soluble SO_4^{2-} is not strongly influenced by afforestation, although statistically significant increases were observed in forest soils of the midlands and southern Cape regions. On the other hand, a considerable increase in *exchangeable* SO_4^{2-} occurs in all clay-rich forest soils, indicating that SO_4^{2-} is accumulating at a much higher rate under forest than under adjacent grassland. This is at least partly due to the positive influence of reduced soil pH on SO_4^{2-} sorption capacity, but may also reflect elevated inputs due to increased interception of atmospheric S or deep-rooted phytocycling. If the SO_4^{2-} is being retained in the soil by adsorption processes, it is likely that continued accumulation will cause increased saturation of the anion exchange capacity and ultimately could lead to the leaching of SO_4^{2-}. The source of atmospheric S inputs is uncertain. While a major anthropogenic contribution is likely in parts of the eastern seaboard (particularly in the eastern escarpment), high concentrations of SO_4^{2-} in soil solutions and rainfall in the Cape regions suggest that S deposition levels in unpolluted maritime environments may exceed those in areas which are purportedly impacted by acid deposition.

The concentrations of soluble strong acid anions in the soils of this study are comparable to those observed for soil solutions from forest ecosystems in the northern hemisphere that are subjected to considerable inputs of atmospheric pollutants. Elevated solute levels in the South African soils may reflect the combined effect of high rates of evaporative concentration (due to the warm climate) and a regional maritime influence.

The above-described changes in solute concentration under forest are accompanied by considerable reductions in solution pH and increased concentrations of soluble monomeric Al. Thus, in all of the regions investigated, the potential for leaching of acidity is considerably

enhanced by the establishment of pine plantations. The composition of saturated paste extracts from topsoil samples provides an indication of the maximum solute levels and minimum pH values possible in saturated soils and probably reflects the composition of soil solutions in the early part of the wet season when salts, accumulated by evaporative concentration during the dry season, are solubilised but not yet removed by leaching. The extent to which the observed enhancement of strong acid anion concentrations and acidity impacts on drainage waters, will depend on the degree of dilution by continued inputs of rain water, as well as on the extent of interaction with more alkaline subsoils and saprolite. The effect of afforestation is, therefore, likely to be most prominent in the early part of the wet season during periods of high discharge when a relatively large proportion of the water that enters streams does not interact with subsoils, saprolite or parent materials.

Increased concentrations of strong acid anions in soil solutions are accompanied by substantially enhanced levels of base cations (particularly Na^{+}, Mg^{2+} and Ca^{2+}). Thus, despite the considerable increases in acidity and the concentration of soluble Al under forest, reductions in the proportion of base cations in solution ([Base Cations]/[Base Cations + Al^{3+} + H^{+} + Mn^{2+}]) are mostly small. This reflects the combined effect of increased solute concentrations under forest and the high relative affinity of acid cations for exchange surfaces which results in a preferential displacement of base cations into solution. It is only in certain forests soils with very low base saturation of the exchange complex that the proportion of base cations in solution drops below 90 %.

Data obtained for stream water samples indicate that, under certain conditions, the changes observed in soil solutions are reflected in the composition of surface waters. Forest streams in the eastern escarpment and western Cape show reduced pH and alkalinity, increased concentrations of strong acid anions and, in some cases, enhanced levels of Al compared to those observed in equivalent streams draining undisturbed catchments. These compositional changes are associated with conditions of high discharge and occur in forest streams that drain catchments underlain by quartzitic parent materials with low buffering capacity.

8.3. DISSOLVED ORGANIC MATTER

It was shown that organic anions contribute substantially to the total negative charge in soil

solutions. Variations in the colour of saturated paste extracts and relationships between dissolved organic carbon (DOC) and excess positive charge suggest that there are broad regional differences in the chemical nature of dissolved organic matter (DOM). The data suggest the charge density of DOM in soils of the southern and western Cape is higher than that in the eastern seaboard soils and may reflect more acidic and oxidised compositions in the former. Afforestation does not appear to have influenced the charge density of DOM in any consistent manner. Total concentrations of DOC are generally modified under forest, however, with different effects observed in the eastern seaboard and Cape regions, respectively. In the eastern escarpment and midlands sites, concentrations of soluble DOC are reduced in forest soils, whereas, in the southern and western Cape, afforestation has generally had the opposite effect. This is reflected in stream waters of the western Cape, as forest streams in this region have considerably higher DOC concentrations than those of streams draining equivalent undisturbed fynbos catchments.

8.4. ALUMINIUM AND MANGANESE CONCENTRATIONS

The pH values in undisturbed soils are close to the upper limit for Al solubility (~ 5) and the drop in pH associated with afforestation, which generally exceeds 0.2 pH units, has resulted in considerable increases in the concentration of soluble monomeric Al to values ranging from 0.38 to 27 mg L^{-1}. Speciation calculations indicate that a large proportion (~ 20 to 80 %) of the dissolved Al is organically-bound and very high concentrations of Al in the western Cape are associated with darkly coloured solutions with high concentrations of DOC. Relationships between Al^{3+} activity and pH, as well as calculated saturation indices, support control of Al solubility by equilibria involving solid-phase $Al(OH)_3$, Al-sulphates and Al-organic matter. Due to the uncertainties associated with modelling of Al-DOM interactions, however, deductions based on calculated Al^{3+} activities can only be regarded as tentative.

In the eastern escarpment and western Cape, forest streams that show reduced pH values also show increased concentrations of dissolved monomeric Al. This is particularly significant in the eastern escarpment where Al concentrations are ubiquitously very low (below the detection limit of 0.075 mg L^{-1}) in grassland streams and can reach values of up to 0.32 mg L^{-1} in acidified streams draining forested catchments. In the western Cape, stream waters are naturally acidic and have high concentrations of DOC and Al. Nonetheless, acidification has led to further pH reductions and in some cases has considerably enhanced

the concentration of Al (up to 1.3 mg L^{-1}).

The data obtained for saturated paste extracts indicate that, under certain conditions, afforestation can lead to dramatically enhanced concentrations of soluble Mn^{2+}. This effect is not widespread, however, and appears to be dependent on a combination of relatively high inherent Mn^{2+} concentrations and increased solute levels. Although the changes in the concentration of Mn^{2+} are not related to changes in pH, the acidic conditions prevalent in both forest and virgin soils are probably necessary in order to facilitate Mn solubilisation. Variations in the redox status of saturated pastes may play an important role in controlling the solubility of Mn^{2+}. If this is the case, it implies that certain forest soils have higher levels of readily oxidisable organic matter than their virgin counterparts.

8.5. IMPLICATIONS WITH RESPECT TO FOREST PRODUCTIVITY

The main emphasis of this study has been to evaluate the impacts of afforestation from an environmental geochemistry perspective and work has largely focused on evaluating changes in the composition of soil solutions and surface waters. Nonetheless, the study has confirmed that pine afforestation causes a considerable reduction in the base saturation of topsoils and it is likely that, over time, this will have an impact on forest productivity. The extent to which this occurs will depend on the degree to which the forests are able to utilise nutrients from upper organic horizons and/or from less acidic subsoils. In the eastern seaboard regions, the development of relatively thick organic horizons and the presence, in most cases, of base-rich parent materials, may provide a source of base cations which offsets their reduced availability in the mineral topsoil. In the Cape regions, however, where forest productivity appears to be limited by a combination of climatological and pedological factors, a further reduction in the availability of key nutrient elements as a result of acidification may have a substantial impact on tree growth. Further work is recommended to assess the extent to which productivity in plantations of the Cape regions is impacted by afforestation-induced acidification.

Aluminium toxicity is an additional factor which may impact on forest productivity. The results of this study indicate the concentrations of Al in soil solutions have not reached critical levels in most South African pine plantations. Nonetheless, afforestation has caused considerable decreases in Ca/Al ratios. This has occurred over time periods ranging from 30

to 65 years (reduction rates for Ca/Al ratios range from 0.03 to 2.1 per year) and continued silvicultural activities may lead to widespread conditions of Al stress that are likely to reduce forest productivity. Long-term monitoring of soil solution compositions is therefore suggested in order to assess the potential for Al toxicity problems in South African pine plantations.

8.6. ENVIRONMENTAL IMPACT OF PINE AFFORESTATION

The observed increases in acidity and reductions in nutrient availability in forest soils will only assume importance, from an environmental point of view, if attempts are made to re-establish the original vegetation in areas previously covered by pine plantations. Both grassland and fynbos vegetation are adapted to acidic, nutrient-poor soil conditions, however, and only minor, if any, amelioration is likely to be necessary to provide suitable soil conditions for re-establishment of these vegetation types or for conversion to intensive agricultural land use.

From an environmental perspective, afforestation-induced changes in the composition of surface waters is potentially of greater concern than soil acidification *per se*. The soil solution and stream water data discussed above indicate that afforestation presents a threat to surface water quality in that it increases the potential for leaching of strong acid anions, acidity and environmentally important metals such as Al and Mn. Observed changes in the composition of stream waters suggest that under certain conditions these processes can cause a deterioration in water quality. The extent of afforestation impacts on surface waters has not been fully established, however, and the ecological implications of the observed changes are therefore uncertain.

8.7. FUTURE WORK

The data reported in this thesis provide a basis for regional assessment of the impacts of pine plantations on the chemical properties of topsoils and surface waters in South Africa. Further work should focus on selected paired catchments and aim to provide an improved understanding of the processes responsible for observed changes. Research should include an assessment of the pools and fluxes of key elements in the entire regolith and in the biomass. In addition a more thorough evaluation of variations in the composition of stream waters is

required. Ideally, this should include the quantification of inputs (primarily in the form of wet and dry deposition) and outputs (in streams) of major ions so that the relationships between inputs, soil solution compositions and outputs in stream waters can be better elucidated. An important aspect of such a study would be to integrate the data on the composition of soil solutions and stream waters with hydrological information so as to be able to model the long term changes that may occur as a result of continued silvicultural activities.

One of the key findings of this study is that afforestation can lead to elevated concentrations of strong acid anions in soil solutions. In the case of Cl^-, this can be ascribed to enhanced interception and evaporative concentration of atmospheric salt inputs. However, the processes responsible for enhanced concentrations of NO_3^- in the eastern escarpment are not well understood. Additional research is required to establish how afforestation and associated acidification affects nitrogen cycling processes. The data presented above indicate a build-up of SO_4^{2-} in clay-rich soils, but further work is required to determine: the extent to which this reflects increased SO_4^{2-} inputs; the relative contribution of S from atmospheric sources and deep-rooted phytocycling; the mechanism by which SO_4^{2-} is being retained in the soils; and the extent to which the SO_4^{2-} sorption capacity of the soil has been saturated.

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APPENDIX A: SITE DETAILS AND LOCALITY MAPS

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Table A1.a: *Details of soil sampling sites. Regions: EE = eastern escarpment; MI = midlands; SC = southern Cape; WC = western Cape. T. Age = total plantation age in years (numbers in brackets are estimates based on an average rotation of 30 years); P. Age = present age; Rot. = rotation number; MAP = mean annual precipitation in mm (based on extrapolation from the 1 minute grid data of the Computing Centre for Water Research, Pietermaritzburg). Missing values indicate unavailable data. n.a. = not applicable*

Region	Site	Plantation	Forest sp.	T. Age	P. Age	Rot.	Parent material	Soil texture	MAP
EE	1	Blyde	*elliottii*	(45)	15	2	quartzite/siltstone	sand-loam	1627
EE	2	Blyde	*elliottii*	(50)	20	2	quartzite	sand	1600
EE	3	Blyde	*elliottii*	(32)	2	2	quartzite	sand	1600
EE	4	Spitskop	*elliottii*	(45)	15	2	shale/siltstone	clay-loam	1280
EE	5	Spitskop	*elliottii*	(45)	15	2	shale/siltstone	loam	1280
EE	6	Ceylon	*patula*	(36)	6	2	shale/siltstone	loam	1435
EE	7	Morgenzon	*patula*	(31)	1	2	dolerite	loam	1048
EE	8	Klipkraal	*elliottii*	(45)	15	2	dolerite?	clay-loam	1419
EE	9	Klipkraal	*elliottii*	(45)	15	2	quartzite	sand	1470
EE	11	Mac Mac	*patula*	22	22	1		clay loam	
EE	12	Tweefontein	*patula*	26		2	dolomite	clay loam	1100
EE	13	Long Tom	*patula*	28	28	1	shale	loam	
EE	14	Frankfort	*patula*	35	35	1	granite	loam	1560
MI	1	Mossbank	*patula*	30	2	2	shale	silty-loam	950
MI	2	n.a.	*patula*	40	40	1	shale	clay-loam	1000
MI	11	Cedara	*patula*	28	28	1	dolerite/shale	clay	910
MI	12	Mossbank	*patula*	30	1	2	dolerite	clay loam	950
MI	13	Sarnia	*patula*	36	36	1	shale	clay loam	980
MI	14	n.a.	*patula*	40	40	1	dolerite	clay loam	1000
MI	15	Weza	*patula*	65	30	2	dolerite	clay loam	1100
MI	16	Weza	*patula*	65	30	2	dolerite	clay	1030
MI	21	n.a.	*elliotii/taeda*	16	16	1	dolerite	clay loam	1000
MI	22	n.a.	*elliotii/taeda*	27	27	1	shale	clay	950
MI	23	Dargle	*elliotii/taeda*	30		2	dolerite	loam	1000
MI	24	Karkloof	*elliotii/taeda*	32	32	1	alluvium	clay loam	950
MI	25	Weza	*elliotii/taeda*	50	20	2	shale	clay loam	1020
MI	26	Weza	*elliotii/taeda*	60	30	2	dolerite	clay loam	980
SC	1	Bergplaas	*radiata*	15	15	1	quartzite	loamy sand	650
SC	2	Bergplaas	*pinaster*	60	15	2	quartzite	loamy sand	600
SC	3	Bergplaas	*radiata*	60	21	2	quartzite	loamy sand	780
SC	4	Karatara	*pinaster*	(45)	15	2	quartzite	loamy sand	1160
SC	5	Jonkersberg	*pinaster*	60	35	2	quartzite	sand	900
SC	6	Jonkersberg	*pinaster*	60	15	2	quartzite	sand	960
WC	1	Silvermine	*radiata*				quartzite	sand	1200
WC	2	Silvermine	*radiata*				quartzite	sand	1200
WC	3	Highlands	*pinaster*	42	42	1	quartzite	sand	840
WC	4	Lebanon	*pinaster*	63	28	2	quartzite	sand	1060
WC	5	Lebanon	*pinaster*	45	14	2	quartzite	sand	760
WC	6	Highlands	*pinaster*	43	43	1	quartzite	sand	877

Table A1.b: *Details of soil sampling sites continued. Regions: EE = eastern escarpment; MI = midlands; SC = southern Cape; WC = western Cape. Alt. = altitude (m). Dist. = distance from nearest coastline (km). Missing values indicate unavailable information. n.a. = not applicable.*

Region	Site	Alt.	Dist.	Latitude		Longitude		Slope	Slope	Terrain	Aspect
				degrees	minutes	degrees	minutes	angle	type	unit	
EE	1	1485	211	24	51.91	30	51.57	4	convex	midslope	NW
EE	2	1584	210	24	50.82	30	52.6	0	straight	midslope	NW
EE	3	1588	210	24	50.86	30	52.67	0	straight	crest	NW
EE	4	1300	204	25	7.79	30	49.36	8	straight	midslope	NW
EE	5	1320	204	25	7.49	30	49.52	8	convex	midslope	NW
EE	6	1885	221	25	3.54	30	41.38	4	straight	crest	NW
EE	7	1860	225	24	53.57	30	41.73	10	convex	midslope	N
EE	8	1335	210	25	0.97	30	49.54	8	straight	midslope	NW
EE	9	1431	208	25	1.21	30	50.39	5	straight	midslope	NW
EE	11	1360	211	30	57.58	24	49.75	0	convex	crest	n.a.
EE	12	1080	211	25	4.33	30	46.58	5	straight	footslope	N
EE	13	1740	219	25	10.50	30	39.33	5	straight	crest	NW
EE	14	1090	205	25	2.25	30	52.17	20	convex	midslope	SE
MI	1	1610	114	29	50.54	29	41.72	0	straight	midslope	NE
MI	2	1530	120	29	35.58	29	51.88	4	straight	midslope	NW
MI	11	1140	84	29	33.75	30	16.00	1	convex	crest	W
MI	12	1640	121	29	50.08	29	41.42	5	convex	crest	SW
MI	13	1600	114	29	51.75	29	44.08	10	convex	midslope	E
MI	14	1540	120	29	35.67	29	51.83	2	straight	midslope	W
MI	15	1240	67	30	36.08	29	41.50	5	convex	crest	N
MI	16	1120	62	30	35.33	29	42.83	10	convex	midslope	NE
MI	21	1320	104	29	21.33	30	9.75	10	concave	midslope	N
MI	22	1120	104	29	59.50	29	44.50	20	convex	footslope	NW
MI	23	1430	109	29	33.92	30	3.50	3	concave	midslope	N
MI	24	1080	92	29	22.33	30	16.17	0	straight	floodplain	n.a.
MI	25	1260	62	30	31.17	29	44.00	0	convex	crest	n.a.
MI	26	1140	58	30	34.42	29	42.92	6	straight	midslope	NE
SC	1	720	14	33	51.99	22	36.52	2	straight	midslope	SE
SC	2	690	15	33	51.44	22	37.73	10	straight	midslope	ESE
SC	3	630	18	33	50.49	22	42.36	5	straight	midslope	NW
SC	4	660	20	33	51.93	22	53.4	20	straight	midslope	SE
SC	5	600	15	33	55.46	22	11.39	0	straight	crest	n.a.
SC	6	550	16	33	54.54	22	12.13	15	straight	midslope	NNE
WC	1		4					0	straight	midslope	n.a.
WC	2		3					5	straight	midslope	N
WC	3	200	5	34	17.89	19	6.837	6	straight	midslope	NE
WC	4	630	22	34	10.32	19	9.093	11	straight	midslope	SW
WC	5	540	16	34	13.56	19	8.733	4	straight	midslope	NE
WC	6	450	8	34	16.83	19	2.897	6	straight	midslope	NNW

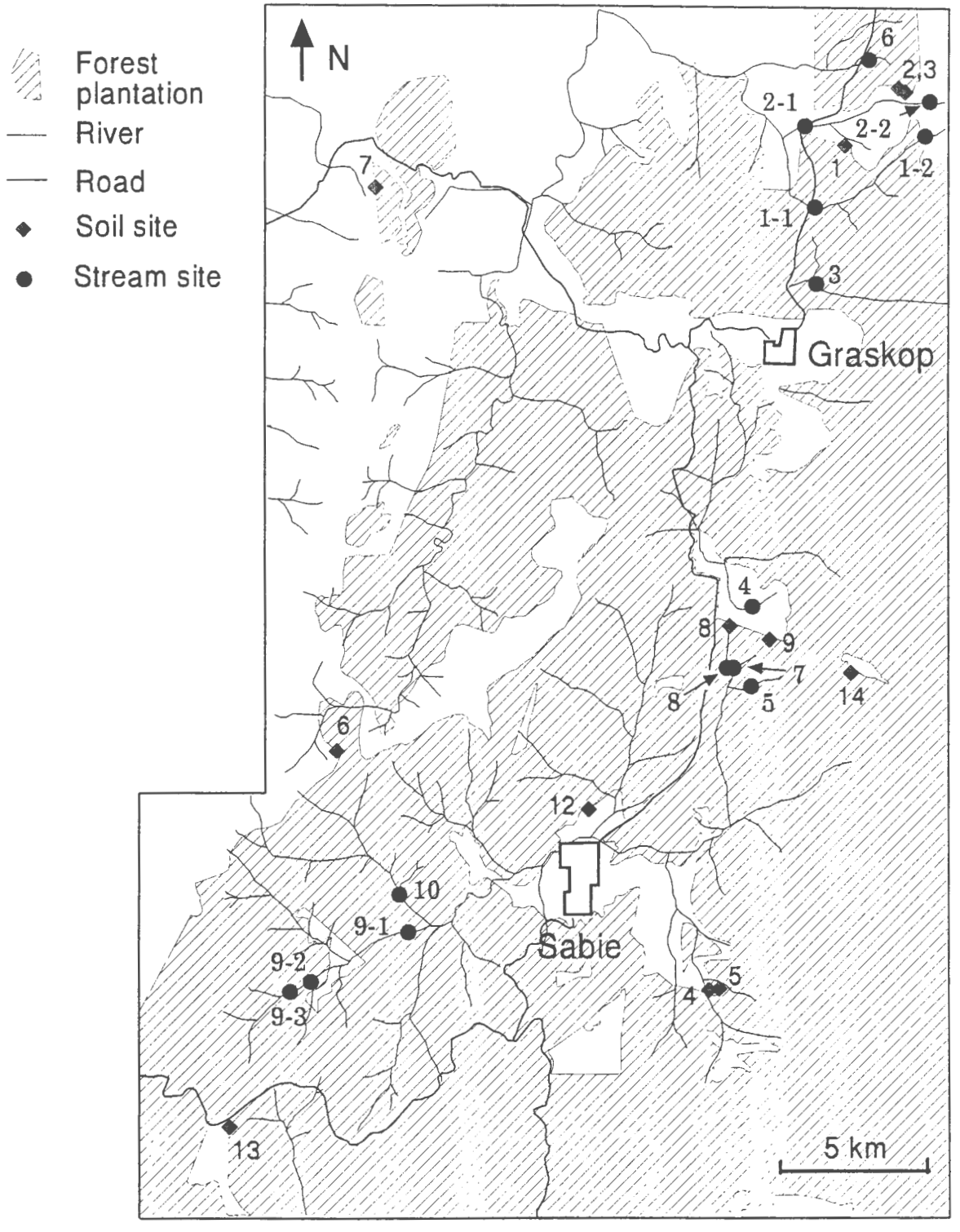

Figure A1: *Locality map for the* ***eastern escarpment*** *region showing the position of soil and stream sampling sites in relation to forestry areas, major roads, towns and selected drainages. Site numbers are shown next to the sampling points.Soil site 11 falls to the south of the area shown*

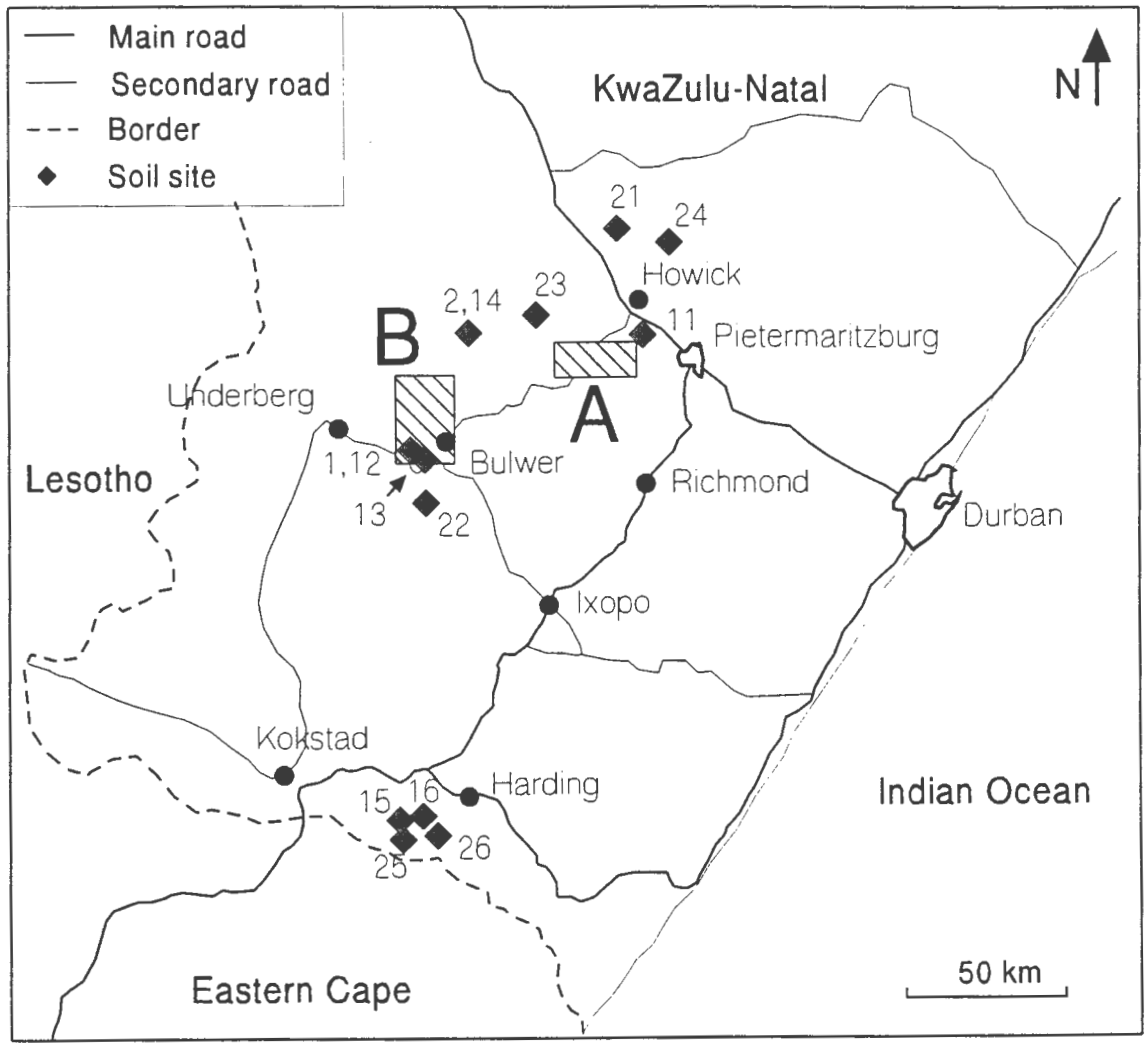

Figure A2: *Locality map showing the position of soil sampling sites in the* ***midlands*** *region in relation to roads and towns. Site numbers are shown next to the sampling points. The shaded blocks A and B denote areas where stream samples were taken. These are shown in detail in Figure A3. Map adapted from du Toit (1993).*

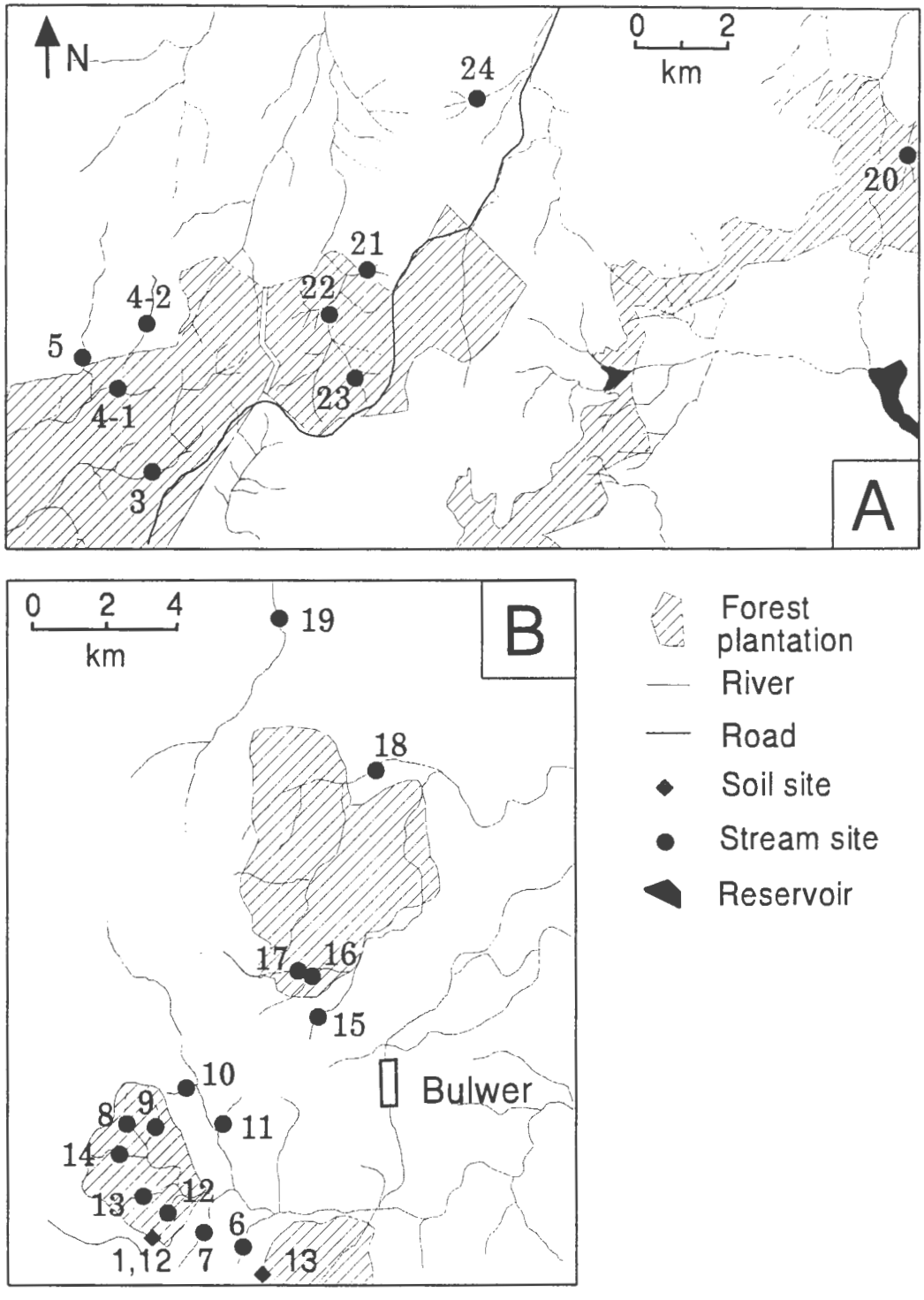

Figure A3: *Detailed locality maps of blocks A and B (see Figure A2) in the* ***midlands*** *region. The maps show the position of stream and soil sampling sites in relation to forestry areas, major roads, towns and selected drainages. Site numbers are shown next to the sampling points.*

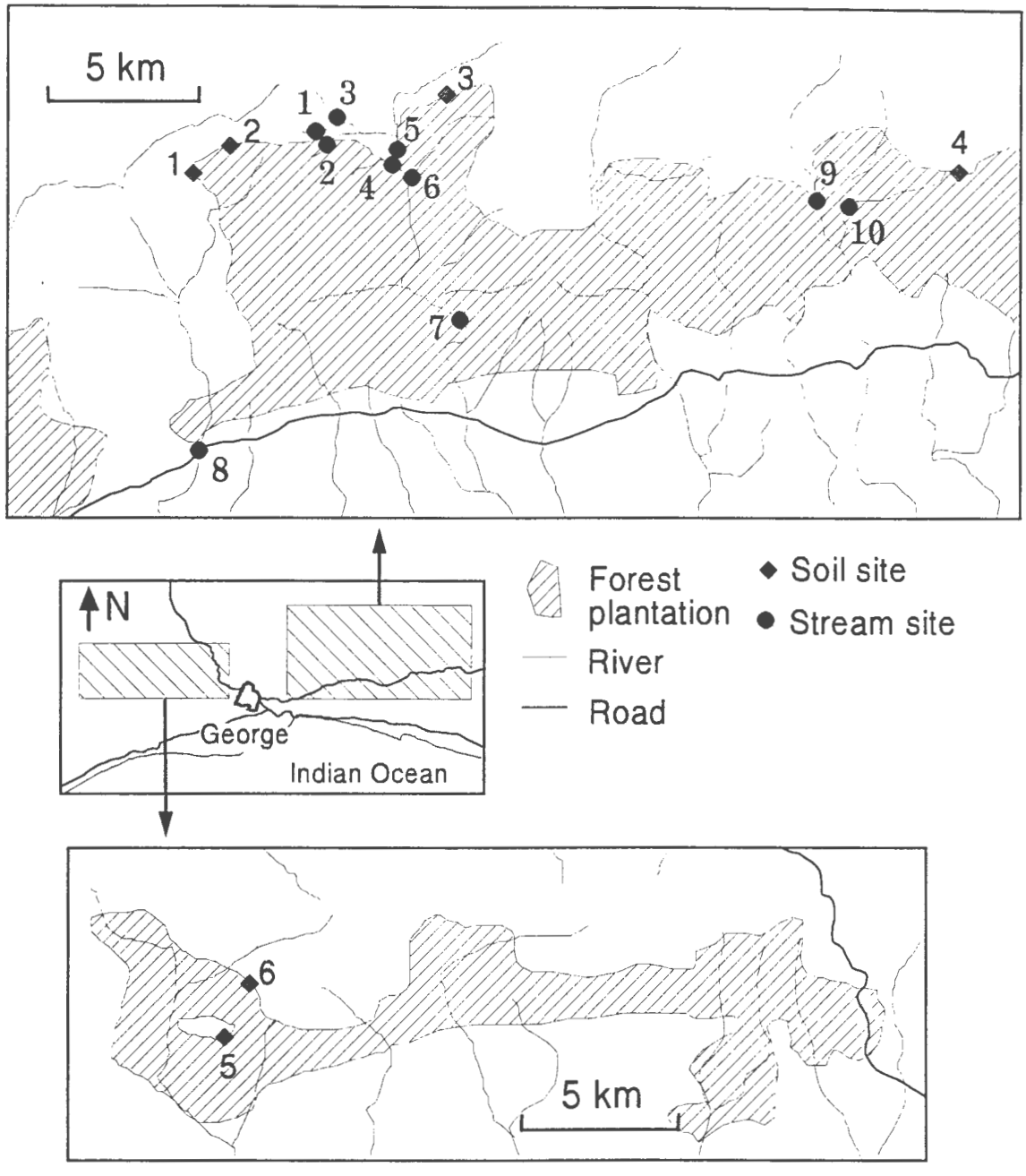

Figure A4: *Locality maps for the* ***southern Cape*** *region showing the position of stream and soil sampling sites in relation to forestry areas, major roads, towns and selected drainages. Site numbers are shown next to the sampling points.*

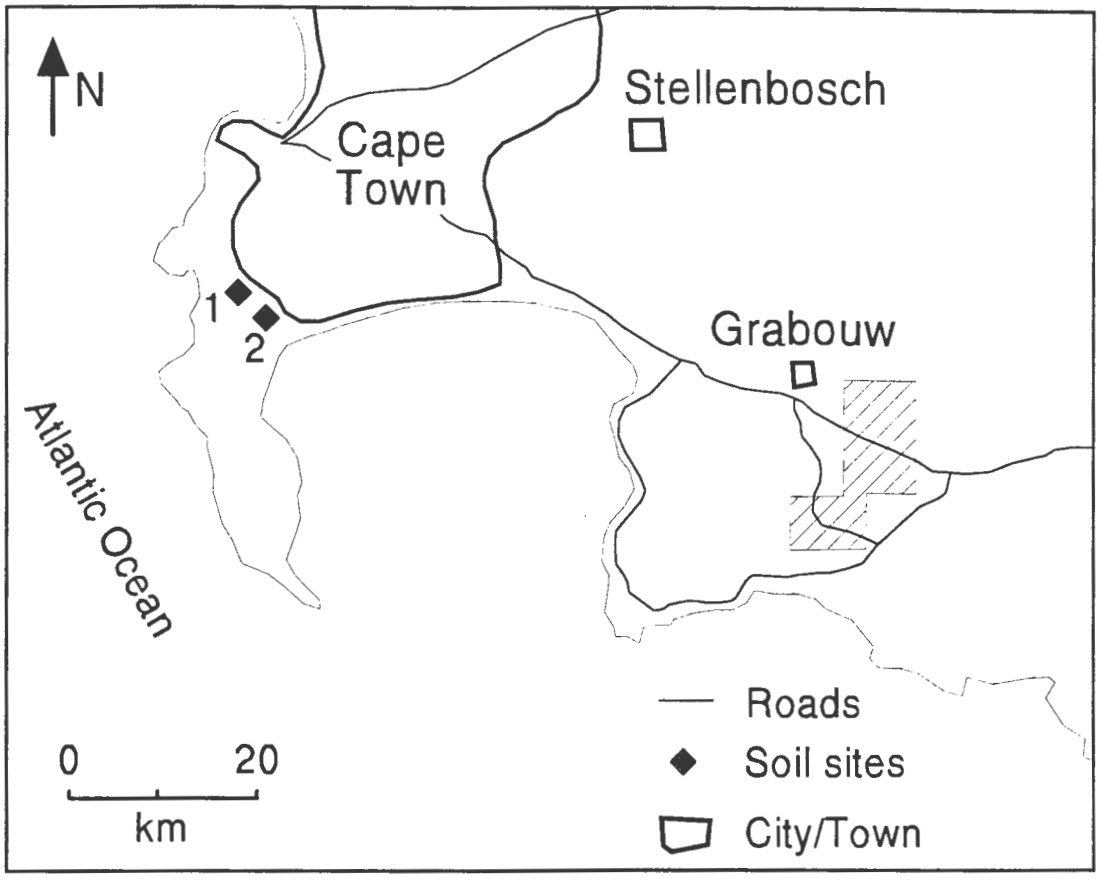

Figure A5: *Locality map of the* ***western Cape*** *region showing the position of soil sampling sites 1 and 2, and the area in which the other soil samples and all stream samples were taken (shaded). Details of this area are shown in Figure A6.*

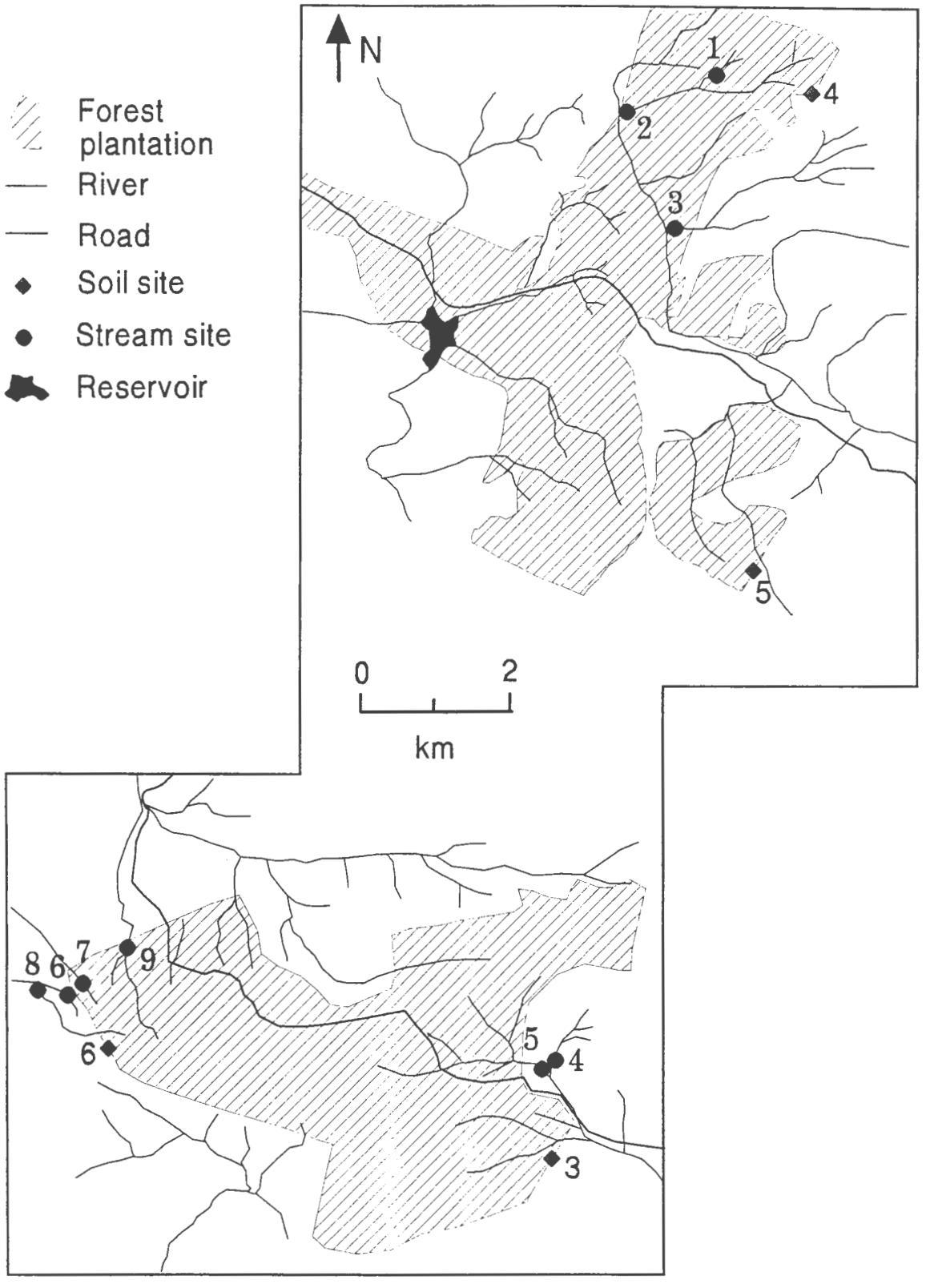

Figure A6: *Detailed locality map showing the main sampling area in the* ***western Cape*** *region (see Figure A5). The maps show the position of stream and soil sampling sites in relation to forestry areas, major roads and selected drainages. Site numbers are shown next to the sampling points.*

APPENDIX B: ANALYTICAL METHODS

Contents

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B1. INSTRUMENTAL PARAMETERS AND DATA QUALITY FOR ROUTINE MAJOR ELEMENT DETERMINATIONS BY WAVELENGTH DISPERSIVE XRF SPECTROMETRY - Extract from Willis, J.P. (1996), Information Circular No. 14, Department of Geological Sciences, University of Cape Town.

Nine major elements, Fe, Mn, Ti, Ca, K, P, Si, Al and Mg are determined using fusion disks prepared according to the method of Norrish and Hutton (1969). The disks are analyzed on a Philips PW1480 wavelength dispersive XRF spectrometer with a Mo/Sc x-ray tube. Fe, Mn and Ti are measured with the tube at 100 kV, 25 mA. The other elements are determined with the tube at 40 kV, 65 mA. Peak only measurements are made on the elements Fe through Mg. Sodium is determined using powder briquettes, the x-ray tube at 40 kV, 65 mA, and with backgrounds measured at -2.00 and +2.00°2θ from the peak position. Analytical conditions are given in Table 1.

Fusion disks made up with 100% Johnson Matthey Specpure SiO_2 are used as blanks for all elements except Si. Fusion disks made up from mixtures of Johnson Matthey Specpure Fe_2O_3 and $CaCO_3$ are used as blanks for Si. Intensity data are collected using the Philips X40 software. Matrix corrections are made on the elements Fe through Mg using the de Jongh model in the X40 software. Theoretical alpha coefficients used in the de Jongh model for all other elements on the analyte element are calculated using the Philips on-line ALPHAS programme. Na_2O is not included in the matrix corrections in de Jongh model, and no matrix corrections are made to the sodium intensities. First order calibration lines, with intercept, are calculated using all data points, including blanks.

Table B1: *Analytical conditions for determination of major elements using a Philips PW1480 WDXRF spectrometer.*

Element/ line	Collimator	Crystal	Detector	PHS LWL	PHS UPL	Counting time (s)	Concentration range *	RMS	No. of standards
FeKα	F	LiF(220)	FL	16	70	150	0 - 17	0.118	14
MnKα	F	LiF(220)	FL	15	70	150	0 - 0.22	0.005	14
TiKα	F	LiF(200)	FL	28	70	150	0 - 2.75	0.020	14
CaKα	F	LiF(200)	FL	36	70	20	0 - 12.5	0.037	14
K Kα	F	LiF(200)	FL	36	70	50	0 - 15.5	0.057	14
P Kα	C	GE(111)	FL	25	75	100	0 - 0.36	0.008	14
SiKα	C	PE(002)	FL	32	74	100	0 - 100	0.408	14
AlKα	C	PE(002)	FL	25	75	80	0 - 17.5	0.136	14
MgKα	F	PX-1	FL	30	74	150	0 - 46	0.095	14
NaKα	F	PX-1	FL	30	78	200	0 - 9	0.189	15

*=all concentrations expressed as wt% oxide

B2. MAJOR CATION AND ANION ANALYSIS BY HIGH PERFORMANCE ION CHROMATOGRAPHY

All major ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Mn^{2+} and Ca^{2+}) in saturated paste extracts and stream water samples were determined by High Performance Ion Chromatography (HPIC). Solutions were diluted with deionised water, where necessary, such that their EC values ranged from 50 to 100 $\mu S\,cm^{-1}$. All solutions were filtered through 0.45 μm membrane filters and Dionex On-Guard P filters for removal of organics. Analyses were carried out using a Dionex DX300 series suppressed IC system with a conductivity detector. The system is operated using the AI-450 chromatography software system.The analytical parameters are given in Table B2.

Table B2: *Analytical parameters for HPIC analysis of major anions and cations.*

	Anions	Cations
Guard column	HPIC-AG4A	HPIC CG12
Separator column	HPIC-S4A-SC	CS12
Eluent	1.8 mM Na_2CO_3; 1.70 mM $NaHCO_3$	20 mM methyl-sulphonic acid
Flow rate	2 ml $minute^{-1}$	1 ml $minute^{-1}$
Suppressor	anion micromembrane suppressor	cation micromembrane suppressor
Run time	8 minutes	15 minutes

B3. COLORIMETRIC DETERMINATION OF MONOMERIC ALUMINIUM USING Cr-AZUROL S

Monomeric Al in saturated paste extracts and stream waters was determined colorimetrically using Cr-Azurol S (CAS). The method is based on the work of Kennedy and Powell (1986).

All sample solutions were filtered through 0.45 μm membrane filters prior to analysis. An aliquot of sample was added to a small (50 ml) volumetric flask and made up to 11 ml with deionised water. The volume of sample used was based on the expected concentration of Al and was adjusted where necessary such that the final concentration (after dilution with H_2O) fell within the dynamic range for absorbance measurement (see below). Ten ml of each of the

reagents hexamine, ascorbic acid and CAS (preparation of reagents is described below) were added to the flask in quick succession. The solution was gently shaken to ensure complete mixing. The absorbance at 567 nm was measured after 20 minutes using a Sequoia-Turner model 340 spectrophotometer with a light path of 1 cm. The relationship between absorbance and Al concentration was found to be linear for absorbance readings ranging from 0.0 to 0.7. These correspond with solution Al concentrations (prior to addition of reagents) of between 0 and approximately 2 mg L^{-1}. Five standards (2, 5, 10, 15 and 20 mg L^{-1} Al) and a blank were used to calibrate the method. One ml of each standard was used and the volume was made up by adding 10 ml deionised water. A typical calibration curve is shown in Figure B1. In most cases, Al concentrations in the samples were lower than 1 mg L^{-1} and, therefore, 10 ml of sample and 1 ml of water was generally used. Thus for most samples there was a concentration factor of 10. This did not apply to samples SC4F and SC5F which had Al concentrations of 10.07 and 5.84 mg L^{-1}, respectively (only 1 ml of these samples was used). Samples were analysed in batches of 6 with a blank and at least three standards being run for each batch. Measurement of absorbance became unreliable below approximately 0.03 indicating that the lower limit of detection for this method is approximately 0.075 mg L^{-1}. The precision of the method, based on 12 duplicate determinations, is better than 10 % (average % difference between duplicates was 5.0 %).

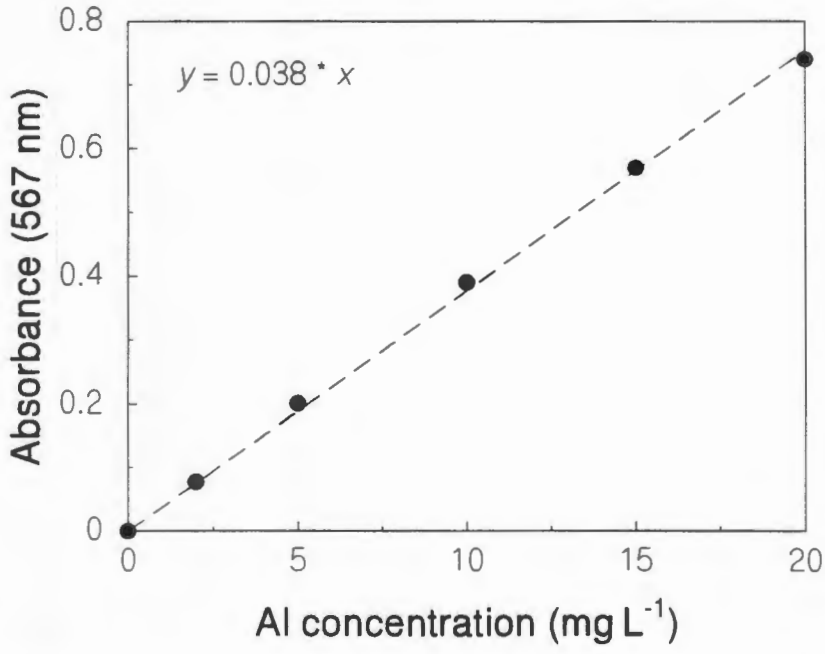

Figure B1: *Typical calibration curve for colorimetric determination of Al using the Cr-azurol S method.*

Preparation of reagents for Cr-azurol S method

Hexamine buffer (0.8 M)	- Dissolve 112.2 g hexamine in 800 ml deionised water. Adjust pH to 4.9 using concentrated HCl before making up to 1 L.
Ascorbic acid	- Dissolve 0.5 g ascorbic acid in 1 L of deionised water.
CAS	- Dissolve 0.0993 g of Cr-azurol in deionised water and make up to 1 L.

B4. ALKALINITY DETERMINATION BY GRAN TITRATION

The alkalinity of filtered stream water samples was determined using a Gran titration method (Gran, 1959). The principle and application of this method are given below.

In the absence of any weak acids other than the carbonate species and water, the total alkalinity of a solution can be expressed as:

$$Alk = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \quad \ldots\ (1).$$

Below a pH of ~ 6.3 the concentration of CO_3^{2-} and OH^- are negligible (Figure B1) and equation 1 becomes:

$$Alk = [HCO_3^-] - [H^+] \quad \ldots\ (2).$$

Below the $H_2CO_3^*$ equivalence point (Figure B2) the solution has negative alkalinity, i.e.:

$$[H^+] > [HCO_3^-] \quad \ldots\ (3).$$

The total alkalinity of a sample can, therefore, be determined by titration with a strong acid to the $H_2CO_3^*$ equivalence point and the alkalinity (in mol L^{-1}) will be given by the equation:

$$Alk = (v_f \times c_a) \div v_s \quad \ldots\ (4)$$

where: v_f = the volume of strong acid (ml) required to bring the sample to the $H_2CO_3^*$ equivalence point,

c_a = the normality of the strong acid used, and

v_s = the volume (in ml) of sample used for the titration.

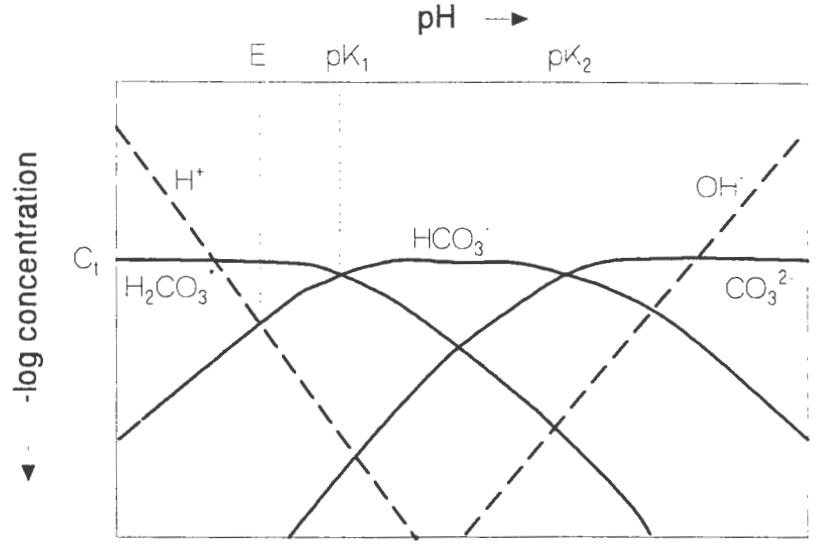

Figure B2: *Schematic diagram illustrating the relationship between pH and the concentration of the carbonate species, H^+ and OH^-. pK_1 - pH = ~ 6.3; pK_2 - pH = ~ 10.4; E - the $H_2CO_3^*$ equivalence point where $[H^+] = [HCO_3^-] + 2[CO_3^{2-}]$ (i.e. alkalinity = 0); c_t - total concentration of inorganic carbon. The diagram represents a closed system in which c_t is fixed. Variations in c_t cause vertical shifts of the carbonate lines but do not change their relative position.*

The pH of the equivalence point is generally not known for any particular sample as it varies with varying concentration of total inorganic carbon (C_t). The effect of C_t is particularly important for samples of low alkalinity. In this case, endpoint titrations are inappropriate and accurate determination of alkalinity can be undertaken by means of a gran function. This is derived as follows.

In the low pH region (i.e. pH < ~ 3.8), alkalinity at any point x in an alkalimetric titration is approximated by:

$$Alk_x \approx -[H^+]_x \quad \ldots . (5).$$

Also,

$$Alk_x = \{Alk_{sample} \times v_s/(v_s + v_x)\} - (v_x \times c_a)/(v_s + v_x) \quad \ldots . (6)$$

where v_x = the volume of strong acid required to bring the sample to some pH value (pH_x) below 3.8. Substituting equation 5 into 6 and simplifying,

$$(Alk_{sample} \times v_s)/(v_s + v_x) - (v_s \times c_a)/(v_s + v_x) = -[H^+]_x \quad \ldots . (7).$$

Combining equations 7 and 4 gives:

$$(v_f \times c_a)/(v_s + v_x) - (v_s \times c_a)/(v_s + v_x) = -10^{-pHx} \quad \ldots . (8),$$

that is,

$$c_a(v_f - v_x) = -10^{pHx}(v_s + v_x) = F_x \quad \ldots . (9).$$

Equation 9 is the Gran function and v_f is determined by solving this function for a number of different pH_x and v_x values obtained by stepwise titration. Strong acid is initially added to the sample until a pH of approximately 3.8 is attained. Thereafter, approximately 3 to 4 aliquots of acid are added ultimately lowering the pH to approximately 3.2. After each aliquot is added the pH (pH_x) and the total volume of acid added (v_x) is noted.

At $F_x = 0$, v_f is equal to v_x. Because the relationship between v_x and F_x is approximately linear in the pH range below 3.8 (Figure B3), v_f can be obtained graphically by extrapolating the linear portion of the F_x function to the intercept with the v_x axis (i.e. $F_x = 0$; see Figure B3). the alkalinity of the sample can then be calculated from equation 4 using the value obtained for v_f.

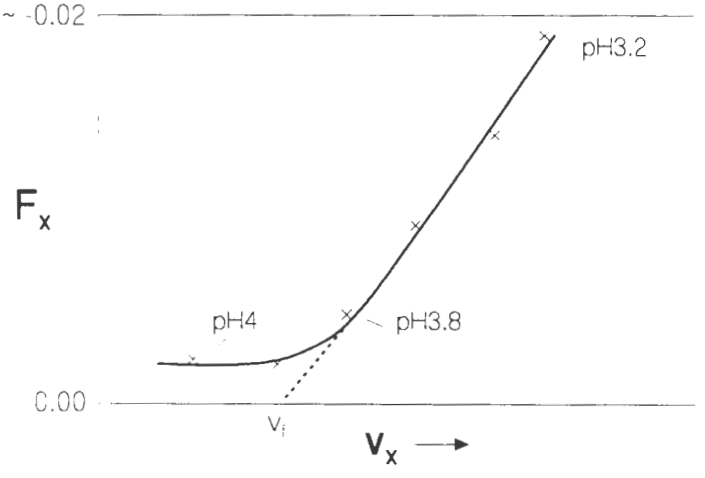

Figure B3: *Schematic diagram illustrating the relationship between F_x, v_x and pH. The volume of strong acid (v_f) required to bring the sample to the $H_2CO_3^*$ equivalence point (i.e. to neutralise all alkalinity) is obtained by extrapolation of the linear portion of the function to the intercept on the v_x axis ($F_x = 0$).*

For this study, stepwise titrations for determining alkalinity were carried out using a Radiometer ABU80 autoburette and TTT85 titrator. A sample volume of 5 or 10 ml was used and titrations were carried out with 0.01 or 0.005 M HCl (depending on the amount of alkalinity present in the sample). The samples were titrated down to a pH of 4 followed by increments of 0.2 pH units down to a pH of 3.2. The lower limit of detection for this method was found to be ~ 20 $\mu mol_c\ L^{-1}$.

APPENDIX C: DATA TABLES

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Table C1: Bulk properties and pH of soil samples. f = forest soil, v = virgin soil. Blank values - not determined.

Site	Specific gravity		Clay (%)		Organic carbon (%)		pH_{aq}		pH_{KCl}		pH_{aq}-pH_{KCl}	
	f	v	f	v	f	v	f	v	f	v	f	v
Eastern escarpment												
2	1.25	1.15	6.6	7.7	1.96	3.96	4.57	5.09	3.97	4.25	0.60	0.84
3	1.42	1.27	1.8	5.5	1.60	3.56	4.44	4.96	3.60	4.15	0.84	0.81
4	0.99	0.96			3.49	4.37	4.64	5.14	3.94	4.30	0.70	0.84
5	0.99	0.93	26	30	3.16	5.53	4.69	5.40	4.08	4.31	0.61	1.09
6	0.88	0.89	27	25	7.08	12.0	4.59	5.13	4.01	4.14	0.58	0.99
7	0.97	0.97	35	38	5.95	6.28	4.29	5.17	4.06	4.24	0.23	0.93
8	0.76	0.83	32	36	8.47	7.76	4.36	5.32	4.12	4.42	0.24	0.90
9	1.10	1.14	12	8.6	7.13	4.26	4.53	5.05	3.89	4.19	0.64	0.86
11	0.97	0.95	30	30	7.50	6.99	4.84	5.28	4.07	4.47	0.77	0.81
12	1.00	0.93	30	30	4.66	4.03	4.69	5.20	4.08	4.33	0.61	0.87
13	0.96	1.02	25	25	4.46	6.72	4.62	5.00	4.02	4.33	0.60	0.67
14	1.03	0.96	25	25	6.24	6.21	4.68	4.97	4.04	4.20	0.64	0.77
Midlands												
1	1.04	1.06	40	40	4.05	4.96	4.92	5.27	3.94	4.14	0.98	1.13
2	1.01	0.99	35	35	4.68	5.12	4.61	4.92	4.06	4.14	0.55	0.78
11	0.93	0.97	50	50	5.70	5.80	4.80	5.18	4.17	4.50	0.63	0.68
12	0.95	0.93	40	40	5.91	6.00	4.58	5.27	3.71	4.03	0.87	1.24
13	0.99	0.96	40	40	4.11	4.68	4.64	4.82	3.83	4.05	0.81	0.77
14	0.94	0.87	35	35	5.59	6.35	4.66	4.94	4.00	4.17	0.66	0.77
15	1.02	0.98	40	40	4.02	4.67	4.55	4.89	3.95	4.25	0.60	0.64
16	1.05	0.99	55	55	3.73	4.28	4.87	5.35	4.08	4.45	0.79	0.90
21	0.93	0.89	35	35	6.36	7.96	4.80	5.41	3.97	4.23	0.83	1.18
22	0.97	0.99	55	55	4.56	4.44	5.25	5.66	3.85	4.19	1.40	1.47
23	0.87	0.92	25	25	8.08	6.93	4.95	5.65	3.90	4.38	1.05	1.27
24	0.81	0.89	30	30	9.94	9.70	5.28	5.70	4.12	4.26	1.16	1.44
25	0.99	0.97	45	45	4.28	5.66	4.91	5.11	3.95	4.19	0.96	0.92
26	0.95	0.93	40	40	6.21	5.61	5.31	5.36	4.33	4.33	0.98	1.03
Southern Cape												
1	1.14	1.13	9.8	8.7	1.99	2.23	5.27	5.56	4.19	4.42	1.08	1.14
2	1.12	1.12	12	11	2.99	2.64	4.96	5.52	3.80	4.15	1.16	1.37
3	1.29	1.12	11	11	1.85	2.65	5.26	5.48	4.06	4.12	1.20	1.36
4	1.05	0.95	7.0	8.8	4.80	6.58	4.17	4.28	3.24	3.23	0.93	1.05
5	1.34	1.13	1.6	4.2	1.50	1.46	4.34	4.41	3.82	3.09	0.52	1.32
6	1.45	1.19	2.0	4.1	1.25	2.30	4.33	4.59	3.33	3.46	1.00	1.13
Western Cape												
1	1.50	1.50	0.5	0.5	0.44	0.78	4.62	4.97	3.79	4.44	0.83	0.53
2	1.50	1.49	3.1	1.5	0.26	0.18	4.92	5.28	4.34	4.54	0.58	0.74
3	1.48	1.52			2.08	1.11	4.52	5.10	2.97	3.54	1.55	1.56
4	1.30	1.45	2.7	1.4	1.75	1.51	4.58	4.49	3.11	3.36	1.47	1.13
5	1.46	1.40	2.3	4.0	0.73	0.86	5.74	5.67	4.10	4.41	1.64	1.26
6	1.32	1.43	2.7	1.8	1.57	1.59	4.35	4.79	2.83	3.38	1.52	1.41

Table C2: *Concentrations of major and minor elements (expressed as weight % oxides) in the bulk soil. CIA = chemical index of alteration (100 x $Al_2O_3/[Al_2O_3+CaO+Na_2O+K_2O]_{molar\ ratio}$). LOI = loss on ignition. f = forest soil, v = virgin soil. bld = below limit of detection.*

Site	Type	CIA	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	LOI	Total
Eastern escarpment															
2	f	88.9	90.82	0.42	1.32	0.60	0.00	0.01	0.02	0.05	0.05	0.05	0.96	5.77	100.08
2	v	89.6	85.31	0.57	1.84	1.19	0.01	0.01	0.02	0.06	0.07	0.07	2.06	8.69	99.89
3	f	80.4	95.07	0.23	0.60	0.83	0.01	bld	0.01	0.05	0.04	0.03	0.33	2.76	99.92
3	v	87.6	90.14	0.31	1.40	0.93	0.00	bld	0.02	0.05	0.07	0.04	0.99	5.82	99.77
4	f	93.1	53.15	0.79	10.56	9.90	0.03	0.07	0.04	0.08	0.54	0.12	4.12	20.03	99.42
4	v	98.2	52.35	1.72	15.76	10.44	0.07	0.12	0.03	0.04	0.16	0.10	3.21	16.18	100.16
5	f	95.9	59.52	1.01	14.20	8.00	0.04	0.23	0.02	0.05	0.45	0.09	3.06	13.33	99.98
5	v	94.6	52.29	1.00	14.68	7.70	0.05	0.28	0.04	0.05	0.63	0.11	6.01	16.76	99.59
6	f	88.9	42.42	0.81	14.29	14.90	0.02	0.13	0.05	0.23	1.22	0.19	6.27	18.78	99.29
6	v	94.2	50.89	1.01	15.76	8.15	0.04	0.34	0.12	0.09	0.55	0.12	5.02	17.39	99.47
7	f	97.8	42.33	0.90	16.86	13.31	0.10	0.18	0.06	0.05	0.17	0.14	5.65	19.91	99.66
7	v	97.4	46.11	0.79	15.93	12.07	0.09	0.21	0.07	0.05	0.20	0.14	5.57	18.60	99.79
8	f	96.7	38.71	1.05	14.77	9.25	0.12	0.28	0.05	0.06	0.29	0.14	6.89	27.95	99.56
8	v	96.3	38.76	1.06	16.90	10.14	0.17	0.38	0.05	0.08	0.40	0.14	7.30	23.60	98.97
11	f	95.4	52.18	1.29	14.08	12.11	0.05	0.07	0.02	0.07	0.48	0.15	3.49	15.36	99.34
11	v	93.4	53.39	0.79	10.61	9.93	0.03	0.07	0.04	0.08	0.52	0.12	4.12	20.03	99.71
Midlands															
12	f	95.4	49.61	1.02	16.13	7.79	0.03	0.34	0.07	0.06	0.51	0.11	5.94	17.38	98.97
12	v	94.3	50.88	1.01	15.74	8.14	0.04	0.35	0.12	0.09	0.55	0.12	5.02	17.39	99.43
14	f	96.3	43.97	1.18	18.70	9.30	0.04	0.29	0.07	0.07	0.45	0.13	5.18	19.76	99.13
14	v	96.7	44.18	1.20	18.64	9.49	0.04	0.28	0.06	0.07	0.38	0.13	5.09	19.68	99.24
23	f	96.2	42.07	1.20	19.22	9.28	0.04	0.38	0.07	0.07	0.48	0.17	5.57	21.58	100.13
23	v	81.5	39.05	1.29	20.03	11.20	0.06	0.39	0.13	2.45	0.27	0.14	4.59	21.74	101.32
25	f	75.3	48.78	1.58	16.57	9.93	0.03	0.20	0.66	2.44	0.20	0.11	3.10	17.11	100.69
25	v	74.6	48.50	1.58	17.03	9.69	0.03	0.23	0.10	3.30	0.19	0.11	3.13	18.96	102.82
26	f	79.9	33.69	1.64	23.03	13.97	0.04	0.29	0.12	3.29	0.15	0.14	7.63	18.88	102.85
26	v	80.3	34.45	1.63	23.57	14.29	0.04	0.30	0.12	3.28	0.15	0.14	6.73	18.16	102.85
Southern Cape															
1	f	80.3	86.34	0.43	4.25	1.12	0.00	0.08	0.06	0.22	0.53	0.03	1.15	5.73	99.92
1	v	80.8	86.47	0.42	4.10	1.62	0.01	0.06	0.07	0.17	0.53	0.05	1.08	5.06	99.64
3	f	82.1	87.30	0.39	3.74	0.99	0.00	0.10	0.10	0.23	0.24	0.03	1.24	5.28	99.63
4	f	77.3	86.13	0.85	1.43	0.89	0.01	0.02	0.03	0.12	0.16	0.02	1.49	8.89	100.02
4	v	75.0	82.25	0.77	1.43	0.48	0.00	0.02	0.04	0.13	0.17	0.03	2.21	12.27	99.80
Western Cape															
2	f	66.0	93.80	0.24	0.52	0.73	0.01	bld	0.05	0.05	0.09	0.01	0.56	3.88	99.91
2	v	67.6	95.85	0.23	0.47	0.59	0.00	bld	0.02	0.05	0.10	0.03	0.31	2.18	99.78
3	f	75.0	82.16	0.77	1.43	0.48	0.00	0.02	0.04	0.13	0.18	0.03	2.21	12.27	99.72
3	v	81.6	95.56	0.27	1.49	0.32	0.00	bld	0.02	0.12	0.09	0.01	0.23	1.73	99.81

Table C3: *Exchangeable cation (NH_4-acetate extracts) and acidity (KCl extracts) concentrations ($mmol_c$ per L soil), effective cation exchange capacity (ECEC = sum of exchangeable bases and acidity) and base saturation (BS = 100 x [base cations/ECEC]). Blank values = not determined.*

Site	Ca^{2+}		Mg^{2+}		Na^{+}		K^{+}		Acidity		ECEC		BS (%)	
	f	v	f	v	f	v	f	v	f	v	f	v	f	v
Eastern escarpment														
2	1.50	1.73	0.63	1.04	1.13	1.04	0.75	1.15	37.9	24.6	41.9	29.5	9.55	16.81
3	1.28	1.65	0.57	1.02	0.57	0.76	0.43	1.27	29.0	28.1	31.9	32.8	8.93	14.31
4	2.18	3.18	0.99	2.31	0.79	1.35	4.36	1.64	20.8	9.84	29.1	18.3	28.54	46.25
5	1.49	3.18	0.79	2.24	0.79	1.03	0.40	1.50	16.1	8.81	19.6	16.8	17.76	47.43
6	0.79	2.40	0.97	1.78	0.79	0.98	0.88	2.32	28.8	22.0	32.2	29.5	10.65	25.39
7	3.10	8.33	1.94	5.91	0.87	0.97	1.16	2.42	28.2	15.8	35.2	33.4	20.10	52.73
8	1.14	2.16	0.91	2.24	0.99	1.00	0.76	1.58	16.3	9.28	20.1	16.3	18.95	42.94
9		1.72		1.49		0.09		1.37	45.8	29.8		34.4		13.56
11	1.90	2.10	1.40	1.70	1.80	1.20	2.00	1.20	15.4	6.20	22.5	12.4	31.56	50.00
12	2.10	2.50	1.20	1.70	1.10	1.00	2.10	0.90	17.7	9.10	24.2	15.2	26.86	40.13
13	1.50	4.20	1.20	2.30	1.70	1.60	3.30	1.10	20.3	11.2	28.0	20.4	27.50	45.10
14									25.3	17.6				
Midlands														
1	14.9	17.8	8.61	7.64	1.35	1.27	3.11	2.76	43.6	25.2	71.6	54.7	39.10	53.95
2									33.8	25.1				
11	3.10	10.1	4.40	9.20	1.30	1.10	2.40	1.70	20.2	5.30	31.4	27.4	35.67	80.66
12	6.70	14.7	3.60	5.30	1.00	1.00	7.60	2.10	55.2	27.9	74.1	51.0	25.51	45.29
13									49.5	32.7				
14	6.50	5.90	4.20	4.00	1.30	1.80	5.60	5.00	32.6	22.3	50.2	39.0	35.06	42.82
15	0.90	3.80	1.80	26.3	1.30	1.10	2.50	2.40	26.6	14.4	33.1	48.0	19.64	70.00
16	7.70	35.0	5.60	30.1	0.90	0.90	3.30	1.90	22.2	7.10	39.7	75.0	44.08	90.53
21									24.5	14.1				
22	32.2	38.1	21.5	14.1	1.00	0.80	7.00	3.90	13.8	5.70	75.5	62.6	81.72	90.89
23	5.60	18.9	6.60	13.6	1.10	1.20	6.00	4.10	37.6	8.00	56.9	45.8	33.92	82.53
24									22.6	13.9				
25	4.70	12.3	4.60	9.50	1.70	2.30	3.50	1.90	31.4	13.5	45.9	39.5	31.59	65.82
26	21.6	12.5	12.7	5.00	2.00	2.10	3.20	3.30	10.4	2.30	49.9	25.2	79.16	90.87
Southern Cape														
1	12.8	13.9	6.97	6.45	2.17	2.38	1.14	1.59	15.6	8.20	38.7	32.5	59.67	74.79
2	8.73	13.8	10.1	12.1	2.57	2.57	0.90	0.78	33.0	14.7	55.3	44.0	40.29	66.50
3	19.5	19.6	10.8	12.2	2.32	1.88	0.77	1.41	15.3	10.2	48.7	45.4	68.55	77.46
4	1.58	3.79	1.89	6.16	1.79	1.71	0.53	1.71	54.4	40.6	60.2	53.9	9.61	24.79
5	1.07	5.63	1.47	3.60	1.47	1.58	0.40	0.68	16.7	10.2	21.1	21.7	20.95	52.88
6	2.46	4.87	1.59	3.57	1.88	1.90	0.29	0.83	20.6	22.3	26.8	33.4	23.18	33.42
Western Cape														
1	4.65	4.95	2.40	2.25	2.10	1.50	0.60	0.45	6.53	4.67	16.3	13.8	59.91	66.21
2	2.25	2.09	1.50	1.19	1.50	1.19	0.60	0.30	11.0	5.61	16.8	10.4	34.78	45.95
3	7.57	1.82	2.82	3.94	1.04	3.18	1.04	0.61	9.80	5.69	22.3	15.2	55.99	62.67
4	12.3	7.52	8.04	4.05	2.59	1.30	0.78	0.72	10.0	14.5	33.8	28.1	70.26	48.32
5	8.89	6.32	4.37	3.23	1.31	0.14	0.44	0.70	6.16	4.54	21.2	14.9	70.91	69.61
6	4.50	10.0	6.36	4.58	2.65	1.58	1.59	0.86	24.9	7.74	40.0	24.8	37.74	68.76

Table C4: *Composition of saturated paste extracts - dataset 1 (sampled, extracted and analysed in 1995; all sites). S/W = soil/water ratio at saturation (g/ml); EC = electrical conductivity ($\mu S\,cm^{-1}$). Ion concentrations are in $mmol_c L^{-1}$. DOC = dissolved organic carbon ($mg\,L^{-1}$). R^- = estimated concentration of organic anions ($mmol_c L^{-1}$, based on DOC/charge relationships - see section 6.3.2 for details).*

Site	Type	S/W	EC	Cl^-	NO_3^-	DOC	R^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Mn^{2+}	Ca^{2+}
Eastern escarpment														
2	f	3.2	202	0.619	0.637	230	0.529	0.185	0.867	0.231	0.209	0.430	0.031	0.306
2	v	2.7	152	0.643	0.022	195	0.449	0.293	0.402	0.426	0.309	0.147	0.041	0.122
3	f	4.6	119	0.238	0.315	95	0.219	0.171	0.329	0.175	0.127	0.271	0.014	0.189
3	v	3.2	151	0.549	0.024	399	0.918	0.275	0.339	0.308	0.415	0.180	0.013	0.161
4	f	2.2	109	0.454	0.061	120	0.276	0.190	0.456	0.113	0.090	0.143	0.020	0.193
4	v	1.8	93	0.270	0.022	215	0.495	0.084	0.302	0.278	0.126	0.085	0.024	0.119
5	f	2.6	177	0.359	0.026	99	0.228	0.154	0.308	0.089	0.069	0.125	0.014	0.156
5	v	2.1	89	0.551	0.034	50	0.115	0.108	0.276	0.254	0.128	0.076	0.024	0.102
6	f	1.8	101	0.235	0.094	99	0.228	0.119	0.232	0.101	0.059	0.186	0.018	0.108
6	v	1.6	146	0.680	0.027	115	0.265	0.288	0.279	0.668	0.292	0.123	0.000	0.134
7	f	1.7	452	0.245	2.654	185	0.426	0.085	0.527	0.313	0.565	1.618	0.929	1.029
7	v	1.9	147	0.653	0.027	285	0.656	0.144	0.377	0.246	0.303	0.496	0.178	0.304
8	f	1.4	280	0.506	1.418	155	0.357	0.051	0.634	0.321	0.154	0.960	0.375	0.323
8	v	1.6	101	0.521	0.025	200	0.460	0.069	0.431	0.248	0.174	0.209	0.168	0.101
9	f	2.3	181	0.577	0.525	200	0.460	0.104	0.685	0.229	0.205	0.458	0.099	0.225
9	v	2.7	116	0.482	0.025	280	0.644	0.193	0.412	0.248	0.293	0.240	0.041	0.141
11	f	1.8	173	0.400	0.068	384	0.883	0.298	0.456	0.477	0.115	0.241	0.337	0.299
11	v	1.8	150	0.421	0.055	351	0.807	0.180	0.415	0.350	0.200	0.304	0.104	0.324
12	f	2.1	213	0.373	0.413	320	0.736	0.337	0.413	0.508	0.100	0.351	0.886	0.440
12	v	2.2	155	0.513	0.041	300	0.690	0.127	0.338	0.559	0.151	0.157	0.258	0.179
13	f	2.1	228	0.489	0.064	435	1.001	0.453	0.582	1.068	0.177	0.289	0.031	0.377
13	v	1.8	205	0.682	0.060	530	1.219	0.172	0.480	0.788	0.283	0.369	0.089	0.351
14	f	2.3	227	0.541	0.219	490	1.127	0.309	0.456	0.646	0.294	0.751	0.114	0.493
14	v	2.2	209	0.875	0.159	310	0.713	0.225	0.525	0.693	0.257	0.391	0.027	0.309
Southern Cape														
1	f	2.6	311	1.654	0.066	280	1.428	0.635	1.367	0.077	0.110	1.061	0.046	0.721
1	v	2.5	266	1.283	0.035	220	1.122	0.394	1.283	0.108	0.271	0.933	0.000	0.617
2	f	2.7	334	1.638	0.000	205	1.046	0.746	1.955	0.089	0.141	1.540	0.000	0.714
2	v	2.6	189	0.698	0.021	205	1.046	0.247	1.248	0.073	0.067	0.752	0.000	0.343
3	f	3.3	410	2.728	0.000	288	1.469	0.656	1.617	0.061	0.089	1.728	0.674	1.226
3	v	3.0	238	0.738	0.034	170	0.867	0.410	0.609	0.069	0.081	0.447	0.030	0.365
4	f	2.5	268	1.130	0.077	270	1.377	0.419	1.231	0.231	0.104	0.549	0.029	0.441
4	v	1.8	265	0.772	0.188	635	3.239	0.368	0.994	0.225	0.290	0.828	0.000	0.388
5	f	3.5	220	1.410	0.180	185	0.944	0.398	1.639	0.270	0.225	0.516	0.000	0.376
5	v	2.5	233	0.785	0.038	185	0.944	0.406	0.818	0.570	0.135	0.300	0.010	0.266
6	f	4.9	244	0.948	0.051	250	1.275	0.266	1.007	0.195	0.130	0.459	0.034	0.310
6	v	2.7	206	0.793	0.039	305	1.556	0.546	1.385	0.291	0.399	0.751	0.000	0.586

Table C4 continued:

Site	Type	S/W	EC	Cl^-	NO_3^-	DOC	R^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Mn^{2+}	Ca^{2+}
Midlands														
1	f	2.2	110	0.246	0.331	177	0.407	0.138	0.191	0.023	0.098	0.384	0.026	0.401
1	v	2.1	169	0.614	0.024	470	1.081	0.055	0.438	0.071	0.181	0.978	0.071	0.633
2	f	2.1	379	1.437	1.267	95	0.219	0.118	0.957	0.097	0.682	1.226	0.196	0.843
2	v	2.1	301	0.500	1.194	105	0.242	0.105	0.268	0.228	0.653	1.064	0.142	0.711
11	f	1.9	201	0.595	0.166	400	0.920	0.388	0.441	0.666	0.136	0.283	0.061	0.207
11	v	2.0	147	0.402	0.035	420	0.966	0.074	0.439	0.448	0.145	0.234	0.082	0.191
12	f	2.2	175	0.252	0.100	441	1.014	0.118	0.358	0.473	0.155	0.562	0.088	0.791
12	v	2.0	198	0.478	0.111	804	1.849	0.076	0.317	0.184	0.273	0.845	0.102	0.669
13	f	2.4	186	0.553	0.117	426	0.980	0.217	0.376	0.228	0.180	0.662	0.148	0.585
13	v	2.1	154	0.600	0.032	420	0.966	0.085	0.349	0.268	0.176	0.443	0.038	0.299
14	f	1.8	357	1.498	0.295	510	1.173	0.401	0.473	0.813	0.524	0.709	0.263	0.674
14	v	1.8	292	0.801	0.716	510	1.173	0.156	0.305	0.894	0.456	0.488	0.066	0.348
15	f	2.2	247	1.065	0.063	395	0.909	0.264	0.888	0.680	0.157	0.427	0.115	0.379
15	v	2.0	201	0.796	0.076	515	1.185	0.170	0.500	0.579	0.327	0.410	0.099	0.426
16	f	2.2	137	0.477	0.168	165	0.380	0.193	0.390	0.213	0.146	0.243	0.029	0.273
16	v	2.0	136	0.468	0.033	267	0.614	0.146	0.292	0.151	0.115	0.461	0.090	0.431
21	f	2.0	334	0.936	0.517	405	0.932	0.438	0.561	0.756	0.328	0.930	0.120	0.613
21	v	1.8	282	1.249	0.046	675	1.553	0.245	0.475	0.713	0.428	0.923	0.134	0.572
22	f	2.5	351	0.892	0.591	775	1.783	0.281	0.509	0.510	0.285	1.424	0.152	1.221
22	v	2.0	341	0.669	0.045	1070	2.461	0.478	0.475	0.083	0.273	2.403	0.116	1.476
23	f	1.7	291	0.878	0.325	540	1.242	0.185	0.359	0.761	0.317	0.747	0.087	0.446
23	v	1.7	278	1.133	0.060	670	1.541	0.231	0.311	0.503	0.524	0.882	0.094	0.690
24	f	1.5	246	0.985	0.057	420	0.966	0.338	0.622	0.662	0.087	0.604	0.021	0.503
24	v	1.5	322	1.408	0.041	600	1.380	0.284	0.510	0.974	0.302	0.905	0.053	0.677
25	f	2.5	178	0.714	0.045	375	0.863	0.190	0.641	0.291	0.155	0.415	0.050	0.363
25	v	1.8	232	0.777	0.127	630	1.449	0.153	0.612	0.399	0.257	0.806	0.039	0.530
26	f	1.9	242	0.709	0.116	430	0.989	0.453	0.746	0.318	0.219	0.566	0.040	0.724
26	v	2.1	150	0.522	0.033	396	0.911	0.064	0.344	0.469	0.158	0.279	0.019	0.279
Western Cape														
1	f	4.5	190	0.773	0.000	129	0.658	0.158	0.953	0.000	0.098	0.348	0.008	0.214
1	v	4.2	127	0.353	0.025	112	0.571	0.164	0.556	0.059	0.133	0.260	0.000	0.209
2	f	5.0	361	2.458	0.072	225	1.148	0.361	1.999	0.087	0.195	1.034	0.000	0.561
2	v	4.9	116	0.522	0.118	72	0.367	0.165	0.578	0.083	0.144	0.257	0.008	0.157
3	f	4.2	284	1.497	0.000	120	0.612	0.364	1.321	0.000	0.271	0.531	0.000	0.337
3	v	4.4	150	0.397	0.035	81	0.413	0.322	0.556	0.056	0.119	0.244	0.006	0.207
4	f	4.2	249	1.013	0.000	245	1.250	0.301	1.410	0.028	0.128	0.551	0.044	0.509
4	v	4.4	136	0.528	0.032	81	0.413	0.413	0.519	0.145	0.145	0.253	0.020	0.205
5	f	4.2	177	0.661	0.038	160	0.816	0.259	0.889	0.067	0.121	0.513	0.000	0.447
5	v	4.5	161	0.655	0.059	126	0.643	0.394	0.669	0.131	0.166	0.272	0.053	0.271
6	f	4.0	266	1.029	0.000	325	1.658	0.317	1.545	0.047	0.164	0.462	0.023	0.382
6	v	4.1	232	0.899	0.044	125	0.638	0.641	0.832	0.254	0.257	0.362	0.181	0.326

Table C5: *Composition of saturated paste extracts - dataset 2 (extracted and analysed in 1996; selected sites only). Asterisks denote samples that were taken in 1996. The remaining analyses were carried out on stored samples that were taken in 1995 (i.e. the same samples used to generate data shown in Table C4). S/W = soil/water ratio at saturation (g/ml); EC = electrical conductivity ($\mu S\,cm^{-1}$). Ion concentrations are in $mmol_c\,L^{-1}$. DOC = dissolved organic carbon ($mg\,L^{-1}$). Al = monomeric Al ($mmol_c\,L^{-1}$). Si = monomeric silica ($mmol\,L^{-1}$).*

Site	Type	S/W	pH	EC	Cl^-	NO_3^-	SO_4^{2-}	DOC	Na^+	NH_4^+	K^+	Mg^{2+}	Mn^{2+}	Ca^{2+}	Al	Si
Eastern escarpment																
2*	f	3.72	4.65	184	0.549	0.439	0.242	282	1.407	0.190	0.214	0.359	0.000	0.242	0.097	0.133
2*	v	2.62	5.17	141	0.517	0.221	0.264	290	0.471	0.528	0.302	0.179	0.000	0.142	0.031	0.059
4*	f	2.13	5.34	95	0.285	0.281	0.139	122	0.405	0.038	0.064	0.224	0.011	0.194	0.015	0.092
4*	v	1.74	5.19	102	0.439	0.013	0.090	160	0.406	0.475	0.138	0.148	0.004	0.112	0.008	0.016
5	f	2.30	5.00	142	0.683	0.050	0.141	162	0.545	0.196	0.445	0.213	0.015	0.152	0.018	0.063
5	v	1.94	5.56	129	0.555	0.004	0.121	163	0.470	0.801	0.148	0.166	0.011	0.133	0.005	0.041
6	f	1.62	4.76	101	0.296	0.150	0.143	193	0.338	0.323	0.065	0.255	0.008	0.151	0.156	0.057
6	v	1.49	5.46	191	0.730	0.088	0.330	210	0.341	0.781	0.211	0.540	0.015	0.264	0.042	0.040
7*	f	1.71	4.96	182	0.199	0.897	0.087	80	0.315	0.299	0.146	0.766	0.071	0.470	0.032	0.106
7*	v	1.90	5.64	85	0.403	0.005	0.111	67	0.298	0.278	0.123	0.262	0.025	0.168	0.003	0.050
8	f	1.38	4.51	287	0.598	1.095	0.114	226	0.802	0.635	0.154	0.978	0.440	0.380	0.180	0.089
8	v	1.50	5.43	118	0.525	0.000	0.065	345	0.559	0.552	0.155	0.217	0.075	0.121	0.008	0.029
9*	f	2.27	4.68	137	0.225	0.352	0.031	162	0.520	0.244	0.155	0.484	0.047	0.195	0.084	0.063
9*	v	2.32	5.30	117	0.548	0.004	0.117	181	0.471	0.477	0.284	0.257	0.022	0.155	0.018	0.037
Midlands																
1	f	2.11	4.90	162	0.471	0.450	0.196	264	0.445	0.013	0.281	0.769	0.040	0.590	0.030	0.116
1	v	1.97	5.08	173	0.471	0.000	0.090	761	0.646	0.186	0.149	1.170	0.036	0.653	0.016	0.085
2	f	2.02	4.65	386	1.454	1.244	0.127	185	1.044	0.174	0.709	1.539	0.145	0.867	0.082	0.102
2	v	2.00	4.95	353	0.737	1.346	0.155	237	0.548	0.610	0.853	1.605	0.096	0.900	0.025	0.079
Southern Cape																
1	f	2.64	5.05	342	1.512	0.047	0.607	335	1.833	0.366	0.000	2.030	0.033	0.962	0.196	0.062
1	v	2.42	5.47	281	1.153	0.014	0.451	342	1.326	0.411	0.329	1.629	0.000	0.890	0.106	0.039
3	f	3.23	4.94	430	1.948	0.017	0.625	471	1.935	0.219	0.074	2.073	0.000	1.181	0.136	0.110
3	v	2.73	5.08	262	0.795	0.017	0.377	454	1.334	0.610	0.151	1.420	0.000	0.768	0.087	0.074
4	f	2.36	3.68	346	1.255	0.040	0.601	508	1.402	0.496	0.117	1.071	0.000	0.328	1.119	0.043
4	v	1.68	3.84	317	1.158	0.016	0.586	910	1.291	0.606	0.345	1.574	0.000	1.972	0.238	0.033
5	f	3.34	3.70	255	0.820	0.010	0.311	350	1.143	0.162	0.132	0.569	0.000	0.252	0.649	0.019
5	v	2.31	3.77	313	0.850	0.008	0.546	487	1.182	0.742	0.215	0.829	0.000	0.406	0.208	0.021
Western Cape																
4	f	3.70	4.01	303	0.999	0.014	0.397	407	1.773	0.000	0.129	0.992	0.000	0.539	0.070	0.021
4	v	3.79	4.34	184	0.555	0.000	0.421	223	0.809	0.000	0.191	0.560	0.000	0.304	0.047	0.014
5	f	3.61	5.01	217	0.841	0.019	0.251	239	1.258	0.031	0.147	1.033	0.000	0.655	0.165	0.032
5	v	4.46	5.38	195	0.669	0.030	0.349	212	1.021	0.120	0.217	0.916	0.000	0.534	0.086	0.033

Table C6: *Phosphate extractable SO_4^{2-} and KCl extractable Mn^{2+} ($mmol_c\ kg^{-1}$). Analyses carried out on the same set of samples used for the 1996 saturated paste extracts (Table C5). Asterisks denote samples taken in 1996. All other analyses were carried out on stored 1995 samples.*

Site	Type	SO_4^{2-}	Mn^{2+}
Eastern escarpment			
2*	f	0.240	0.078
2*	v	0.134	0.103
4*	f	3.939	0.273
4*	v	0.767	0.308
5	f	5.310	0.214
5	v	0.534	0.415
6	f	7.552	0.114
6	v	2.604	0.162
7*	f	6.344	1.040
7*	v	1.583	0.383
8	f	7.379	1.790
8	v	2.619	1.350
9*	f	2.340	0.180
9*	v	0.680	0.160
Midlands			
1	f	1.442	0.663
1	v	0.006	0.653
2	f	5.125	0.854
2	v	0.209	0.893
Southern Cape			
1	f	0.576	0.122
1	v	0.359	0.107
3	f	0.386	0.135
3	v	0.298	0.101
4	f	0.291	0.092
4	v	0.210	0.100
5	f	0.172	0.087
5	v	0.341	0.095
Western Cape			
4	f	0.215	0.091
4	v	0.199	0.096
5	f	0.197	0.099
5	v	0.271	0.093

Table C7: *The pH and estimated concentrations (mmol L^{-1}) of chemical species in saturated paste extracts calculated on a DOM-free basis (i.e. dissolved organic matter excluded from calculations). Calculations were based on the composition of saturated paste extracts obtained in 1996 (Table C5) and were carried out using MINTEQA2 (see section 6.2.4 for details). Elements which occur predominantly (> 99 %) in free ionic form and complexes occurring in very low concentrations (< 10^{-3} mmol L^{-1}) are excluded.*

Site	Type	pH	SO_4^{2-}	Mg^{2+}	$MgSO_4$	Ca^{2+}	$CaSO_4$	Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	$AlSO_4^+$	H_4SiO_4
Eastern escarpment												
2	f	4.63	0.112	0.179	0.002	0.121	0.002	0.020	0.007	0.002	0.004	0.132
2	v	5.15	0.249	0.172	0.005	0.138	0.005	0.009	0.010	0.010	0.004	0.176
4	f	5.32	0.131	0.223	0.004	0.191	0.004	0.003	0.005	0.007	0.001	0.277
4	v	5.17	0.086	0.147	0.002	0.111	0.001	0.002	0.002	0.003	0.000	0.025
5	f	4.98	0.133	0.211	0.003	0.150	0.003	0.007	0.006	0.004	0.002	0.189
5	v	5.54	0.116	0.162	0.002	0.130	0.002	0.000	0.001	0.002	0.000	0.123
6	f	4.74	0.118	0.252	0.003	0.150	0.002	0.089	0.040	0.016	0.018	0.172
6	v	5.43	0.298	0.522	0.017	0.255	0.009	0.006	0.012	0.023	0.003	0.119
7	f	4.93	0.075	0.759	0.006	0.465	0.004	0.016	0.010	0.006	0.002	0.317
7	v	5.62	0.105	0.260	0.003	0.165	0.002	0.000	0.001	0.002	0.000	0.150
8	f	4.47	0.085	0.972	0.008	0.376	0.003	0.140	0.030	0.006	0.014	0.266
8	v	5.41	0.061	0.216	0.002	0.119	0.001	0.001	0.002	0.004	0.000	0.087
9	f	4.66	0.025	0.484	0.001	0.194	0.001	0.059	0.021	0.007	0.002	0.189
9	v	5.28	0.109	0.252	0.003	0.152	0.002	0.004	0.006	0.008	0.001	0.109
Midlands												
1	f	4.87	0.167	0.756	0.013	0.578	0.011	0.014	0.008	0.004	0.003	0.349
1	v	5.05	0.074	1.160	0.008	0.648	0.005	0.007	0.006	0.005	0.001	0.254
2	f	4.61	0.098	1.526	0.013	0.860	0.008	0.059	0.016	0.004	0.006	0.307
2	v	4.91	0.124	1.588	0.017	0.890	0.011	0.013	0.007	0.004	0.002	0.237
Southern Cape												
1	f	5.01	0.457	1.957	0.071	0.922	0.038	0.079	0.054	0.036	0.034	0.186
1	v	5.43	0.361	1.580	0.049	0.860	0.031	0.016	0.031	0.055	0.006	0.118
3	f	4.90	0.472	2.000	0.074	1.135	0.048	0.063	0.033	0.017	0.027	0.331
3	v	5.04	0.302	1.382	0.037	0.746	0.023	0.033	0.026	0.019	0.011	0.221
4	f	3.64	0.303	1.045	0.025	0.321	0.009	0.883	0.026	0.001	0.253	0.129
4	v	3.79	0.400	1.529	0.047	1.905	0.067	0.177	0.007	0.000	0.063	0.100
5	f	3.66	0.178	0.559	0.009	0.247	0.005	0.541	0.018	0.001	0.115	0.058
5	v	3.74	0.415	0.800	0.031	0.389	0.017	0.139	0.005	0.000	0.070	0.061
Western Cape												
4	f	3.98	0.324	0.962	0.029	0.521	0.018	0.050	0.003	0.000	0.020	0.065
4	v	4.31	0.369	0.538	0.021	0.291	0.013	0.028	0.004	0.001	0.015	0.043
5	f	4.98	0.200	1.013	0.019	0.640	0.014	0.071	0.049	0.032	0.018	0.097
5	v	5.35	0.297	0.891	0.026	0.517	0.017	0.016	0.026	0.040	0.006	0.099

Table C8: *The pH and estimated negative logarithm (base 10) of activities of chemical species in saturated paste extracts calculated on a DOM-free basis (i.e. dissolved organic matter excluded from calculations). Calculations were based on the composition of saturated paste extracts obtained in 1996 (Table C5) and were carried out using MINTEQA2 (see section 6.2.4 for details). Elements which occur predominantly (> 99 %) in free ionic form and complexes with very low activity values (-log activity > 7) are excluded.*

Site	Type	pH	SO_4^{2-}	Mg^{2+}	$MgSO_4$	Ca^{2+}	$CaSO_4$	Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	$AlSO_4^+$	H_4SiO_4
Eastern escarpment												
2	f	4.65	4.05	3.84	5.64	4.01	5.75	4.90	5.25	5.70	5.44	3.88
2	v	5.17	3.70	3.86	5.30	3.95	5.34	5.25	5.08	5.01	5.45	3.75
4	f	5.34	3.96	3.73	5.44	3.80	5.45	5.77	5.43	5.19	6.23	3.56
4	v	5.19	4.14	3.91	5.80	4.03	5.86	5.88	5.69	5.60	6.52	4.60
5	f	5.00	3.96	3.76	5.48	3.91	5.57	5.33	5.33	5.43	5.80	3.72
5	v	5.56	4.02	3.87	5.64	3.97	5.68	6.69	6.13	5.67	7.21	3.91
6	f	4.76	4.02	3.69	5.46	3.91	5.62	4.25	4.49	4.83	4.77	3.76
6	v	5.46	3.64	3.39	4.78	3.70	5.03	5.49	5.03	4.67	5.62	3.93
7	f	4.96	4.24	3.24	5.23	3.45	5.38	5.07	5.11	5.25	5.81	3.50
7	v	5.64	4.06	3.66	5.47	3.86	5.61	6.82	6.18	5.64	7.37	3.82
8	f	4.51	4.21	3.16	5.12	3.57	5.47	4.18	4.67	5.26	4.90	3.57
8	v	5.43	4.30	3.75	5.80	4.01	6.00	6.18	5.75	5.42	6.98	4.06
9	f	4.68	4.69	3.41	5.85	3.81	6.19	4.45	4.77	5.19	5.64	3.72
9	v	5.30	4.05	3.69	5.48	3.90	5.64	5.62	5.32	5.12	6.17	3.96
Midlands												
1	f	4.90	3.90	3.24	4.89	3.36	4.95	5.12	5.22	5.42	5.51	3.46
1	v	5.08	4.26	3.06	5.07	3.32	5.26	5.43	5.35	5.37	6.19	3.59
2	f	4.65	4.17	2.98	4.90	3.23	5.09	4.60	4.95	5.40	5.27	3.51
2	v	4.95	4.07	2.96	4.78	3.21	4.97	5.25	5.30	5.45	5.81	3.62
Southern Cape												
1	f	5.05	3.51	2.88	4.15	3.21	4.41	4.49	4.44	4.49	4.51	3.73
1	v	5.47	3.60	2.96	4.31	3.22	4.51	5.14	4.67	4.30	5.24	3.93
3	f	4.94	3.50	2.88	4.13	3.12	4.32	4.60	4.66	4.82	4.61	3.48
3	v	5.08	3.67	3.01	4.43	3.28	4.64	4.82	4.74	4.76	4.99	3.66
4	f	3.68	3.69	3.16	4.60	3.67	5.05	3.45	4.77	6.19	3.64	3.89
4	v	3.84	3.58	3.00	4.33	2.90	4.18	4.16	5.32	6.58	4.24	4.00
5	f	3.70	3.89	3.39	5.04	3.75	5.33	3.58	4.88	6.28	3.98	4.23
5	v	3.77	3.52	3.24	4.51	3.55	4.76	4.17	5.40	6.73	4.19	4.21
Western Cape												
4	f	4.01	3.63	3.15	4.53	3.42	4.74	4.61	5.60	6.69	4.73	4.19
4	v	4.34	3.54	3.38	4.67	3.65	4.88	4.80	5.46	6.22	4.85	4.37
5	f	5.01	3.84	3.13	4.72	3.33	4.86	4.45	4.44	4.53	4.79	4.01
5	v	5.38	3.65	3.18	4.58	3.41	4.76	5.09	4.71	4.43	5.25	4.00

Table C9: *Estimated concentrations (mmol L^{-1}) of chemical species (including DOM) in saturated paste extracts. Calculations were based on the composition of saturated paste extracts obtained in 1996 (Table C5) and were carried out using MINTEQA2 (see section 6.2.4 for details). Because of sample storage effects, activities of DOM species were recalculated using DOM values obtained from DOC concentrations in 1995 extracts (see section 6.2.4 and 6.3.3.3 for details). This does not apply to samples marked with asterisks which were taken in 1996 and therefore are not subject to storage effects. Elements which occur predominantly (> 99 %) in free ionic form and complexes with very low concentrations (< 10^{-3} $mmol_c L^{-1}$) are excluded.*

Site	Type	SO_4^{2-}	DOM	Mg^{2+}	Mg-DOM	$MgSO_4$	Ca^{2+}	Ca-DOM	$CaSO_4$	Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	$AlSO_4^+$	Al-DOM	H_4SiO_4	H-DOM
Eastern escarpment																
2	f	0.115	0.095	0.177	0.001	0.002	0.112	0.009	0.002	0.003	0.001	0.000	0.000	0.029	0.132	0.024
2	v	0.253	0.107	0.170	0.002	0.005	0.123	0.016	0.004	0.001	0.002	0.002	0.001	0.028	0.176	0.012
4	f	0.132	0.045	0.221	0.001	0.004	0.181	0.011	0.003	0.001	0.002	0.003	0.000	0.009	0.277	0.003
4	v	0.086	0.062	0.145	0.002	0.002	0.100	0.011	0.001	0.000	0.000	0.000	0.000	0.006	0.025	0.009
5	f	0.134	0.039	0.209	0.001	0.003	0.141	0.006	0.003	0.002	0.001	0.001	0.000	0.011	0.189	0.006
5	v	0.116	0.020	0.160	0.001	0.002	0.114	0.005	0.002	0.000	0.000	0.001	0.000	0.001	0.123	0.002
6	f	0.124	0.021	0.251	0.000	0.004	0.149	0.001	0.002	0.054	0.024	0.009	0.011	0.034	0.172	0.001
6	v	0.300	0.039	0.519	0.002	0.016	0.241	0.009	0.009	0.003	0.006	0.011	0.001	0.014	0.119	0.002
7	f	0.075	0.024	0.758	0.001	0.006	0.460	0.005	0.004	0.009	0.006	0.004	0.001	0.014	0.317	0.002
7	v	0.105	0.026	0.259	0.001	0.003	0.157	0.008	0.002	0.000	0.001	0.002	0.000	0.001	0.150	0.001
8	f	0.089	0.032	0.971	0.000	0.008	0.373	0.002	0.003	0.086	0.018	0.004	0.009	0.051	0.266	0.002
8	v	0.061	0.080	0.210	0.004	0.001	0.092	0.016	0.001	0.000	0.000	0.001	0.000	0.004	0.087	0.008
9	f	0.027	0.040	0.483	0.001	0.001	0.192	0.002	0.001	0.029	0.010	0.003	0.001	0.046	0.189	0.003
9	v	0.110	0.067	0.250	0.002	0.003	0.140	0.013	0.002	0.001	0.002	0.002	0.000	0.014	0.109	0.006
Midlands																
1	f	0.170	0.056	0.753	0.003	0.013	0.550	0.019	0.011	0.003	0.002	0.001	0.001	0.016	0.349	0.006
1	v	0.076	0.161	1.139	0.014	0.008	0.547	0.065	0.004	0.001	0.001	0.000	0.000	0.011	0.254	0.015
2	f	0.101	0.025	1.524	0.001	0.013	0.851	0.005	0.008	0.031	0.009	0.002	0.003	0.021	0.307	0.002
2	v	0.125	0.033	1.583	0.002	0.017	0.862	0.013	0.010	0.004	0.002	0.001	0.001	0.008	0.237	0.003
Southern Cape																
1	f	0.476	0.106	1.948	0.005	0.073	0.890	0.023	0.038	0.030	0.020	0.013	0.013	0.088	0.186	0.004
1	v	0.368	0.121	1.568	0.009	0.048	0.797	0.043	0.028	0.007	0.013	0.022	0.003	0.044	0.118	0.003
3	f	0.495	0.147	1.984	0.009	0.075	1.058	0.049	0.046	0.013	0.007	0.003	0.006	0.070	0.331	0.009
3	v	0.314	0.095	1.365	0.007	0.037	0.665	0.032	0.021	0.005	0.004	0.003	0.002	0.030	0.221	0.006
4	f	0.348	0.063	1.039	0.000	0.030	0.317	0.001	0.010	0.583	0.017	0.000	0.201	0.195	0.129	0.010
4	v	0.448	0.275	1.516	0.007	0.050	1.790	0.082	0.068	0.030	0.001	0.000	0.011	0.150	0.100	0.122
5	f	0.204	0.047	0.557	0.000	0.011	0.245	0.001	0.005	0.337	0.011	0.000	0.086	0.129	0.058	0.009
5	v	0.463	0.096	0.794	0.002	0.034	0.374	0.007	0.018	0.034	0.001	0.000	0.018	0.082	0.061	0.049
Western Cape																
4	f	0.342	0.120	0.956	0.004	0.030	0.490	0.020	0.017	0.008	0.001	0.000	0.003	0.040	0.065	0.061
4	v	0.382	0.043	0.535	0.001	0.021	0.275	0.006	0.013	0.005	0.001	0.000	0.003	0.015	0.043	0.015
5	f	0.209	0.075	1.010	0.002	0.020	0.622	0.012	0.014	0.028	0.019	0.012	0.007	0.073	0.097	0.003
5	v	0.302	0.088	0.886	0.004	0.026	0.487	0.023	0.016	0.006	0.011	0.016	0.002	0.041	0.099	0.003

Table C10: *Estimated negative logarithm (base 10) of activities of chemical species (including DOM) in saturated paste extracts. Calculations were based on the composition of saturated paste extracts obtained in 1996 (Table C5) and were carried out using MINTEQA2 (see section 6.2.4 for details). Because of sample storage effects, activities of DOM species were recalculated using DOM values obtained from DOC concentrations in 1995 extracts (see section 6.2.4 and 6.3.3.3 for details). This does not apply to samples marked with asterisks which were taken in 1996 and therefore are not subject to storage effects. Elements which occur predominantly (> 99 %) in free ionic form and complexes with very low activity values (-log activity > 7) are excluded.*

Site	Type	SO_4^{2-}	DOM	Mg^{2+}	Mg-DOM	$MgSO_4$	Ca^{2+}	Ca-DOM	$CaSO_4$	Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	$AlSO_4^+$	Al-DOM	H_4SiO_4	H-DOM
Eastern escarpment																
2*	f	4.04	4.21	3.85	5.87	5.64	4.05	5.07	5.78	5.82	6.17	6.62	6.35	4.54	3.88	4.70
2*	v	3.69	4.16	3.87	5.68	5.31	4.01	4.82	5.39	6.04	5.87	5.80	6.24	4.56	3.75	5.01
4*	f	3.96	4.51	3.74	5.90	5.45	3.83	4.99	5.48	6.18	5.84	5.60	6.64	5.04	3.56	5.54
4*	v	4.14	4.36	3.92	5.80	5.81	4.08	4.97	5.92	6.63	6.44	6.35	7.28	5.22	4.60	5.11
5	f	3.96	4.53	3.77	6.03	5.48	3.94	5.21	5.60	6.02	6.02	6.12	6.48	4.98	3.72	5.29
5	v	4.02	4.80	3.88	6.15	5.66	4.03	5.29	5.74	7.14	6.58	6.12	7.67	6.11	3.91	5.85
6	f	4.00	4.81	3.69	6.99	5.43	3.92	6.22	5.60	4.47	4.71	5.05	4.97	4.47	3.76	6.09
6	v	3.64	4.56	3.40	5.75	4.78	3.73	5.08	5.06	5.82	5.36	5.00	5.96	4.87	3.93	5.84
7*	f	4.24	4.85	3.24	6.10	5.23	3.45	5.32	5.38	5.30	5.34	5.48	6.04	4.87	3.50	5.86
7*	v	4.06	4.74	3.67	5.91	5.48	3.89	5.13	5.64	6.98	6.34	5.80	7.55	5.93	3.82	5.91
8	f	4.19	4.70	3.16	6.36	5.10	3.57	5.78	5.46	4.39	4.88	5.47	5.08	4.29	3.57	5.74
8	v	4.31	4.21	3.77	5.43	5.83	4.13	4.79	6.13	7.04	6.61	6.29	7.85	5.41	4.06	5.12
9*	f	4.67	4.59	3.41	6.29	5.84	3.81	5.69	6.18	4.76	5.08	5.50	5.94	4.34	3.72	5.59
9*	v	4.05	4.35	3.69	5.66	5.49	3.95	4.91	5.69	6.20	5.90	5.70	6.75	4.87	3.96	5.30
Midlands																
1	f	3.89	4.44	3.25	5.60	4.89	3.38	4.74	4.97	5.75	5.85	6.05	6.14	4.81	3.46	5.28
1	v	4.26	4.03	3.08	4.89	5.09	3.40	4.21	5.35	6.47	6.39	6.41	7.22	4.97	3.59	4.92
2	f	4.16	4.86	2.98	6.07	4.89	3.23	5.33	5.09	4.88	5.23	5.68	5.54	4.67	3.51	5.77
2	v	4.06	4.74	2.96	5.64	4.78	3.23	4.90	4.98	5.73	5.78	5.93	6.29	5.10	3.62	5.66
Southern Cape																
1	f	3.50	4.25	2.89	5.33	4.14	3.23	4.67	4.42	4.92	4.87	4.92	4.92	4.06	3.73	5.52
1	v	3.60	4.18	2.97	5.09	4.32	3.26	4.39	4.55	5.54	5.07	4.70	5.63	4.36	3.93	5.62
3	f	3.49	4.12	2.89	5.06	4.12	3.16	4.33	4.34	5.28	5.34	5.50	5.27	4.16	3.48	5.14
3	v	3.66	4.26	3.02	5.20	4.43	3.33	4.51	4.69	5.65	5.57	5.59	5.81	4.53	3.66	5.29
4	f	3.63	4.46	3.15	6.55	4.53	3.67	6.06	4.98	3.61	4.93	6.35	3.74	3.71	3.89	5.11
4	v	3.54	3.88	3.01	5.19	4.30	2.94	4.11	4.17	4.95	6.11	7.37	4.99	3.83	4.00	4.04
5	f	3.83	4.54	3.39	6.80	4.96	3.75	6.16	5.26	3.78	5.08	6.48	4.10	3.89	4.23	5.14
5	v	3.48	4.22	3.24	5.84	4.47	3.57	5.16	4.74	4.79	6.02	7.35	4.77	4.09	4.21	4.39
Western Cape																
4	f	3.61	4.14	3.16	5.43	4.53	3.45	4.72	4.76	5.44	6.43	7.52	5.55	4.40	4.19	4.30
4	v	3.53	4.52	3.39	5.91	4.67	3.68	5.20	4.90	5.59	6.25	7.01	5.62	4.81	4.37	4.90
5	f	3.82	4.35	3.13	5.71	4.70	3.34	4.92	4.85	4.86	4.85	4.94	5.18	4.14	4.01	5.62
5	v	3.65	4.26	3.18	5.39	4.59	3.44	4.65	4.79	5.49	5.11	4.83	5.64	4.39	4.00	5.61

APPENDIX D: AN EVALUATION OF THE EFFECTS OF VARYING EQUILIBRATION TIME AND MICROBIAL ACTIVITY ON THE COMPOSITION OF SATURATED PASTE EXTRACTS

D1. INTRODUCTION

A number of factors can significantly affect the composition of saturated paste extracts obtained from dried soil samples (Bartlett and James, 1980). In particular, rewetting of dry soil is widely reported to result in an explosion of microbial activity (Stevenson, 1956; van Shreven, 1967) and can cause significant temporal variation in solution composition (Carlson *et al.*, 1971; Bartlett and James, 1980). A further source of uncertainty is the amount of time required for the added water to equilibrate with the soil. An understanding of how these factors may influence the composition of saturated paste extracts from soils of this study is critical in order to allow meaningful interpretations and intersample comparisons to be made on the basis of chemical data obtained from these solutions.

D2. MATERIALS AND METHODS

In order to evaluate the effect of varying equilibration time, four aliquots of between 100 and 200 grams were split from five forest soil samples (composites) from the eastern escarpment. The four aliquots were wet to saturation point with high-purity deionised water, and allowed to equilibrate for periods of 1, 4, 10 and 24 hours respectively. The effect of microbial activity was investigated on two of the forest soil samples. One-hundred gram aliquots from these samples were treated with varying concentrations (0, 0.1 and 0.5g) of the phenolic compound thymol. Thymol is an effective suppressant of microbial activity (Carlson *et al.*, 1971) and is mixed into the soil in powdered form approximately one hour before wetting. Four 100g aliquots were used for each of the three treatments and were allowed to equilibrate for different time periods as described above. All solutions were extracted under vacuum and immediately filtered through 0.45μm millipore filters. pH, electrical conductivity and major anion concentrations (HPLC) were determined for each of the extracts. Dissolved organic carbon concentrations were determined for selected samples using the ANATOC total organic carbon analyser.

D3. RESULTS AND DISCUSSION

The pH and anion data for all of the saturated paste extracts obtained from this study are presented in Table D1 and Figures D1.a to 1.l. Table D1 also includes total dissolved organic carbon concentrations for all four aliquots of two thymol-free treatments as well as for selected thymol-treated aliquots.

The *pH* data do not show any consistent trends with varying equilibration time (Figure D1.a) and in most cases pH values appear to stabilise after approximately four hours of equilibration. Two exceptions are the data for EE2 which is extremely erratic, and that for EE7 which shows an increase in pH between the 10 and 24 hour equilibrations. The very constant and similar pH values obtained for both of the EE2 thymol treatments, and the fact that the dramatically different pH values obtained for the two and twenty-four hour thymol-free treatments is not reflected in the 10 hour treatment, suggest that these erratic fluctuations are the result of sampling (splitting) or analytical error. The more gradual increase in the pH of the thymol-free treatments for the EE7 soil is not evident in the thymol-treated aliquots and could be taken to suggest the influence of microbial activity. However, this is based on a single elevated pH reading, and is not corroborated by consistent changes in any of the other parameters measured. It is therefore considered unlikely that the pH variations reflect microbial activity.

With a few exceptions, the concentrations of major *anions* do not vary significantly with varying equilibration time, and they appear to be particularly stable after 10 hours (Figures D1.d, g and j). The elevated *chloride* concentration observed for the 24 hour EE2 (Figure D1.d) treatment is not evident for either of the thymol treatments (Figure D1.e) and is believed to be due to contamination. Although the other samples show very slight increases in chloride concentration with time, these are effectively stable, and increased equilibration times are very unlikely to affect relative or absolute concentrations to any significant extent. *Sulphate* shows similar trends to those of chloride, although a gradual increase in the sulphate concentration of EE3 extracts is evident, suggesting that equilibrium may not have been reached in this case. The sharp increase in sulphate concentration observed for EE2 may be partly related to contamination as proposed for chloride, but less dramatic increases in the sulphate

Table D1: *pH, electrical conductivity (EC), anion (mmol L^{-1}) and dissolved organic carbon (DOC, mg L^{-1}) data for the saturated paste time-dependence and thymol studies.*

Site	*Equ.Time*	*Thymol*	*pH*	*EC*	*Cl*	NO_3^-	SO_4^{2-}	*DOC*
EE2	1	0	4.53	220	0.583	0.705	0.094	170
EE2	4	0	5.30	208	0.569	0.703	0.094	190
EE2	10	0	4.45	220	0.561	0.611	0.097	123
EE2	24	0	5.77	253	0.769	0.716	0.141	204
EE2	1	0.1	4.50	218	0.522	0.493	0.083	
EE2	4	0.1	4.45	243	0.604	0.711	0.105	
EE2	10	0.1	4.57	223	0.594	0.692	0.103	
EE2	24	0.1	4.51	247	0.617	0.603	0.119	237
EE2	1	0.5	4.62	221	0.590	0.658	0.101	
EE2	4	0.5	4.61	221	0.593	0.698	0.099	
EE2	10	0.5	4.55	222	0.561	0.679	0.098	
EE2	24	0.5	4.56	250	0.610	0.705	0.116	805
EE3	1	0	4.32	135	0.276	0.338	0.077	
EE3	4	0	4.36	134	0.276	0.340	0.080	
EE3	10	0	4.26	137	0.275	0.339	0.082	
EE3	24	0	4.33	142	0.285	0.345	0.096	
EE4	4	0	5.17	107	0.448	0.118	0.087	
EE4	10	0	5.22	108	0.451	0.083	0.093	
EE4	24	0	5.04	107	0.466	0.069	0.094	540
EE7	1	0	4.25	428	0.289	2.725	0.061	104
EE7	4	0	4.39	430	0.290	2.901	0.058	161
EE7	10	0	4.41	442	0.379	2.924	0.071	164
EE7	24	0	4.65	463	0.332	3.043	0.068	165
EE7	1	0.1	4.27	425	0.275	2.793	0.061	
EE7	4	0.1	4.28	444	0.243	2.951	0.058	
EE7	10	0.1	4.41	465	0.312	2.954	0.072	
EE7	24	0.1	4.46	480	0.318	3.072	0.075	297
EE7	1	0.5	4.32	430	0.274	2.678	0.055	
EE7	4	0.5	4.47	445	0.278	2.765	0.063	
EE7	10	0.5	4.46	449	0.281	2.876	0.062	
EE7	24	0.5	4.42	486	0.342	2.913	0.076	
EE9	1	0	4.82	198	0.620	0.606	0.062	
EE9	4	0	4.45	183	0.515	0.575	0.043	
EE9	10	0	4.45	185				
EE9	24	0	4.47	188	0.554	0.519	0.050	379

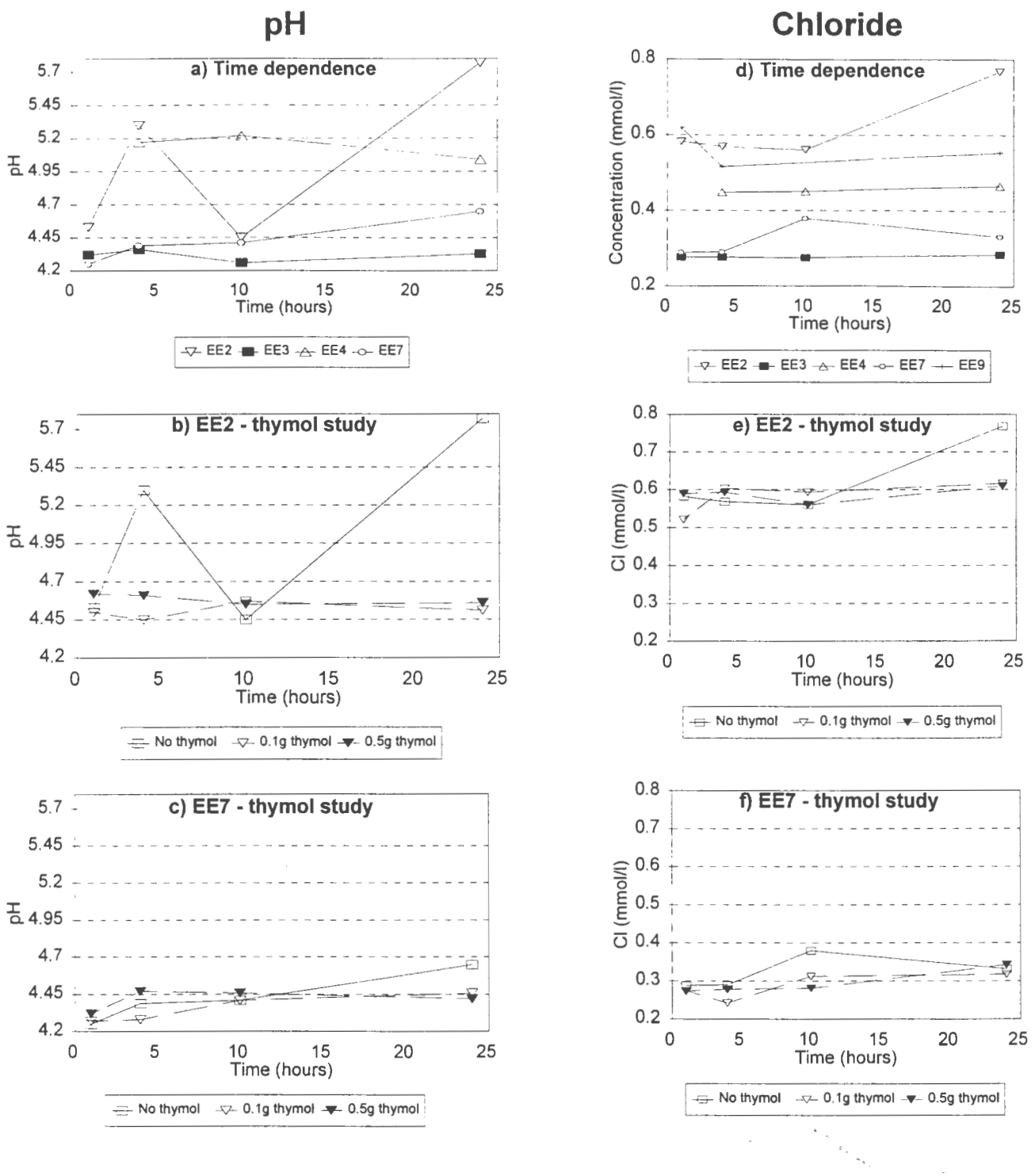

Figure D1: *Graphical representation of pH (a-c) and chloride (d-f) data for the saturated paste time-dependence and thymol studies. See text for details.*

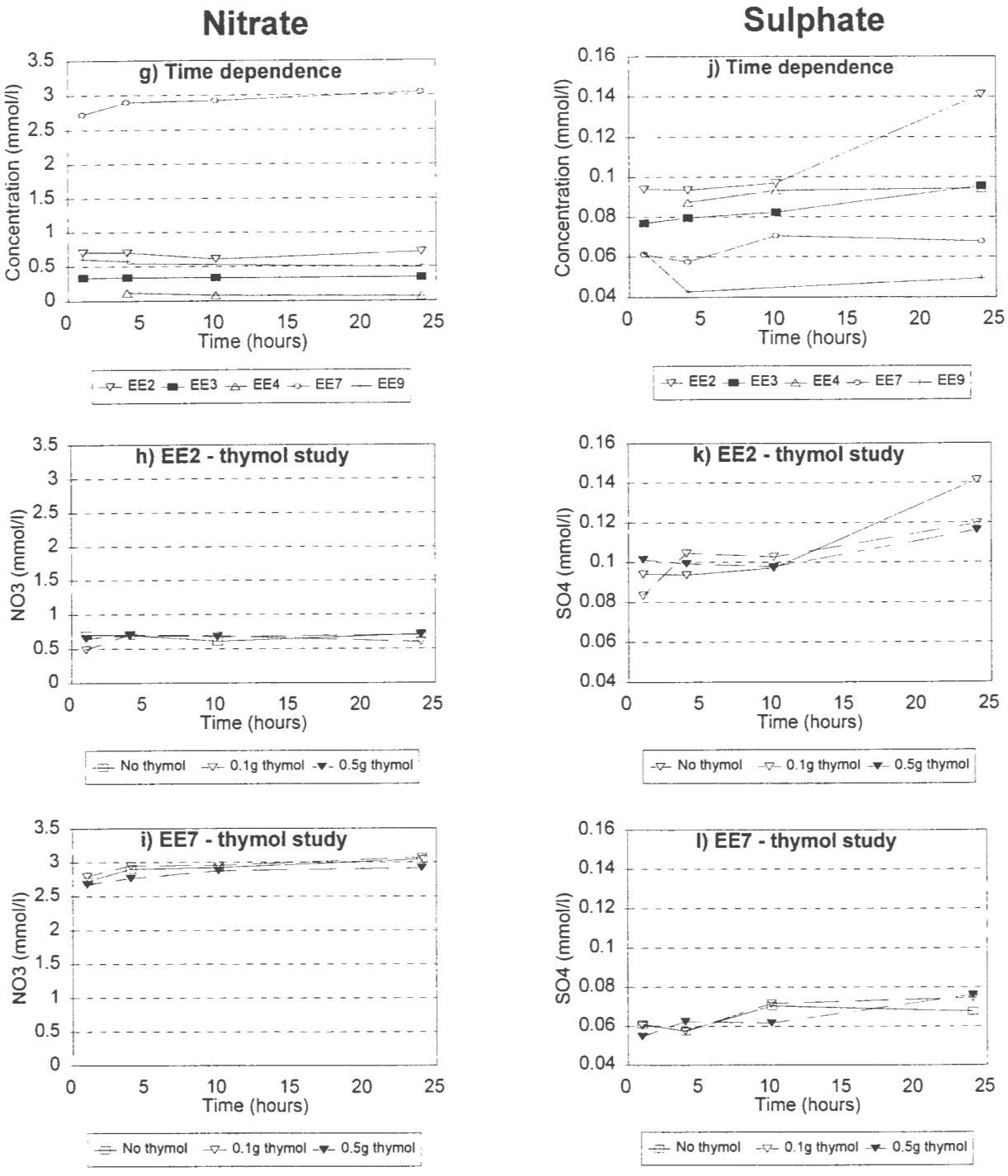

***Figure D1 continued**: Graphical representation of nitrate (g-i) and sulphate (j-l) data for the saturated paste time-dependence and thymol studies. See text for details.*

concentrations of the thymol-treated aliquots (Figure D1.k) suggests that the trend is partly real, and is similar to that displayed by EE3. Samples EE2 and EE3 are both very sandy soils and were taken within relatively close proximity to each other (~500m).

Concentrations of nitrate in the saturated paste extracts are remarkably constant (Figure D1.g), and only EE7, which is extremely enriched in nitrate, shows any consistent (although minor) variation. Nitrate is the anion most likely to be affected by microbial activity (i.e. by nitrifying and/or denitrifying microbes). Therefore, the lack of variability in nitrate levels, suggests that microbial activity does not have a significant effect on the chemical parameters under investigation. This is supported by the data for the thymol-treated samples (Figures D1.h and i) which suggest that addition of thymol and the consequent suppression of microbial activity, does not influence the composition of the saturated paste extracts.

Total *dissolved organic carbon* (DOC) concentrations for the extracts from thymol-free treatments range from 104 to 540 mg/l (Table D1). DOC concentrations in the EE2 thymol-free extracts display fluctuations which do not appear to relate to equilibration time, whereas the EE7 extracts show an initial sharp increase followed by relatively constant DOC levels. As would be expected, thymol treatment results in dramatic increases in DOC concentrations.

D4. CONCLUSIONS

The results of this study indicate that, with respect to pH, major anion and probably DOC concentrations, equilibration of saturated paste extracts usually takes place within approximately ten hours. However, two of the samples used for the study showed gradually increasing sulphate concentrations, even after twenty-four hours, suggesting that in some cases this may not apply to sulphate. The anion data and the data for thymol-treated samples indicates that microbial activity during saturated paste equilibration does not have a significant influence on the chemical parameters under investigation.

APPENDIX E: PRECISION ESTIMATES AND SAMPLING VARIABILITY FOR SATURATED PASTE EXTRACT DATA

E1. ESTIMATION OF ANALYTICAL AND EXTRACTION PRECISION

An empirical approach, whereby analytical precision was estimated from data obtained for duplicate extracts, has been used to obtain a combined estimate of the variability/error associated with extraction and analysis of saturated paste extracts, and determination of exchangeable sulphate and manganese.

The following procedure was employed to obtain these precision estimates:

- Duplicate extracts were carried out for between six and twenty samples (in most cases ≥14).
- All analyses were carried out on both the original and the duplicate extracts.
- Values obtained for the duplicate extracts were subtracted from those obtained for the original extracts and were converted to absolute differences.
- For each variable, the mean as well as the sum of the mean and standard deviation (mean+SD) of these absolute differences were calculated (Table E1). These parameters were also determined for the differences expressed as a percentage of the average value for the duplicate and original extracts. Differences which were more than three standard deviations greater than the mean difference were regarded as outliers and these duplicates were excluded from the final calculations.

For most variables, greater than 90% of the values obtained for duplicate extracts (including outliers) do not deviate from those obtained for the original extracts by more than the mean+SD value obtained for the absolute and percentage differences. This suggests that the mean+SD parameter (i.e. the sum of the mean and standard deviation of the duplicate/original differences) provides a reasonable estimate of analytical precision.

Table E1: *Summary data for discrepancies between duplicate extracts. For each variable, the arithmetic mean, as well as the sum of the mean and the standard deviation (Mean+SD), of the absolute differences obtained for "n" duplicate extract pairs, are presented. The parameters are also given for differences expressed as a percentage of the average value for each duplicate extract pair. Values used as estimates of the combined analytical and extraction precision are given in bold text. See text for details.*

Variable	Unit	n	Outliers	Absolute differences		% differences	
				Mean	Mean+SD	Mean	Mean+SD
H^+_{sp}	$mmol_c\ L^{-1}$	20	2	0.006	0.015	16	**30**
EC	$uS\ cm^{-1}$	20	1	12	29	6.4	**17**
Cl^-	$mmol_c\ L^{-1}$	20	1	0.066	0.130	7.8	**14**
NO_3^-	$mmol_c\ L^{-1}$	20	0	0.018	**0.044**	59	141
SO_4^{2-}	$mmol_c\ L^{-1}$	20	1	0.017	0.033	6.9	**13**
DOC	$mg\ L^{-1}$	20	0	31	58	14	**25**
Na^+	$mmol_c\ L^{-1}$	20	0	0.077	0.136	10	**16**
NH_4^+	$mmol_c\ L^{-1}$	20	0	0.063	**0.119**	40	68
K^+	$mmol_c\ L^{-1}$	20	0	0.031	0.056	16	**27**
Mg^{2+}	$mmol_c\ L^{-1}$	20	1	0.092	0.195	15	**29**
Mn^{2+}	$mmol_c\ L^{-1}$	20	1	0.034	**0.073**	104	184
Ca^{2+}	$mmol_c\ L^{-1}$	20	1	0.055	0.098	14	**25**
Base cation sum	$mmol_c\ L^{-1}$	20	0	0.228	0.430	11	**18**
Al^{3+}	$mmol_c\ L^{-1}$	6	1	0.005	0.007	16	**23**
Si	$mmol\ L^{-1}$	6	0	0.034	**0.058**	16	33
Ex-Mn	$mmol_c\ dm^{-3}$	9	0	0.033	0.065	4.8	**6.8**
Ex-SO_4^{2-}	$mmol_c\ dm^{-3}$	30	0	1.984	3.992	5.0	**10**

The validity of these precision estimates was evaluated graphically by plotting the duplicate extract data against those of the original extracts and fitting "precision lines" (e.g. Figure E1 to E3). Two sets of precision lines were plotted, corresponding to deviations from a one to one correlation (i.e. perfect reproducibility) by amounts corresponding to the mean+SD values for the absolute and percentage differences respectively. For the majority of variables, the plots suggest an increase in scatter with increasing concentrations, and mean+SD of *percentage* differences was found to be the most appropriate estimate of analytical precision. These range from 4.3 to 30% and for most variables do not exceed 25%. However, for some variables, absolute precision terms (i.e. mean+SD of absolute differences) provide a better description of the data variability than do the relative precision estimates (Figure E1 to E3). This applies to the concentrations of nitrate, ammonium, manganese and silicon in saturated paste extracts (precision ranges from 0.044 to 0.119 $mmol_c L^{-1}$).

In the case of nitrate (Figure E1.b) and manganese (Figure E2.e) most of the values obtained are close to or below the detection limits of the analytical technique employed (i.e. high performance liquid ion chromatography). The precision estimates for these variables are therefore very uncertain as they are based primarily on a small number of duplicate extract pairs at elevated concentration.

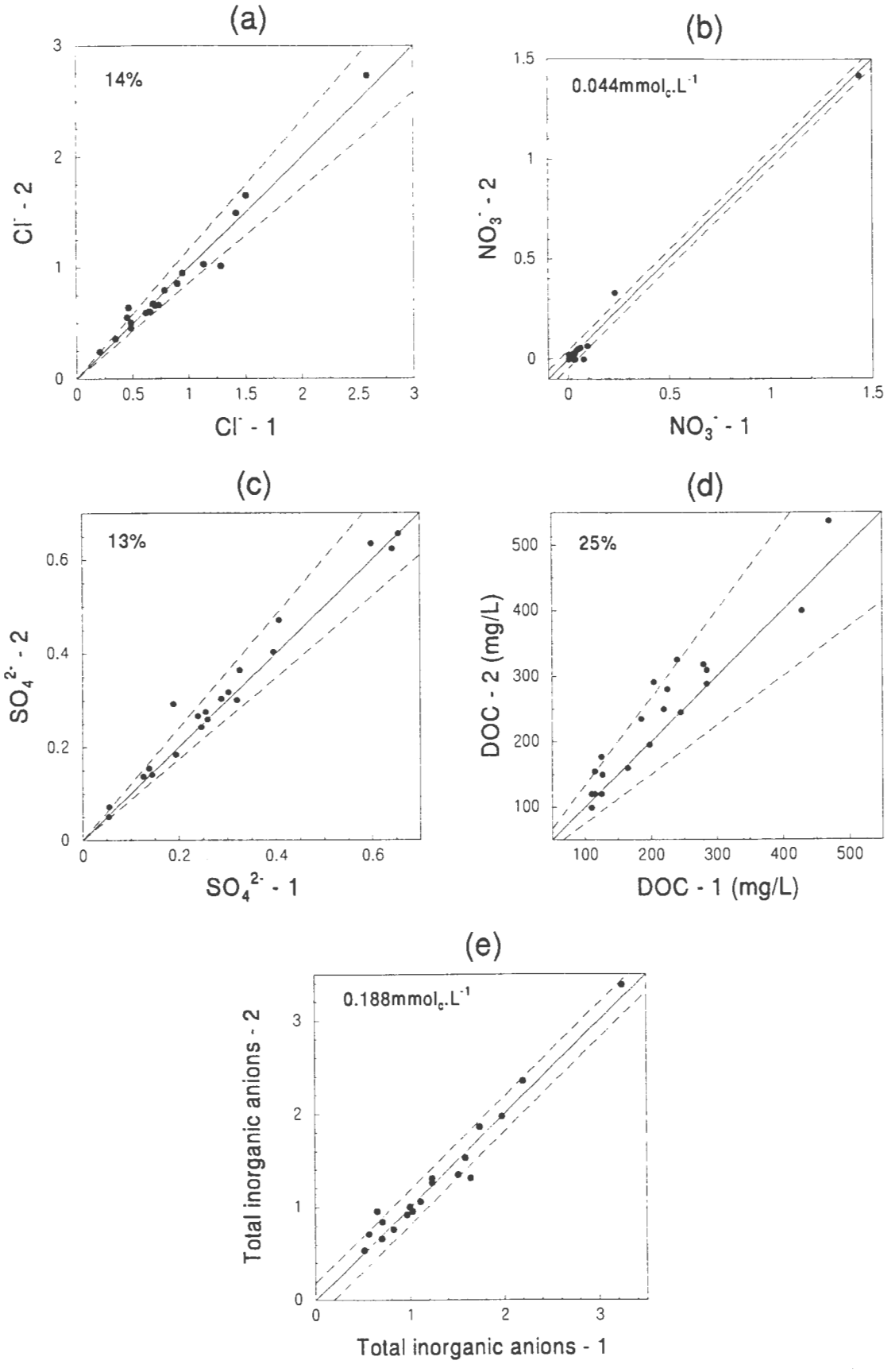

Figure E1: *Plots comparing anion data for duplicate saturated paste extracts. Data for extract one is plotted on the horizontal axis and that for extract two is plotted on the vertical axis. With the exception of dissolved organic carbon (DOC), all data are given in mmol$_c$ L^{-1}. Best estimates of the combined analytical and extraction error for each variable are given in the top left hand corner of each plot and are represented graphically by the dashed lines on either side of a one-to-one correlation line (solid line).*

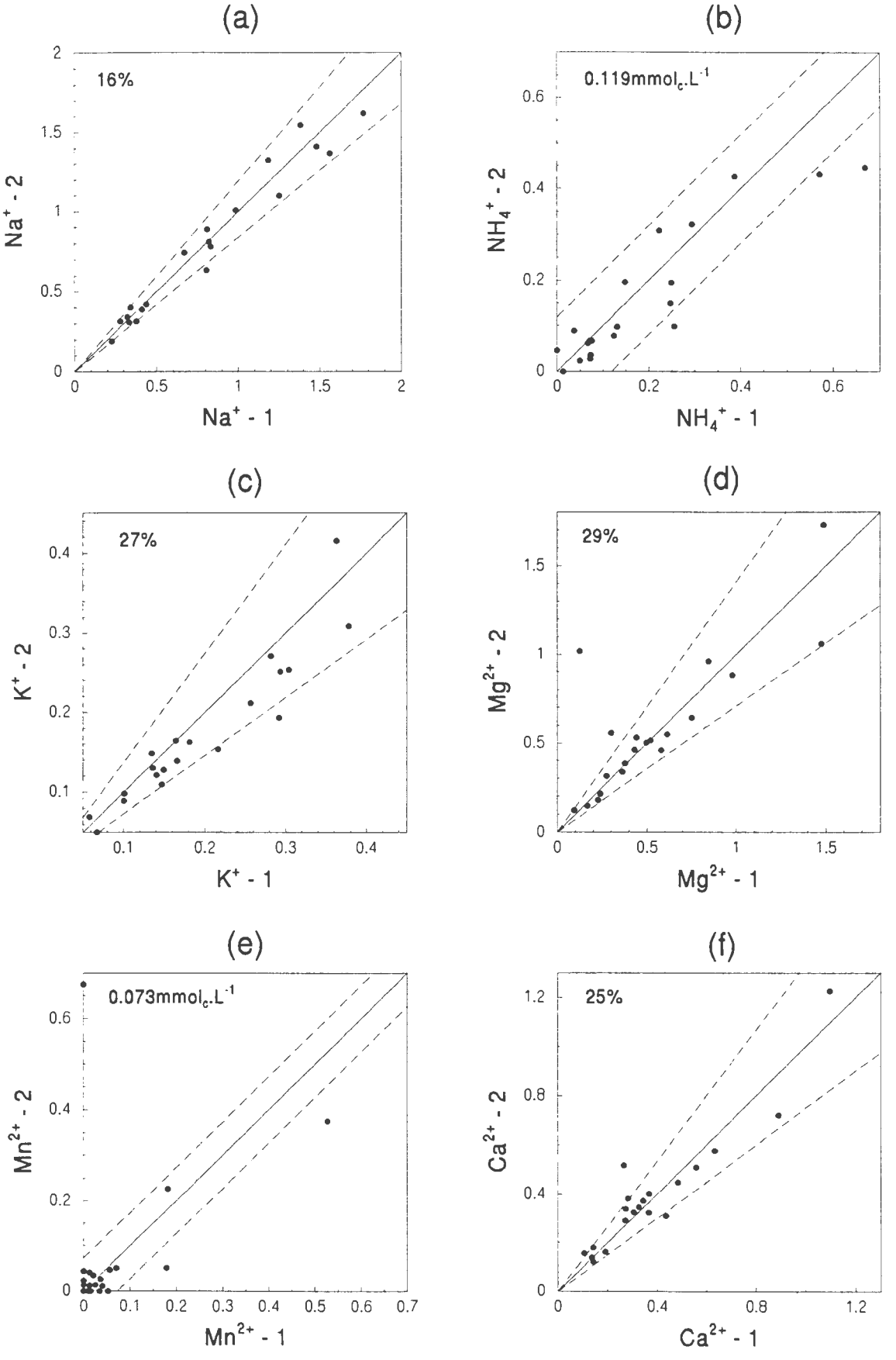

Figure E2: *Plots comparing cation data for duplicate saturated paste extracts. Data for extract one is plotted on the horizontal axis and that for extract two is plotted on the vertical axis. All data are given in mmol$_c$L^{-1}. Best estimates of the combined analytical and extraction error for each variable are given in the top left hand corner of each plot and are represented graphically by the dashed lines on either side of a one-to-one correlation line (solid line).*

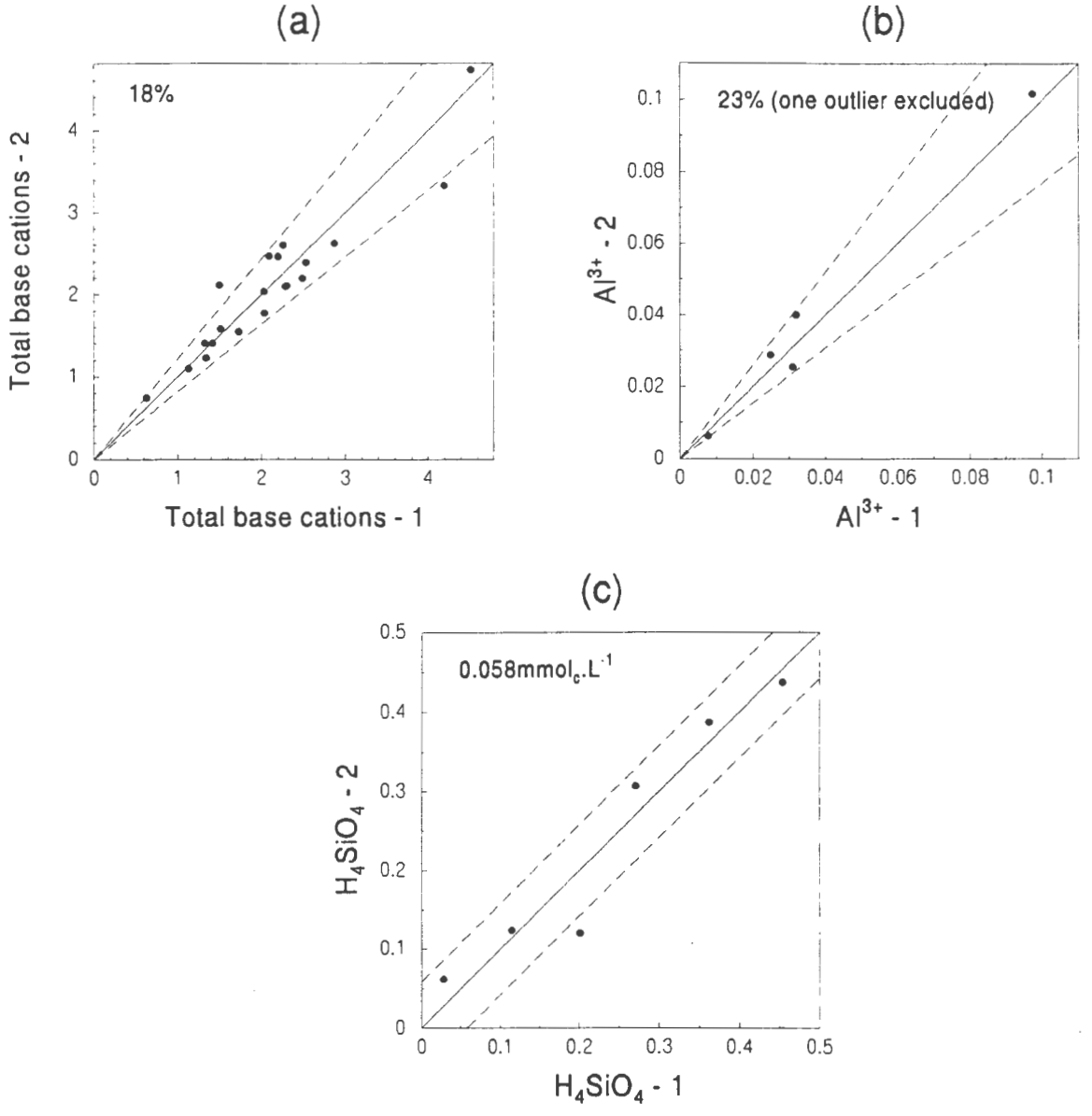

Figure E3: *Plots comparing total base cation, aluminium and silicon data for duplicate saturated paste extracts. Data for extract one is plotted on the horizontal axis and that for extract two is plotted on the vertical axis. The total base cations and Al data are given in mmol$_c$ L^{-1}, whereas the H_4SiO_4 data is in mmol L^{-1}. Best estimates of the combined analytical and extraction error for each variable are given in the top left hand corner of each plot and are represented graphically by the dashed lines on either side of a one-to-one correlation line (solid line).*

E2. EVALUATION OF SAMPLING VARIABILITY

Duplicate paired (forest-virgin) composite samples were taken from six sites in order to asses variability associated with sampling, and thereby obtain an indication of how representative the original composite samples are. The sites, four in the eastern escarpment and two in the western Cape, were sampled one year after the original samples were taken. Because the samples were taken at the same time of year (during the same month) and under the same climatic conditions, seasonal effects on soil chemistry are likely to be minimised, and observed differences are likely to be due primarily, although not exclusively, to random sampling error. Sampling grids at each site were located such that individual samples (ten for each composite) were taken as near to the original sampling sites as possible.

In Figure E4 selected analytical results obtained for the duplicate samples are compared to those obtained for the original samples. The data are represented both as absolute values for forest and virgin samples, and as differences between forest-virgin sample pairs (reflecting afforestation impacts). The plots illustrate that for most variables, differences between the 1995 and 1996 samples are not significantly greater than analytical precision estimates, and inter-site variations both in absolute values (Figure E4.a1-a12) and in forest-virgin differences (Figure E4.b1-b12) are well duplicated in most cases. Thus the data suggest that, the composite samples taken for this study smooth out spatial variability and provide a representative indication of soil chemistry at individual sites. In addition, the observed reproducibility indicates that temporal variability (at least on an annual time-scale) is minimal.

There are some exceptions to the overall reproducibility of the saturated paste data. Dissolved organic carbon (DOC) and chloride display differences in absolute values and in afforestation impacts which for some sites significantly exceed analytical precision estimates. In the case of DOC, this is likely to be the result of microbial activity which would be expected to produce relatively small scale temporal and spatial variations. The chloride variations are less simple to account for, but may result from a combination of variable inputs, a high degree of mobility and variable degrees of flushing by dilute precipitation. Thus caution needs to be exercised when interpreting differences in DOC and chloride concentrations between individual sites.

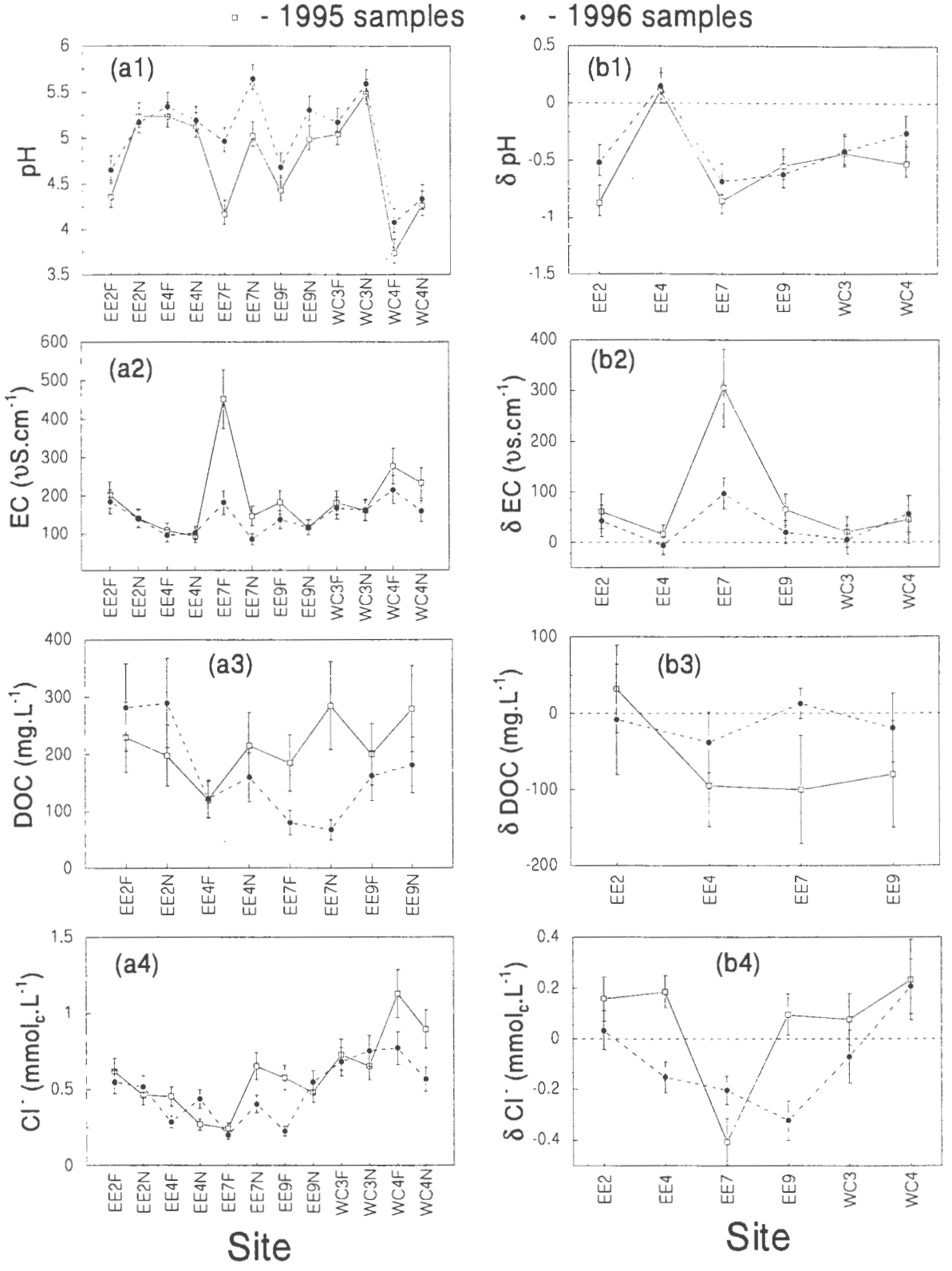

Figure E4: *Comparison of saturated paste extract data for duplicate samples taken in 1995 and 1996. Absolute values for both forest (F) and virgin (N) sites are plotted in (a1) to (a12). The differences for forest-virgin sample pairs (δx = x in forest soil minus x in virgin soil) are plotted in (b1) to (b12). Error bars represent estimates of analytical error based on duplicate extracts (Table E.1). Lines joining points are included in order to better facilitate comparison of inter-site variations.* *Continued on next page.*

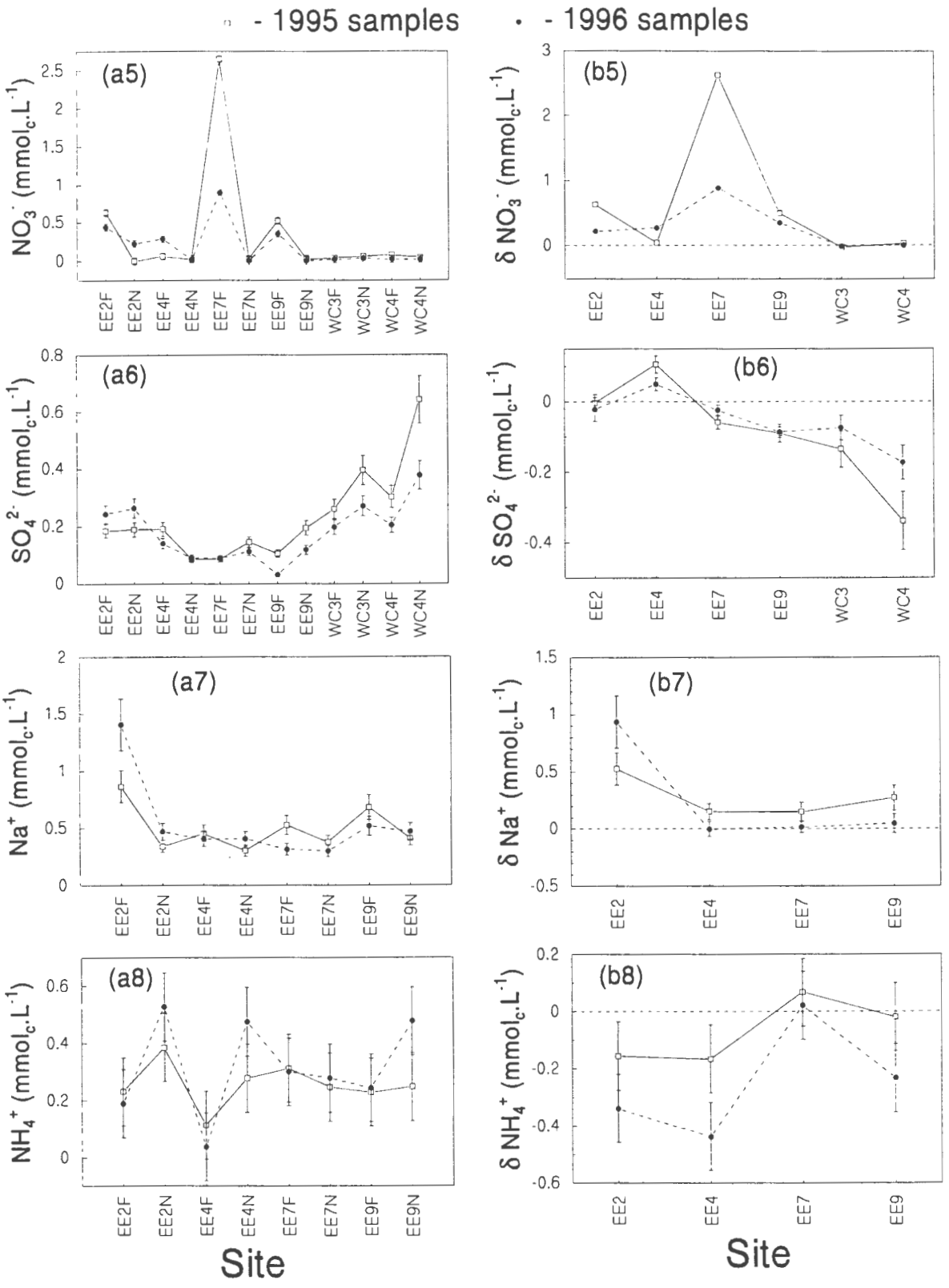

Figure E4 continued: *Comparison of saturated paste extract data for duplicate samples taken in 1995 and 1996. Absolute values for both forest (F) and virgin (N) sites are plotted in (a1) to (a12). The differences for forest-virgin sample pairs (δx = x in forest soil minus x in virgin soil) are plotted in (b1) to (b12). Error bars represent estimates of analytical error based on duplicate extracts (Table E.1). Lines joining points are included in order to better facilitate comparison of inter-site variations. Continued on next page.*

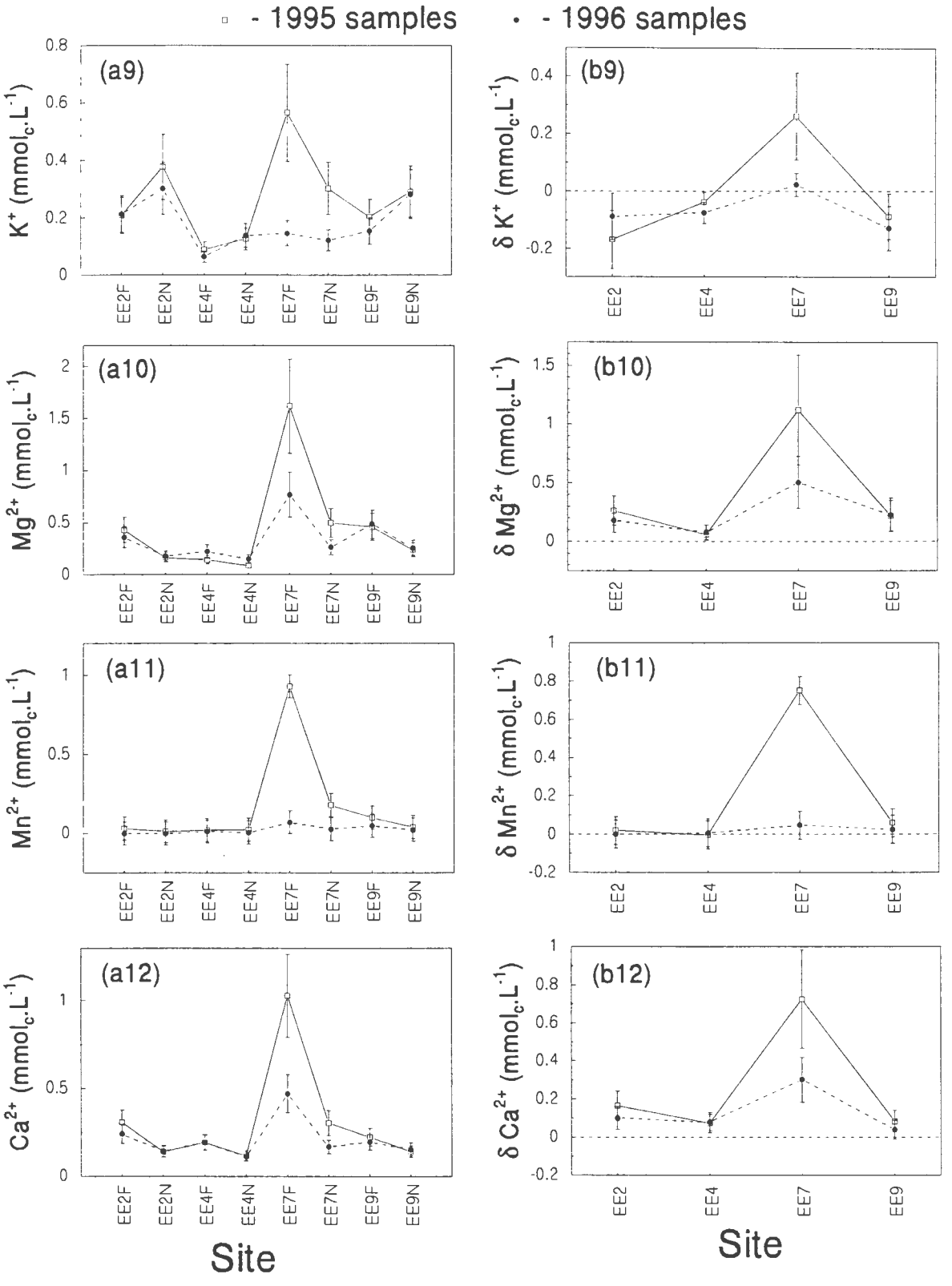

Figure E4 continued: *Comparison of saturated paste extract data for duplicate samples taken in 1995 and 1996. Absolute values for both forest (F) and virgin (N) sites are plotted in (a1) to (a12). The differences for forest-virgin sample pairs (δx = x in forest soil minus x in virgin soil) are plotted in (b1) to (b12). Error bars represent estimates of analytical error based on duplicate extracts (Table E.1). Lines joining points are included in order to better facilitate comparison of inter-site variations.* *Continued on next page.*

Site EE7 differs from all of the other sites which were resampled in that it consistently shows very large differences between values obtained on 1996 samples and those obtained in 1995. The 1996 forest samples from this site show nitrate levels which are significantly reduced relative to the extremely high values obtained for the original sample. The reduced nitrate levels are reflected in a lower electrical conductivity (EC) and are accompanied by higher pH values and consistently lower concentrations of all cations except for sodium and ammonium (Figure E4.a7, a8, b7 and b8). The original (1995) samples from EE7 were taken approximately one year after the site was clearfelled. It is therefore likely that the high initial nitrate levels result from rapid oxidation of organic matter following harvesting, and this effect is less prominent in the duplicate samples taken in the following year. An alternative hypothesis is that the high nitrate concentrations are caused by fertiliser application immediately after replanting of pine seedlings in early 1995 (prior to initial sampling).

APPENDIX F: AN ASSESSMENT OF POTENTIAL BIOLOGICAL DIFFERENCES BETWEEN GRASSLAND AND FORESTED STREAMS IN MPUMALANGA USING THE RAPID BIOASSESSMENT METHOD SASS4

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F1. Introduction

The following assessment was undertaken to ascertain if observed differences in stream water chemistry between grassland and afforested streams are reflected in biological differences. The biotic component examined for this purpose was the benthic macroinvertebrates, comprising mostly the aquatic stages of insects, worms, snails and crustaceans.

F2. Methodology

The rapid bioassessment method, SASS4 (South African Scoring System, Moore & McMillan 1993) was used and is based on one component of the aquatic biota, namely benthic macroinvertebrates, which commonly live in aquatic ecosystems, in habitats such as stony beds, marginal vegetation and sand. SASS4 is a field-based method that uses information on aquatic invertebrates to assess the impairment of water quality in rivers. It yields a Total Score, the number of taxa and the Average Score Per Taxon (ASPT) for a site. The Total Score is derived by summing the sensitivity/tolerance scores assigned to each invertebrate family whilst the ASPT is a value of this Total Score divided by the number of families present at the site. Because SASS4 is based on families of invertebrates it provides an assessment of change in a river at a medium-to-coarse level. Any effects at species level will therefore not be detected. This method has been used extensively within the south-western Cape, Mpumalanga and other provinces and its usefulness in establishing impaired water quality has been demonstrated (e.g. Dallas 1995). The advantages of using biological assessment methods as opposed to methods which rely on physical and chemical attributes of the water, include the fact that biological methods integrate effects, both in terms of time scale (i.e. intermittent pulses which may not be recorded with chemical monitoring), and in terms of assessing the effect of multiple stresses.

SASS4 assessments were undertaken on 22 and 23 May 1996. Five sites were selected for sampling. Four of these represented two pairs, each pair including a site in a natural grassland area (sites EER4 and EER2-1) and a site in a forested area (sites EER5 and EER1). The fifth site was upstream (site EER2-2) of the grassland site EER2-1. A description of each sampling site, the biotopes (possible areas that animals can live) sampled, the Total Scores, number of taxa (i.e. families of animals) and the Average Score Per Taxon (ASPT) values are given in Table F1 and Figure F1. A more detailed description of the aquatic invertebrates recorded at each of the sites is given in Table F2.

Table F1: *Site description, biotopes sampled, Total Scores, number of taxa and Average Score Per Taxon (ASPT) values for each site sampled in the Sabie area.*

Site	River	Description	Biotopes sampled	Total Score	Number of taxa	ASPT
EER4	Mac-Mac Tributary Grassland stream	Mountain stream, closed canopy	shallow riffle and run (stones in turbulent water flow), marginal vegetation (grasses), gravel and sand	161	21	7.67
EER5	Klipkraal Forest Stream	Mountain stream, single channel, closed canopy	shallow riffle and run, marginal vegetation (grasses), stones in backwater (no flow), gravel and sand	131	21	6.24
EER2-1	Heddle River @ bridge Grassland stream	Foothill zone, braided river in gorge	deep riffle and run, marginal vegetation (grasses), stones in backwater and sand	184	25	7.36
EER1	Lisbon River @ bridge Forest stream	Foothill zone, single channel	deep and shallow riffle and run, marginal vegetation (grasses), gravel and sand	147	17	8.65
EER2-2	Heddle River @ Paradise grassland stream	Mountain stream, braided channel of bedrock	deep and shallow riffle and run (loose cobble on bedrock), marginal vegetation (grasses), aquatic (instream) vegetation, gravel and sand	160	21	7.62

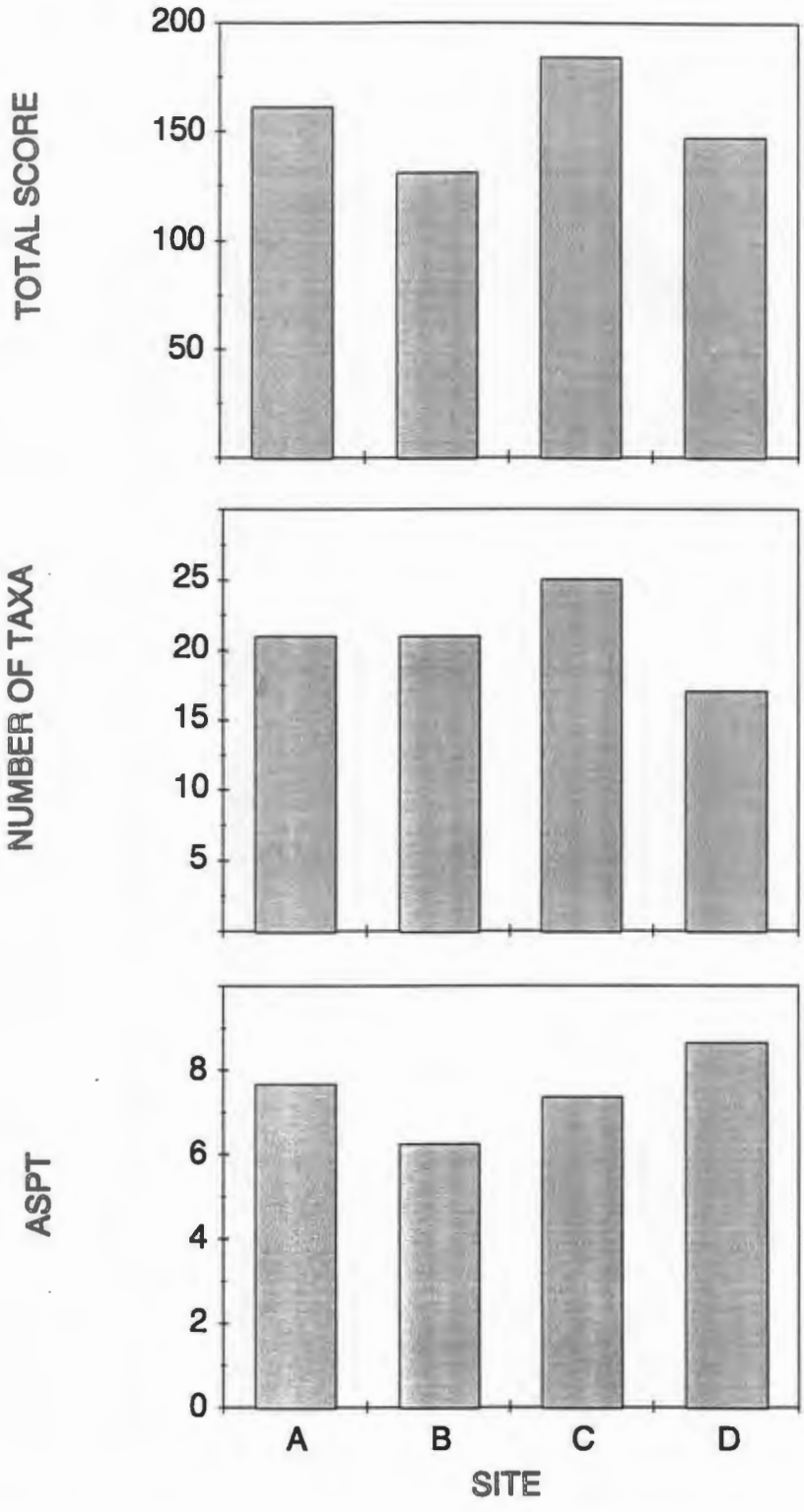

Figure 1. Total Score, Number of Taxa and Avergae Score per Taxon (ASPT) for two pairs of sites (A and B; C and D). Grassland sites are indicated by and forested ones by

Figure F1: *Graphical representation of SASS4 scores assigned to paired forest and grassland streams. A = EER4; B = EER5; C = EER2-1; D = EER1.*

Table F2: *SASS4 scores for each of the taxa recorded in this study. Squares indicate the sites at which each was recorded. Differences referred to in the text are highlighted with large squares* (■).

TAXON		SASS4 Score	EER4	EER5	EER2 -1	EER1	EER2-2
Turbellaria	Planaria	5	▪	▪			▪
Oligochaeta		1	▪	▪			
Hydracarina		8		▪			
Decapoda		3	■		■		▪
Plecoptera	Notonemouridae	12	▪	▪		▪	
	Perlidae	12				▪	▪
Ephemeroptera	Baetidae 3 species	12	■		■	■	▪
	Heptageniidae	10			■		
	Leptophlebiidae	13	■		■	■	▪
	Tricorythidae	9			■		▪
Odonata	Chlorolestidae	8	▪	▪	▪		▪
	Protoneuridae	8			▪		
	Coenagriidae	4		▪	▪		
	Chlorocyphidae	10	▪				
	Gomphidae	6	▪	▪	▪	▪	▪
	Aeshnidae	8	▪		▪	▪	
Hemiptera	Notonectidae	3		▪	▪		▪
	Naucoridae	7		▪	▪		▪
	Nepidae	3		▪			
	Corixidae	3					▪
	Gerridae	5			▪		
	Veliidae	5	▪		▪	▪	
Trichoptera	Hydropsychidae 1 type	4				▪	▪
	Hydropsychidae 2 types	6	▪	▪	▪		
	Philopotamidae	10	■		■		▪
	Cased caddis 1 type	8					
	Cased caddis 2 types	15	▪		▪		
	Cased caddis ≥ 3 types	20		■		■	▪
Coleoptera	Dytiscidae	5		▪	▪		▪
	Gyrinidae	5	▪	▪		▪	▪
	Elmidae/Dryopidae	8	▪	▪	▪	▪	▪
	Helodidae	12	▪	▪	▪	▪	
	Hydrophilidae	5		▪			
	Psephenidae	10	■		■		
Diptera	Blephariceridae	15					■
	Tipulidae	5	▪		▪	▪	▪
	Simuliidae	5	▪	▪	▪	▪	▪
	Chironomidae	2	▪	▪	▪	▪	▪
	Tabanidae	5		▪	▪	▪	
	Athericidae	13				▪	
	Empididae	6		▪			

F3. RESULTS

The combination of Total Score and Average Score Per Taxon (ASPT) provides an indication of the extent of impairment of water quality, and the water quality associated with different combinations of these two measures are outlined in Table F3 (modified from Chutter, 1996). Based on the results of rapid bioassessment of the five sites the following conclusions can be drawn.

- Sites EER4 (grassland) and EER5 (forested) differed in terms of Total Score (161 and 131 respectively) and ASPT (7.67 and 6.24 respectively), although the number of taxa (invertebrate families) was 21 for both (Table F1, Figure F1). This suggests that more tolerant taxa were present at site EER5 (the afforested site). Most notable was the absence of mayflies (Ephemeroptera) at site EER5, whilst 3 species of baetid mayflies and one species of leptophlebiid mayflies were present at site EER4. Crabs (Decapoda), psephenid beetles and philopotamid caddisflies were also absent at site EER5 (Table F2). Six types of cased caddisfly larvae were present at site EER5 (Table F2). Both sites are within Class A, i.e water quality natural, habitat diversity high (Table F3).

- Sites EER2-1 (grassland) and EER1 (forested) differed with respect to Total Score (184 and 147 respectively), number of taxa (25 and 17 respectively) and ASPT (7.36 and 8.65) respectively Table F1, Figure F1). The comparatively low ASPT at site EER2-1 relative to site EER1 is largely attributable to the presence of quiet backwaters (areas of no flow), and to the relatively high percentage of air-breathing taxa at site EER2-1. Crabs (Decapoda), psephenid beetles, philopotamid caddisflies were absent at site EER1 (Table F2). Three types of cased caddisfly larvae were present at site EER1 (Table F2). Both sites are within Class A, i.e water quality natural, habitat diversity high (Table F3).

- Site EER2-2, upstream of site EER2-1, had a Total Score = 160, number of taxa = 21 and an ASPT = 7.62 (Table 1). Characteristic blepharicerid dipteran larvae were found at this mountain stream site (Table F2). This site is within Class A, i.e water quality natural, habitat diversity high (Table F3).

Table F3: *Interpretation of water quality in rivers based on Total Score and ASPT (from Chutter, 1996.)*

Class	Total Score	ASPT	Description
A	> 100	> 6	water quality natural, habitat diversity high
B	< 100	> 6	water quality natural, habitat diversity reduced
C	> 100	< 6	borderline case between water quality natural and some deterioration in water quality, interpretation should be based on the extent by which Total Score exceeds 100 and ASPT is < 6
D	50 - 100	< 6	some deterioration in water quality
E	< 50	ASPT variable	major deterioration in water quality

F4. DISCUSSION

On the basis of single SASS4 assessments at each site the following is apparent. Total Scores and ASPTs recorded during this study are all within Class A (Table F3) suggesting that, in general context, all of the sites have natural water quality and habitat diversity is high. However, if one makes comparisons within the pairs of sites (i.e EER4 versus EER5, EER2-1 versus EER1) certain trends become apparent. In both the forested streams three taxa are absent, namely the Decapoda, Philopotamidae and Psephenidae, in addition to an absence or decrease in Ephemeropterans. Cased caddisflies, on the other hand, appear to be significantly more abundant in the forested streams. This change in benthic macroinvertebrate community structure may be associated with the differences in water quality noted between the grassland and forested streams. It may, however, also be related to changes in the type and extent of allochthonous (input from outside the stream) material. Further investigation, however, would be needed to clarify the "cause and effect". Seasonal differences, particularly those related to rainfall events and hence import of material into the stream, may also occur but these could only be identified if sampling were to be repeated on a seasonal basis. More subtle effects resulting from changes in taxa at the species level may also be occurring.

Regardless of the specific cause of the community differences, it is apparent that whilst similar difference are noted within the pairs, the resultant effects on the SASS4 scores are less similar. In particular, the differencess with respect to ASPT values in the mountain stream pair (sites EER4 and EER5), both Total Score and ASPT were significantly lower at the forested site, clearly indicate that there is indeed an effect of afforestation at site EER5. Such differences are not apparent within the other pair, a foothill zone stream, although the number of taxa is lower. Reasons for this include differences in biotope availability and the relative proportions of air-breathing taxa. These results also indicate the importance of taking the river zone, i.e. mountain stream versus foothill, into account, since effects may be more pronounced in one or the other zone, such as in mountain streams.

Lastly, the importance of ensuring that there are realistically comparable sites is highlighted. Whilst effects may appear insignificant in terms of general trends, it is important to establish control or reference sites with which experimental or test sites can be realistically compared.