ACIDIFICATION OF SANDS IN CITRUS ORCHARDS FERTILIZED BY DRIP IRRIGATION

BY
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DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and has not previously, in its entirety or in part, been submitted at any other university for a degree.

20 / 11 / 2002

Date

ABSTRACT

The use of drip irrigation in citrus orchards is becoming increasingly important in the Citrusdal region of the Western Cape. Drip irrigation provides an opportunity to optimize water and fertilizer use by inducing a smaller root zone that can be managed more effectively. Ammoniacal fertilizers are an integral part of any drip fertilization (fertigation) programme. However, a disadvantage is that they generate soil acidity upon nitrification. If insufficient plant uptake of nitrate occurs during the fertigation season, soil acidification may become an important yield-limiting factor. This study investigated the effect of drip fertigation on four sandy soils with different buffer capacities, near Citrusdal. Spatial variation in soil chemical properties below irrigation emitters was investigated to determine the nature and extent of soil acidification from drip fertigation. The response of the four sands to acid and base addition (and laboratory incubation) was also studied in order to assess the magnitude and origin of pH buffering.

The soil types in the four orchards included two poorly buffered and two moderately buffered soils. Both the poorly buffered soils, at Brakfontein and Swartvlei, were classified in the Kroonstad form and contain less than 5% clay. The two moderately buffered soils, at BoHexrivier and OnderHexrivier, were classified in the Vilafontes and Constantia forms, respectively, and contained more than 10% clay in the subsoil. X-ray diffractometry revealed that kaolinite and quartz dominate the clay fraction of all four soils. Organic carbon content in the topsoils ranged from 0.2-0.98 percent.

Drip fertigation for a period of between 4 and 10 years at all four sites has resulted in large decreases in soil pH to depths of up to 1 m below the emitter with a sharp increase in acid saturation at pH_{KCl} values below 4.5. The Brakfontein and Swartvlei orchard soils were the least acid saturated with levels of about 50-60 percent. At the BoHexrivier site acid saturation values of 70 percent were recorded for the topsoil immediately below the emitter, while the whole soil profile

of the OnderHexrivier site had extreme acid saturation levels, exceeding 90 percent in the deeper parts of the profile. It was also revealed that a large proportion of the 1 M KCl-extractable acidity consisted of Al, although Al saturation showed a poorer relationship to pH_{KCl} than did acid saturation. The Al component of exchangeable acidity in the OnderHexrivier subsoil was significantly larger [Al = 0.84(acidity)] than in the other soils [Al = 0.69(acidity)]. It was found that most of the wetted soil volume was deficient in exchangeable Ca, Mg, K and enriched with Al. No accumulation of NH_4^+ or NO_3^- was found in any of the soils directly below the emitter, indicating either a sufficient degree of nitrification or the leaching of both NH_4^+ and NO_3^- to greater depths. The mobile anions Cl^- and SO_4^{2-} also appeared at the periphery of the wetting front. Phosphate generally accumulated in the soil just below the emitter, except in two of the soils where P showed some degree of leaching. Spatial variation in soil chemical properties indicated that nitrification and over-irrigation had resulted in a significant volume (between 0.1 and 1.1 m^3) of severely acidified soil (pH_{KCl} <4.5) below the emitter at all four study sites.

Buffering in these naturally acidic sandy soils from the Citrusdal area is weak as a result of the low clay and organic matter contents. The low content of clay, dominated by kaolinite and quartz, implied that organic carbon plays an important role in pH buffering, especially in the topsoils. Laboratory incubation with acid or base confirmed the fact that CEC becomes increasingly saturated by acidic cations (H^+ and Al^{3+}) once soil pH_{KCl} values decrease below 4.5. Again Al was found to be the major acidic cation [Al = 0.69(acidity)], especially in the subsoils. This confirmed that, even in these poorly buffered, quartz-rich sandy soils, toxic amounts of Al could enter the soil solution quite rapidly following acidification. Lime requirement calculated from the slope of titration curves following incubation provided a useful way of assessing the magnitude of the acidification problem, even though liming the acidified subsoil may present practical difficulties under field conditions in drip-fertilized irrigation systems. These lime requirement values, ranging from 0.9-10.3 tonnes of $CaCO_3$/ha, can be applied to field conditions with some calibration refinements.

UITTREKSEL

Die gebruik van drup besproeiing in die citrus boorde van Citrusdal in die Wes-Kaap is besig om toenemende belangstelling te werf. Drup besproeiing bied die geleentheid om water en misstof toediening te optimiseer deur die meer effektiewe benutting van 'n kleiner wortel sone. Mistowwe wat ammonium bevat is 'n integrale deel van enige drup en misstof toedienings (misstofbesproeiing) program. 'n Nadeel hiervan egter is die vorming van grondsuurheid weens nitrifisering. Indien nitraat onvoldoende deur die plant opgeneem word gedurende die misstof besproeiings seisoen, kan grondversuring 'n belangrike opbrengs-bepalende faktor word. Hierdie studie het die invloed van misstof besproeiing op vier sanderige gronde met vier verskillende buffer vermoëns naby Citrusdal ondersoek. Die ruimtelike variasie in die chemiese einskappe van die grond direk onder die drupper is ondersoek om die aard en omvang van grondversuring van drup besproeiing te bepaal. Die reaksie van die vier sande op die byvoeging van suur en basis (en laboratorium inkubasie) is ook bestudeer om die grootte en oorsprong van pH buffereinskappe te bepaal.

Die vier boordgronde het bestaan uit twee swak-gebufferde en twee matig-gebufferde gronde. Beide die swak-gebufferde gronde, by Brakfontein en Swartvlei, is geklassifiseer in die Kroonstad vorm en bevat minder as 5% klei. Die twee matig-gebufferde gronde by BoHexrivier en OnderHexrivier, is geklassifiseer in die Vilafontes en Constantia vorms onderskeidelik, en bevat meer as 10% klei in die ondergrond. X-straal diffraksiometrie het getoon dat kaoliniet en kwarts die klei-fraksie oorheers. Organiese koolstof in die bogrond het gewissel van 0.2-0.98 percent.

Drupmisstofbesproeiing, vir 'n tydperk van tussen 4 en 10 jaar, het by al vier persele groot afnames in grond pH tot 'n diepte van 1 m, met 'n skerp toename in suur versadiging, tot gevolg gehad. Suurversadiging by die Brakfontein en Swartvlei boordgronde is die minste met vlakke van omtrent 50-60 percent. By die BoHexrivier perseel, het suurversadiging waardes van 70 percent bereik in

die bogrond direk onder die drupper. Die hele profiel van die OnderHexrivier perseel het uiters hoë suurversadigings vlakke gehad, met waardes van hoër as 90 percent in die dieper dele van die profiel. Daar is ook getoon dat 'n groot gedeelte van die 1 M KCl-ekstraeerbare suurheid bestaan uit Al, hoewel Al versadiging 'n swakker verwantskap toon met pH_{KCl} as suurversadiging. Die Al komponent van uitruilbare suurheid in die OnderHexrivier ondergrond is betekenisvol groter [Al = 0.84(suurheid)] as die ander gronde [Al = 0.69(suurheid)]. Daar is gevind dat die grootste gedeelte van die benatte grond volume gebrekkig is aan Ca, Mg en K, en verryk is in Al. Geen akkumulasie van ammonium of nitraat is gevind direk onder die drupper van enige van die persele nie, wat aandui dat daar genoegsame nitrifisering, of diep loging van beide ione plaasgevind het. Die mobiele ione, chloor en sulfaat is gevind aan die buiterand van die benattings volume. Fosfaat het oor die algemeen in die omgewing van die drupper gekonsentreer, behalwe in twee gronde waar daar tog 'n mate van P-loging waargeneem is. Die ruimtelike variasie in grondchemiese kenmerke het aan die lig gebring dat groot volumes (tussen 0.1 en 1.1 m^3) grond versuur het direk onder drupper van al vier persele as gevolg van nitrifisering en oorbesproeiing.

Die buffereinskappe van hierdie sanderige, natuurlike suur gronde van Citrusdal is swak weens hul lae klei en organiese materiaal inhoud. Die lae inhoud van klei, wat deur kaoliniet en kwarts oorheers word, impliseer dat organiese materiaal 'n belangrike rol speel in pH buffereienskappe, veral in die bogronde. Laboratorium inkubasie met suur en basis het die feit bevestig dat die KUK toenemend versadig word met suur katione (Al^{3+} en H^+) sodra grond pH_{KCl} na waardes laer as 4.5 verminder. Weereens is gevind dat Al die belangrikste suur katioon is [Al = 0.69(suurheid)], veral in die ondergronde. Dit impliseer dat selfs swak-gebufferde, kwartsryke sande ook die vermoë beskik om toksies hoeveelde Al tot die grondoplossing te voorsien as gevolg van grondversuring. Kalkbehoeftes wat bereken is vanaf die helling van die titrasie kurwes na inkubering, bied bruikbare inligting om die graad van die grondsuurheids probleem te bepaal, hoewel bekalking van die versuurde ondergrond praktiese probleme mag voorsien onder toestande van

drupmisstofbesproeiing. Die kalkbehoefte waardes wat wissel van 0.9-10.3 ton/ha kan toegepas word in die praktyk met sommige kalibrasie verfynings.

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This thesis is largely dedicated to my parents who are a blessing to me.

Finally, I would like to give glory to the most important person in my life: my Rock, my Joy, my Strength, my Refuge and my Salvation, Jesus Christ, who said:

"I am the vine, you are the branches. He who abides in Me, and I in him, bears much fruit; for without Me you can do nothing."

[John 14:5 (NKJV)]

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INTRODUCTION

Citrusdal is situated in the Olifant's River valley near the Cedarberg mountain range in the Western Cape. The area receives moderate to low winter rainfall and summers are hot and dry. Quartzitic sandstones of the Table Mountain Group dominate the geology of the area. Soils that develop under these climatic conditions and parent materials are mostly poorly buffered sandy soils with a low organic carbon content (Ellis *et al.*, 1989).

The Olifant's River supplies most of the water needed for the production of high quality citrus in the area. Water reserves are decreasing and many citrus growers are changing from regular irrigation systems to drip irrigation as means of cutting down on their water use. Drip irrigation also gives the grower the opportunity to fertilize more efficiently by applying fertilizers directly through the irrigation system (fertigation) (Haynes, 1985; Bravdo & Proebsting, 1993). A disadvantage of drip fertigation is the probable acidification of the soil volume immediately below the dripper (Edwards *et al.*, 1982; Haynes & Swift, 1987; Parchomchuk *et al.*, 1993). Fertilizers that contain ammonium or urea as nitrogen source have the ability to produce acidity upon nitrification (Tisdale *et al.*, 1993, p371). It is very difficult to design a fertilization programme without including ammonium or urea as a source of nitrogen. Many farmers may therefore have to suffer the consequences of soil acidification. In sandy Citrusdal soils, H.G.M van Zyl (personal communication) and Pijl (2001) have reported severe acidification after only a few years of drip fertigation. Inputs of acidity from nitrification as well as increased leaching can deplete the acid neutralizing capacity of these unbuffered sandy soils within only a few irrigation cycles. The resulting decrease in soil pH and associated problems such as aluminium toxicity could severely affect citrus yields if preventative measures are not taken.

In studying the effects of two drip fertigation systems on root development of citrus trees, Pijl (2001) found poor root development beneath the dripper with roots tending to concentrate in the

spaces between the emitters on a sandy soil under a conventional drip fertigation system, applying daily drip irrigation and either daily or weekly fertigation with a nutrient solution containing macronutrients only. On the other hand, roots developed well under a system of daily drip fertigation in which a nutrient solution containing both macro- and micronutrients was applied daily by means of pulse irrigation. Furthermore, it was found that on a silt loam soil, roots developed well under both types of drip fertigation. Soil acidity and/or oxygen deficiency were suggested as possible causes of restricted root growth, resulting from the tendency to over-irrigate under the conventional drip fertigation system.

The objectives of this study were:

1   To investigate the magnitude and spatial extent of soil acidification and associated chemical changes (cation and anion composition) of a representative selection of sandy orchard soils in the Citrusdal area as a result of drip fertigation practices.

2   To study the buffering properties of the soils through laboratory incubation after acid or base addition as a means of understanding the soil chemical response to fertigation and of formulating practical strategies for minimizing the degree of soil acidification and its impact on orchard productivity.

1   Origin and control of soil acidity: A review

1.1   Introduction

A fundamental part of sustainable agricultural production today consists of understanding and managing soil acidity. Soil acidity affects large areas of the tropics as well as the temperate regions. Soils can acidify through both natural and anthropogenic (agricultural and industrial) processes. One of the most important acidifying processes in agriculture is the microbial oxidation (nitrification) of ammoniacal fertilizers (Tisdale *et al.,* 1993). As soil pH declines and soils become more acidic, phytotoxic forms of aluminium (Al) and manganese (Mn) are released into the soil solution (McBride, 1994). An integral part of amending and managing soil acidity is to neutralize and/or reduce these phytotoxic elements to more favourable quantities for plant growth. Also, acid soils are usually impoverished in a range of macronutrients and replenishment of these elements is important. Redeeming the effects of soil acidification is expensive and requires knowledge of the reversibility of the changes and an understanding of why liming practices do not always produce the expected results (Fey, 2001).

Understanding and managing soil acidity thus requires a sophisticated knowledge and strategy to ensure that we conserve our most important resource for generations to come. The aim of this chapter is to review the underlying aspects of the origin and control of soil acidity.

1.2   The nature of soil acidity

1.2.1   Soil pH

Soil pH is probably the most indicative measurement of the chemical properties of a soil. Soil pH has much to do with controlling the solubility of various compounds, the relative bonding of ions to the exchange sites, and the activity of various microorganisms. Thomas (1967) noted that three pH ranges are particularly informative: a pH from 7.8 to 8.2 indicates the presence of calcium carbonate ($CaCO_3$); a pH <5.5 suggests the likely occurrence of soluble aluminium (Al^{3+}) and

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manganese (Mn^{2+}); and a pH <4 indicates the presence of free acids, generally from oxidation of sulfides.

The measurement of pH is normally made by means of either an electrometric or colorimetric method. Measuring pH colorimetrically involves suitable dyes or acid-base indicators, the colors of which change with H-ion activity. The use of indicators for identifying pH ranges and endpoints of acid-base titrations in clear solutions is widespread, but they are less suitable than electrometric methods for measuring soil pH, because they tend to be slower, less precise, and obscured from view by the soil particles (McLean, 1982). Their use is therefore not common, except in field test kits where pH level is to be approximated. The electrometric method involves a glass H^+-sensing (indicator) electrode in conjunction with a reference electrode attached to a suitable meter for measuring ΔE. The potential between the electrodes, ΔE, is related to pH at room temperature by the Nernst equation:

$$pH = (\Delta E - constant)/0.059 \qquad [1.1]$$

where ΔE is expressed in units of volts (McBride, 1994). In order to make electrical contact, a soil paste or suspension is prepared. For routine analysis a 1: 2.5 (g soil: cm^3 solution) suspension is commonly used and the pH is measured in the stirred suspension after a few minutes of equilibration. Other soil: solution ratios are also commonly used including 1:1, 1:5 and 1:10 (McLean, 1982).

If a soil suspension is left to settle, the pH measured in the sediment is usually lower than that of the supernatant and this phenomenon is called the *suspension effect*. The *suspension effect* is maximal with high soil cation exchange capacity, weakly bound exchangeable ions, and low electrolyte concentration (Coleman &Thomas, 1967). It can, however, be minimized by suspending the soil in 0.01 M $CaCl_2$ or 1 M KCl (Woodruff, 1967; McLean, 1982). For most acid or neutral soils this causes a depression of pH of about 0.5 units compared to that in water. The added cation displaces the H^+ into the solution and the dilution effect is counteracted. This is called the *salt effect*. The

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lower pH is closer to the value in the soil solution and therefore probably a more accurate reflection of the actual pH influencing soil chemical and biological processes (Rowell, 1988).

1.2.2 Acidity on soil surfaces

Soil pH is sensitive to the acidity retained on particle surfaces. This acidity, referred to as *reserve acidity,* can build up at low pH on the surfaces of soil colloids (McBride, 1994). Important sources are dissociation of organic acids, hydrolysis of Al^{3+}-organic complexes, non-exchangeable forms of acidity on sesquioxide minerals, and cation exchange and hydrolysis of exchangeable H^+ and Al^{3+}. The response of the *reserve acidity* to the H^+ and Al^{3+} in the soil solution, termed the *active acidity,* is slow because of slow ionic diffusion through micropores of the soil particles and slow dissociation of Al^{3+}-complexes. Bases (e.g. liming materials) added to a soil initially react with the active acidity in the soil solution, and subsequently with the acidity released from the reserve acidity pool, a quantity representing the *buffer capacity* of the soil (McBride, 1994).

The *exchangeable acidity* parameter, commonly used in lime requirement predictions, is usually determined by displacing the bound H^+ and Al^{3+} with a concentrated neutral salt solution such as 1 *M* KCl. The *exchangeable acidity* value is predominantly composed of exchangeable Al^{3+} in mineral soils and exchangeable H^+ in organic soils. Bound H^+ and Al^{3+} not easily displaced or displaced very slowly by 1 *M* KCl make up the *non-exchangeable acidity*. This form is associated with weak acid groups on humus, organically complexed Al, and Al-hydroxy cations strongly retained at mineral surfaces (McBride, 1994).

1.2.3 Aluminium solubility in soils

Aluminium is the most abundant metal in the earth's crust, comprising about 7% of the mass of the crust. Aluminium is found in soils mostly as insoluble aluminium silicates and oxides, with the oxides, particularly poorly crystalline ones, being the most reactive in acidic soils (Paterson *et al.*, 1991). As soil pH declines and soils become more acidic, phytotoxic forms of Al are released into the soil solution, primarily in the form of Al^{3+}. Since most plants are sensitive to micromolar

concentrations of Al, plant productivity will be decreased in most acidic soils (Kinraide, 1991). There are several different forms of Al in soils that contribute to the toxic quantity of Al in solution, either directly or indirectly (Adams, 1984; Ritchie, 1989). The ultimate *source* of Al in most soils is Al-containing minerals, whereas *sinks* for Al^{3+} released during mineral dissolution are organically bound, exchangeable, interlayer, and soluble complexed Al. The amount of Al^{3+} in the soil solution is separately or collectively controlled by these sinks, which provide Al^{3+} to the soil solution in the short term (Ritchie, 1994). In pure water, the solubility and chemical form of Al is determined by a sequence of hydrolysis steps that ultimately results in the precipitation of $Al(OH)_3$ above pH 5, and the dissolution of $Al(OH)_3$ as the aluminate anion above pH 8 (McBride, 1994).

Once the soil pH is lowered much below 5.5, the dissolution of aluminosilicate clays and Al-hydroxide minerals will take place, releasing Al^{3+} and Al-hydroxy cations, that can displace other cations from soil colloids into the soil solution (McBride, 1994). Exchangeable Al forms a large proportion of the total cations in acid soils, but little is extracted above pH 5.5 (McBride, 1994). The wide range of Al:CEC ratios at a given pH for the different soils is explained by the fact that some soils have very small amounts of soluble Al compounds present, so giving limited amounts of exchangeable Al. Also, variability may be as a result of determining the CEC at pH 8.2. For many soils the CEC at pH 8.2 is greater than that at the pH of the soil (Thomas & Hargrove, 1984).

Soluble inorganic and organic ligands can complex with Al^{3+} in soil solutions. The effect of ligands is to increase the concentration of total soluble Al, since many of these complexes are soluble. Ligands that increase the overall solubility of Al include F^-, $oxalate^{2-}$, $citrate^{3-}$, fulvic acid, and monomeric silicate. Ligands that decrease the overall solubility of Al include phosphate, sulfate, hydroxyl, and polymeric silicate (McBride, 1994). Although organic matter seems to increase the concentration of total Al in soil solution, its complexing capacity means that its effect is to decrease the activity of Al^{3+} in solution (Bloom *et al.*, 1979). Aluminium-organic matter complexes are not readily extractable with 1*M* KCl and KCl extractable Al is generally lower in soils rich in organic matter. The same is true for organic rich surface soils compared to subsurface soils (Hargrove &

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Thomas, 1981; Thomas, 1975). There is evidence that these various complexed forms of Al are much less phytotoxic than soluble Al^{3+} or Al-hydroxy cations, which may partly account for the lower critical pH values for plant growth in organic soils and the significance of organic matter additions in the management of soil acidity (Bloom *et al.*, 1979; Haynes & Mokolobate, 2001).

1.2.4 Soil pH buffering

Most soils are able to resist changes in pH when a source of acidity or alkalinity has been introduced into the soil system. The measure of a soil's resistance to pH change, or *buffering capacity*, is needed not only for measuring the lime requirement of a soil, but also for explaining the change in soil pH in response to biological processes such as N transformations and plant nutrient acquisition, that add OH^- and H^+ to soil (Conyers *et al.*, 2000).

According to McBride (1994) there are three main mechanisms of soil pH buffering:

1. Carbonate mineral buffering (soil pH above 7.0), in calcareous soils, in which free Ca and Mg carbonates provide reserve alkalinity that neutralises most acid inputs.

2. Exchangeable base cation buffering (pH 5.5 – 7.0), where the exchange of base cations (Ca^{2+}, Mg^{2+} etc.) for added acid cations (H^+, Al^{3+}) on clay or humus exchange sites can buffer pH.

3. Buffering by aluminosilicate mineral decomposition (pH <5.5), where part of the acidity is consumed in the breaking of Si-O-Si and Al-O-Al bonds in strongly acid soils. The product of these reactions, soluble monosilicic acid $[Si(OH)_4^0]$, is readily leached.

The determination of pH buffer capacity (pH_{BC}) required in soil acidification studies and the calculation of acidification rates are typically measured by a titration procedure (Thomas & Hargrove, 1984; van Breemen, 1991). In the past, the pH buffering capacity has been mostly related to the clay and organic matter content of a soil (Magdoff & Bartlett, 1985). In recent studies, an excellent correlation has been found between pH buffering and various soil chemical factors

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such as pH, effective cation exchange capacity (ECEC), exchangeable acidity, exchangeable Al, and organic carbon (Aitken *et al.*, 1990; Hochman *et al.*, 1995). Conyers *et al.* (2000) in their studies of titration with $Ca(OH)_2$, concluded that pH buffering is best estimated using reacted OH^-, rather than added OH^-, and that reacted OH^- can be estimated using two parameters:

$$Reacted\ OH^- = \Delta Al_{ex} + \Delta ECEC$$

where ΔAl_{ex} is the precipitated Al^{3+}, and $\Delta ECEC$ ($cmol_c/kg$) is the increase in effective cation exchange capacity after alkali addition. Thus, the buffer capacity could theoretically be expected to depend on two variables:

1. the amount of exchangeable Al (or exchangeable acidity), and

2. the extent to which deprotonation of organic groups and variable charge minerals (such as Fe and Al hydrous oxides) occurs as pH increases.

The latter deprotonation reactions lead to an increase in the net negative charge on surfaces, and this increase is reflected in the magnitude of $\Delta ECEC$ (Aitken *et al.*, 1990).

Van Breemen *et al.* (1983) introduced the concept of the *acid neutralizing capacity* (ANC) of mineral soils i.e., a soil's capacity to assimilate protons, in terms of which soil acidification can be defined as a decrease, and soil alkalinization as an increase in the ANC. The difference between the buffering capacity and ANC of a soil lies in the fact that the former relates to the amount of H^+ needed per unit pH reduction of the mineral and organic fraction of a soil, whereas ΔANC represents the change in a capacity factor unrelated to pH, and is only applicable for mineral soils and is therefore not widely used (Rowell, 1988). The ANC(S) of a mineral soil is calculated as the sum of the ANC of the solid and the aqueous phases, although the contribution of the aqueous phase is usually negligible. The ANC of a soil is equal to the basic (proton acceptor) minus the acidic (proton donor) components, and soil acidification can be defined in terms of the addition and removal of these components (van Breemen, 1991).

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1.3 Sources of soil acidification

Soils can acidify by both natural and anthropogenic (agricultural and industrial) processes. Most soils in natural ecosystems, however, can be seen as having achieved a degree of equilibrium. The removal and addition of plant material take place at similar rates, so biomass and soil organic matter remain at a constant level. Changes in the inputs to, and outputs from the ecosystem are the cause of increased soil acidification (in some cases alkalinization) rates (van Breemen *et al.*, 1983; van Breemen, 1991). The most significant inputs in the ecosystem H^+-pool are the result of chemical reactions within the carbon, nitrogen and sulfur cycles (Helyar & Porter, 1989). A discussion of various factors influencing the processes of acidification of natural and agricultural soils follows.

1.3.1 Internal sources of acidity

1.3.1.1 Carbon dioxide

Atmospheric carbon dioxide (CO_2) in contact with water forms a dilute carbonic acid solution with a pH of 5.6. The concentration of CO_2 in equilibrium with soil water (as a result of root and microbial respiration) can be five to twenty times the concentration in the atmosphere (Helyar & Porter, 1989). The role of carbonic acid becomes important only above pH 5 when it becomes significantly dissociated, thus being a major source of H^+ in neutral to alkaline soils. Soil acidification occurs when percolating water leaches bicarbonates from the soil. The metabolic activity of roots and microorganisms not only produces CO_2, but also soluble organic acids and acidic organic residues at higher pH values, which all behave as weak acids, displacing base cations from soil colloids (Coleman & Thomas, 1967; McBride, 1994).

1.3.1.2 The organic matter pool

The organic matter pool is another potential source of H^+ ions in most soils, when mineralization and nitrification of organic nitrogen release nitric acid (HNO_3) as a product:

$$R\text{-}NH_2 + O_2 = R\text{-}OH + H^+ + NO_3 \qquad [1.2]$$

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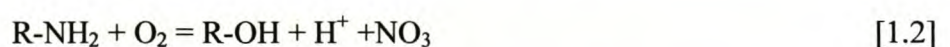
Soil acidification can only occur by leaching of base cations with nitrate, but in most soils the process is counteracted by efficient uptake by plants of any nitrate formed. As soon as the N supply exceeds the demand of plants, acidification by nitrification can occur (van Breemen, 1991). As a consequence, ecosystems that increase in biomass acidify the soil.

1.3.1.3   The assimilation of nutrients by plants

The assimilation of nutrients by plants can be a source of either acidity or alkalinity when roots release H^+ and OH^- to maintain electrical neutrality at their surfaces (van Breemen *et al.*, 1983). Plants control the pH of the cell solution during nutrient uptake by regulating the carboxylate content (Davies, 1986), which is of particular importance in N uptake and assimilation. During uptake of NH_4-N, H^+ ions are exuded, and either OH^- or HCO_3^- ions are exuded during NO_3-N uptake to maintain electrical neutrality (Raven & Smith, 1976). Thus no net acidification will occur, except if the OH^- or HCO_3^- ions are leached. In steady-state ecosystems the rate of mineralization equals the assimilation of products, and the soil does not acidify, except if plant material is harvested or exported, hence removing bases stored in vegetation and leading to permanent soil acidification (van Breemen, 1991).

1.3.1.4   Redox processes

Redox processes can play an important role in the internal production of acids in soils. The formation of acid sulfate soils, the process of ferrolysis, and alkalinization by volatilization of H_2S or gaseous N from reduced soils are excellent examples of this (van Breemen *et al.*, 1983, van Breemen, 1991). If the elements undergoing redox reactions are retained in the soil, no net acidification will take place if the oxidized elements are reduced again. However, if leaching or volatilization removes the mobile components, the changes can be permanent (van Breemen, 1991). When tidal marshes are drained, the pyrite present in the anoxic marsh soil oxidizes to form H_2SO_4:

$$FeS + 9/2\ O_2 + 5/2H_2O = Fe(OH)_3 + SO_4^{2-} + 2H^+ \qquad [1.3]$$

Acidification of sands in citrus orchards fertilized by drip irrigation
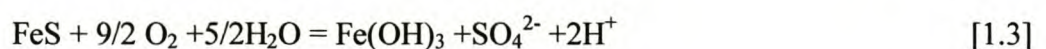
Pyrite occurs in many soil parent materials, and its oxidation can cause environmentally hazardous soil acidification in the "acid mine spoils" of many coal and metal mining regions, resulting in the dissolution of potentially toxic trace metals (McBride, 1994).

1.3.2   Atmospheric deposition of acids

The burning of fossil fuels has an important effect on ecosystems by influencing the acidity of rainwater. The deposition of atmospheric acids occur by:

1. dry deposition of SO_2 which produces acidity upon dissolution and oxidation in the soil,

2. acidity produced by nitrification of NH_4^+ dissolved in rainwater, and

3. wet deposition of H^+ as sulphuric and nitric acid (Rowell, 1988).

Wet deposition is usually relatively low in dry/warm years and acidity can by neutralized by dust from rural areas near cities. Dry deposition of SO_2 can substantially contribute to acid input, especially on neutral soils and on exposed mountains (Ulrich, 1991). Because of its nitrification, ammonium can contribute as much as 25-50% of total acid deposition in areas with high intensities of animal production (Ulrich, 1991).

In Table 1.2, it can be seen that the deposition of air pollutants is an important, but not necessarily dominant, contributor to the soil's gradual acidification, and up to 80% of the proton deposition may be buffered by foliage in some areas (Ulrich, 1991). Large areas of eastern North America and northern Europe do, however, receive significant annual acidity inputs as a result of atmospheric deposition.

Table 1.2. Acidity added to soils from various sources (from Rowell, 1988)

	Source	H addition or equivalent (kg $H^+.ha^{-1}.a^{-1}$
Natural	CO_2 in soil pH>6.5 (calcareous soils)	7.2-12.8
	Org. acids in acid soils and from vegetation	0.1-0.7
Atmosphere	Wet deposition	0.3-1.0
	Dry deposition	0.3-2.4
	NH_3 and NH_4^+ oxidation	0.7
Land use	Cation excess in vegetation	0.5-2[a]
	NH_4^+ oxidation (agric. soils) and leaching	4-6
	Oxidation of N and S from organic matter and leaching	0-10[b]

[a]Cation excess calculated for all ions except NH_4^+ and NO_3^-

[b]High values only after clearance of vegetation. Acid sulfate soils are not included

1.3.3 Fertilizers

1.3.3.1 N, P and K fertilizers

Agricultural inputs of plant nutrients by fertilizers and manure applications are often acid forming. The most important acid forming reaction is probably the microbial oxidation of ammoniacal fertilizers. Oxidation of NH_4-N to NO_3-N, referred to as nitrification, can be achieved by autotrophic and heterotrophic microorganisms with the autotrophic bacteria *Nitrosomonas* and *Nitrobacter* being most important in agricultural soils (Tisdale *et al.*, 1993). Combined mineralization and nitrification of organic N (e.g. urea) in theory produces 1 mole H^+ for every mole of N transformed. Ammonium sulfate fertilizer produces more acidity compared to urea, forming 2 moles of H^+ per mole of N transformed. This is consistent with field observations in which soil acidification was generally found to be more severe under the continual use of ammoniacal fertilizers compared to urea (Barak *et al.*, 1997; Khonje *et al.*, 1989). The depression in soil pH is generally greater as the amount of N applied increases (Jolley & Pierre, 1977; Mahli *et al.*, 1991). Again, soil acidification will depend on the fate of the nitrate formed during

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nitrification.   If insufficient plant uptake after nitrification and/or leaching takes place, soil acidification will be inevitable.   The addition of basic nitrate fertilizers such as $Ca(NO_3)_2$ and $NaNO_3$ has little effect on soil pH and sometimes increases soil pH (Awad & Edwards, 1977; Khonje *et al.*, 1989).   A summary of the reactions involved in the nitrification of ammoniacal fertilizers, and amount of lime required to neutralize the acidity formed are given in Table 1.1.

Application of soluble phosphate salts to soil can have various long-term effects.   Calcium phosphate $[Ca_3(PO_4)_2]$ precipitates in neutral to alkaline soils, and $AlPO_4$ precipitates in acid soils (Haynes, 1984; McBride, 1994).   Hence, phosphate fertilizers can act in some ways like an expensive liming material, in that they have the effect of suppressing phytotoxic Al. However, the use of diammonium phosphate (DAP) has been shown to play a role in the long-term acidification of soil under pastures in New Zealand (Manoharan *et al.*, 1995). Soil pH and Ca saturation was significantly lowered, and soluble Al increased, with application of DAP compared to superphosphate and rock phosphate.   It was concluded that the acidity formed from DAP was probably by nitrification of the NH_4^+ component.

Extremely high application rates of KCl to acid soils can result in large increases through cation exchange in the concentration of phytotoxic elements such as Al^{3+} and Mn^{2+} in the soil solution, while not substantially influencing the overall soil acidity (Tisdale *et al.*, 1993). These effects are most likely to occur in a fertilizer band or in soil adjacent to fertilizer granules.

1.3.3.2   Effect of N, P and K fertigation

Urea or ammonium and nitrate salts are commonly used as nitrogen source in drip irrigated soil systems (Haynes, 1985). Both applied ammonium and urea are subject to microbial transformation to nitrate, and subsequent soil acidification if leaching of nitrate occurs. The source of applied nitrogen will determine its mobility in the wetted soil volume. The ammonium cation is less mobile and tends to be adsorbed to soil colloids directly below the emitter, whereas nitrate and urea tend to be more evenly distributed through the soil profile (Haynes, 1985). The acidity produced by NH_4^+

fertigation will therefore be restricted to the volume directly below the emitter, compared to urea where the acidity produced will be formed at greater depths and be more difficult to ameliorate (Haynes, 1990). Parchomchuk *et al.* (1993) found that acidification was most severe in the 20-30 cm directly below the emitter, and that the soil pH decreased from 5.8 to 4.5 within 1 year and to 3.7 after 3 years of fertigation with NH_4^+-containing fertilizers. Similar results were obtained by Haynes (1990), and, additionally, it was found that soil acidification by urea occurred down to a depth of 40 cm. Edwards *et al.* (1982) and Haynes & Swift (1987) found a substantial increase in extractable Al, and decrease in extractable Ca, Mg and K, as a result of acidification below drippers.

Table 1.1. Soil acidity produced by N fertilizers (from Adams, 1984)

N Source	Nitrification reaction	Residual soil acidity				
		Maximum			Minimum	
		Acid residue	CaCO₃ equivalent (kg CaCO₃/kg of N)		Acid residue	CaCO₃ equivalent (kg CaCO₃/kg of N)
Anhydrous ammonia	$NH_3(g) + 2O_2 = H^+ + NO_3^- + H_2O$	H^+ NO_3^-	50/14 =3.6		none	0
Urea	$(NH_2)_2CO + 4O_2 = 2H^+ + 2NO_3^- + CO_2 + H_2O$	$2H^+$ $2NO_3^-$	100/28 =3.6		none	0
Ammonium nitrate	$NH_4NO_3 + 2O_2 = 2H^+ + 2NO_3^- + H_2O$	$2H^+$ $2NO_3^-$	100/28 =3.6		none	0
Ammonium sulfate	$(NH_4)_2SO_4 + 4O_2 = 4H^+ + 2NO_3^- + SO_4^{2-} + 2H_2O$	$4H^+$ $2NO_3^-$ SO_4^{2-}	200/28 =7.2		$2H^+$ SO_4^{2-}	100/28 = 3.6
Monoammonium phosphate	$NH_4H_2PO_4 + O_2 = 2H^+ + NO_3^- + H_2PO_4^- + H_2O$	$2H^+$ NO_3^- $H_2PO_4^-$	100/14 =7.2		$2H^+$ $H_2PO_4^-$	50/14 = 3.6
Diammonium phosphate	$(NH_4)_2HPO4 + O_2 = 3H^+ + 2NO_3^- + H_2PO_4^- + H_2O$	$4H^+$ $2NO_3^-$ $H_2PO_4^-$	150/28 =5.4		H^+ $H_2PO_4^-$	50/28 =1.8

A constant supply of these basic cations is therefore necessary to maintain optimal soil levels, if acidification below drippers occurs. Fertigation with nitrate in the form of $Ca(NO_3)_2$ did not acidify the soil, even at a high application rate (Haynes & Swift, 1987).

Phosphorus mobility is dependent upon the phosphate adsorption capacity of the soil just below the emitter, and P tends to concentrate in this zone. Organic phosphates such as glycerophosphate can move deeper than inorganic orthophosphates (Rauschkolb *et al.*, 1976). The most common phosphate salts used for fertigation include potassium and ammonium phosphates as well as phosphoric acid. Parchomchuk *et al.* (1993) found no enhanced acidification with simultaneous P addition with NH_4-N fertigation, and thus no contribution of orthophosphate to soil acidification. When using phosphoric acid, there may, however, be a certain degree of soil acidification.

The most common sources of potassium (K_2SO_4, KNO_3 and KCl) are all soluble, neutral salts, and have no effect on soil acidity below emitters (Haynes, 1985).

1.4   Managing and ameliorating soil acidity

Soil acidity is a yield-limiting factor in many agricultural and forest soils of the world. Two main factors limit plant productivity on acidic soils: nutrient deficiencies (base cations) and metal toxicity (soluble Al and Mn) (Sumner *et al.*, 1991). Additionally, phosphate nutrition presents problems because it is subject to strong fixation by Al and Fe hydrous oxides in many acid soils (Haynes, 1984). The toxic effect of Al^{3+} on plant roots is well known, and typical symptoms of Al damage are stunted root growth and a dying off of the root tip meristem, resulting in poorer mineral nutrition and water absorption (Delhaize & Ryan, 1995; De la Fuente-Martinez & Herrera-Estrella, 1999). In principle, the amelioration and management of soil acidity would include methods to precipitate or detoxify Al (and Mn) and at the same time replenish base cations (especially Ca and Mg), the selection of Al tolerant plant species, and the reduction of acid inputs (Helyar, 1991).

1.4.1   Plant selection

Plant species differ in their tolerance to soil acidity and Al, and many agronomically important crops like maize, soybean and wheat even show intraspecific tolerance to Al (Hocking, 2001). Selecting crop cultivars tolerant to soil acidity is an important tool for increasing yields and shifting

the cost/price ratio to values that favour higher amendment rates. There are two main mechanisms whereby plants can tolerate toxic concentrations of Al in the root zone (De la Fuente-Martinez & Herrera-Estrella, 1999):

1. excluding Al entry into the root apex and root hairs (apoplasmic mechanism), and

2. tolerating toxic Al within the cell (symplasmic mechanism).

The exclusion mechanisms take place primarily by excretion of organic acids (mainly malate, citrate and oxalate) by plant roots that act as Al-binding ligands which effectively chelate Al^{3+} and prevent its entry into the root (Delhaize & Ryan, 1995; Hocking, 2001). However, an Al-induced increase in rhizosphere pH has also been reported (Degenhardt *et al.,* 1998).

An important alternative for the management of crop production on acid soils should be the production of Al-tolerant, transgenic plant varieties. Evidence provided in recent studies that organic acids improved the Al tolerance of some plants, suggests the use of gene technologies and plant breeding to enhance organic acid exudation by plant roots to improve Al tolerance, and thus plant productivity on acid soils (Hocking, 2001).

1.4.2   Controlling soil acidity

Managing soil acidity for a given agricultural system will usually involve the use of ameliorants. Additionally, managing agricultural acid inputs in order to reduce these inputs to a minimum is also important.

Natural ecosystems are many times more efficient at recycling nutrients (especially nitrogen) than agricultural ecosystems, where nutrient losses (mostly nitrate) as a result of leaching often occur, resulting in soil acidification (van Breemen, 1991). Helyar (1991) proposed the following techniques to minimize nitrate losses in agricultural ecosystems:

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1. Match the nitrogen supply by the soil and fertilizer addition with plant and microbial demand.

2. When high nitrification rates are expected (whenever warm moist conditions favouring mineralization occur), ensure that the plant and microbial demand is high enough to consume the entire amount of nitrate produced.

3. Use techniques such as stubble incorporation, intercropping, zero-tillage techniques, and perennial rather than annual pastures, and avoid excessively high stocking rates.

Reducing the export of organic anions from and accumulation within the ecosystem can minimize acid production in the organic carbon cycle (Helyar & Porter, 1989). This can be achieved by reducing the accumulation of the surface litter layer, soil organic matter and of live plant material, as well as reducing exports of organic anions in products and waste products (Helyar, 1991). These options are, however, counterproductive and some acid addition in the form of organic acids must be accepted if soil chemical and physical fertility is to be maintained (Helyar, 1991).

1.4.3   Calcium amendments

Root damage in acidic soils is strongly correlated with the activity of Al^{3+} and the sum of activities of Al^{3+} and monomeric Al-hydoxo-species in solution culture, rather than total Al-concentration (Blamey *et al.,* 1983). Aluminium extracted by $1\ M$ KCl is, however, a better measure of the amount of lime required to neutralize phytotoxic amounts of Al^{3+} (Sims, 1996) since soil solution Al is continually replenished by exchangeable Al. In acid soils, Al, H and Ca interact in a complex manner to influence root growth (Runge & Rode, 1991), and increased Ca activity in the soil solution has been found to have an ameliorative effect on Al^{3+} and H^+ stressed roots (Foy, 1984). The Ca ion plays an important role in the formation of Ca-pectates in the middle lamella of the cell wall, and the stabilization of membranes. Calcium is transported very slowly in the phloem and a constant supply to the roots is therefore important to ensure healthy root growth (Emanuelsson, 1984). Because of the antagonistic effects between Ca and Al, various indexes have been proposed

to provide explanations for rooting performance of plants growing in acid soils. Sumner *et al.* (1986) proposed the calcium aluminium activity ratio $[0.5 \log (a_{Ca}^{2+}) - 0.33 \log (a_{Al}^{3+})]$ and Noble *et al.* (1988), working with nutrient solutions, related root length to a function called the calcium aluminium balance (CAB) $[2 \log (a_{Ca}^{2+})] - [3 \log (a_{Al}^{3+}) + 2 \log (a_{Al(OH)}^{2+}) + \log(a_{Al(OH)2}^{+})]$. It is therefore evident that in addition to actual levels of Ca and Al in acid soils, the relative levels of each must be considered as well.

1.4.3.1 Lime

The use of $CaCO_3$ and $Ca(OH)_2$ (and various other calcium compounds used as liming materials) can simultaneously precipitate phytotoxic Al by raising the soil pH while increasing soil Ca to favorable levels for root growth (Sumner *et al.*, 1991). When $CaCO_3$ dissolves in the soil solution OH^- or HCO_3^- can neutralize H^+ and Al^{3+}:

$$CaCO_3 + H_2O = Ca^{2+} + OH^- + HCO_3^- \qquad [1.14]$$

The neutralization reaction will result in the precipitation of gibbsite ($Al(OH)_3$) and the CEC becoming more base saturated. Liming may, however, prove insufficient in alleviating the subsoil acidity that is found in many soils under pastures, perennial crops and forests. Since lime has a relatively low solubility (0.014 g/l), liming usually requires mechanical incorporation or bioturbation to increase effectiveness with depth. Along with this, acid soils are also deficient in K and micronutrients such as Zn, Cu and B as a result of leaching, and the use of calcitic lime will not correct these losses (Fey, 2001).

1.4.3.2 Gypsum

The use of gypsum ($CaSO_4 \cdot 2H_2O$), can, under some conditions, prove to be more beneficial than lime in managing soil acidity. Gypsum is considerably more soluble (2.6 g/l) than regular limestone, allowing Ca to move down in the soil solution. This makes gypsum an excellent ameliorant for subsoil acidity occurring in vast areas in the humid tropics (Ritchey & de Sousa,

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1997). Beneficial effects can be seen in improved root growth and nutrient uptake, and decreasing water stress during dry periods as a result of increased concentration of soil solution Ca that has leached to greater depths. Higher levels of Ca in the soil solution can displace Al from the exchange complex. Here Al can either form a less phytotoxic $AlSO_4^+$ ion pair with the increased SO_4^{2+} in the soil solution (Kinraide & Parker, 1987; Sumner, 1993), or it can precipitate as insoluble Al sulfate compounds such as alunite $[KAl_3(OH)_6(SO_4)_2]$, basaluminite $[Al_4(OH)_{10}SO_4·5H_2O]$ and jurbanite $[AlOHSO_4·5H_2O]$ (Ritchey & de Sousa, 1997). Another mechanism whereby Al availability is decreased by gypsum use is through a "self-liming" effect proposed by Reeve and Sumner (1972). The SO_4^{2-} ion participates in a ligand exchange reaction with OH^- ions on surfaces of Al and Fe hydrous oxides in oxidic soils, and the resulting slight increase in soil pH causes $Al(OH)_3$ to precipitate.

A possible disadvantage of gypsum application may be the increased leaching of potassium and magnesium (Shainberg *et al.,* 1989; Sumner, 1993). Dolomitic lime can be applied with gypsum to overcome Mg losses as well as cause gypsum to leach more rapidly (Ritchey & de Sousa, 1997), since increased pH causes sulfate adsorption to decrease (Couto *et al.,* 1979). Gypsum has proved highly effective in ameliorating subsoil acidity on low CEC, oxidic soils, resulting in improved yields of various crops (Ritchey & de Sousa, 1997). However, in higher CEC, clay soils where subsoil levels of Al toxicity are very high, it is unlikely that gypsum treatment will have any long-term beneficial effects (Farina, 1997).

1.4.4   Organic amendments

As an alternative to Ca compounds, the addition of organic matter (OM) to soil, either as green manures or animal wastes, has been shown to be very effective in amending Al toxicity and P deficiencies in acid soils (Haynes & Mokolobate, 2001). Mechanisms whereby organic amendments can detoxify Al in acid soils include an increase in soil pH (Noble *et al.,* 1996), and the complexation of exchangeable and soil solution Al by soluble humic material and aliphatic

organic acids (Bloom *et al.*, 1979; Hue *et al.*, 1986). Soil pH usually increases during residue decomposition (Noble *et al.*, 1996) and exchangeable and soil solution Al are decreased through precipitation as insoluble hydroxy-Al compounds. As mentioned previously, organic acids such as humic, fulvic, oxalic, citric and tartaric acids (formed during decomposition of plant material) all have the ability to form stable chelate complexes with Al^{3+}, and with other polyvalent cations in the soil solution (McBride, 1994). Aluminium complexed by OM is much less toxic to plants than monomeric Al (Hue *et al.*, 1986, Ritchie, 1989). Strong complexing agents such as citrate and fulvate might even prove to be more effective in removing Al from exchange sites than Ca used alone in subsoil acidity amelioration with lime and gypsum (Smith *et al.*, 1995). Yearly applications of OM are needed to increase the effectiveness of the amendment in reducing Al toxicity, since equilibration of added OM with soil minerals is very slow (Bloom *et al.*, 1979).

1.5 Soil acidification and drip irrigation

The use of drip irrigation has grown recent times in response to increasing scarcity of water agriculture. Advantages of drip irrigation systems over sprinkler and furrow irrigation are not only more efficient water use, but also the opportunity to localize fertilizer and chemical applications, reduced risk of pollution, and the potential use of more saline irrigation water (Bernstein & Francois; 1973, Bravdo & Proebsting, 1993). Another advantage is more continuous supply of nutrients during the growing season. Drip irrigation has made the application of soluble fertilizers through the irrigation water (fertigation) possible, and as a result, roots tend to be concentrated in the small wetted volume of soil, thereby making them less sensitive to soil heterogeneity (Haynes, 1985; Rolston *et al.*, 1986). The application and concentration of certain fertilizer elements in this relatively small rooting volume may, however, have adverse effects on soil fertility and crop yields. Soil acidification as a result of drip fertigation has been reported on several occasions (Edwards *et al.*, 1982; Haynes & Swift, 1987; Parchomchuk, *et al.*, 1993) and will prove to be an important yield-limiting factor if unmanaged.

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To date, no information is available on the effective amelioration of subsoil acidity below drippers. Managing soil acidity below drippers is difficult once the problem has developed, since regular liming materials will not readily move down the soil profile to neutralize the acidity. Increasing the discharge rate of the emitter promotes lateral movement of water (Bresler, 1978). Hence, Haynes (1990) proposed an increased discharge rate to promote lateral movement of water and nitrogen, thus minimizing the downward movement of applied urea. Subsurface acidity can consequently be minimized and the surface acidity more easily treated. He also proposed an investigation into the use of more mobile liming materials, such as potassium and sodium hydroxide or carbonate. The use of gypsum has already proved an effective ameliorant of subsoil acidity (Shainberg *et al.,* 1989; Sumner, 1993), and may also be applicable for soil acidity in drip fertigated soil systems. Another interesting possibility might be the use of calcium citrate, as proposed by Smith *et al.* (1995), as an effective ameliorant of subsoil acidity. Advantageous effects could be seen in increased soil Ca content, Al precipitation as a result of increased soil pH, Al complexation by citrate rendering it less phytotoxic, and increased cation exchange capacity.

1.6   Conclusions

Soil acidification has proved to be an important yield-limiting factor under various agricultural systems in the world. Phytotoxic amounts of Al and low levels of Ca limit crop performance and plant productivity in these soils. Amelioration of these effects therefore focuses on neutralizing Al by precipitation, or reducing Al activity in the soil solution while simultaneously replenishing Ca and other nutrient deficiencies. Reducing acid inputs and selecting plant cultivars more tolerant to acid soil infertility can also increase yields. The goal of this review was to emphasize the importance of understanding the origin and control of soil acidity, with special emphasis on the effect of nitrogenous fertilizers on the acidification of agricultural soils. The following chapters will bring to light the special case of soil acidification of poorly buffered sands in citrus orchards fertilized by drip irrigation.

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2   Soil chemical response to drip fertigation in Citrusdal orchards

2.1   Introduction

Irrigation and fertilization are the most important management practices available to farmers to improve crop performance and yield. Drip irrigation can be used to combine irrigation and fertilization (fertigation) to improve fertilizer use efficiency relative to conventional broadcast applications of fertilizer (Haynes, 1985). Nutrients applied through drip irrigation systems tend to concentrate in the wetted soil volume immediately below the emitter where most of the roots proliferate and consequently nutrient uptake by plants is usually optimal in drip fertigated systems (Haynes, 1985; Rolston *et al.*, 1986; Bravdo & Proebsting, 1993).

Concentrating large amounts of fertilizer in a relatively small volume of soil can, however, cause problems when ammoniacal fertilizers are used (Tisdale *et al.*, 1993). Soil acidification as a result of drip fertigation has been reported by numerous researchers (Edwards *et al.,* 1982; Haynes & Swift, 1987; Parchomchuk *et al.,* 1993), primarily as a result of nitrogenous fertilizers. Both ammonium and urea fertilizers produce acidity upon nitrification, which will result in soil acidification if plant uptake is insufficient or excessive leaching of nitrate occur (van Breemen *et al.,* 1984; van Breemen; 1991, McBride, 1994). As the soil pH drops below 4.5, acid attack on clay minerals will release Al^{3+} into the soil solution and inevitably Al^{3+} will dominate the exchange sites (acid saturation) on clay surfaces in these acidified zones (McBride, 1994). Monomeric Al is toxic to plant roots (Delhaize & Ryan, 1995) and consequently soil acidification can severely limit crop performance in drip fertigated soil systems.

Most citrus farmers in the Citrusdal region use fertilizer mixes that contain large amounts of ammonium or urea as a major source of nitrogen. Since citrus trees require a steady supply of nitrogen throughout the growing season one could expect that the soil chemistry as well as root

growth immediately below the emitter will be severely altered as a result of soil acidification. Pijl (2001), studying the effect of drip fertigation on root distribution and water movement at similar locations in Citrusdal, found that roots tended to concentrate at the periphery of the wetted soil volume. This phenomenon probably occurred due to the combined effects of soil acidification, Al toxicity and possibly anaerobic conditions created by over-irrigation. Soil chemical changes as a result of drip fertigation on soils of different buffering capacities have not been studied extensively in the past and it was the objective of this study to investigate the spatial variation in soil chemical properties below the emitter in a set of drip fertigated Citrusdal soils.

2.2   Materials and methods

2.2.1   Site selection and soil classification

Sampling sites were selected in order to represent a range of soil types in citrus orchards in the Citrusdal area and these were located as close as possible to the sites where Pijl (2001) had already studied the distribution of roots in drip-fertigated citrus. Four orchard soils belonging to three different soil forms were selected for investigation. The geographical location of the four orchards Brakfontein, BoHexrivier, OnderHexrivier and Swartvlei in the Citrusdal area is shown in Figure 2.1.

The physical and chemical properties of each horizon in the four soils are summarized in Table 2.1. The soil types in the four orchards can be paired into two poorly buffered and two moderately buffered soils (by considering the average clay content to a depth of 1 m). Both the poorly buffered orchard soils, at Brakfontein and Swartvlei, were classified in the Kroonstad form (Soil Classification Working Group, 1991) and contain less than 5% clay. The G horizon in both soils was sufficiently deep not to impede normal root growth. The two moderately buffered soils, at BoHexrivier and OnderHexrivier, were classified in the Vilafontes and Constantia forms, respectively (Soil Classification Working Group, 1991), and contained more than 10% clay in the subsoil.

2.2.2   Sampling and chemical analysis

A thorough survey of soil chemical properties below the trickle source of the four citrus orchards was achieved by grid sampling. A Thompson auger was used to drill between the 2 emitters closest to a tree at 20 cm intervals parallel to the dripper pipeline, except at the BoHexrivier site where drill intervals were 18.75 cm. A second series of samples was collected at 20 cm intervals perpendicular to the dripper line (to a distance of 60 cm) on either side of the emitter. The depth intervals are 0-20, 20-40, 40-60, 60-80 and 80-100 cm from the surface. Collection of samples was carried out in March 2000. Samples were air-dried and crushed to pass a 2 mm screen, and the ≤ 2 mm fraction was stored in plastic bags for further analysis. Gravel content of all the samples was <5% and thus ignored for analysis.

For each of the sampling positions and depth intervals a soil pH measurement was taken in both water and 1 M KCl using a 1:2.5 soil to solution ratio. Other soil chemical properties determined on the samples taken perpendicular to the dripper line were:

- 1 M NH$_4$OAc-extractable Ca, Mg, K and Na, determining the cations in the extract using atomic absorption spectrophotometry (Thomas, 1982).

- 1 M KCl-extractable acidity, Al, Ca and Mg. Acidity was determined by back titrating against standard 0.01 M NaOH to a phenolphthalein end point (Thomas, 1982). Aluminium was determined colorimetrically by the Chrome-Azurol-S method (Kennedy & Powell, 1986) and Ca and Mg were determined using atomic absorption spectrophotometry.

- Inorganic nitrogen (NO$_3$-N and NH$_4$-N) was extracted by 1 M KCl and determined colorimetrically. Nitrate was determined using a copperized cadmium reduction method and ammonium using an indophenol blue method (Keeney & Nelson, 1982; Stock, 1983).

- Available phosphate was extracted using the Bray No.2 extractant (0.1 M HCl and 0.3 M NH$_4$F) and P determined colorimetrically (Bray & Kurtz, 1945).

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- 0.3 M NH$_4$F-extractable Cl$^-$, SO$_4$$^{2-}$ and PO$_4$$^{3-}$ were determined by ion chromatography using a modification of the method of Prietzel and Hirsch (2000).

A detailed description of each of the above methods is given in Appendix A. The spatial variation of the soil chemical properties was plotted using SURFER™ software. The diagrams were generated using a linear point *Kriging* method and an omni-directional variogram model with a slope of 1.

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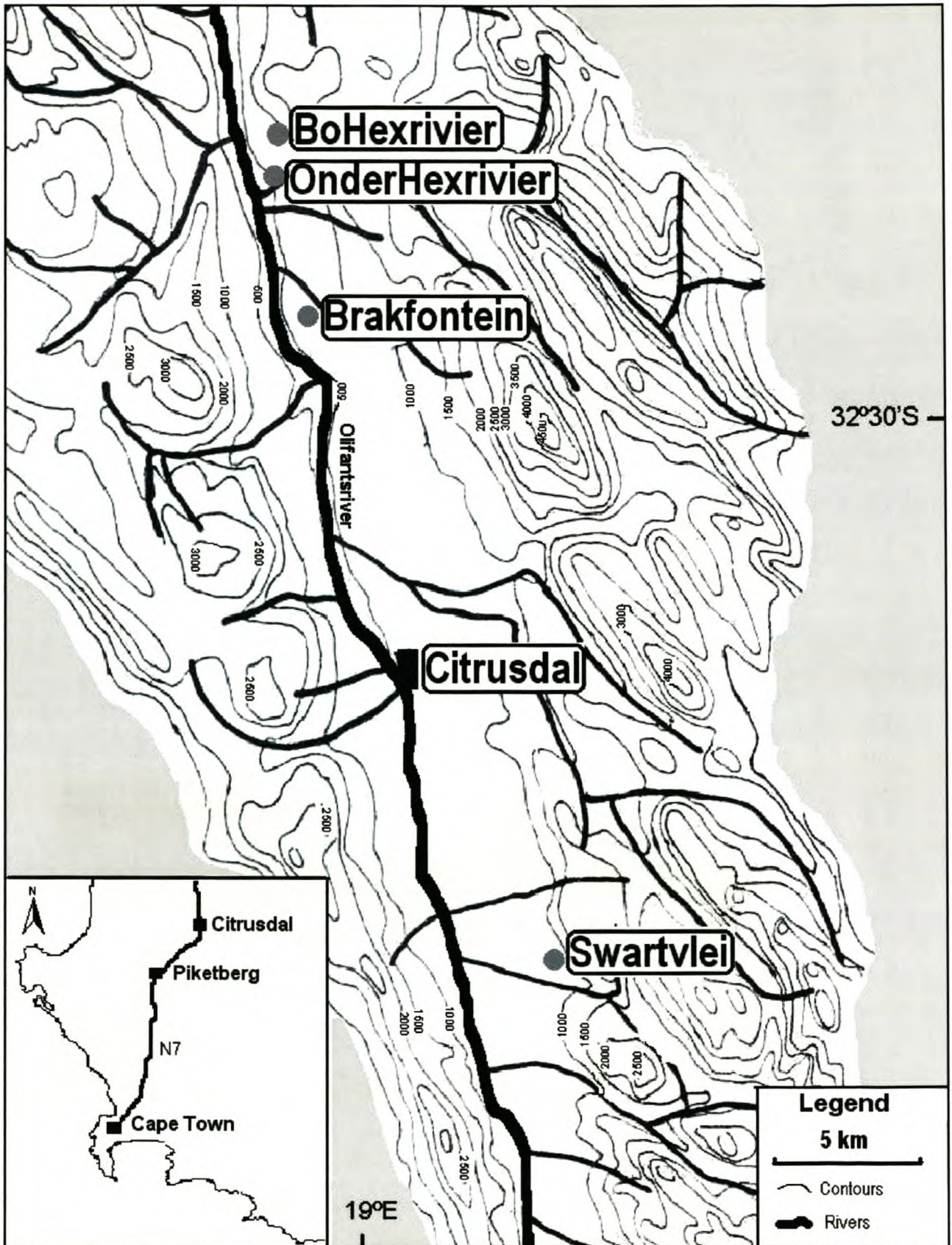
Figure 2.1. Map showing the position of the four study sites Brakfontein, BoHexrivier, OnderHexrivier and Swartvlei in the Citrusdal area.

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Table 2.1. Soil physical and chemical properties of the orchard soils sampled at Brakfontein, BoHexrivier, OnderHexrivier and Swartvlei.

Orchard	Brakfontein			BoHexrivier			OnderHexrivier			Swartvlei		
Soil form/family	Kroonstad 2000			Vilafontes 2110			Constantia 2100			Kroonstad 1000		
Horizon	A	E	G	A	E	B	A	E	B	A	E	G
Depth [cm]	0-20	20-130	>130	0-30	30-40	>40	0-20	20-50	>50	0-30	30-140	>140
Soil colour (dry)	10YR7/4	10YR6/4		10YR6/6	10YR7/4	7.5YR6/8	10YR6/3	10YR7/4	7,5YR6/8	10YR7/3	10YR7/3	
Soil colour (moist)	7.5YR5/6	7.5YR8/5		10YR5/6	7.5YR5/6	7.5YR5/8	10YR3/3	7.5YR5/4	7.5YR5/8	10YR5/4	10YR5/4	
Organic C (%)	0.20	0.12	0.23	0.37	0.24	0.19	0.98	0.30	0.22	0.30	0.17	0.24
pH(KCl)	6.85	4.78	3.70	4.55	4.22	3.94	6.40	4.30	3.83	4.72	4.35	3.87
Resistance (Ohms)	970	5000	1500	480	1860	1840	1520	3350	4600	3500	4600	2870
Particle size distribution (%)												
Coarse fragments	1.5	1.5	4.2	2.4	2.5	3.0	1.0	1.6	1.4	1.3	1.5	13.9
Coarse sand	0.5	0.7	1.4	37.4	35.6	29.8	14.9	16.9	14.0	41.9	48.4	30.4
Medium sand	8.8	11.0	2.8	24.7	24.1	23.8	40.1	39.9	34.5	33.8	29.9	15.3
Fine sand	76.7	80.1	32.6	11.8	14.0	13.6	25.8	23.6	23.9	17.1	14.9	16.9
Very fine sand	8.2	3.8	17.3	5.1	6.3	6.5	6.4	5.6	6.3	2.9	2.2	4.7
Coarse silt	2.3	1.3	10.5	7.7	7.6	8.8	6.1	5.4	5.1	1.9	1.4	3.2
Fine silt	1.7	0.9	6.0	2.7	3.2	3.5	3.8	3.0	2.5	0.8	1.2	1.5
Clay	1.9	2.2	29.4	10.7	9.2	14.1	2.9	5.5	13.7	1.7	2.0	28.0
Exchangeable cations and CEC (mmol$_c$kg^{-1})												
Ca	10.6	3.5	15.3	9.9	7.8	7.7	22.3	5.3	3.1	4.7	3.7	7.2
Mg	4.1	2.0	40.2	7.3	4.9	4.5	8.1	4.4	5.0	0.8	0.9	3.1
K	3.3	1.6	1.5	4.9	1.7	1.3	2.1	1.1	1.4	1.5	0.6	1.1
Na	2.0	0.8	6.4	1.5	1.3	1.1	0.9	1.1	1.4	1.5	1.6	1.7
Acidity (1 M KCl))	0.6	1.4	22.1	2.3	5.6	11.6	0.6	4.2	19.8	1.6	4.0	26.5
CEC (pH7 NH$_4$OAc)	12.6	12.2	99.7	22.5	22.4	29.5	31.8	19.2	34.1	16.7	22.4	52.8

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2.2.3 Fertilization history

The Brakfontein orchard was planted in 1996 and managed according to the open hydroponic system developed by Prof. R. Martinez from Spain (H.G.M. van Zyl, personal communication). Royalties for transfer of knowledge are required to implement the system and a detailed description of the fertilizer history is therefore unavailable. Fertilizer solutions are purportedly a "balanced mix" of all the macro- and micronutrients needed for the citrus tree to grow sufficiently.

The BoHexrivier and Swartvlei orchards were both planted in 1997, and the OnderHexrivier orchard in 1950. At the OnderHexrivier site a microsprinkler system was used until 1994, when it was replaced with a drip system. At the time of sampling the BoHexrivier and OnderHexrivier sites received an amount of 81 and 211 kg N/ha/year, respectively, as a soluble 6:1:3 NPK mix (containing a total of 15% N, P and K) consisting of NH_4NO_3, H_3PO_4 and KCl.

This NPK mixture was applied daily through the dripper system from week 37 to week 4 (mid-September to the end of January). The NO_3-N: NH_4-N ratio is 1:1. Supplemental foliar sprays are applied every 4 weeks as a solution containing 10 g urea, 1.5 g $Zn(NO_3)_2$ and 1.5 g $MnSO_4$ per litre water. Each tree receives about $1l$ of this solution per monthly spray.

Trees at the Swartvlei site are drip fertigated from September to March by monitoring the EC of the irrigation water. The EC is allowed to fluctuate between 0.8 mS/m (±50 ppm N) and 1.6 mS/m (±100 ppm N) through the fertigation season. The fertilizer concentrate contains N, P, K, Ca and Mg in a ratio 6:1:3:2:1 and consists of $Mg(NO_3)_2$, $Ca(NO_3)_2$, NH_4NO_3, H_3PO_4 and KCl. Total nitrogen applied is 90 kg N/ha/year and consists of about 70% NO_3-N. Gypsum is applied twice in the season as a 250 kg/ha topdressing. The microelement quantities applied per hectare per year are 6 kg $CuSO_4$, 8 kg $MnSO_4$, 6 kg $ZnSO_4$, 2 kg Solubor™ and 0.3 kg Na_2MoO_4.

2.3   Results and discussion

2.3.1   Soil pH

The spatial variation in soil pH_{KCl} perpendicular and parallel to the dripper pipeline of the four orchard soils is presented as contour charts for each of the four orchard soils in Figure 2.2 to 2.5 (Actual data for the properties plotted in this and subsequent figures are tabulated in Appendices A and B). The current points of discharge are indicated by 0 cm perpendicular to the pipeline. Emitter spacings were 80, 75, 100 and 100 cm for Brakfontein, BoHexrivier, OnderHexrivier and Swartvlei soils, respectively. It is evident from the spatial variation in soil pH that the surface position of the emitters changed during the course of the growing seasons. Usually the pipeline is placed close to the young trees just after planting and is moved a distance away after a year or two. Many times in the summer the heat causes the pipeline to stretch during the day and shrink again in the evening, also causing the surface position of the emitters to change slightly. Nevertheless, in all of the sites the spatial variation in soil pH below and around the emitter was sufficiently captured to give a realistic display.

As shown in Figures 2.2-2.5, there is a marked decrease in soil pH directly below the emitter at all the sites sampled. Large volumes of soil directly below the emitter have a pH_{KCl} of 4.5 and lower. A general trend was that soil pH increased gradually with increasing distance from the center of the wetting front and least affected soil pH would presumably occur at the outside border of the wetting front. The acidified volume of soil below the emitter in the least buffered Brakfontein and Swartvlei orchard soils appeared as an elongated column reaching down to a depth of at least 1 m (Fig. 2.2 and 2.5). In these two soils the gradient of the vertical contours is much steeper than the horizontal contours, suggesting that gravitational movement of water is more marked than lateral (capillary) movement. These soils have similar texture and presumably similar hydraulic conductivity. This general pattern of acidification to a greater depth suggests that there is a tendency towards over-irrigation. Interesting to note is that the emitters on the Brakfontein soil are

more closely spaced (80 cm) than on the Swartvlei soil (100 cm). This causes the wetting fronts in the Brakfontein soil to overlap resulting in a larger proportion of acidified soil compared to that in the Swartvlei soil. Preferably, spacing distances should be aimed at forming a continuous strip of wetted soil along the dripper pipeline (Bravdo & Proebsting, 1993). However, as seen in the Brakfontein soil, this may result in a more expanded zone of acidified soil. The advantage of an expanded shallower strip of acidified soil over deep, discrete zones of acidified soil is that the former is more controllable. Subsoil acidity is more difficult to alleviate than topsoil acidity (Shainberg *et al.,* 1989; Sumner, 1993; Farina, 1997).
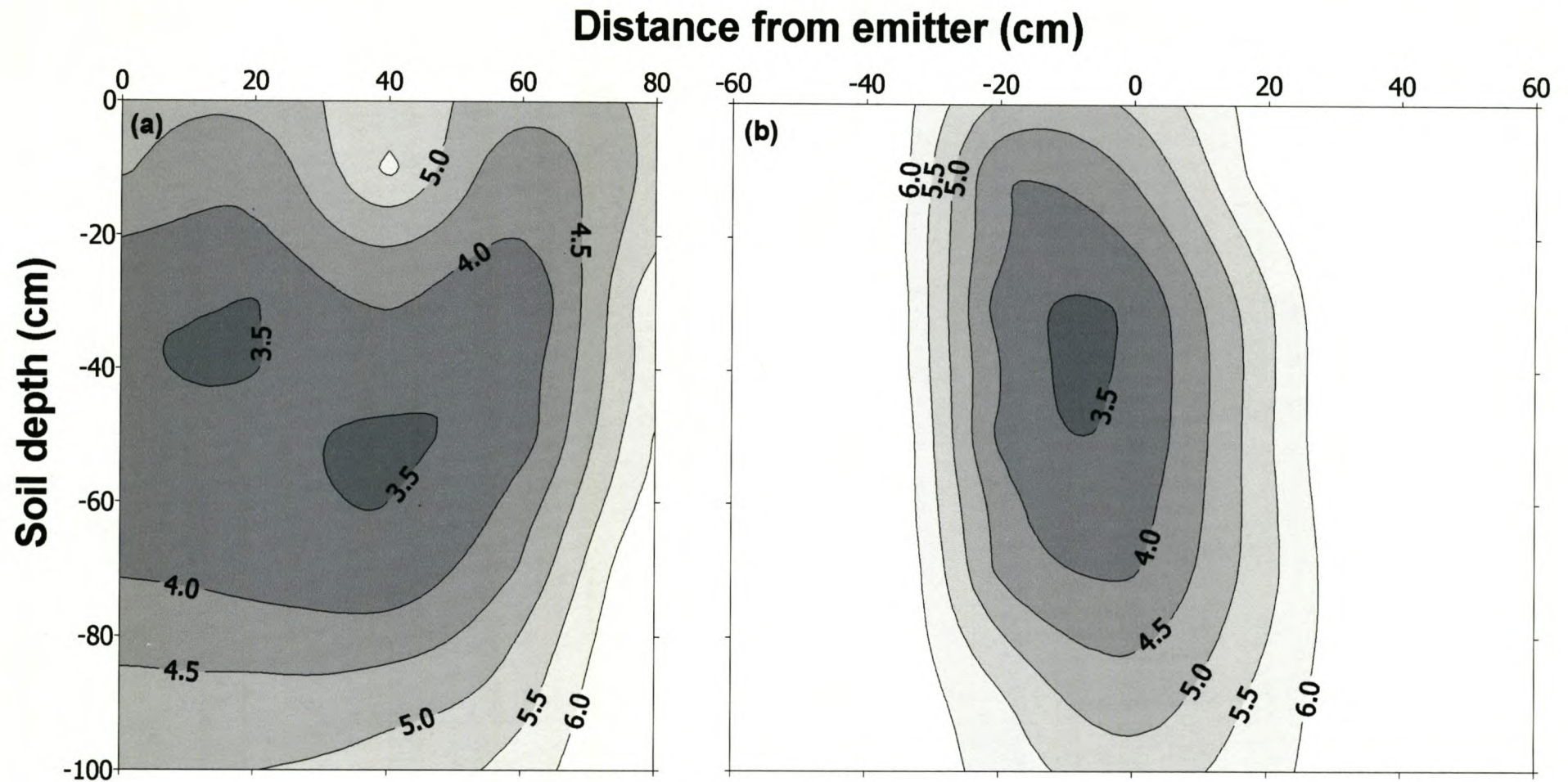
Figure 2.2. Contour chart showing the spatial variation in soil pH_{KCl} below the emitter a) along the pipeline and b) perpendicular to the pipeline of the Brakfontein orchard soil. Points of discharge are located at 0 cm.

Distance from emitter (cm)
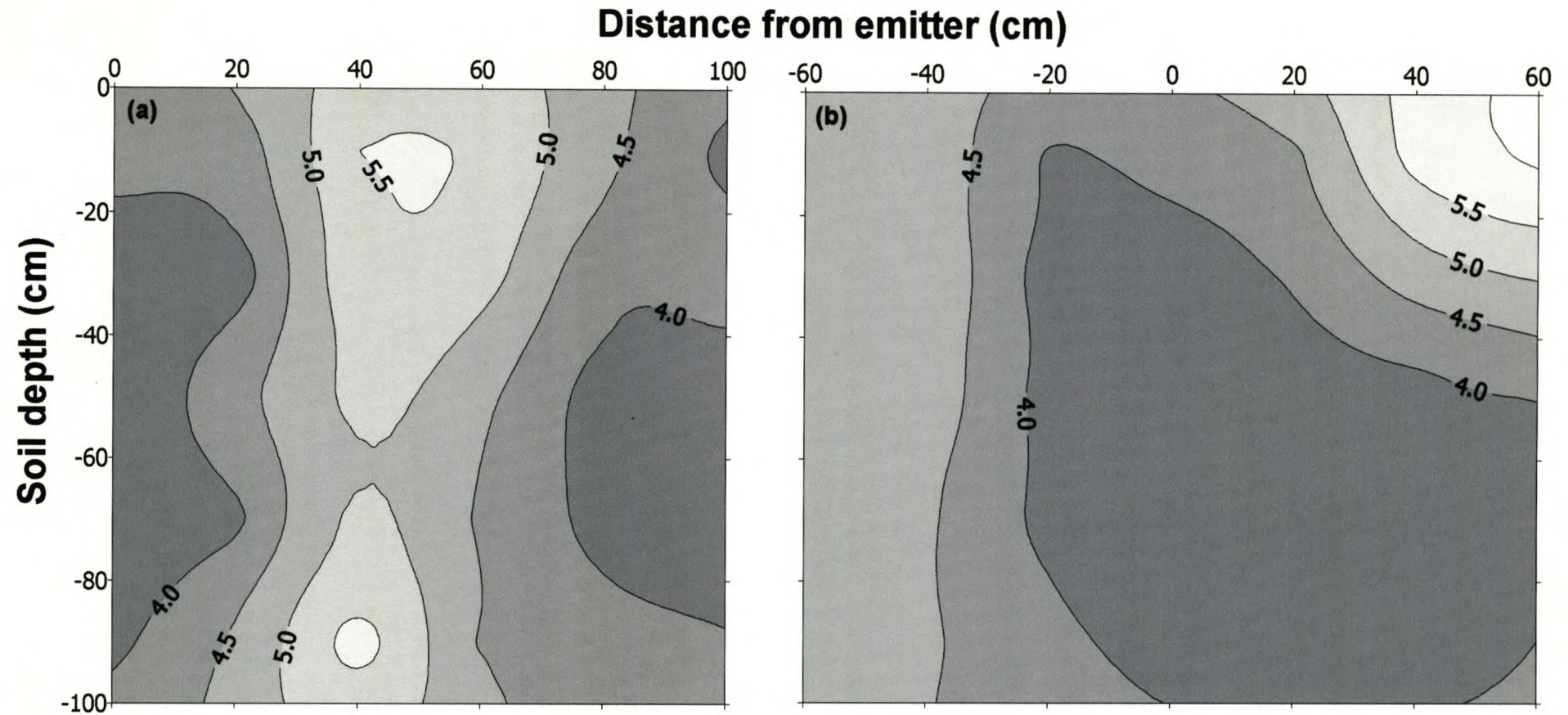
Figure 2.5. Contour chart showing the spatial variation in soil pH pH$_{KCl}$ below the emitter a) along the pipeline and b) perpendicular to the pipeline of the Swartvlei orchard soil. Points of discharge are located at 0 cm.

The BoHexrivier soil, a naturally acidic soil that had been limed prior to planting, also showed deceases in pH directly below the emitter (Fig. 2.3). Here, however, the effects are not as marked with only a narrow zone of acidified soil extending through the limed layer. Better buffering characteristics in the BoHexrivier soil may have slowed the process of soil acidification. At greater depths the acidification front has shifted away from the emitter position above, suggesting lateral movement of drainage water. This phenomenon is presumably as a result of the direction the slope influencing seepage of the perched water table above the more clayey B horizon. The OnderHexrivier site shows the most severe acidification following 10 years of drip fertigation (Fig. 2.4). A bulb-shaped volume of severely acidified soil, having a pH less than 3.5, occurs directly below the emitter. Much of the soil profile at OnderHexrivier had a pH below 4.5 and the effects of previous liming had long disappeared. The magnitude and position of pH decline in these orchard soils is generally similar to that reported in previous studies by Edwards et al. (1982), Haynes and Swift (1987) and Parchomchuk et al. (1993). From Figures 2.2-2.5 the volume of soil having a pH_{KCl} of less than 4.5 were estimated and found to be 0.1, 0.38, 1.13 and 0.5 m^3/emitter for the Brakfontein, BoHexrivier, OnderHexrivier and Swartvlei soils respectively. It is this volume of soil that most urgently requires lime to improve crop performance.

2.3.2   Acid and base saturation

The proportion of the cation exchange capacity (CEC) occupied by basic cations (i.e. Ca^{2+}, Mg^{2+}, K^+ and Na^+) is termed the base saturation, and the remaining proportion occupied by acidic cations (i.e. H^+ and Al^{3+}) is termed the acid saturation (McBride, 1994). In this study acid saturation was expressed as a proportion of the effective CEC (ECEC = sum of 1 M NH_4AOc extractable Ca^{2+}, Mg^{2+}, K^+ and Na^+ and 1 M KCl extractable acidity). Thus base saturation and acid saturation are complementary to one another. The spatial variability in acid saturation of the soil profile perpendicular to the dripper pipeline below the emitter of the four different orchard soils is shown in Figure 2.6.

Acidification of sands in citrus orchards fertilized by drip irrigation

The spatial variation in acid saturation shows a similar pattern to that of soil pH, as would be expected. The Brakfontein and Swartvlei orchard soils are the least affected although acid saturation in the center of the wetted soil volume has still reached levels of about 50-60 percent [Fig. 2.6(a) and (d)]. At the BoHexrivier site acid saturation values of 70 percent were recorded for the topsoil immediately below the emitter, thereafter decreasing with depth [Fig. 2.6(b)]. The deeper, naturally acidic part of this profile has acid saturation values in excess of 60 percent. The whole soil profile of the OnderHexrivier site exhibits elevated acid saturation levels, with values in excess of 90 percent in the deeper parts of the soil profile [Fig. 2.6(c)]. Thus, it is evident that the wetted soil volume of all four soils is highly acid saturated and will be commensurately deficient in exchangeable basic cations. Sufficient Ca in the soil solution is critical and much work has been done on the Ca/Al interaction to predict optimal Ca/Al ratios for optimal fibrous root growth (Sumner *et al.*, 1986; Noble *et al.*, 1988). Consequently roots could be expected to occupy the periphery of the wetted soil volume (Pijl, 2001) where Ca/Al ratios are more favourable.

It is well known that acidic cations on soil exchange sites increase exponentially in concentration as pH_{KCl} decreases below a value of 4.5 (Adams, 1984, McBride, 1994). Such a relationship is confirmed by the data in Figure 2.7. Comparison of Figure 2.7(a) and (b) indicates that a large proportion of 1 M KCl-extractable acidity consists of Al, although Al saturation shows a poorer relationship to pH_{KCl} than acid saturation. There is a linear relationship between KCl-extractable Al and KCl-extractable acidity (Figure 2.8). The values used in Figure 2.8 were separated into topsoils (0-20 cm) and subsoils (below 20 cm) for each orchard. Interestingly, the Al component of exchangeable acidity in the OnderHexrivier subsoil is significantly higher [Al = 0.84(acidity)] than in the other soils' [Al = 0.69(acidity)], possibly because the OnderHexrivier site had a longer period of soil acidification (10 years) compared to the other sites (not more than 4 years).

Acidification of sands in citrus orchards fertilized by drip irrigation
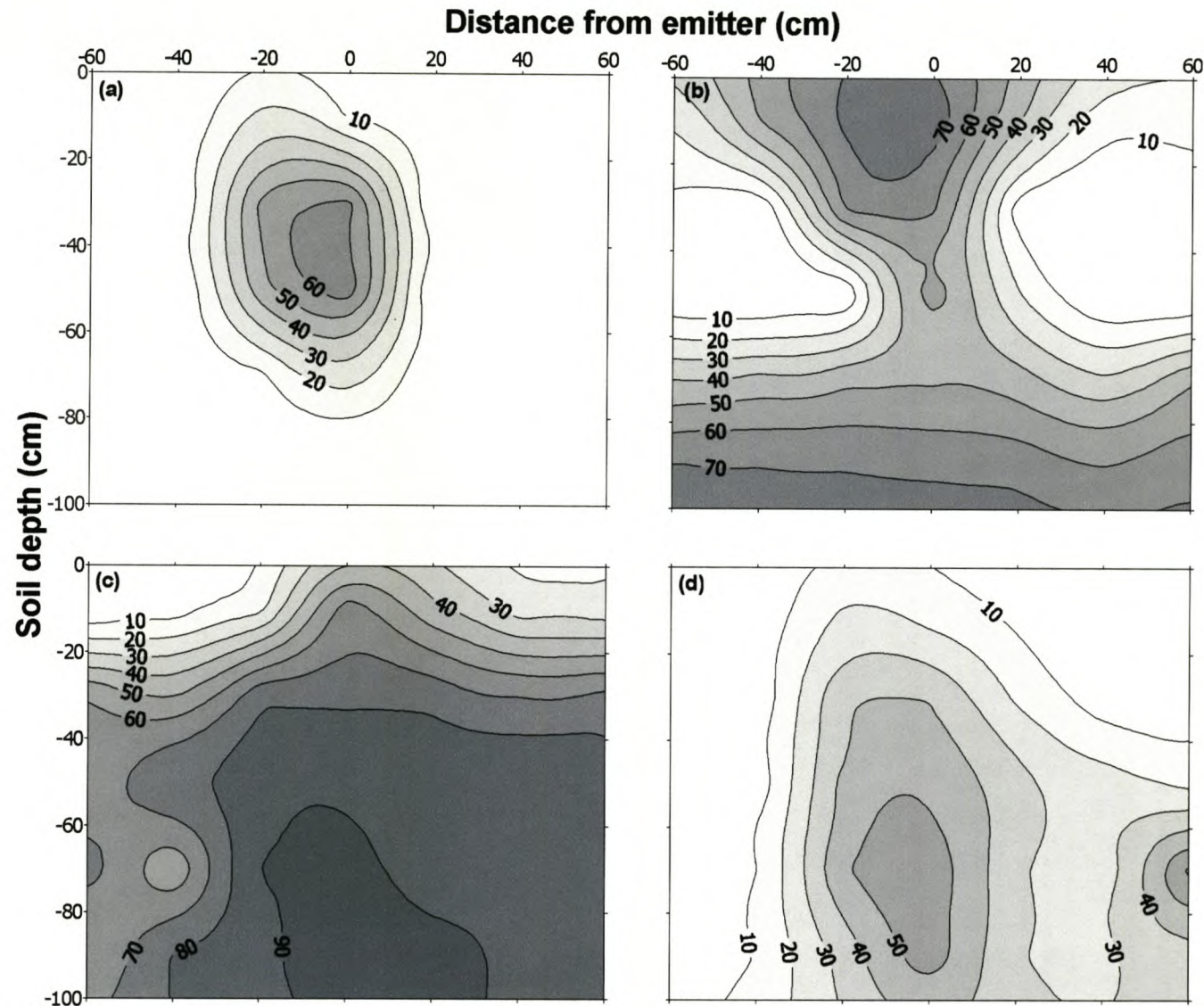
Figure 2.6. Contour charts showing the spatial variation in acid saturation (% of ECEC) in the soil profile perpendicular to the dripper line below the emitter of (a) Brakfontein, (b) BoHexrivier, (c) OnderHexrivier and (d) Swartvlei soils.

Acidification of sands in citrus orchards fertilized by drip irrigation
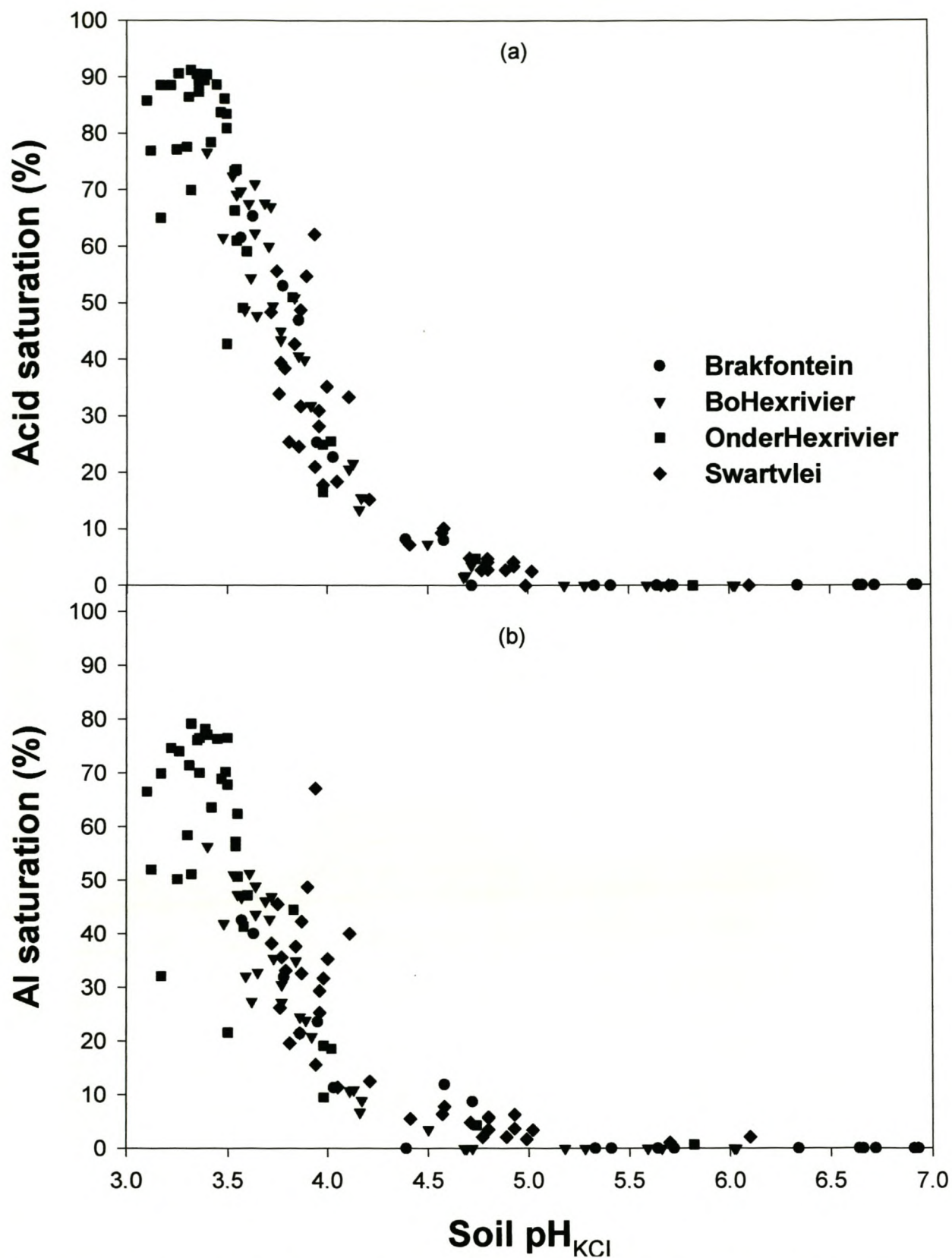
Figure 2.7. The relationship between soil pH_{KCl} and (a) acid saturation and (b) Al saturation of the four different orchard soils.
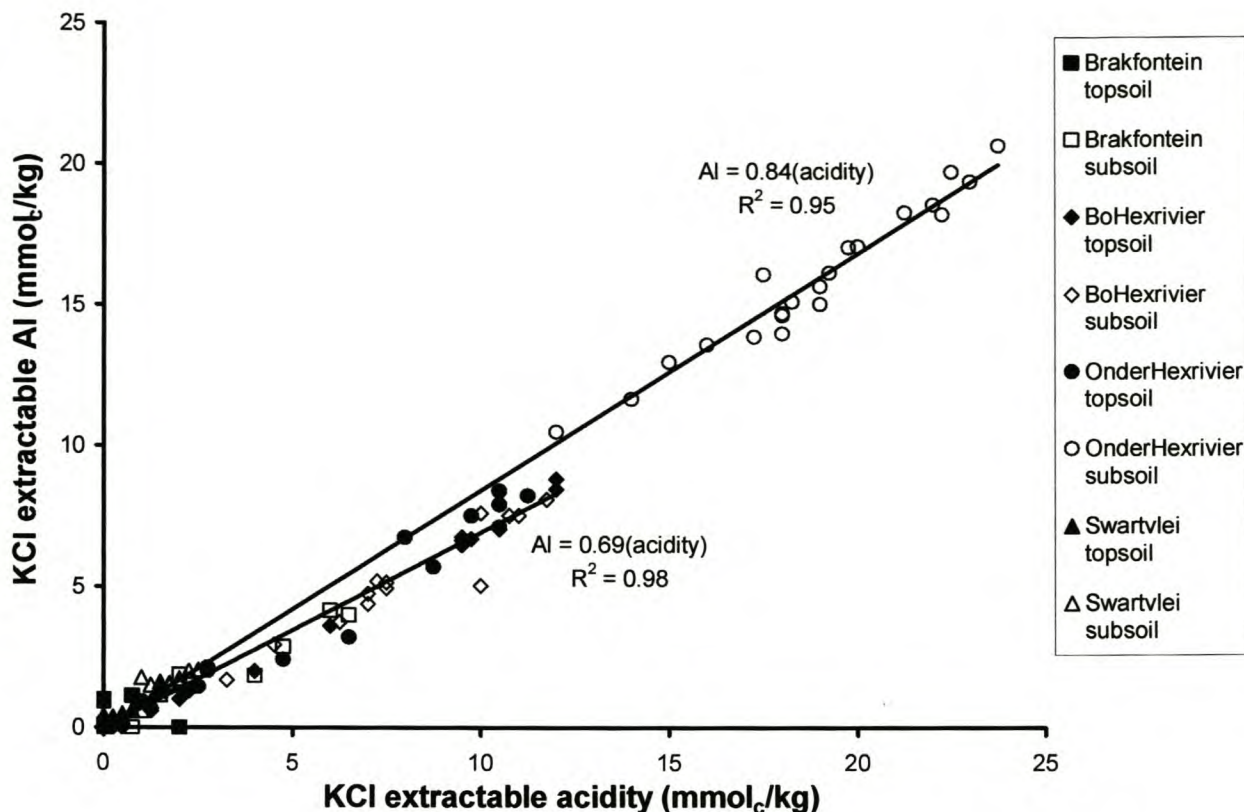
Figure 2.8. Relationship between KCl extractable acidity and KCl extractable Al for the four different orchard soils (topsoils, 0-20 cm; subsoils from below 20 cm).

2.3.3 Inorganic nitrogen

The inorganic forms of nitrogen in soils most relevant to this study are NO_3^- and NH_4^+. Although inorganic N represents only a small fraction (<2%) of the total nitrogen in soils (Keeney & Nelson, 1982), its importance lies in the fact that it is the nitrogen fraction most available to the plant. Inorganic N is usually extracted by a neutral potassium salt solution in the field or as soon after sampling as possible to prevent biological transformation that may alter the concentration and speciation of the nitrogen in the sample (Keeney & Nelson, 1982, Stock, 1983). In this study, however, extraction and sampling were only done after the soil had been dried and stored for a few months in plastic bags. Considering these circumstances and the fact that soil sampling took place at the end of the fertigation cycle, the values obtained would represent little more than an index of the relative availability of N at the time of sampling. The spatial variation in 1 M KCl-extractable

NO_3-N and NH_4-N below the emitters of the four different orchard soils is shown in Figures 2.9 and 2.10, respectively.

Drip fertilized NH_4^+, being a cation, will be sorbed onto soil colloids immediately below the emitter once it enters the soil. The fate of applied NH_4^+ (or ammonium from urea hydrolysis) will depend on the nitrifying capacity of the soil. No accumulation of NH_4^+ was found in any of the soils directly below the emitter, indicating either a sufficient degree of nitrification or the leaching of NH_4^+ to greater depths. In general, the NH_4^+ values obtained were relatively low although pockets of increased concentrations occurred, mainly at the surface (BoHexrivier), or on the periphery of the wetted soil. This suggests that a degree of NH_4^+ movement might have occurred, especially at the Swartvlei site where relatively large amounts of NH_4^+ occurred at increased distance from the emitter. The Swartvlei soil is poorly buffered and presumably possesses little nitrifying ability, which might explain the movement of NH_4^+ to greater distances from the emitter. At the other sites it would appear that the applied NH_4^+ was sufficiently nitrified and/or utilized by the plant.

The spatial variation in NO_3^- concentration was similar to that of NH_4^+. The volume of soil directly below the emitter to depths of 1 m contains relatively low NO_3^- concentrations. This implies that the plant rapidly takes up all the NO_3^-, whether applied, or formed through nitrification. Since NO_3^- is highly mobile in the soil solution, it was probably subjected to leaching at all the sites sampled, but this is not confirmed. Pockets of increased NO_3^- occur at the soil surface possibly in tandem with a general salt accumulation (Haynes, 1985). Further interpretation of the N distribution pattern is probably not warranted, since denitrification together with N immobilization may also have occurred.
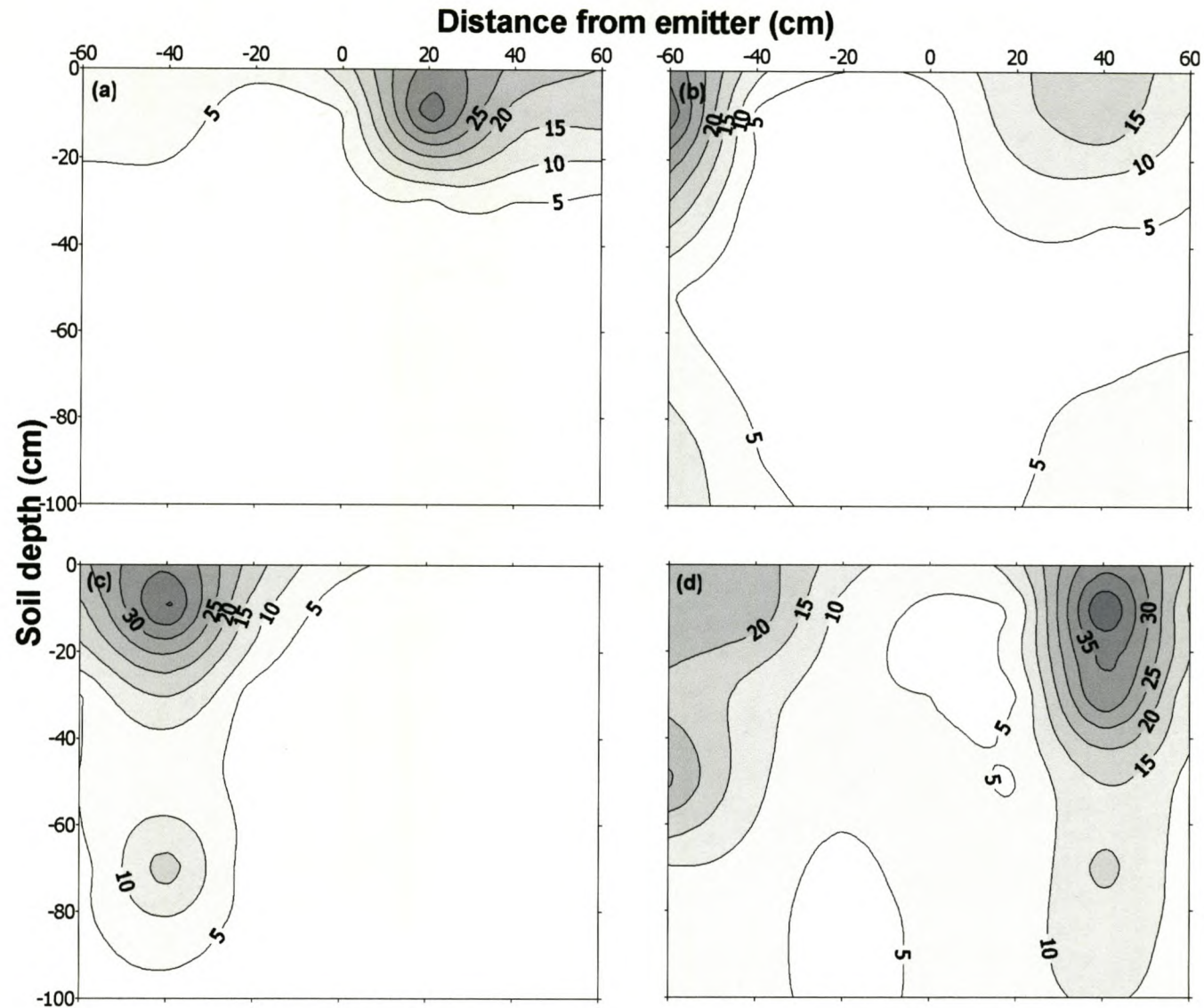
Figure 2.9. Contour charts showing the spatial variation in KCl-extractable NO$_3$-N (mg/kg) in the soil profile perpendicular to the dripper line below the emitter of (a) Brakfontein, (b) BoHexrivier, (c) OnderHexrivier and (d) Swartvlei soils.
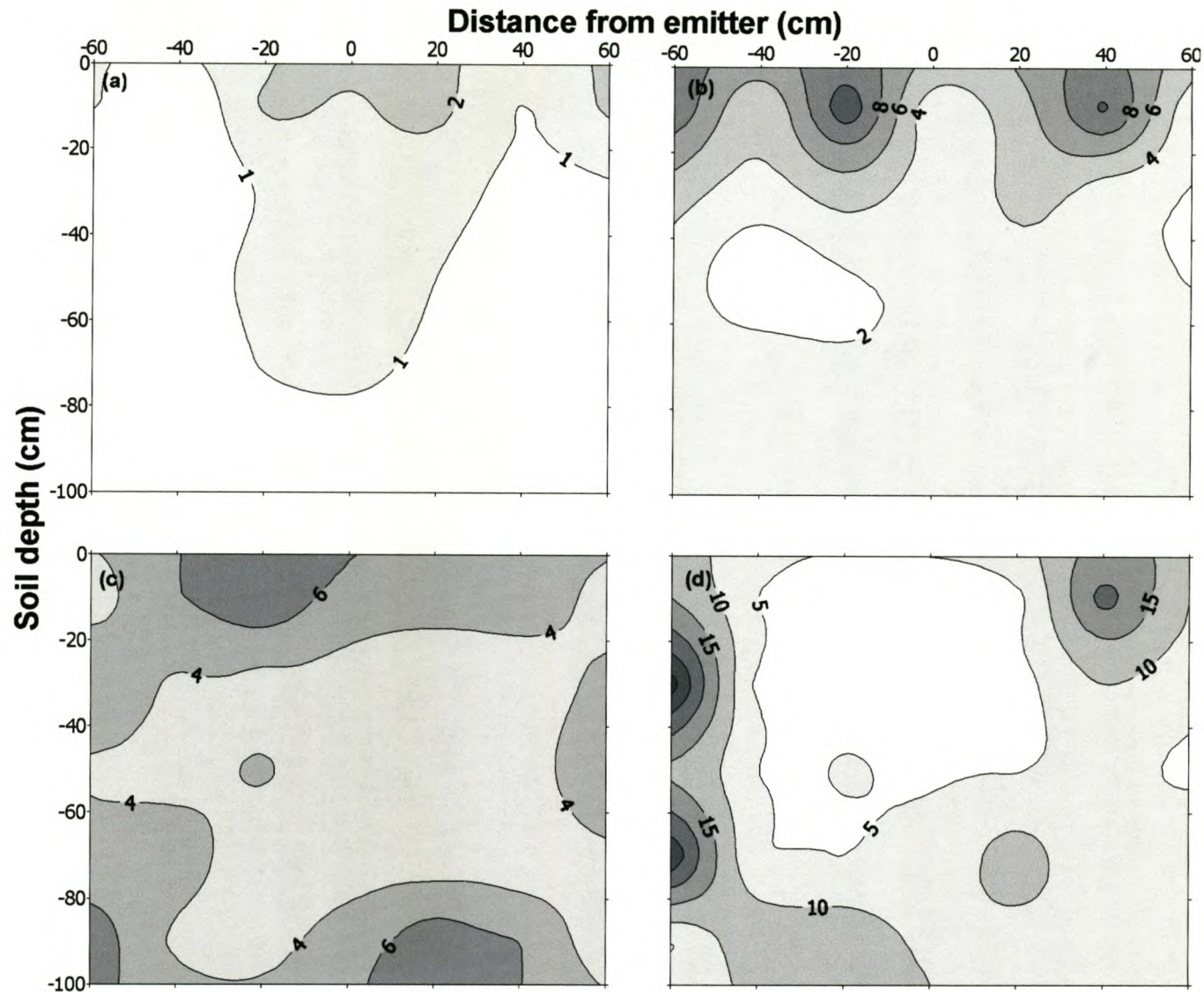
Figure 2.10. Contour charts showing the spatial variation in KCl-extractable NH_4-N (mg/kg) in the soil profile perpendicular to the dripper line below the emitter of (a) Brakfontein, (b) BoHexrivier, (c) OnderHexrivier and (d) Swartvlei soils.

2.3.4 Phosphate

The spatial variation in Bray No.2 extractable P below the emitter of the four drip fertilized citrus orchards is shown in Figure 2.11. The P applied from a point source in the Brakfontein and BoHexrivier soils accumulated in the vicinity of the emitter. The movement of P was presumably limited by fixation on clay mineral and sesquioxide surfaces. Hydrated oxides of Al and Fe play an important role in P adsorption and in acid soils highly insoluble Al and Fe phosphates may precipitate (Haynes, 1984). Consequently, P movement under very acidic conditions, such as found directly below the emitter, could have been limited by such a mechanism.

At the OnderHexrvier and Swartvlei sites two peculiar cases of P leaching were evident. The coarse textured, sandy Swartvlei soil has very little clay or sesquioxides capable of sorbing and retaining P on exchange sites. Applied P will therefore be subject to leaching when large amounts of water are applied during the irrigation cycle. As a result P would move more readily to the periphery of the wetted soil volume. At the OnderHexrivier site P applied from a point source appears to have accumulated in the upper part of the B horizon and some leaching has occurred deeper into the B horizon immediately below the emitter. Minimal P sorption appears to have occurred in the organic matter-rich A horizon and E horizon whereas P has accumulated in a band at some depth from the emitter above the B horizon. During the decomposition of organic matter, humic substances and organic acids are produced that sorb on soil surfaces and block potential P adsorption sites (Haynes & Mokolobate, 2001). Thus the A horizon, with its low clay and high organic matter contents, will probably have a low P sorption capacity and P will move more readily through the A and E horizons and accumulate in the more clayey and sesquioxidic B horizon.

Acidification of sands in citrus orchards fertilized by drip irrigation
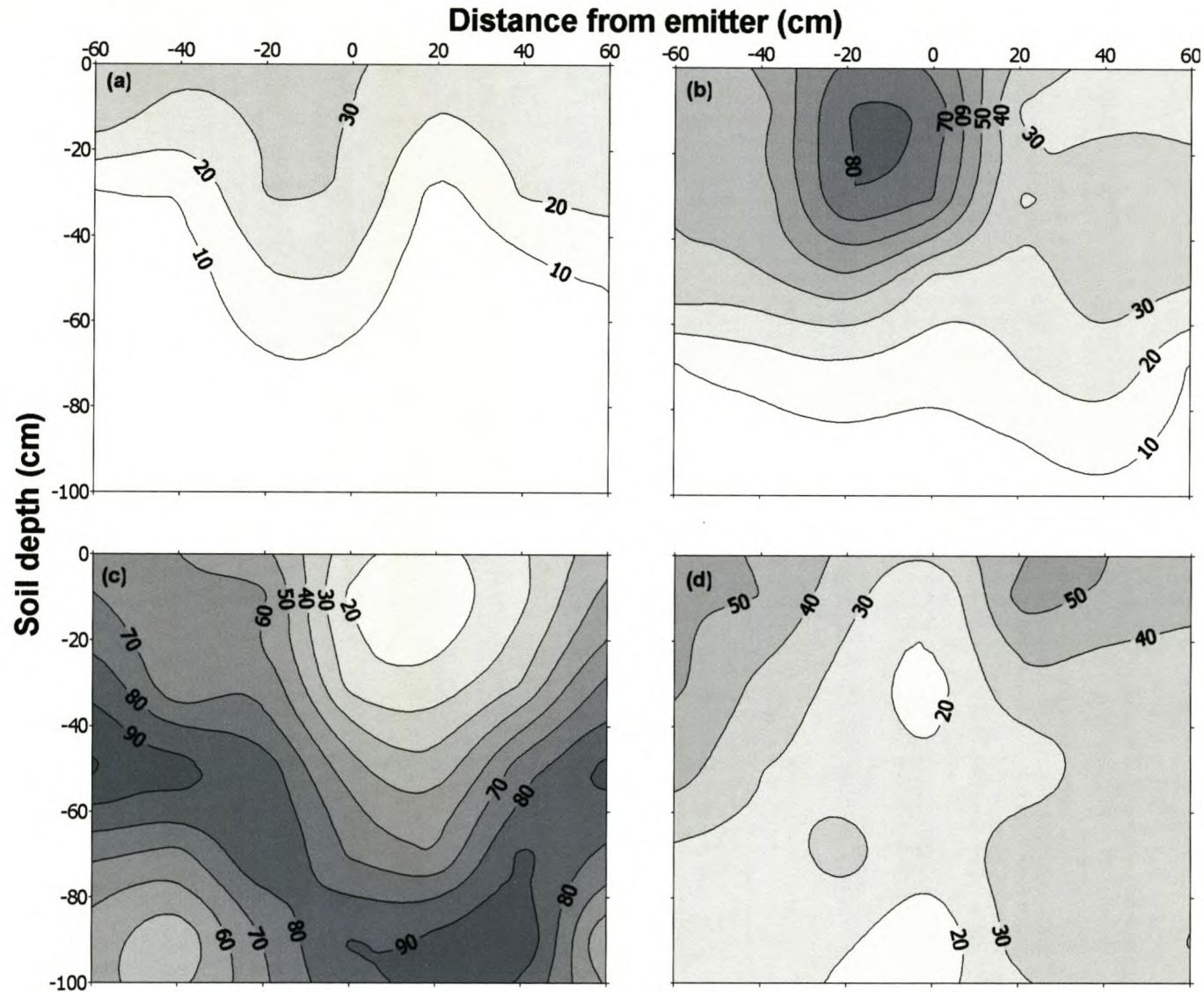
Figure 2.11. Contour chart showing the spatial variation in Bray No. 2 extractable P (mg P/kg soil) in the soil profile perpendicular to the dripper line below the emitter for (a) Brakfontein, (b) BoHexrivier, (c) OnderHexrivier and (d) Swartvlei orchard soils.

2.3.5   Chloride and sulfate

The spatial variation of Cl^- and SO_4^{2-} below the emitter is an indication of the movement and accumulation of soluble salts and is illustrated in Figures 2.12 and 2.13, respectively. Unlike phosphate, chloride and, to a lesser extent sulfate, are mobile anions and are transported through the soil without being greatly retained (McBride, 1994). Chloride in the soil, whether introduced by irrigation water or naturally occurring, reaches its highest concentration at the periphery of the wetted soil volume in all four sites. Generally the greatest accumulation of chloride was found at the soil surface some distance away from the emitter. There were large differences between the soils in the spatial variation of sulfate below the emitter. The spatial variation in sulfate at the Brakfontein site was similar to that of chloride with significant accumulation at a distance of 40 cm either side of the emitter. At the BoHexrivier site virtually no sulfate occurred in the top 60 cm of the soil profile and below that a gradual increase in sulfate was evident. Soil pH in this part of the profile is very low, possibly resulting in positive charge on amphoteric sesquioxides, thus improving the capacity of the soil to sorb sulfate (McBride, 1994). The soils of OnderHexrivier and Swartvlei were largely devoid of sulfate. It would appear that the fertilizer solutions contained little sulfate and the irrigation water had already leached the naturally occurring sulfate beyond the vicinity of sampling.
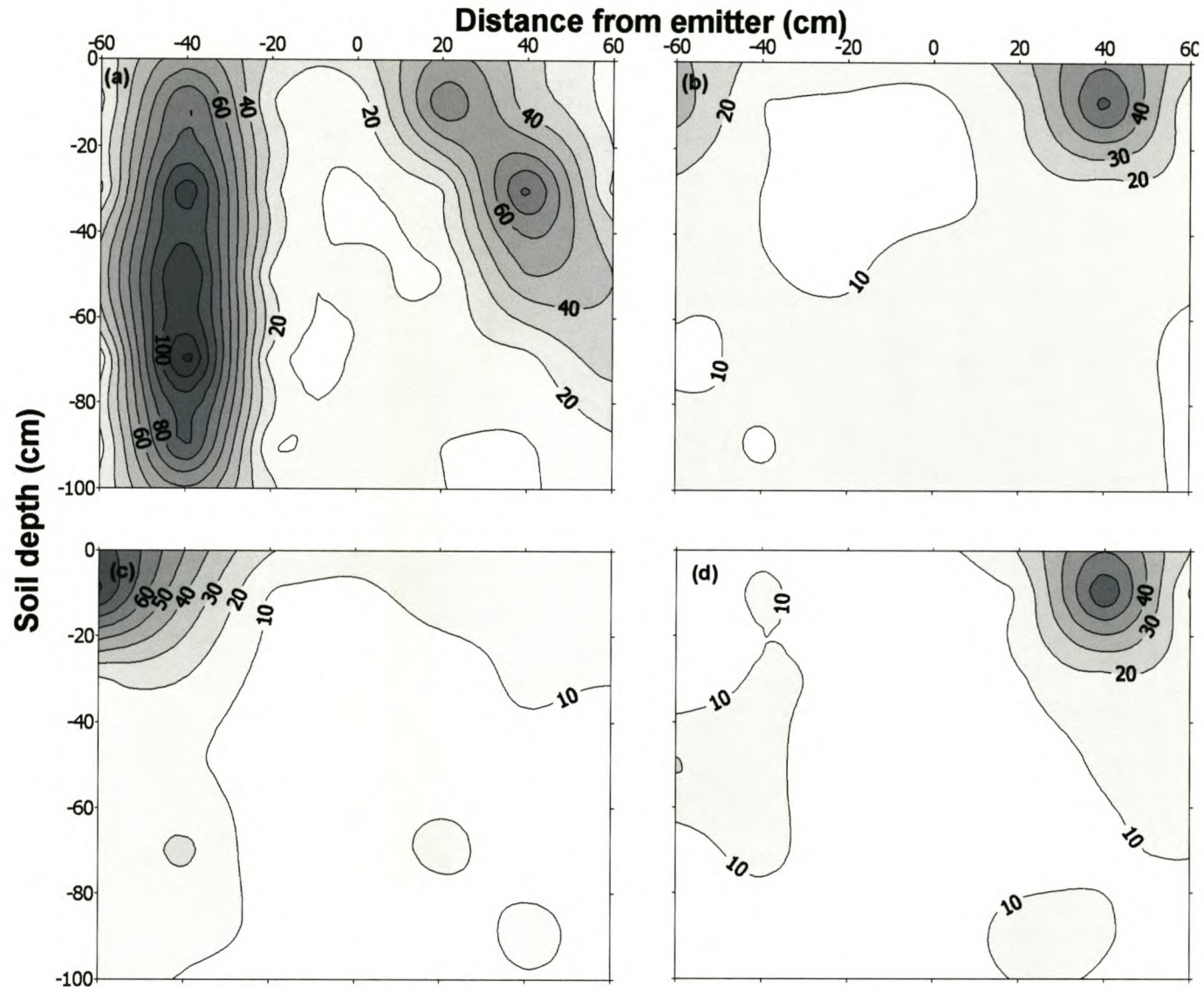
Figure 2.12. Contour chart showing the spatial variation in 0.3 M NH$_4$F extractable chloride (mg/kg) in the soil profile perpendicular to the dripper line below the emitter for (a) Brakfontein, (b) BoHexrivier, (c) OnderHexrivier and (d) Swartvlei orchard soils.
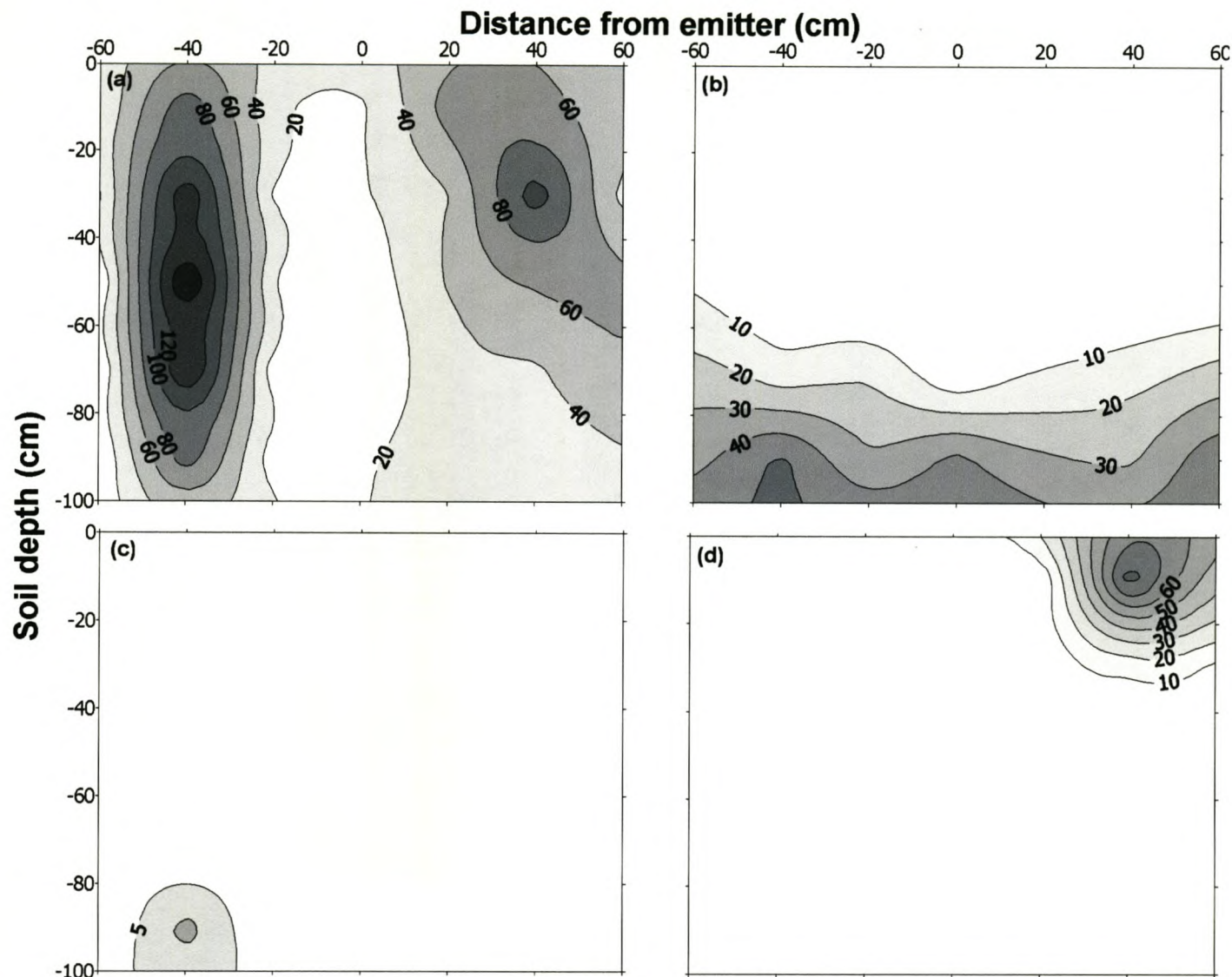
Figure 2.13. Contour chart showing the spatial variation in $0.3\,M\,NH_4F$ extractable sulfate (mg/kg) in the soil profile perpendicular to the dripper line below the emitter for (a) Brakfontein, (b) BoHexrivier, (c) OnderHexrivier and (d) Swartvlei orchard soils.

2.4   Conclusions

Drip fertigation of all four sandy Citrusdal soils has resulted in large decreases in soil pH immediately below the emitter with a concomitant increase in acid saturation once soil pH_{KCl} decreased below 4.5. It was also revealed that a large proportion of 1 *M* KCl-extractable acidity consists of Al, although Al saturation shows a poorer relationship to pH_{KCl} than acid saturation. It was found that most of the wetted soil volume was deficient in exchangeable Ca, Mg, K and enriched with Al. Thus the chemical properties of the wetted soil volume are highly unsuitable for root growth and consequently depressed yields should be expected. These have been reported at the OnderHexrivier site. Since all four study sites received ammonium-containing fertilizers in varying amounts it can be concluded that nitrification of these fertilizers has resulted in a soil pH decline. This was to some extent confirmed by the fact that there was little residual ammonium left in the vicinity just below the emitter of all four sites, which indicates that sufficient nitrification took place during the fertigation season. It was initially thought that these soils would have a low nitrification potential but it would appear that sufficient nitrification had occurred to nitrify the applied ammonium and cause a significant degree of soil acidification. Spatial variation in phosphate of the four soils suggested that under some conditions some leaching of P may occur, but in general applied P tended to accumulate in the vicinity immediately below the emitter. The more mobile anions chloride and sulfate have moved to a greater distance from the emitter and concentrated at the surface and at the periphery of the wetted soil volume. Sulfate was probably already deficient in some of the soils and over-irrigation may have caused further leaching losses. The fact that most of the plant nutrients in soils such as that at the OnderHexrivier site are depleted throughout the sampling depth suggests that over-irrigation is most probably a contributing factor to soil acidification in some of these soils. The contribution of over-irrigation to soil acidification needs to be investigated because improved irrigation scheduling would offer a range of benefits in terms of improved fertilizer and water use efficiency, soil chemistry and soil aeration.

3   Laboratory investigation of soil buffering

3.1   Introduction

It is generally accepted that soil organic matter and clay content are the main determinants of pH buffering in soils. Aitken *et al*. (1990) found that organic carbon, clay content and exchangeable acidity accounted for 85% of the variance in soil buffer capacity and that of these, organic carbon seemed to be the most important constituent. Clay mineralogy may also play an important role. Kaolinite has relatively low reactivity and very little permanent charge compared to illite and smectite which are much more effective buffers. However, only the highest charge vermiculites have a buffer capacity approaching that of soil organic matter (Bloom, 2000).

In the previous chapter the spatial variation in soil chemical properties of a set of Citrusdal sands revealed interesting differences in response to drip fertigation. Large differences were found in the degree of acidification and these were attributed to differences in buffering capacity of the four soils studied. In order to estimate the amount of lime required to neutralize and manage soil acidity, it is useful to understand the sources of pH buffering (Bloom, 2000; Conyers *et al.,* 2000). It was therefore decided to study the reactions of a range of Citrusdal sands to both acid and alkali addition (and laboratory incubation) in order to evaluate differences in pH buffering, and the factors affecting it. The measurement of buffer capacity by titration techniques can be used to directly determine lime requirement (Aitken & Moody, 1994). It is hypothesized that pH buffering on these soils will not be substantial since clay and organic matter contents are both relatively low. The cost of remedial liming strategies can be assessed more accurately once the relative contributions of fertilizer history and soil buffering to soil acidification are better understood.

3.2   Materials and methods

3.2.1   Sample selection

Surface (A) horizons of all four soils were included in this study. Selected subsoils were also examined: the E horizon of the two Kroonstad forms (at Brakfontein and Swartvlei) and the B horizon of the Vilafontes and Constantia forms (at BoHexrivier and OnderHexrivier, respectively). The G horizon was excluded since its occurrence was generally below the depth of root development. The depths and properties of each horizon were reported in Section 2 (Table 2.1). Soils were air dried, sieved (<2 mm) and stored in plastic bags for analysis.

3.2.2   Clay mineralogy

To separate the clay fraction, 100 g soil (air-dried, <2 mm) was used to make a slurry in distilled water. The pH of this slurry was brought to 9 by dropwise addition of 1 M NaOH. The slurry was then transferred to a 3 L jar and filled with a dilute Na_2CO_3 solution (pH 10), covered and allowed to stand for 16 h at 22°C. The top 18 cm of the supernatant was then siphoned off and the decantate stored in a large bucket and the pH restored to <7 with 1 M HCl. This procedure was repeated 3 times. Regular table salt was added to promote flocculation after which the clear supernatant was siphoned off and discarded. The flocculated suspension was further concentrated by centrifugation and the excess salt was removed by centrifuge washing until the supernatant gave a very weak test for chloride using $AgNO_3$ solution. Before the clear supernatant was discarded it was checked for chlorides using silver nitrate solution. The concentrated clay suspension was then oven-dried and weighed. The clay was resuspended in deionised water and the suspension concentration was adjusted to 2 mg/ml. An aliquot of about 2 ml was pipetted onto a glass slide for X-ray diffractometry (XRD) using Copper K_α radiation with a Phillips PW1404 instrument fitted with graphite monochromator operated at 50 kV and 40 mA and a scanning rate of 0.2^{o}2θ/min.

3.2.3   Titration of soils

Acid and base additions were made to a 20 g soil sample using of 0, 4, 8, 16 and 24 mmol$_c$/kg of HCl or Ca(OH)$_2$, dissolved in aqueous solution, to achieve a 1:2.5 soil to solution ratio. For acid addition, a background concentration of 0.01 M CaCl$_2$ was used to achieve a constant ionic strength. This was done in order to avoid ambiguities caused by salt effects on the slope of the titration curve as well as to create an incubation ionic strength comparable with that of the soil solution (Aitken & Moody, 1994). For alkali addition, 0.01 M CaCl$_2$ and 0.01 M Ca(OH)$_2$ were added such that the final ionic strength of the solution was 0.03 M. The 0.01 M Ca(OH)$_2$ solution was made up using freshly boiled, distilled water to minimize interference from CO$_2$, and the solution was standardized by titration with HCl. The soil suspensions were incubated in polyethylene bottles and shaken mechanically for 12 hour and then equilibrated for a further 5 days (shaken every morning for 1 hour) at room temperature. After equilibration a pH and an EC measurement were made of the supernatant solution after which the soil and supernatant were separated by filtration and the supernatant discarded. The soil was rinsed with 70% ethanol to remove soluble salts occluded in the sample. The samples were then oven-dried overnight at 105°C. A 1 M KCl extract was made on 10 g subsample of the oven-dried soil with a 1:10 soil:solution ratio for determination of exchangeable acidity and Al. Exchangeable acidity was determined on an aliquot of the KCl extract by titration with standard 0.01 M NaOH (Thomas, 1982) and exchangeable Al was determined colorimetrically using the Chrome-Azurol-S-method (Kennedy & Powell, 1986). Calcium and Mg were determined in the same 1 M KCl extract by flame atomic absorption spectrophotometry. The base cations were extracted from each soil horizon using a 1 M NH$_4$OAc solution (buffered at pH 7) (Thomas, 1982). A detailed description of each of the above methods as well as additional data are given in Appendix A and B.

3.3   Results and discussion

3.3.1   Soil properties and mineralogy

A summary of relevant properties of the different orchard soil horizons is given in Table 3.1. The effective cation exchange capacity or ECEC value given in Table 3.1 is defined as the sum of Ca, Mg, K, Na and exchangeable acidity (1 M KCl extractable). From the ECEC and CEC values (pH 7 NH_4OAc) it is evident that the Brakfontein and Swartvlei soils have less negative charge than BoHexrivier and OnderHexrivier soils, mainly as a result of their lower clay content, but organic matter also plays an important role in the OnderHexrivier topsoil. Most of the subsoils are naturally acidic and some topsoils have significantly higher soil pH_{KCl} as well as base saturation, probably as a result of the surface application of lime.

Diffractograms used to identify the dominant clay minerals for each of the orchard soils are shown in Figure 3.1 and 3.2. Kaolinite and quartz dominate the clay fraction of all the soils, with 2:1 layer silicates (mica, interstratified clays or a vermiculite/smectite component) constituting a minor component.

Table 3.1. Properties of the soils used for pH buffering investigation

Soil horizon	Soil pH_{KCl}	Organic carbon (%)	Clay (%)	Base saturation (soil pH) (%)	Exch. acidity	CEC (pH 7)	ECEC
						(mmol$_c$/kg)	
Brakfontein A	6.85	0.20	1.9	97	0.6	12.6	20.6
Brakfontein E	4.78	0.12	2.2	85	1.4	12.2	9.3
BoHexrivier A	4.55	0.37	10.7	91	2.3	22.5	26.0
BoHexrivier B	3.94	0.19	14.1	56	11.6	29.5	26.2
OnderHexrivier A	6.40	0.98	2.9	98	0.6	31.8	34.0
OnderHexrivier B	3.83	0.22	13.7	36	19.8	34.7	30.7
Swartvlei A	4.72	0.30	1.7	84	1.6	16.7	10.2
Swartvlei E	4.35	0.17	2.0	63	4.0	22.4	10.7
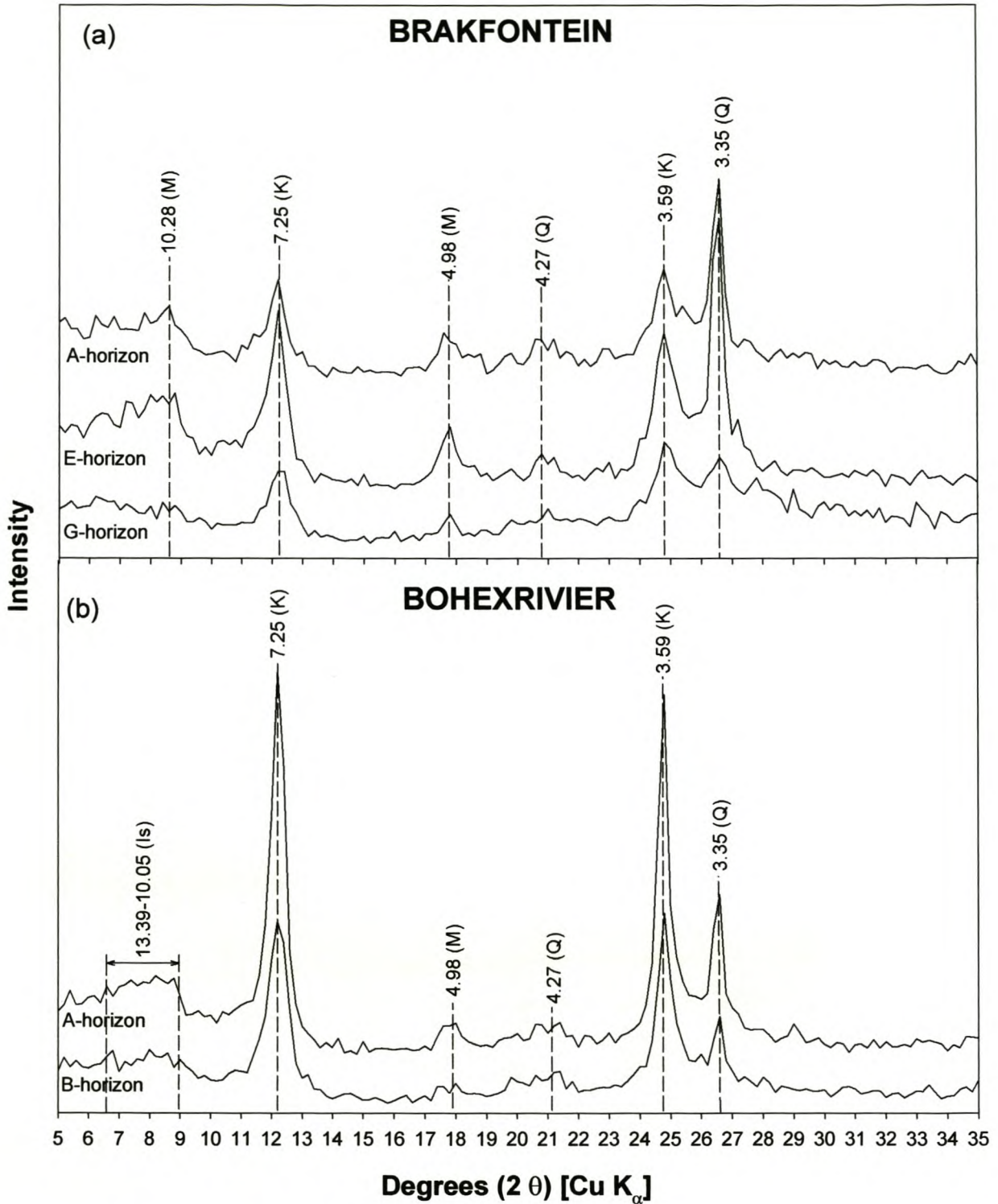
Figure 3.1. Diffractograms showing X-ray intensity against degrees 2θ for the clay fraction of the a) Brakfontein and b) BoHexrivier orchard soil horizons. Characteristic d-spacings are given in Angstrom (Å) and clay minerals are K: kaolinite, M: mica, Q: quartz, Is: interstratified 2:1 layer silicate.

Acidification of sands in citrus orchards fertilized by drip irrigation
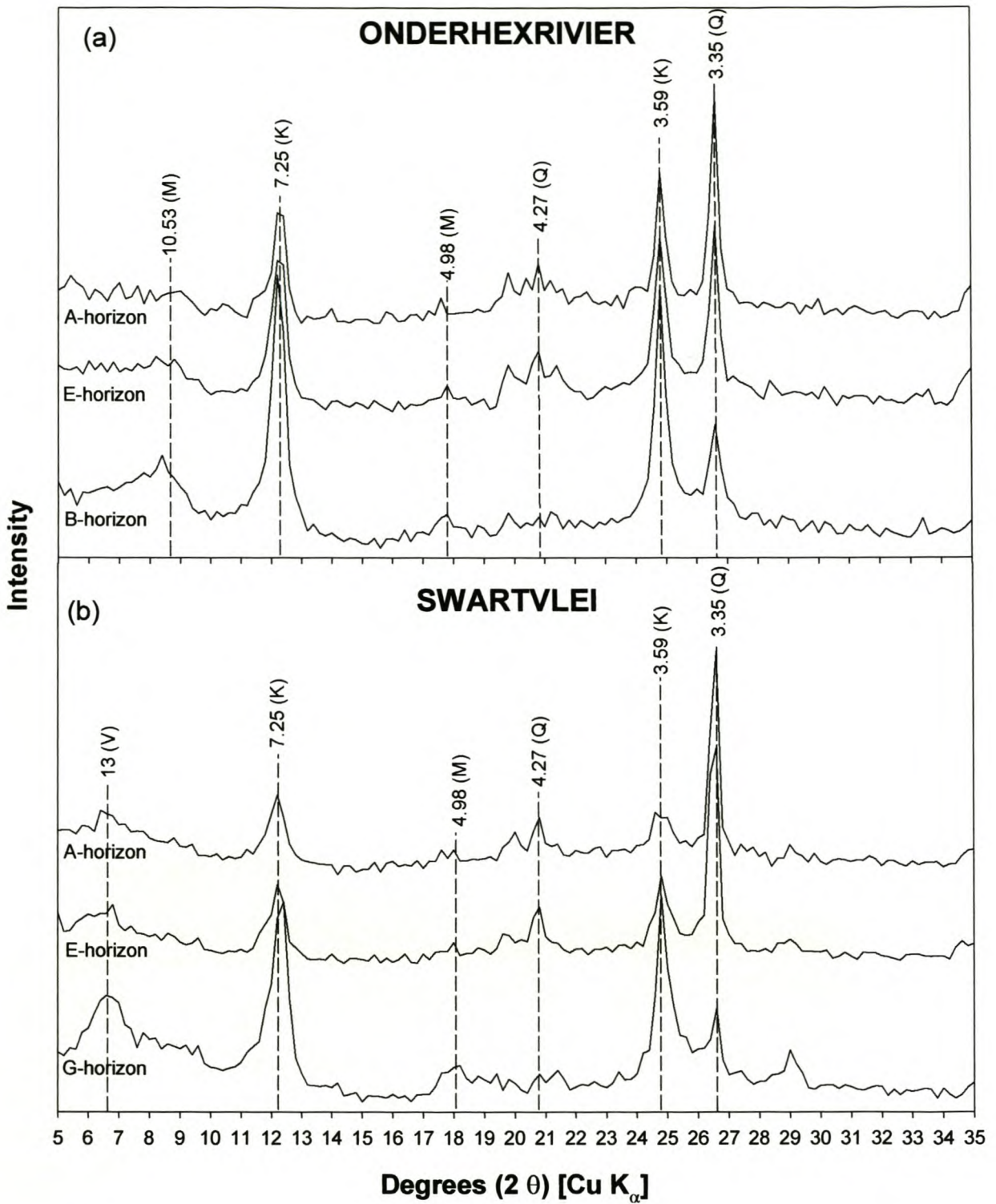
Figure 3.2. Diffractograms showing X-ray intensity against degrees 2θ for the clay fraction of the a) OnderHexrivier and b) Swartvlei orchard soil horizons. Characteristic d-spacings are given in Angstrom (Å) and clay minerals are K: kaolinite, M: mica, Q: quartz, V: vermiculite (possibly smectite).

Acidification of sands in citrus orchards fertilized by drip irrigation

3.3.2   Titration curves

Titration curves for the soils are shown in Figure 3.3 and 3.4. The resultant pH of either the equilibrated supernatant (Figure 3.3) or measured in a KCl suspension after drying the soil following titration (Figure 3.4) are plotted against the quantity of acid and base added.

The equilibration pH of the supernatant of some of the poorly buffered samples was below 3 and above 9 for acidification and alkalinization, respectively. Usually soils tend to be well buffered at upper and lower extremes of the pH scale and will stabilize at pH 7-8 as a result of $CaCO_3$ buffering or between pH 3-4 as a result of buffering by aluminosilicate dissolution (Ulrich, 1991, van Breemen, 1991 & McBride, 1994). As a result one can conclude that the soil had not reached a state of complete equilibrium, since the supernatant pH at the highest levels of acid and base added to some samples was still outside above-mentioned limits. This might have been due to the fact that the polyethylene bottles were relatively tightly sealed and atmospheric CO_2 was excluded during the incubation period of 5 days, not allowing $CaCO_3$ to precipitate at higher pH values. In the acidic range, over-addition of acid can depress the pH to unrealistically low values, especially in quartzitic sands such as from the Swartvlei and Brakfontein orchards where little aluminosilicate clays or Al hydroxide minerals exist to buffer pH in the acid range. Thus, soil pH would be more accurately represented by the pH of the 1 M KCl extract made of a dried subsample after equilibration than by the pH of the supernatant following titration. Soil pH_{KCl} ranged from 4 to 8 in the topsoils and from 3.5 to 9 in the subsoils.

Acidification of sands in citrus orchards fertilized by drip irrigation
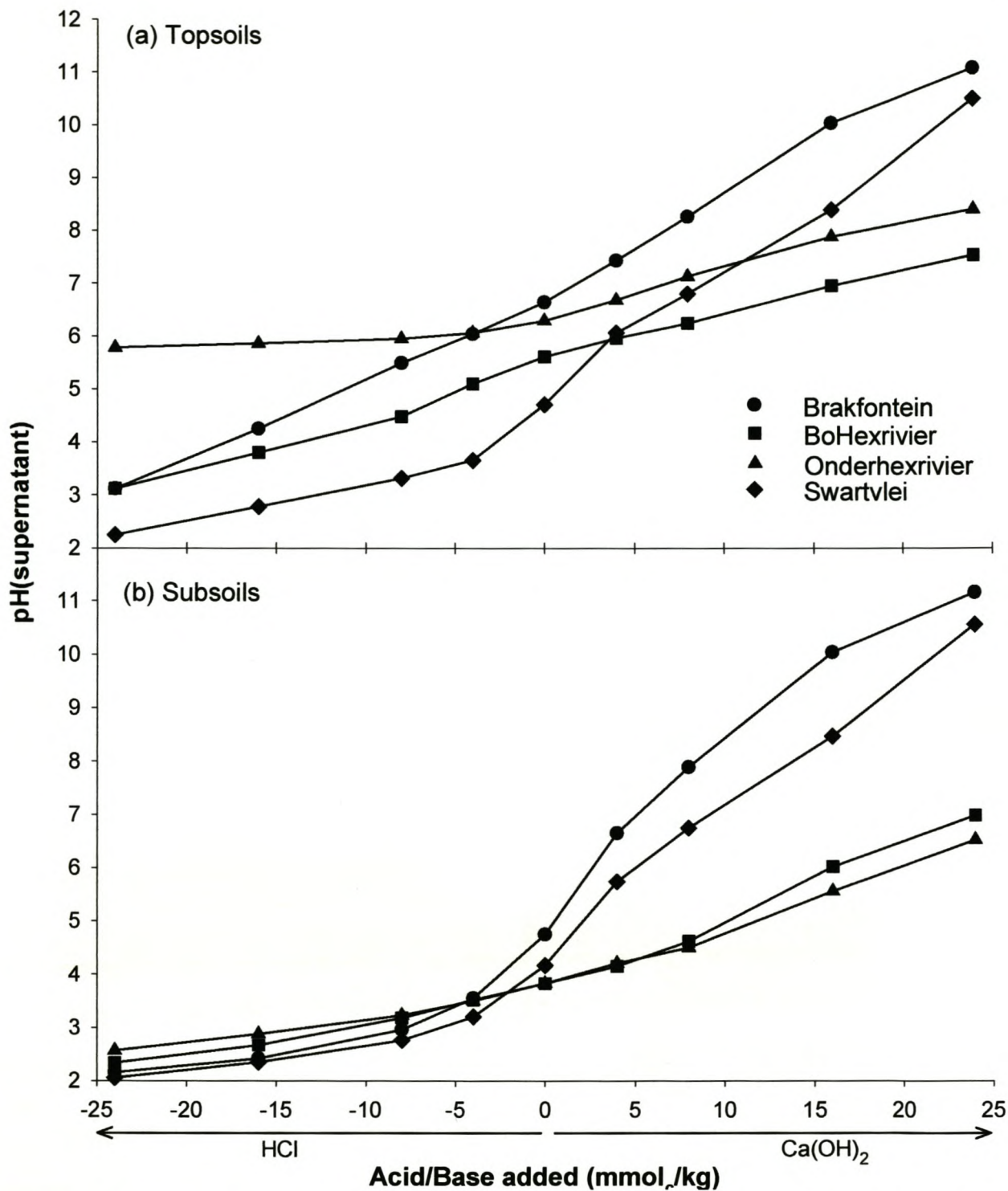
Figure 3.3. Titration curves showing reaction of soil pH (pH of equilibrated supernatant) to acid and base addition as HCl and Ca(OH)₂ respectively for (a) topsoils and (b) subsoils of the four selected orchard soils

Acidification of sands in citrus orchards fertilized by drip irrigation
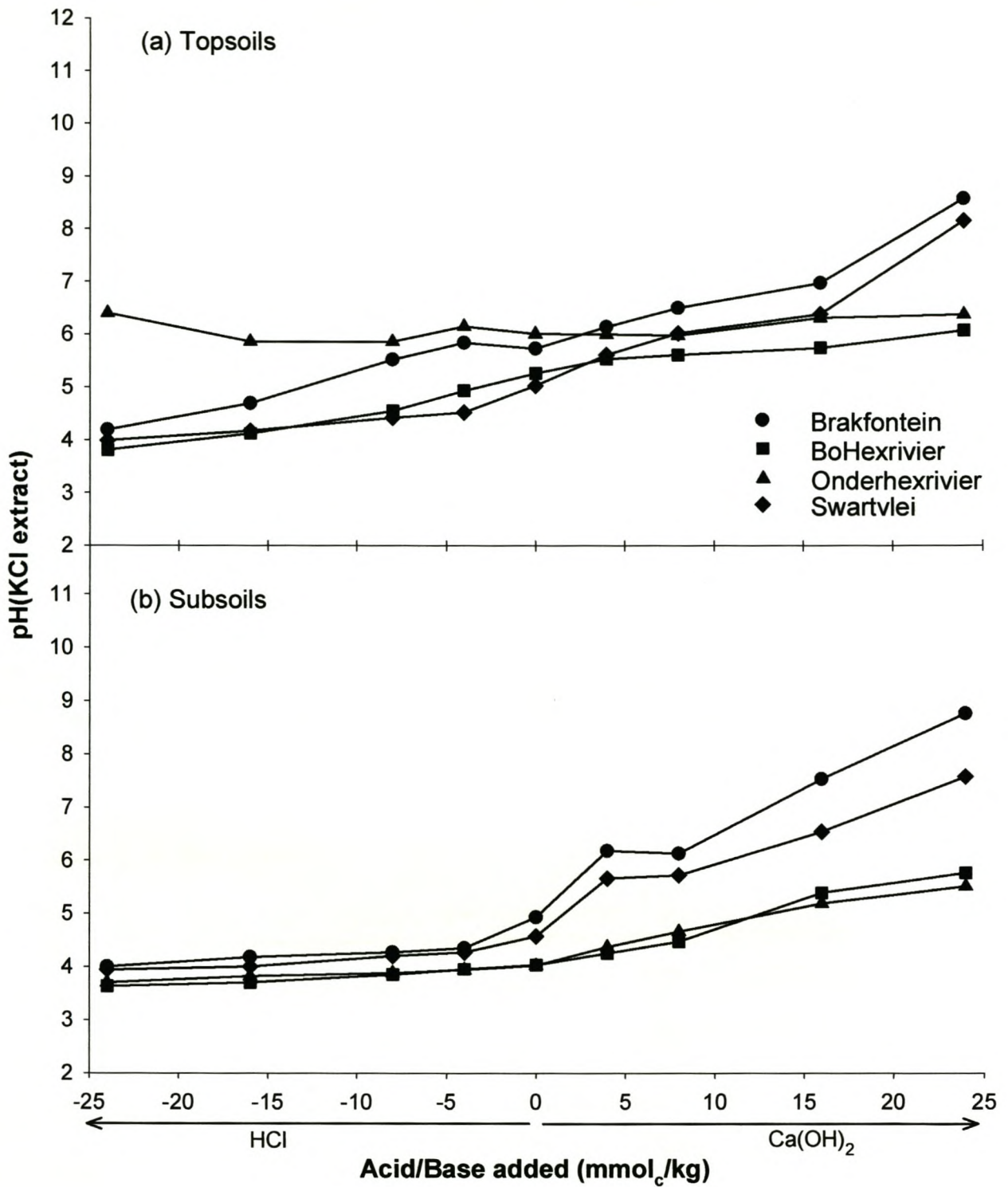
Figure 3.4. Titration curves showing reaction of soil pH (pH of KCl extract) to acid and base addition as HCl and Ca(OH)$_2$ respectively for (a) topsoils and (b) subsoils of the four selected orchard soils.

3.3.3   pH buffering

Values for pH buffering intensity, pH buffering capacity and lime requirement were calculated from the slopes of the titration curves in Figure 3.2 in the pH_{KCl} range of 4.5 to 6.5 and are given in Table 3.2. A pH range of 4.5 to 6.5 was used since most titration curves are linear in this pH region as a result of weaker cation exchange buffering processes (Magdoff & Bartlett, 1985). This pH range is also more relevant when determining lime requirement since most agricultural soils fall in this pH range. Buffering capacity values ranges from as low as 6.7 to as high as 76.9 $mmol_c kg^{-1}$ H^+ added/pH unit. Soil pH buffering in these sandy soils is to a large extent controlled by clay and organic matter. This was seen in the fact that the BoHexrivier and OnderHexrivier orchard soils containing more clay in the subsoil (Table 3.1) had better pH buffering capacities than the Brakfontein and Swartvlei soils. Also the topsoils were significantly better buffered than their counterpart subsoils probably because the topsoils contained more organic carbon (Table 3.1). This was especially evident in the OnderHexrivier topsoil with significantly higher organic carbon content where pH buffering is much higher than all the other soil horizons even though it had less than 3% clay compared to 13.7% clay in the subsoil.

Table 3.2. The inverse slope (pH buffering capacity) and R^2 values between pH 4.5 and 6.5 of the titration curves (Figure 3.4) and lime requirement (LR) calculated from the slope.

Soil horizon	pH Buffering capacity ($\Delta H/\Delta pH$)	R^2	LR^a (tonnes of $CaCO_3$)
Brakfontein A	14.5	0.94	1.9
Brakfontein E	6.7	0.72	0.9
BoHexrivier A	23.3	0.90	3.1
BoHexrivier B	12.3	0.94	1.6
OnderHexrivier A	76.9	0.72	10.3[b]
OnderHexrivier B	18.9	0.98	2.5
Swartvlei A	10.6	0.94	1.4
Swartvlei E	8.9	0.89	1.2

[a]Lime Requirement per hectare per pH unit for a soil depth of 20 cm and bulk density of 1333 $kg.m^{-3}$
[b]In this soil buffering was so strong that this value represents a crude estimate

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Lime requirement per hectare per pH unit for each soil horizon was calculated (calculations in Appendix C) assuming a soil depth of 20 cm, soil bulk density of 1333 kg.m^{-3} and $CaCO_3$ as liming material. Once the soil has acidified to pH values below 4.5 and Al toxicity becomes a problem, these values can be used to estimate the amount of lime required to raise soil pH_{KCl} to more desirable levels (Conyers *et al.,* 2000, Tisdale *et al.,* 1993). The least buffered soils Brakfontein and Swartvlei will acidify at a greater rate in the field but their lime requirement will be less when acidified than the better buffered soils at BoHexrivier and OnderHexrivier. All the soil profiles except the topsoils at Brakfontein and OnderHexrivier are already in an acidified state and will need lime to raise soil pH to more acceptable levels. Since these soils are naturally acidic, lime requirement will best be estimated from titration curves using only base addition and not acid addition. Special care should be taken on better buffered soils, such as that in the OnderHexrivier orchard, to prevent soil acidification. Here the lime requirement for the topsoil would be more than 10 tonnes/ha and for the subsoil, 2.5 tonnes/ha, to raise soil pH by only 1 unit.

3.3.4   Acid and Al saturation

There was a strong relationship between the quantity of KCl-extractable acidity or Al (expressed as a proportion of the ECEC, i.e. acid or Al saturation) and pH_{KCl} (Figure 3.5). Below pH 5 the exchange complex becomes increasingly dominated by acidic cations, reaching a saturation of up to 65% at the lowest pH values. These results conform to the typical relationship between pH and acid and/or Al saturation described by McBride (1994, p176). The data in Figure 3.5 were replotted to show the relationship between Al and total acidity in Figure 3.6, from which it is apparent that Al accounts on average for 69% of total acidity. These results compare well with those obtained in Chapter 2, for which the Al component of KCl-extractable acidity, for most of the soils, was also found to be 69%, and only the OnderHexrivier subsoil had a higher proportion of Al (84%). These results may indicate that the titrated soils had closely approached a state of equilibrium, at least on the acid side of the pH scale. The higher values in Figure 3.6 were mainly for subsoils, in particular

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the BoHexrivier and OnderHexrivier subsoils. This is consistent with the fact that, in general, the subsoils contain more Al minerals (e.g. aluminosilicate clays) with the potential to release Al^{3+} upon acidification. An alternative explanation may be that the more organic-rich topsoils contain less exchangeable Al since not all organically bound Al is readily extractable with 1 M KCl (Hargrove & Thomas, 1981). Since the subsoils contain more Al as a proportion of exchangeable acidity in the acidified state (and especially the more buffered subsoils of BoHexrivier and OnderHexrivier) it is possible that these subsoils will be more toxic to plants than the others at any given pH. Consequently, the amelioration and management of soil acidity in these soils may require special attention.

While acidic cations Al^{3+} and H^+ dominated the exchange complex at lower pH values, basic cations would be expected to be dominant in the neutral to high pH range. In this case exchangeable Ca (the dominant basic cation) increased linearly as pH increased, as illustrated in Figure 3.7. BoHexrivier and OnderHexrivier orchard soils showed one trend (A) while the Brakfontein and Swartvlei soils exhibited another (B). This is consistent with the buffering and cation exchange properties exhibited by these two pairs of soils, the former pair being more buffered (of CEC values in Table 3.1) than the latter.

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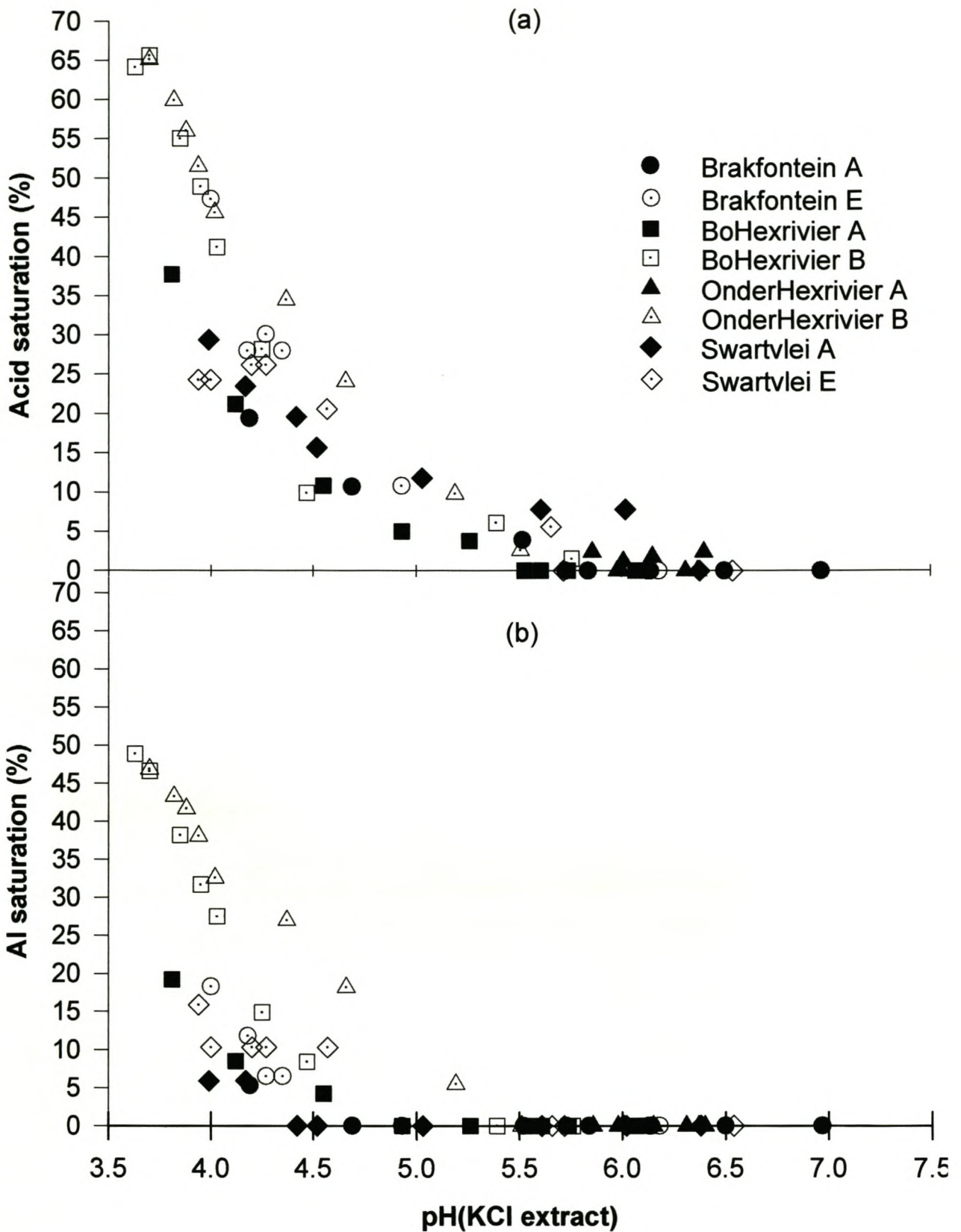
Figure 3.5. The relationship between soil pH (taken as pH of KCl extract) and (a) acid saturation and (b) Al saturation for the different orchard soil horizons.

Acidification of sands in citrus orchards fertilized by drip irrigation
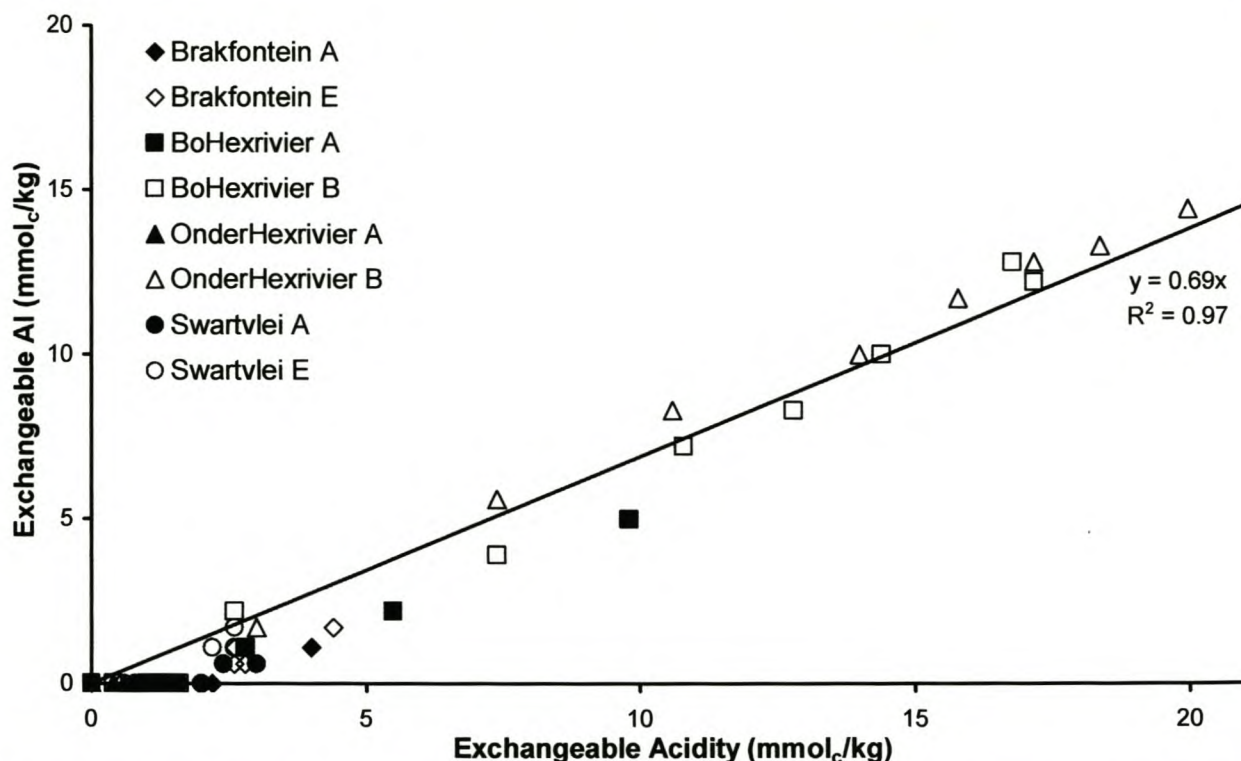
Figure 3.6. The relationship between exchangeable Al and exchangeable acidity determined in 1 *M* KCl extracts of the different orchard soil horizons.
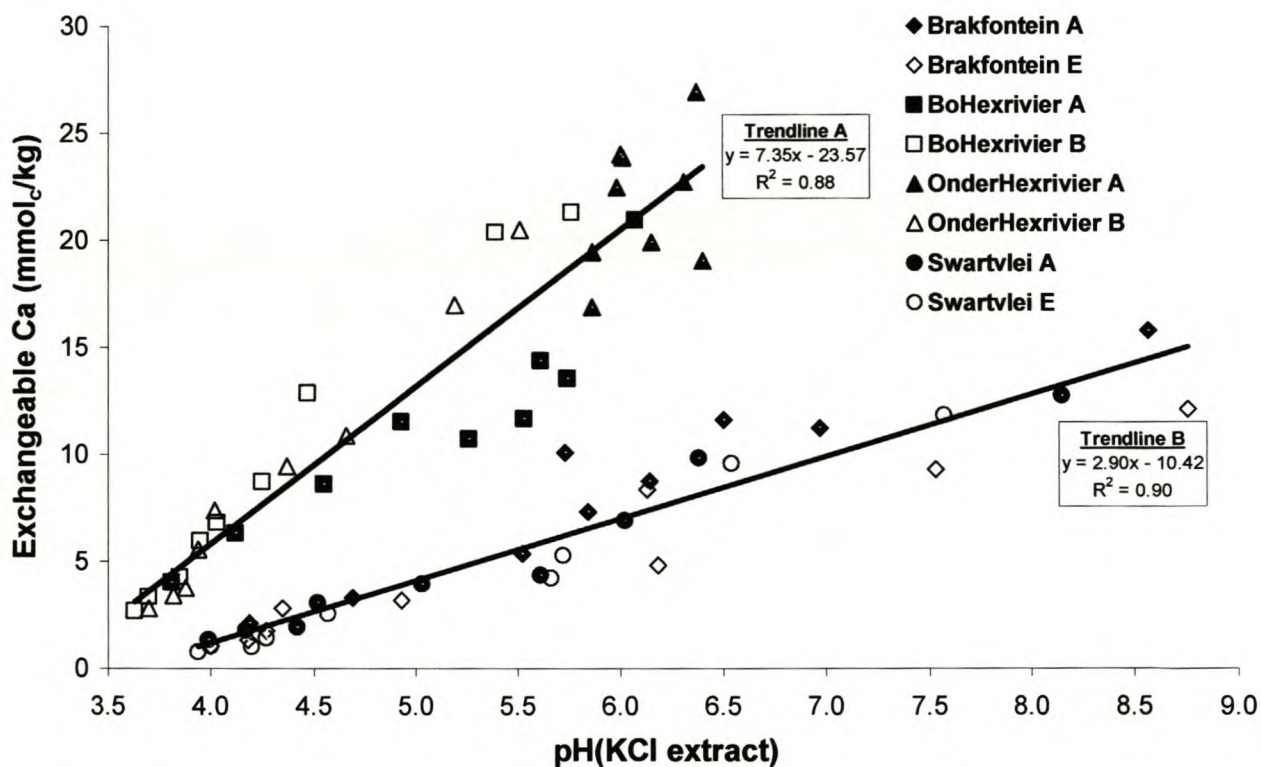
Figure 3.7. Relationship between pH and Ca determined in 1 *M* KCl extracts of the different orchard soil horizons. Trendline A represents the BoHexrivier and OnderHexrivier soils and trendline B represents the Brakfontein and Swartvlei soils.

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3.4   Conclusions

Buffering in the naturally acidic sandy soils from the Citrusdal orchards varies to some extent, but in general is weak as a result of low clay and organic matter contents. The clay fraction is dominated by kaolinite and quartz, further implying that organic matter plays an important role in pH buffering, especially in the topsoils. The subsoils of the BoHexrivier and OnderHexrivier profiles contain larger amounts of clay than those at Brakfontein and Swartvlei, and pH buffering in the former two soil profiles is correspondingly greater.

Extractable acidity and Al dominate the exchange sites at pH_{KCl} values below 4.5. Aluminium is the major acidic cation, especially in the subsoils. This confirms that even in these poorly buffered, quartz-rich sandy soils, toxic amounts of Al can enter the soil solution quite rapidly following acidification. Lime requirement calculated from the slope of the titration curves provides a useful way of assessing the magnitude of the acidification problem, even though liming the acidified subsoil may present practical difficulties under field conditions in drip-fertilized irrigation systems.

GENERAL DISCUSSION AND CONCLUSIONS

The objectives of this study have been met to a large extent. Investigating soil acidification and associated chemical changes of a representative selection of sandy orchard soils in the Citrusdal area as a result of drip fertigation practices revealed the magnitude and spatial extent of the problem. Studying the buffering properties of the soils through laboratory incubation has revealed adequate information to assist in the formulation of practical strategies for minimizing the degree of soil acidification and its impact on orchard productivity.

Spatial variation in soil chemistry. Applying fertilizers through drip irrigation has resulted in large decreases in soil pH immediately below the emitter at all four study sites. Concomitantly, an increase in exchangeable acidity, which is dominated by Al, was also observed. These findings compare well with those of Edwards *et al.* (1982), Haynes & Swift (1987) and Parchomchuk *et al.* (1993). The wetted soil volume was also found to be largely deficient in exchangeable Ca, Mg, and K, which leached to the periphery. Without exception it was found that the cation exchange capacity of the wetted soil volume of the four soils was mostly acid saturated. Thus the chemical properties of the wetted soil volume are highly unsuitable for root growth, which possibly explains why Pijl (2000) found that roots tend to concentrate at the periphery of the wetting front. The direct effect of toxic quantities of Al in the soil solution on the yield of citrus on these sandy Citrusdal soils is an issue that is still unaddressed and needs further research. Since the trees were still young at the time of sampling, the effects of soil acidification might only be realized when the orchards are in full production.

It can be concluded that nitrification of ammonium-containing fertilizers has resulted in the soil pH decline since all four study sites received these fertilizers in varying amounts. Little residual ammonium was found in the vicinity just below the emitter of all four sites, which indicates that sufficient nitrification and leaching of nitrate took place to cause the pH decline. However, the

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nitrification potential of these poorly buffered, sandy soils is still ill-defined and further research in this area is required.

From the spatial variation in Bray No. 2 extractable P of the four soils, it can be concluded that under some conditions a degree of P leaching may occur, but in general applied P tends to accumulate in the vicinity immediately below the emitter. The more mobile anions chloride and sulfate have moved a greater distance from the emitter and concentrated at the surface and at the periphery of the wetted soil volume. Sulfate was probably already deficient in some of the soils and over-irrigation may have caused further leaching losses. The fact that most of the plant nutrients are depleted throughout the sampling depth suggests that over-irrigation was definitely a contributing factor to soil acidification. The contribution of over-irrigation to soil acidification needs to be investigated because improved irrigation scheduling will hold benefits in terms of improved fertilizer and water use efficiency, soil chemistry and soil aeration.

Buffering of selected soils. In general, it was found that buffering in these naturally acidic sandy soils is weak as a result of a low content of both clay and organic matter. The clay fraction is dominated by kaolinite and quartz, further implying that organic carbon plays an important role in pH buffering, especially in the topsoils. The subsoils of the BoHexrivier and OnderHexrivier profiles contain larger amounts of clay than those at Brakfontein and Swartvlei, and pH buffering in the former two soils is correspondingly greater. The rate of soil acidification with a constant acid input will therefore be slower on the better-buffered soils, which may explain why Pijl (2000) found better root development below the emitter of a silt loam compared to a sandy soil under a conventional drip fertigation system. However, once the better-buffered soil has acidified, it will be both more difficult and more costly to ameliorate.

It was found that the CEC becomes increasingly saturated by acidic cations (H^+ and Al^{3+}) once soil pH_{KCl} values decrease below 4.5, which is consistant with what is generally reported (Adams, 1984; McBride, 1994). Aluminium is the major acidic cation, especially in the subsoils. This confirms

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that even these poorly buffered, quartz-rich sandy soils, toxic amounts of Al can enter the soil solution quite rapidly following acidification. Lime requirement calculated from the slope of the titration curves provides a useful way of assessing the magnitude of the acidification problem, even though liming the acidified subsoil may present practical difficulties under field conditions in drip-fertilized irrigation systems. These lime requirement values can be applied to field conditions with some calibration refinements.

Proposed management strategies: The most important management strategy should always be to prevent the soil from acidifying in the first place. As Pijl (2001) pointed out, there seem to be definite benefits from applying a balanced nutrient solution, containing both macro- and micro-nutrients, on a daily basis as is sometimes proposed. Such approaches originated in hydroponic culture but have been applied to field conditions with reasonable success. Poorly buffered sandy soils are the most likely to benefit from such a system in view of their low nutrient storage capacity. By maintaining a constant, balanced supply of nutrients (especially Ca) in the irrigation water, along with more efficient irrigation scheduling, leaching losses on very sandy soils can be minimized. Soil acidification occurs through leaching of base cations along with nitrate. Therefore, if more efficient irrigation scheduling is used to promote the uptake of nitrate by plants, soil acidification can be reduced. Pulse irrigation may reduce the problem of leaching as a result of over-irrigation. Another benefit of pulse irrigation is its positive effect on soil aeration (Pijl, 2001).

In most sandy soils, water movement below an emitter with a low discharge rate occurs preferentially in a vertical (downward) direction (Bresler, 1978). By increasing the discharge rate of the emitters, horizontal water movement may be increased and vertical movement decreased. This might hold benefits, especially if acidity can be restricted to the topsoil, which could allow for easier ameliorative strategies (Haynes, 1990). Such a strategy would create a wetting front resembling that of flood irrigation. This might increase evaporation and the accumulation of salts at the surface. Additional mulching might also therefore be required.

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Liming is the best curative measure for soil acidity because it provides Ca necessary for maintaining healthy roots, while simultaneously increasing soil pH to precipitate toxic Al^{3+}. Unfortunately most liming materials [$CaCO_3$ and $Ca(OH)_2$] are not readily mobile and will not readily ameliorate the subsoil. Gypsum, being more soluble, may therefore be a better option because it will provide Ca in the soil solution, but will do little to increase soil pH. Haynes and Swift (1987) proposed the use of more soluble KOH or $KHCO_3$, achieving K nutrition in the form of a highly soluble alkaline carrier. Smith *et al.* (1995) demonstrated the beneficial effect of a Ca citrate solution on subsoil acidity while simultaneously increasing the CEC of the soil, which could be especially important in poorly buffered sands. Since the nitrification of NH_4-N is probably the main cause of soil acidification in drip-fertigated soils, decreasing the total NH_4-N content in the fertilizer solution may also reduce soil acidification. This could be achieved by substituting NH_4NO_3 as main source of nitrogen in fertigation solutions with $Ca(NO_3)_2$ and could ensure that no net acidification will takes place. This change of N source could, however, result in a four to five fold increase in cost per unit of N (rough calculations to illustrate this point have been included in Appendix C) and might not be economically feasible. These more novel forms of amelioration have not yet been tried in the orchards of Citrusdal and further research should be considered.

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APPENDICES

A. SOIL ANALYSIS

A.1. Analytical methods and data reproducibility

A.1.1.   Soil pH

Background

The electrometric method for determining hydrogen activity involves a glass, H^+-sensing (indicator) electrode in conjunction with a reference electrode attached to a suitable meter for measuring ΔE (McBride, 1994).   In order to make electrical contact a soil paste or suspension is prepared. Potassium chloride or $CaCl_2$ is used is used as suspending solution to mask variation in salt concentration resulting from fertilizer residues, irrigation water and microbial decomposition of organic matter (McLean, 1982).

Method

A 1: 2.5 (g soil: cm^3 solution) suspension was made up using 20 g soil and 50 ml of solution. Samples were suspended in a 100 ml plastic beaker with both 1 *M* KCl and distilled water, stirred, and left to equilibrate for 30 minutes. The pH measurement was taken at ambient temperature using Metrohm 744 pH meter calibrated with two buffers at 4 and 7 equipped with an automatic temperature compensator. The electrodes were positioned in the supernatant while simultaneously stirring the solution with a magnetic stirrer. Reproducibility of the measurements is reported in Table A.1.

Table A.1. Reproducibility of soil pH measurements. All measurements were reproducible to an acceptable extent (RSD<10%)

Sample	pH(KCl)	pH(KCl)	Mean	SD	RSD (%)	pH(H₂O)	pH(H₂O)	Mean	SD	RSD (%)
A1HB	4.58	4.46	4.52	0.08	1.9	5.80	5.70	5.75	0.07	1.2
B1HB	3.57	3.47	3.52	0.07	2.0	4.65	4.58	4.62	0.05	1.1
C1HB	3.63	3.57	3.60	0.04	1.2	4.63	4.50	4.57	0.09	2.0
D1HB	3.95	3.96	3.96	0.01	0.2	5.21	5.03	5.12	0.13	2.5
E1HB	4.72	4.84	4.78	0.08	1.8	6.20	6.03	6.12	0.12	2.0
A5HH	3.40	3.30	3.35	0.07	2.1	4.52	4.23	4.38	0.21	4.7
B5HH	3.48	3.47	3.48	0.01	0.2	4.69	4.51	4.60	0.13	2.8
C5HH	3.62	3.51	3.57	0.08	2.2	5.02	4.62	4.82	0.28	5.9
D5HH	3.59	3.51	3.55	0.06	1.6	4.98	4.78	4.88	0.14	2.9
E5HH	3.69	3.41	3.55	0.20	5.6	4.66	4.41	4.54	0.18	3.9
A6HH	3.17	3.02	3.10	0.11	3.4	4.45	4.14	4.30	0.22	5.1
B6HH	3.25	3.08	3.17	0.12	3.8	4.48	4.14	4.31	0.24	5.6
C6HH	3.17	3.03	3.10	0.10	3.2	4.16	4.03	4.10	0.09	2.2
D6HH	3.26	3.05	3.16	0.15	4.7	4.22	4.00	4.11	0.16	3.8
E6HH	3.32	3.16	3.24	0.11	3.5	4.11	4.01	4.06	0.07	1.7

A.1.2.   Potassium chloride (1 *M*) extractable base cations

Background

A neutral, unbuffered salt solution such as 1 *M* KCl can be used to displace part of the absorbed and soluble Ca^{2+}, Mg^{2+} and Na^+ present in the soil. Displacement is usually very effective and values obtained compare good with other extraction methods (Thomas, 1982). The cations determined are referred to as extractable Ca, Mg and Na.

Method

Ten grams of soil (±0.1 g) was mixed with 100 ml of 1 *M* KCl to achieve a 1:10 soil: solution ratio. The soil and solution were mechanically shaken for 1 hour in a plastic beaker. After 1 hour the supernatant was immediately filtered off using Whatman no. 2V filter paper into a 500 ml Erlenmeyer flask. A 25 ml portion was separated and used for determination of Ca and Mg by atomic absorption spectrophotometry and 50ml was used for titratable acidity determination. Data reproducibility is shown in Table A.2. All measurements were reproducible within 15% RSD and results are acceptable for this study.

Table A.2. Reproducibility of 1 *M* KCl extractable Ca and Mg.

Sample	Ca					Mg				
	mmol$_c$/kg	mmol$_c$/kg	Mean	SD	RSD (%)	mmol$_c$/kg	mmol$_c$/kg	Mean	SD	RSD (%)
BF1	20.0	21.3	20.6	0.9	4.3	4.0	4.3	4.2	0.2	3.9
BF2	11.9	12.6	12.3	0.5	3.8	3.6	3.8	3.7	0.1	2.0
BF3	8.6	9.2	8.9	0.4	5.0	4.2	4.3	4.2	0.1	2.3
BF4	7.4	7.8	7.6	0.3	3.3	4.3	4.5	4.4	0.1	2.4
BF5	7.1	8.0	7.6	0.6	8.1	6.1	6.3	6.2	0.2	2.5
BH1	7.8	8.1	8.0	0.2	2.1	5.3	4.9	5.1	0.3	5.0
BH2	8.7	9.6	9.1	0.6	7.1	4.9	4.8	4.8	0.0	0.2
BH3	11.9	12.6	12.2	0.5	4.1	6.4	5.9	6.2	0.4	5.8
BH4	5.2	5.0	5.1	0.1	2.5	3.6	3.5	3.6	0.1	3.1
BH5	2.2	2.1	2.2	0.0	1.6	1.9	1.6	1.7	0.3	14.4

A.1.3. Potassium chloride (1 *M)* extractable acidity and aluminium (Al)

Background

A neutral, unbuffered salt solution such as 1 *M* KCl can be used to displace acidity from soil surfaces. Extractable acidity is composed of four types of acidity. Firstly H^+ ions derived from the hydrolysis of exchangeable Al^{3+}. The second type is from the hydrolysis of partially hydrolysed and non-exchangeable Al. A third type is from weakly acidic group on organic matter and lastly is exchangeable H^+ (Thomas, 1982). Using an unbuffered salt such as KCl renders it possible to determine acidity by back titration with a standard alkali such as NaOH while simultaneously determining the contribution made by Al. This can be achieved by the addition of a complexing agent such as NaF and titrating the liberated alkalinity with a standard acid solution such as HCl (Thomas, 1982). Aluminium in the KCl extract can also be determined colorimetricly. The metallochromic reagent chrome azurol S (CAS), when used in hexamine buffer at pH 4.9, reacts rapidly with monomeric Al and produces a coloured CAS/Al(III) complex that obeys Beer's law at 567 nm. Interference by Fe^{3+} is prevented by reduction to Fe^{2+} with the addition of ascorbic acid added prior to colour development (Kennedy & Powell, 1986).

Method

Extraction was the same as for 1 M KCl extractable cations. Total extractable acidity was determined in 50 ml of the KCl extract by titration to a light pink end point with 0.01 M NaOH using 5 drops of phenolphthalein as indicator. For the determination of extractable Al 5 ml of 1 M NaF was added to the solution and the liberated alkalinity was titrated with 0.01 M HCl. The endpoint was indicated when the pink colour did not return after 2 minutes. Colorimetric determination of Al was achieved by adding 0.5 ml sample, 5 ml 1 M KCl, 5ml hexamine buffer, 5ml ascorbic acid and 5 ml CAS agent and allowed to stand for 20 minutes before reading the absorbance at 567 nm. A typical standard calibration curve is shown in Figure A.1 and the results obtained by the two methods are compared in Figure A.2. The results of these two methods are in good agreement over the concentration range of 1-20 mmol$_c$/kg. It is notable that the CAS method has a higher sensitivity than NaF titration method at concentrations below 1.5 mmol$_c$/kg.

A.1.4.   Potassium chloride (1 *M)* extractable inorganic nitrogen

Background

Inorganic nitrogen can be extracted using a 1 M KCl solution at a soil: solution ratio of 1:10. A 1-molar solution is used firstly to provide sufficient ions, K^+ and Cl^-, to produce a mass action effect to remove any NH_4^+ and NO_3^- from exchange sites. Secondly a 1 M KCl solution will provide a sufficient osmotic potential to inhibit further microbial transformations (Keeney & Nelson, 1982, Stock, 1983). For the determination of nitrate Cd granules are used (that have been treated with $CuSO_4$) to reduce NO_3^- to NO_2^-. Nitrite is determined using a modified Griess Ilosvay method, this involves treating the extract with a diazotizing reagent (sulphanilamide) and a coupling reagent [*N*-(1-napthyl)-ethylene] resulting in the formation of an azo chromophore. The amount of NO_2^- is proportional to the intensity of the reddish colour produced (Keeney & Nelson, 1982). For the determination of NH_4^+, phenol is used to react with NH_3 in the presence of an oxidising agent

(hypochlorite) under alkaline conditions to form a blue coloured complex (Keeney & Nelson, 1982).
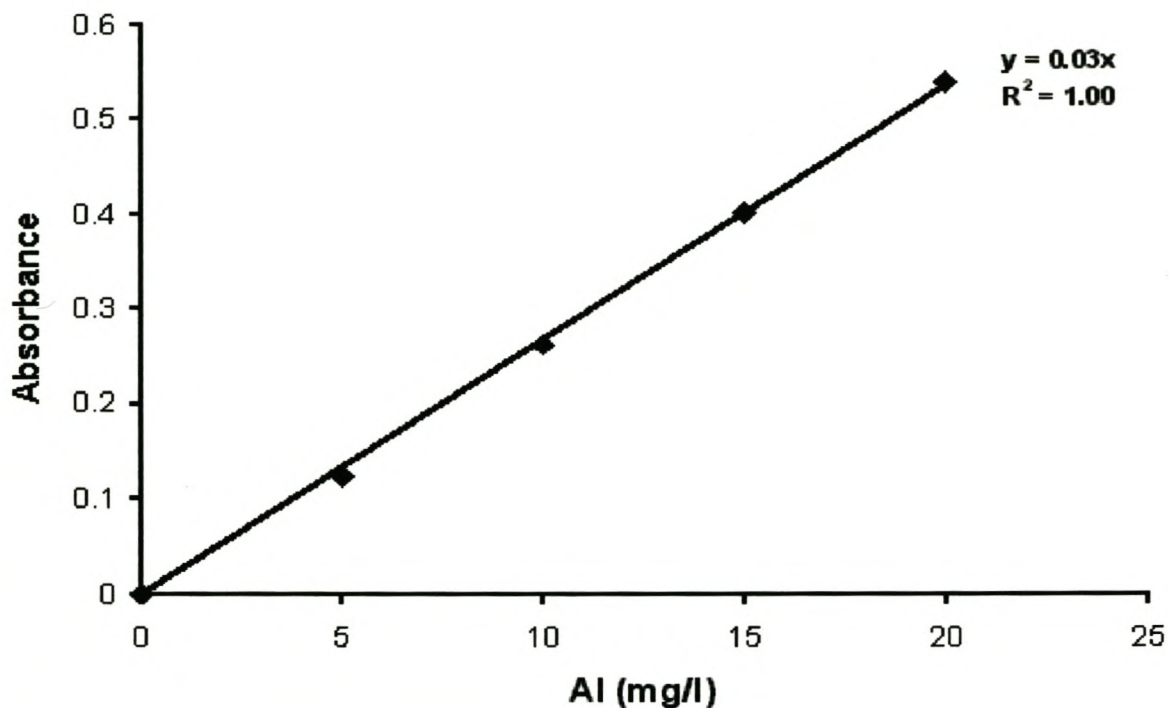
Figure A.1. A typical standard calibration curve for the colorimetric determination of Al in 1M KCl extracts.
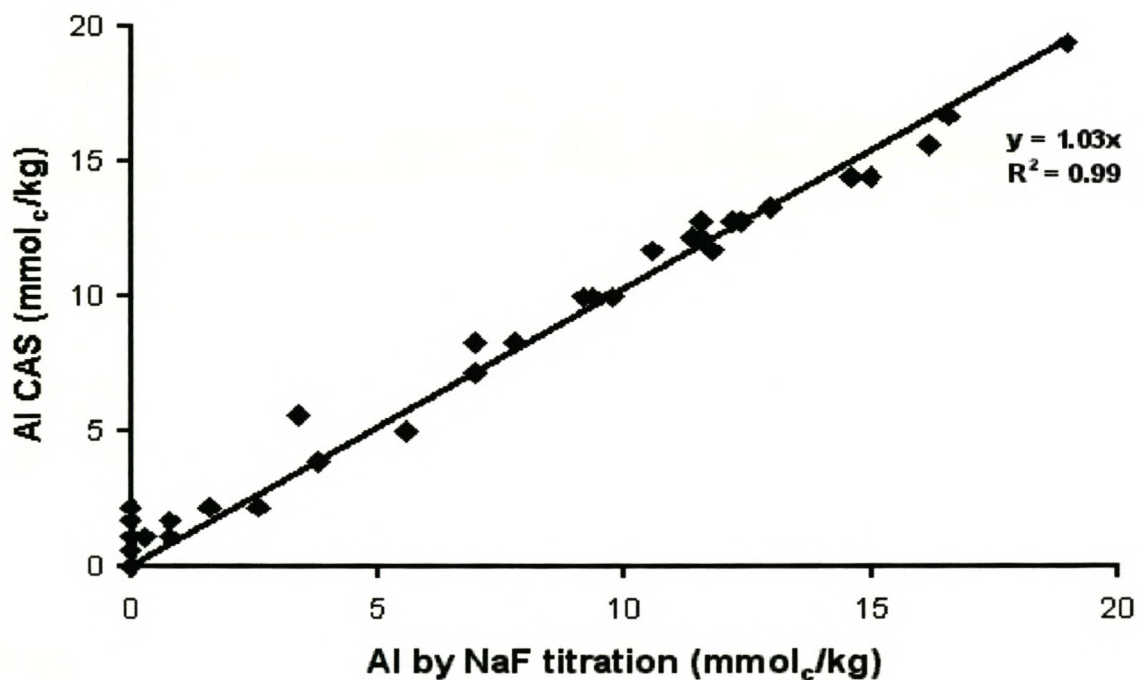
Figure A.2. Comparison between the CAS method en NaF titration method for determining Al.

Method

a. **Nitrate**:   The copper/cadmium, used to as reducing agent, was prepared by washing coarse cadmium powder briefly with 5% HCl, followed by water. It was then mixed with 0.5% (w/v) $CuSO_4 \cdot 5H_2O$ and filtered. The Cu/Cd was washed extensively with a solution containing 0.007 N (normal)and 0.005 M Na_2EDTA. The Cu/Cd was always stored in this acid/EDTA solution and washed with fresh acid/EDTA solution prior to use (Bate & Heelas, 1975). A 3ml aliquot of soil extract was added to approximately 2 g of wet Cu/Cd in a 25 ml test tube. Sequentially 1.9 ml of a 0.4 M NH_4Cl buffer (adjusted to pH 9.6) was added and the mixture shaken for precisely 10 minutes whereupon a 1ml aliquot was removed and NO_2^- determined by the Griess Ilosvay method. The Griess Ilosvay method requires that 1ml of 1% (w/v) sulphanilamide in 1.5 N HCl and 1 ml of 0.01% (w/v) N-(1-napthyl)-ethylene solution are added to 1 ml of soil extract (Stock, 1983). Absorbance was read after 10 minutes at 540 nm. The instrument was calibrated with a range of standards on NO_3-N. A typical calibration curve can be seen in Figure A.3.

b. **Ammonium**: A 2 ml aliquot of soil extract was pipetted into a 25 ml test tube and 1.6 ml 10% (w/v) sodium potassium tartrate, 0.2 ml 0.16% (w/v) sodium nitroprusside (serving as catalyst), 0.4 ml sodium phenate (prepared daily with 25 g NaOH and 12.5 g phenol made up to 100 ml in distilled water) and 0.2 ml sodium hypochlorite were added sequentially. The tubes were made up to 10 ml with distilled water and incubated in a water bath at $40^{\circ}C$ for 20 minutes. After cooling the absorbance was read at 625 nm. A typical calibration curve is shown in Figure A.4 and reproducibility of inorganic nitrogen determinations are shown in Table A.3 and Table A.4.
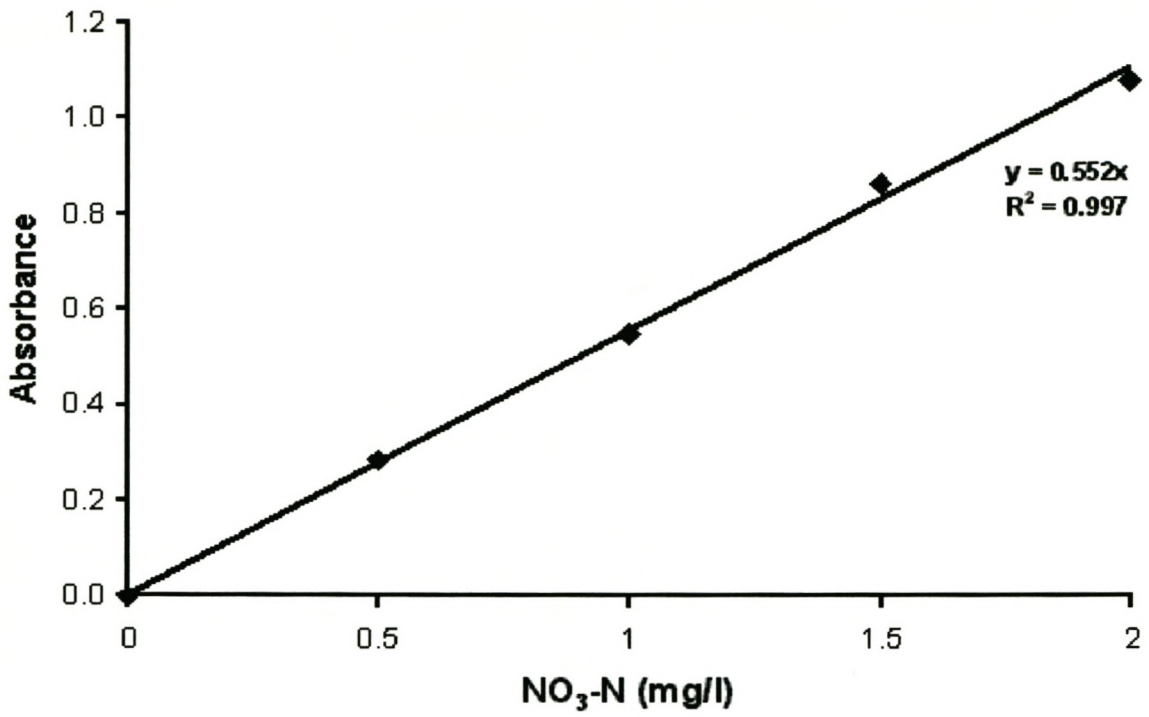
Figure A.3. A typical calibration curve for the colorimetric determination of NO_3-N.
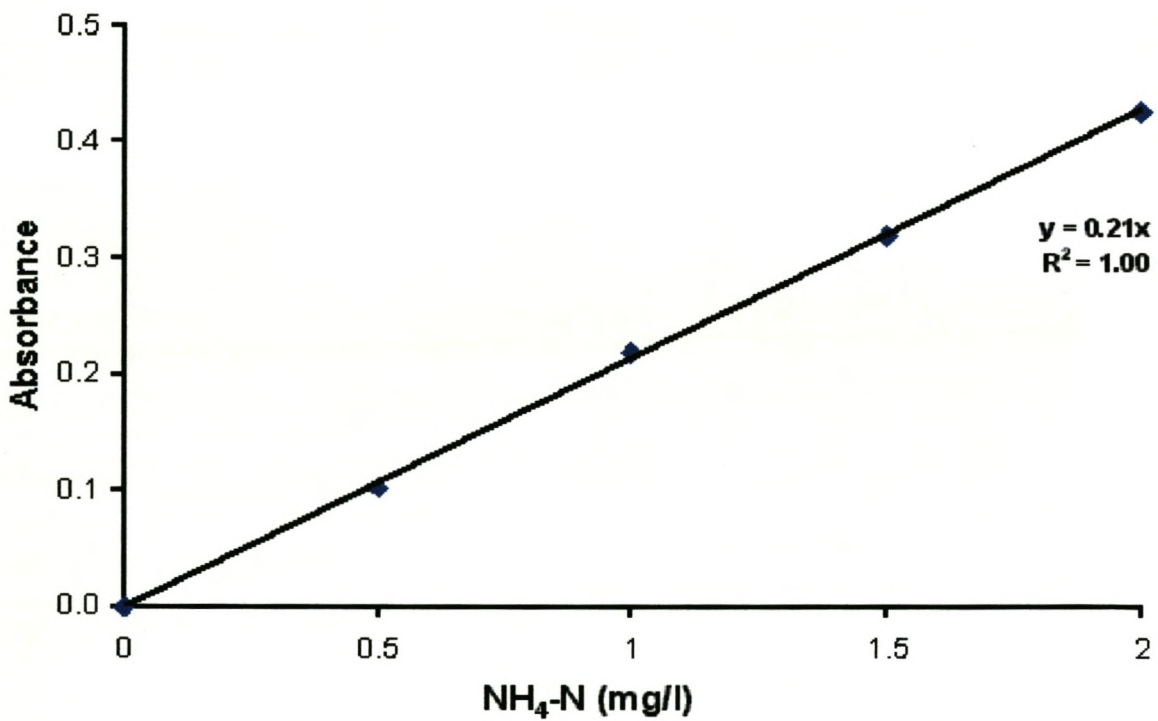
Figure A.4. A typical calibration curve for the colorimetric determination of NH_4-N.

Table A.3. Reproducibility of NO_3-N data

Sample	(mg/kg)	(mg/kg)	Mean	SD	RSD (%)
BF16	8.6	11.4	10.0	2.0	19.7
BF17	2.0	1.7	1.8	0.2	11.7
BF18	2.1	1.5	1.8	0.4	23.3
BF19	2.4	2.2	2.3	0.1	4.2
BF20	2.8	3.0	2.9	0.1	4.6
BH16	39.0	38.8	38.9	0.1	0.3
BH17	19.8	19.8	19.8	0.0	0.1
BH18	5.2	4.8	5.0	0.3	5.2
BH19	8.7	7.7	8.2	0.7	8.7
BH20	13.8	10.3	12.1	2.4	20.3

Table A.4. Reproducibility of NH_4-N data

Sample	(mg/kg)	(mg/kg)	Mean	SD	RSD (%)
BF16	1.9	1.3	1.6	0.4	27.6
BF17	1.5	1.6	1.5	0.0	2.0
BF18	1.4	1.0	1.2	0.3	26.3
BF19	1.3	0.9	1.1	0.3	23.6
BF20	0.5	0.4	0.5	0.1	12.9
BH16	2.3	2.6	2.5	0.2	7.2
BH17	2.7	3.1	2.9	0.3	9.8
BH18	2.2	2.5	2.3	0.2	9.0
BH19	2.5	2.9	2.7	0.3	10.9
BH20	2.2	4.7	3.4	1.8	51.3
OH16	5.3	5.0	5.2	0.2	3.8
OH17	2.9	2.8	2.8	0.1	3.0
OH18	3.0	2.7	2.9	0.2	7.0
OH19	2.7	2.4	2.5	0.2	7.9
OH20	5.1	2.5	3.8	1.8	49.0
SV16	4.1	4.8	4.5	0.5	10.2
SV17	4.2	5.3	4.7	0.8	16.0
SV18	4.3	4.8	4.6	0.3	7.5
SV19	6.4	6.7	6.5	0.3	4.1
SV20	9.0	7.2	8.1	1.3	15.9

A.1.5.   Cation exchange capacity and exchangeable cations: (NH_4OAc, pH 7)

Background

During the determination of the cation exchange capacity (CEC) of soil both adsorbed and water soluble cations are extracted with 0.2 M NH_4OAc (buffered at pH 7) while the negatively charged exchange sites are fully saturated with NH_4^+ ions (Thomas, 1982). Leaching with a K-salt such as

K_2SO_4 displaces the NH_4^+ ions retained on the exchange complex and the occluded NH_4^+ are determined in the leachate by Kjeldahl distillation. This amount is taken as equal to the CEC of the soil. In soils containing gypsum or free Ca/Mg carbonates some Ca and Mg are exchanged giving inaccurate exchangeable cation and CEC values. This method is thus not suitable for soils in the arid regions (Thomas, 1982). A 1 M NH_4OAc (buffered at pH 7) solution was used where only the exchangeable cations were to be determined.

Method

a. CEC: This method was proposed by THE NON-AFFILIATED SOIL ANALYSIS WORK COMMITTEE (1990). Twenty grams of air-dried soil (<2 mm) and 50 ml 0.2 M NH_4OAc (buffered at pH 7) were placed in a 125 ml glass beaker, stirred and allowed to stand for 30 minutes. The contents of the beaker were transferred to a Buchner funnel and leached with 50ml aliquots of 0.2 M NH_4OAc under vacuum. The filtrate was collected over a period of 1 hour in a 500 ml Stohmann volumetric flask contained in Witt filter flask, made up to the mark and an aliquot taken for the analysis of cations using atomic absorption spectrophotometry. The mass of the dry Buchner funnel and filter was taken before filtration and the mass of the funnel with soil, filter and occluded solution was taken after filtration. A second leaching was undertaken using 50 ml aliquots of 0.2 M K_2SO_4 into a clean 500 ml Stohmann volumetric flask. Hundred millilitres of the K_2SO_4 leachate was placed in an 800 ml Kjeldahl flask and 200 ml distilled water, 80 ml 40% NaOH and a few glass beads to prevent bumping. Approximately 200 ml liquid was distilled off and collected in a 500 ml wide mouth Erlenmeyer flask containing 60 ml of a 4% boric acid solution. Ten drops of mixed indicator (methyl red and methylene blue) was added to the solution and titrated to purple endpoint with 0.1 M HCl. An analytical blank was also prepared and titrated in the same manner.

b. Cations: The centrifuge procedure (Thomas, 1982) was used for the determination of base cations. Five grams of air-dried soil (<2 mm) was placed in a centrifuge tube with 25 ml 1 M

NH$_4$OAc (buffered at pH 7) and mechanically shaken for 30 minutes. The tube was then placed in a centrifuge and spun at 2000 rpm for 10 minutes. The supernatant was then poured off in a 50 ml volumetric flask and the process repeated with another 25 ml NH$_4$OAc solution, and finally brought to a volume of 50 ml. The base cations, Ca, Mg, K and Na in this solution were determined by atomic absorption spectrophotometry. Reproducibility of Ca and Mg data is shown in Table A.5 and of K and Na data in Table A.6.

Table A.5. Reproducibility of 1 *M* NH$_4$OAc extractable Ca and Mg

Sample	Mg					Ca				
	mg/kg	mg/kg	Mean	SD	RSD(%)	mg/kg	mg/kg	Mean	SD	RSD(%)
BF16a	35.0	36.6	35.8	1.1	3.2	75.5	84.8	80.2	6.6	8.2
BF17a	15.5	15.3	15.4	0.1	0.9	20.1	19.5	19.8	0.4	2.1
BF18a	12.9	12.3	12.6	0.4	3.4	13.7	13.3	13.5	0.3	2.1
BF19a	24.2	26.0	25.1	1.3	5.1	46.9	51.2	49.1	3.0	6.2
BF20a	45.9	47.2	46.6	0.9	2.0	95.7	103.7	99.7	5.7	5.7
BH16a	15.6	17.2	16.4	1.1	6.9	22.1	26.3	24.2	3.0	12.3
BH17a	21.8	22.7	22.3	0.6	2.9	54.6	57.4	56.0	2.0	3.5
BH18a	27.7	28.3	28.0	0.4	1.5	88.1	89.1	88.6	0.7	0.8
BH19a	30.0	31.7	30.9	1.2	3.9	79.3	72.3	75.8	4.9	6.5
BH20a	20.1	23.5	21.8	2.4	11.0	37.4	37.7	37.6	0.2	0.6
OH16a	19.8	20.6	20.2	0.6	2.8	15.2	25.2	20.2	7.1	**35.0**
OH17a	13.1	12.4	12.8	0.5	3.9	9.0	13.8	11.4	3.4	**29.8**
OH18a	9.9	9.8	9.9	0.1	0.7	6.6	8.5	7.6	1.3	**17.8**
OH19a	8.8	9.2	9.0	0.3	3.1	6.4	13.4	9.9	4.9	**50.0**
OH20a	9.0	8.8	8.9	0.1	1.6	6.8	8.7	7.8	1.3	**17.3**

Table A.6. Reproducibility of 1 *M* NH₄OAc extractable K and Na

Sample	K mg/kg	mg/kg	Mean	SD	RSD(%)	Na mg/kg	mg/kg	Mean	SD	RSD(%)
BF16a	60.3	63.9	62.1	2.5	4.1	9.9	9.4	9.7	0.4	3.7
BF17a	45.9	49.6	47.8	2.6	5.5	7.0	7.2	7.1	0.1	2.0
BF18a	54.3	49.5	51.9	3.4	6.5	7.4	5.4	6.4	1.4	**22.1**
BF19a	48.3	54.8	51.6	4.6	8.9	7.8	7.1	7.5	0.5	6.6
BF20a	59.0	60.5	59.8	1.1	1.8	9.5	8.5	9.0	0.7	7.9
BH16a	38.9	36.7	37.8	1.6	4.1	6.5	7.2	6.9	0.5	7.2
BH17a	46.1	45.9	46.0	0.1	0.3	5.9	6.2	6.1	0.2	3.5
BH18a	58.0	59.6	58.8	1.1	1.9	5.0	5.1	5.1	0.1	1.4
BH19a	51.1	48.5	49.8	1.8	3.7	4.0	4.3	4.2	0.2	5.1
BH20a	31.8	54.3	43.1	15.9	**37.0**	5.0	4.0	4.5	0.7	**15.7**
OH16a	24.7	25.2	25.0	0.4	1.4	11.0	11.5	11.3	0.4	3.1
OH17a	26.0	25.7	25.9	0.2	0.8	9.3	9.8	9.6	0.4	3.7
OH18a	35.7	35.0	35.4	0.5	1.4	9.2	9.6	9.4	0.3	3.0
OH19a	37.0	38.6	37.8	1.1	3.0	7.5	8.1	7.8	0.4	5.4
OH20a	35.4	35.6	35.5	0.1	0.4	7.0	7.5	7.3	0.4	4.9

A.1.6. Ammonium fluoride (0.3 *M)* extractable inorganic anions

Background

A modification of the method developed by Prietzel and Hirsch (2000) was used whereby soil samples are extracted with a 0.3 *M* NH₄F solution and the mobilized sulfate along with phosphate, nitrate and chloride in the extract determined by ion chromatography. Ammonium fluoride extracts inorganic sulfate more efficiently than phosphate or bicarbonate solutions. Aluminium is strongly complexed by the F⁻ ion (McBride, 1994) in a NH₄F environment. Hence, sulfate strongly adsorbed to the soil matrix in the form of Al hydroxy sulfate minerals, is extracted more efficiently using NH₄F (Prietzel & Hirsch, 2000). An additional benefit is the simultaneous determination of chloride and phosphate in the extract using ion chromatography.

Method

Five grams of air-dried (<2 mm) soil was added to 25 ml 0.3 M NH₄F solution in a 50 ml polythene

bottle and mechanically shaken for 1 hour. The contents of the bottle were then filtered through

Whatman no.40 filter paper along with 3 blank solutions. The blank 0.3 M NH₄F solutions filtered

through Whatman no.40 filter paper didn't seem to contribute to the final concentration of inorganic

anions in the extract. The extract was diluted 10 times before analysis for inorganic anions using

DIONEX DX-120 ion chromatograph. The eluent was 0.003 M NaHCO₃ and 0.0018 M Na₂CO₃.

The standards were prepared in a 0.03 M NH₄F matrix. Data reproducibility of 0.3 M NH₄F

extractable anions is given in Table A.7.

Table A.7. Data reproducibility of 0.3 M NH₄F extractable anions

	Cl^-					SO_4^{2-}					PO_4^{3-}				
Sample	mg/l	mg/l	Mean	SD	RSD(%)	mg/l	mg/l	Mean	SD	RSD(%)	mg/l	mg/l	Mean	SD	RSD(%)
BF16	12.5	12.7	12.6	0.1	0.9	3.5	8.7	6.1	3.7	60.6	5.3	10.4	7.9	3.6	45.3
BF17	11.4	12.1	11.8	0.6	4.7	3.7	5.8	4.7	1.5	31.7	7.8	13.4	10.6	4.0	37.2
BF18	12.6	15.5	14.1	2.1	14.6	1.9	9.0	5.4	5.0	91.7	0.0	13.0	6.5	9.2	141.4
BF19	11.9	11.4	11.7	0.4	3.2	<0.1	7.0	3.5	5.0	141.4	<0.1	<0.1	-	-	-
BF20	13.4	10.8	12.1	1.8	15.1	3.4	5.2	4.3	1.3	30.1	<0.1	<0.1	-	-	-
BH16	9.8	10.8	10.3	0.7	7.0	<0.1	<0.1	-	-	-	44.0	45.5	44.7	1.0	2.3
BH17	9.7	10.0	9.9	0.2	1.9	<0.1	<0.1	-	-	-	32.1	39.4	35.8	5.2	14.4
BH18	11.0	10.0	10.5	0.8	7.2	<0.1	<0.1	-.	-	-	7.6	5.3	6.5	1.6	25.4
BH19	10.3	10.6	10.4	0.2	2.0	<0.1	<0.1	-	-	-	<0.1	<0.1	-	-	-
BH20	10.6	10.6	10.6	0.0	0.1	8.2	8.6	8.4	0.3	3.8	<0.1	<0.1	-	-	-

A.1.7. Bray-2 extractable phosphate (P)

Background

The Bray-2 extraction procedure developed by Bray and Kurtz (1945) is suitable for the

determination of P in moderate to highly weathered soils. This method of P extraction is based on

the solubilisation effect of H^+ on soil P and the ability of F^- to lower the activity of Al^{3+}. The Bray-

2 extracting solution contains 0.1 M HCl and 0.3 M NH₄F where the F^- ion complexes with Al^{3+} and

thereby increases the solubility of aluminium phosphate compounds and by precipitation as CaF,

releases P from calcium phosphate compounds. Total inorganic phosphates in the extracts are

determined by colorimetric analysis by first converting condensed phosphates present to orthophosphate by hydrolysis with sulfuric acid at 90°C. The total phosphate concentration is then determined by the reduction of phosphomolybdic acid with 1-amino-2-naphthol-4-sulfonic acid to yield an intense blue colour, suitable for photometric determination at 660 nm.

Method

Six grams of air-dried (<2 mm) soil was added to 45 ml of Bray-2 solution in a 50 ml polythene bottle and shaken for 1 minute, where after the solution was filtered through a Whatman no. 44 filter paper. A 20 ml aliquot of extract was pipetted into a clean 50 ml volumetric flask and 10 ml colour reagent (boric acid ammonium molybdate solution) was added and to the solution and mixed. Ten milliliters of the reducing agent (1-amino-2-naphthol-4-sulfonic acid) was added the solution diluted to 50 ml with distilled water and mixed. Absorbance was read after 20 minutes at 660 nm against a set of standards. Data reproducibility of Bray-2 extractable P is given in Table A.8 and a typical colorimetric calibration curve a shown in Figure A.6.
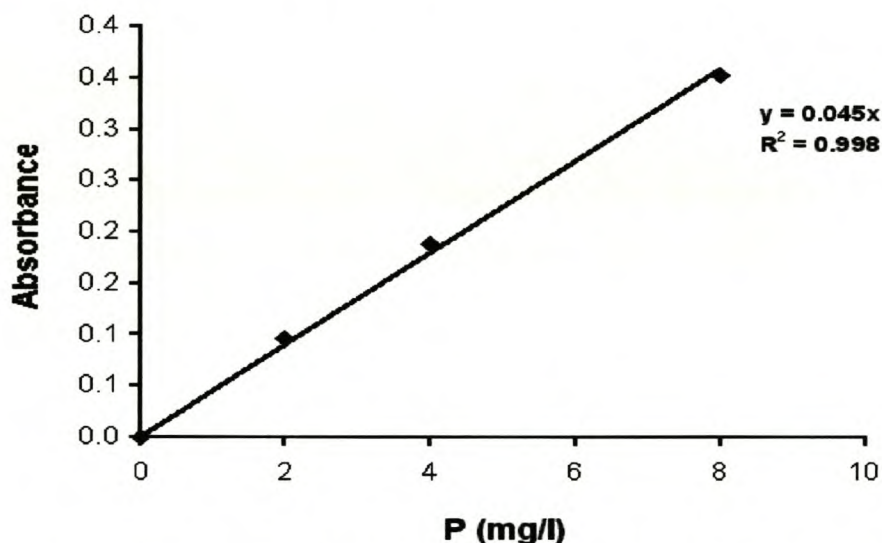
Figure A.6. A typical calibration curve for the colorimetric determination of Bray-2 extractable P

Table A.8. Data reproducibility of Bray-2 extractable P

Sample	Bray-2 P		Mean	SD	RSD(%)
	mg/l	mg/l			
A2VB	5.3	5.1	5.2	0.1	2.7
B2VB	1.2	1.3	1.3	0.1	5.7
C2VB	1.0	1.2	1.1	0.1	12.9
D2VB	0.9	0.9	0.9	0.0	0.0
E2VB	0.7	0.7	0.7	0.0	0.0

A.1.8. Organic carbon: Walkley-Black method

Background

Organic matter in soil can be oxidized by treatment with a hot mixture of $K_2Cr_2O_7$ and sulfuric acid (Schollenberger, 1927). After completion of the reaction, the excess dichromate is titrated with $FeSO_4$ and the dichromate reduced during the reaction with soil is assumed to be equivalent to the organic C present in the sample (Nelson & Sommers, 1982). It is also assumed that the soil organic matter has an average valence of zero.

Method

One gram of air-dried soil (ground, <0.5 mm) was placed in a wide-mouth 500 ml Erlenmeyer flask and 10 ml 0.167 M $K_2Cr_2O_7$ added. Sequentially 20 ml concentrated sulfuric acid was added and the solution shaken for 1 minute and allowed to cool for 30 minutes on an asbestos plate. After cooling 200 ml distilled water and 10 ml concentrated H_3PO_4 were added. The excess dichromate was determined by titrating with 0.5 N $FeSO_4$ using sodium diphenylamine-sulfonate as indicator to a light green endpoint. The determination was repeated with less soil (0.5 g) if >75% of the dichromate was reduced.

A.1.9. Electrical resistance of soil paste

Background

The electrical resistance of the saturated soil paste is inversely proportional to the salt concentration of the soil. The electrical resistance can therefore be considered to be an index of the salt hazard of a soil (US salinity laboratory staff, 1954).

Method

Sufficient soil to fill the *US Bureau of Soils standard electrode cup* was saturated using distilled water. The saturated soil was homogenized with a spatula and the mixture consolidated by tapping the container on the workbench. The soil paste was allowed to stand for 1 hour after which the electrical resistance was measured in ohms with a resistance bridge and corrected for a temperature of $25^{o}C$.

A.1.10. Particle size distribution: Pipette method

Background

The method for particle size analysis involves sieving and sedimentation procedures. Pre-treatment of soil samples is necessary to break the binding agents such as organic matter and coatings of gypsum, carbonate and Fe/Al oxides. This will enhance dispersion of soil particles. After pre-treatment soil particles are further dispersed using sodium hexametaphosphate. The sedimentation analysis of the silt and clay fraction is based on the fact that spherical particles in suspension settle at a velocity that can be calculated from Stokes' law. The sand fraction is characterized by sieving procedures (Gee & Bauder, 1986).

Method

a. **Pre-treatment:** The mass percentage left on the sieve after sieving an air-dried soil sample with a 2mm sieve was taken as the coarse fraction (>2 mm). Pre-treatment of the <2 mm fraction was restricted to the removal of organic matter. This was achieved by adding 5ml H_2O

to 40 g of sample (wetted with distilled water) in a 250 ml glass beaker. The excess water was evaporated on a water bath but not to dryness and H_2O_2 was continually added till all organic matter was destroyed. After final addition of H_2O_2 the sample was kept on the water bath to destroy the excess H_2O_2 after which the sample was oven dried overnight at 105^oC.

b. **Dispersion:** Samples was dispersed using 10 ml Calgon dispersing solution [$(NaPO_4)_4$ and Na_2CO_3] and the suspension transferred quantitatively with distilled water to a 500 ml dispersion cup and mixed for 5 minutes at high speed with a electric mixer.

c. **Separation of sand fractions:** The dispersed sample was washed through a 0.053 mm sieve, passing the silt and clay through the sieve *via* a funnel into a 1000 ml measuring cylinder. The washing continued till the percolate was clear. The sand fraction on the sieve was quantitatively transferred to glass beaker and excess water evaporated. The sample was then oven dried (105^oC) and transferred to a nest of sieves in the order 0.5, 0.25, 0.106 and 0.053 mm (from top to bottom). The sieves were shaken on a sieve shaker for 10 minutes and the different sand fractions determined by weighing on a 0.001 g precision balance.

d. **Silt and clay determination:** The 1000 ml cylinder with the silt and clay suspension was made to the mark with distilled water and the mouth sealed with plastic wrapping film. The cylinder was allowed to equilibrate for 1h in a room with constant temperature of 22^oC. After equilibration the cylinder was hand shaken end-over-end for 30 seconds and the suspension left to settle for the appropriate time intervals. The settling time for clay (0.002 mm) is 5 hours and 17 min at 7 cm depth, for fine silt (0.02 mm) 4 min 26 sec at 10 cm depth, and for coarse silt (0.05 mm) is 1 min 16 sec at 10 cm depth and 22^oC. At the appropriate time interval the Lowry pipette was lowered to the appropriate depth and 25 ml of sample withdrawn within 12 seconds. The sample was discharged in a porcelain crucible, evaporated to dryness on a water bath and finally dried in an oven at 105^oC. After cooling the crucible was weighed and the mass percentage calculated.

B. ADDITIONAL DATA

B.1. pH data

Table B.1. Data for the distribution of pH (KCl) and pH (H_2O) perpendicular to the dripper pipeline.

Orchard	Depth (cm)	pH (KCl) Distance from dripper (cm)						pH (H_2O) Distance from dripper (cm)							
		60	40	20	0	-20	-40	-60	60	40	20	0	-20	-40	-60
Brakfontein	0-20	7.74	6.93	4.03	4.58	6.34	7.17	7.18	8.18	7.41	5.50	5.80	6.70	7.70	7.70
	20-40	7.45	7.04	3.78	3.57	5.41	7.28	7.66	8.34	7.55	5.00	4.65	6.46	7.80	8.23
	40-60	7.42	7.23	3.86	3.63	5.41	7.34	7.60	8.42	7.80	5.02	4.63	6.52	8.25	8.20
	60-80	7.20	7.12	4.39	3.95	5.33	6.91	7.25	8.25	7.72	5.88	5.21	6.53	8.40	8.07
	80-100	6.72	6.66	5.64	4.72	5.72	6.64	6.93	8.02	7.63	6.86	6.20	7.04	8.13	8.15
BoHexrivier	0-20	4.13	3.84	3.53	3.40	3.86	4.16	4.17	4.80	4.94	4.59	4.52	4.66	5.02	5.30
	20-40	4.50	4.69	3.64	3.48	4.72	5.59	5.28	5.44	6.09	4.75	4.69	5.87	6.47	6.20
	40-60	6.03	6.02	4.68	3.62	4.11	5.18	5.66	6.90	7.05	6.13	5.02	6.90	6.19	6.55
	60-80	3.89	3.77	3.65	3.59	3.77	3.92	3.73	4.93	5.07	4.97	4.98	4.94	5.12	4.76
	80-100	3.64	3.57	3.55	3.69	3.72	3.71	3.61	4.40	4.63	4.70	4.66	4.65	4.55	4.44
OderHexrivier	0-20	5.82	4.74	3.98	3.17	3.50	4.02	3.98	6.20	5.20	4.80	4.45	4.70	5.17	5.00
	20-40	3.60	3.58	3.30	3.25	3.12	3.32	3.54	4.51	4.25	4.28	4.48	4.33	4.40	4.44
	40-60	3.54	3.42	3.31	3.17	3.10	3.36	3.49	4.37	4.16	4.16	4.16	4.23	4.25	4.40
	60-80	3.55	3.83	3.40	3.26	3.22	3.36	3.50	4.46	4.57	4.20	4.22	4.28	4.22	4.38
	80-100	3.55	3.50	3.45	3.32	3.35	3.39	3.47	4.57	4.27	4.30	4.11	4.24	4.22	4.48
Swartvlei	0-20	4.99	4.80	3.94	4.21	4.41	5.70	6.10	5.67	5.49	4.82	5.35	5.25	6.13	6.44
	20-40	4.77	4.93	3.79	3.77	4.05	4.71	5.02	5.47	5.60	4.80	4.80	5.04	5.24	6.00
	40-60	4.89	4.80	3.84	3.72	3.76	3.81	3.98	5.52	5.68	4.83	4.46	4.76	4.44	4.87
	60-80	4.93	4.57	3.87	3.75	3.87	3.86	3.94	5.72	5.60	4.89	4.55	4.13	4.56	4.90
	80-100	4.80	4.58	4.11	3.90	3.96	3.96	4.00	5.64	5.55	5.44	4.75	4.82	4.46	4.80

B.2. Soil chemical data

Table B.2. Soil chemical data for samples taken below dripper at Brakfontein site

Distance from dripper	Depth (cm)	pH$_{KCl}$	Ca	Mg	H/Al	Al	Ca	Mg	K	Na	Bray-2 P (mg/kg)	NO$_3$-N	NH$_4$-N	Cl	NO$_3$	SO$_4$	PO$_4$
			1 M KCl extractable (mmol$_c$/kg)				1 M NH$_4$OAc (pH 7) extractable (mmol$_c$/kg)					1 M KCl extractable (mg/kg)		0.3 M NH$_4$F extractable (mg/kg)			
-60cm	0-20	7.74	20.0	4.0	<0.1	<0.1	35.3	5.4	1.5	0.6	39.8	8.6	1.1	17.3	69.7	21.9	20.8
	20-40	7.45	11.9	3.6	<0.1	<0.1	17.6	4.3	0.8	0.8	9.0	2.0	<0.1	17.5	12.2	18.2	<0.1
	40-60	7.42	8.6	4.2	<0.1	<0.1	10.4	4.6	1.0	0.7	7.5	2.1	<0.1	42.8	12.2	<0.1	<0.1
	60-80	7.20	7.4	4.3	<0.1	<0.1	8.9	4.8	1.0	0.6	6.8	2.4	<0.1	12.4	<0.1	<0.1	<0.1
	80-100	6.72	7.1	6.1	<0.1	<0.1	7.8	6.4	1.4	0.6	5.3	2.8	<0.1	15.2	15.9	<0.1	<0.1
-40cm	0-20	6.93	15.2	3.8	<0.1	<0.1	19.0	4.3	1.9	3.3	27.0	7.6	<0.1	82.3	32.9	90.7	<0.1
	20-40	7.04	12.5	4.0	<0.1	<0.1	14.7	4.4	1.0	4.2	10.5	3.7	<0.1	108.5	17.6	132.2	<0.1
	40-60	7.23	10.6	3.9	<0.1	<0.1	11.6	4.4	0.8	4.0	4.5	1.6	<0.1	114.4	9.8	160.7	<0.1
	60-80	7.12	9.5	4.6	<0.1	<0.1	11.3	4.8	0.9	4.3	4.5	1.5	<0.1	127.1	<0.1	143.0	<0.1
	80-100	6.66	7.6	6.2	<0.1	<0.1	7.9	6.7	1.1	2.9	3.8	1.7	<0.1	94.7	<0.1	89.9	<0.1
-20cm	0-20	4.03	3.5	1.6	2.0	1.0	3.5	1.8	1.2	0.4	32.3	2.1	2.2	19.0	14.7	24.1	40.9
	20-40	3.78	1.6	1.4	4.8	2.9	1.0	1.4	1.4	0.4	30.8	1.8	1.1	23.2	9.1	14.6	34.9
	40-60	3.86	1.6	1.6	4.0	1.8	1.2	1.6	1.2	0.5	18.8	1.5	1.6	14.9	<0.1	19.3	<0.1
	60-80	4.39	4.1	2.1	0.8	<0.1	4.1	2.3	1.5	0.5	9.0	1.2	1.1	13.6	<0.1	9.1	<0.1
	80-100	5.64	5.7	2.6	<0.1	<0.1	5.9	2.9	1.6	0.5	7.5	2.1	0.4	9.4	<0.1	9.9	<0.1
0cm	0-20	4.58	3.9	2.6	0.8	1.1	3.8	2.9	1.5	0.4	30.0	4.4	1.9	13.8	22.2	17.5	26.7
	20-40	3.57	1.3	1.1	6.0	4.1	1.0	1.3	1.2	0.3	28.5	1.6	1.5	8.2	<0.1	18.4	39.2
	40-60	3.63	1.0	0.9	6.5	4.0	0.7	1.1	1.4	0.3	18.8	3.0	1.4	14.5	11.7	9.6	<0.1
	60-80	3.95	2.7	1.9	2.0	1.9	2.3	2.0	1.2	0.3	7.5	1.7	1.3	11.0	<0.1	<0.1	<0.1
	80-100	4.72	4.8	3.5	<0.1	0.9	4.8	3.8	1.5	0.4	5.3	1.4	0.5	18.4	<0.1	16.8	<0.1
20cm	0-20	6.34	10.9	4.8	<0.1	<0.1	11.9	4.9	4.4	2.4	20.3	39.2	2.3	69.7	255.6	69.3	<0.1
	20-40	5.41	6.6	4.3	<0.1	<0.1	7.0	4.3	1.8	1.7	6.8	3.8	1.5	17.9	5.7	38.5	<0.1
	40-60	5.41	6.7	4.3	<0.1	<0.1	7.2	4.5	1.9	1.4	0.8	1.6	1.0	8.4	<0.1	42.1	<0.1
	60-80	5.33	6.4	3.9	<0.1	<0.1	6.4	3.9	1.7	0.6	<0.1	1.7	0.8	16.8	<0.1	34.4	<0.1
	80-100	5.72	6.4	3.5	<0.1	<0.1	6.4	3.6	1.5	0.6	1.5	1.3	0.5	9.8	<0.1	35.1	<0.1
40cm	0-20	7.17	12.4	3.5	<0.1	<0.1	15.9	3.9	3.2	1.2	26.3	17.4	0.9	34.0	102.1	68.4	40.4
	20-40	7.28	14.8	5.0	<0.1	<0.1	21.4	5.7	1.5	2.2	21.0	4.8	0.6	85.2	17.9	110.7	<0.1
	40-60	7.34	10.7	6.7	<0.1	<0.1	11.7	7.5	1.3	3.2	6.0	2.1	0.4	50.7	12.9	62.0	<0.1
	60-80	6.91	8.4	10.4	<0.1	<0.1	9.3	11.2	2.0	2.2	2.3	1.4	0.6	16.2	<0.1	37.2	<0.1
	80-100	6.64	6.3	7.2	<0.1	<0.1	6.7	7.5	1.8	0.9	1.5	2.2	0.7	9.0	<0.1	26.7	<0.1
60cm	0-20	7.18	10.9	4.2	<0.1	<0.1	14.1	4.5	2.4	0.5	24.0	17.3	2.2	15.0	96.3	40.5	37.9
	20-40	7.66	15.1	4.7	<0.1	<0.1	26.8	5.5	1.4	0.7	23.3	3.7	0.8	17.4	18.4	33.7	<0.1
	40-60	7.60	11.4	5.8	<0.1	<0.1	13.7	6.4	1.2	1.6	10.5	3.6	0.4	40.4	17.1	65.1	<0.1
	60-80	7.25	9.5	7.7	<0.1	<0.1	11.7	8.8	1.7	1.4	9.0	4.9	0.4	35.3	26.5	58.2	<0.1
	80-100	6.93	5.7	6.6	<0.1	<0.1	6.6	6.9	1.6	0.8	4.5	2.9	0.4	17.8	<0.1	37.5	<0.1

Table B.3. Soil chemical data for samples taken below dripper at BoHexrivier site

Distance from dripper	Depth (cm)	pH$_{KCl}$	1 M KCl extractable Ca	Mg	H/Al	Al (mmol$_c$/kg)	1 M NH$_4$OAc (pH 7) extractable Ca	Mg	K	Na (mmol$_c$/kg)	Bray-2 P (mg/kg)	1 M KCl extractable NO$_3$-N	NH$_4$-N (mg/kg)	0.3 M NH$_4$F extractable Cl	NO$_3$	SO$_4$	PO$_4$ (mg/kg)
-60cm	0-20	4.13	7.8	5.3	4.0	2.0	7.3	4.8	1.9	0.5	42.8	39.0	9.6	35.6	157.2	<0.1	114.3
	20-40	4.50	8.7	4.9	1.3	0.6	9.0	4.8	1.8	0.3	41.3	19.8	4.9	17.1	67.1	<0.1	62.0
	40-60	6.03	11.9	6.4	<0.1	<0.1	12.9	6.7	1.2	0.3	37.5	5.2	3.0	11.5	13.3	8.8	45.1
	60-80	3.89	5.2	3.6	6.3	3.7	4.7	3.7	0.8	0.2	9.0	8.7	3.3	8.5	21.5	24.1	<0.1
	80-100	3.64	2.2	1.9	11.8	8.1	1.9	1.9	0.7	0.3	6.0	13.8	3.2	12.9	33.4	37.0	<0.1
-40cm	0-20	3.84	3.8	2.7	9.8	6.7	5.7	2.0	1.4	0.3	45.8	3.1	3.6	9.6	<0.1	<0.1	89.3
	20-40	4.69	9.8	4.9	0.3	<0.1	8.4	4.0	1.3	0.4	44.3	2.0	2.8	9.8	<0.1	<0.1	63.6
	40-60	6.02	14.3	6.9	<0.1	<0.1	13.5	6.5	1.2	0.2	37.5	2.0	0.0	10.4	<0.1	<0.1	50.9
	60-80	3.77	4.7	3.2	7.0	4.4	4.8	3.2	0.9	0.2	14.0	3.5	3.5	11.5	<0.1	13.4	<0.1
	80-100	3.57	2.4	1.6	10.5	7.0	2.1	1.6	0.7	0.2	6.0	5.3	2.6	9.4	<0.1	51.9	<0.1
-20cm	0-20	3.53	2.0	1.6	12.0	8.5	1.7	1.6	1.0	0.3	80.3	1.6	11.6	9.2	<0.1	<0.1	256.1
	20-40	3.64	3.1	1.9	9.5	6.6	2.7	1.7	1.0	0.2	79.5	1.9	4.9	8.1	<0.1	<0.1	218.7
	40-60	4.68	10.6	4.2	0.3	<0.1	10.1	4.1	1.7	0.2	47.3	1.7	1.8	9.5	<0.1	<0.1	59.9
	60-80	3.65	4.1	2.4	7.5	5.2	4.2	2.5	1.3	0.2	18.0	2.4	2.2	11.2	<0.1	18.2	13.7
	80-100	3.55	2.3	1.5	11.0	7.5	2.1	1.9	0.8	0.2	7.5	2.3	2.2	12.6	<0.1	31.4	<0.1
0cm	0-20	3.40	1.4	1.2	12.0	8.8	1.1	1.3	1.0	0.3	77.3	1.7	2.3	7.6	<0.1	<0.1	220.1
	20-40	3.48	2.9	1.7	9.5	6.5	2.7	1.8	1.2	0.3	70.5	1.9	2.7	7.5	<0.1	<0.1	160.7
	40-60	3.62	4.6	2.2	10.0	5.0	4.4	2.3	1.5	0.2	26.3	2.4	2.2	14.0	<0.1	<0.1	38.2
	60-80	3.59	3.7	2.1	7.5	5.0	4.0	2.5	1.3	0.2	13.5	1.9	2.5	10.0	<0.1	<0.1	<0.1
	80-100	3.69	2.0	1.4	9.5	6.5	1.9	1.7	0.8	0.2	6.0	1.9	2.2	11.6	<0.1	43.2	<0.1
20cm	0-20	3.86	4.2	2.4	6.0	3.6	4.0	2.6	1.8	0.4	28.5	13.5	5.0	18.1	41.5	<0.1	40.8
	20-40	4.72	9.0	4.0	0.5	<0.1	7.9	3.9	1.6	0.3	29.3	6.9	4.7	12.8	13.1	<0.1	31.7
	40-60	4.11	7.0	3.5	3.3	1.7	7.0	3.9	1.4	0.2	25.5	2.9	3.6	11.7	<0.1	<0.1	30.5
	60-80	3.77	4.9	2.7	7.0	4.8	4.5	2.7	1.1	0.2	19.5	3.3	2.5	11.7	<0.1	10.7	<0.1
	80-100	3.72	2.6	1.6	10.8	7.5	2.5	1.7	0.9	0.2	8.3	3.7	3.7	12.1	<0.1	31.9	<0.1
40cm	0-20	4.16	6.8	3.6	2.0	1.0	6.8	3.9	1.7	0.5	27.3	19.5	10.6	65.1	72.1	8.5	24.0
	20-40	5.59	12.8	7.1	<0.1	<0.1	12.1	7.2	1.0	0.6	40.5	5.8	2.4	13.1	10.5	<0.1	<0.1
	40-60	5.18	10.1	5.9	<0.1	<0.1	10.3	6.2	1.0	0.4	35.3	4.0	3.2	11.5	<0.1	<0.1	36.7
	60-80	3.92	5.7	2.9	4.5	2.9	5.3	3.1	1.0	0.3	27.0	4.6	3.6	13.9	<0.1	15.4	31.0
	80-100	3.71	3.3	2.0	9.5	6.8	3.0	2.0	1.0	0.2	12.8	9.2	3.7	15.4	26.7	28.7	<0.1
60cm	0-20	4.17	6.6	3.2	2.3	1.3	6.5	3.4	2.1	0.4	25.5	9.5	2.5	11.0	25.0	<0.1	30.2
	20-40	5.28	10.6	5.9	<0.1	<0.1	12.0	7.0	1.2	0.5	37.5	5.0	1.8	16.0	10.2	<0.1	39.0
	40-60	5.66	11.9	6.4	<0.1	<0.1	13.1	7.5	1.1	0.4	30.8	4.3	1.9	11.2	6.9	<0.1	21.7
	60-80	3.73	3.4	2.3	7.3	5.2	3.5	2.8	0.9	0.3	9.0	5.5	3.5	7.4	14.0	23.9	<0.1
	80-100	3.61	2.2	1.3	10.0	7.6	2.1	1.6	0.9	0.3	6.0	6.3	3.2	7.9	10.1	48.0	<0.1

Table B.4. Soil chemical data for samples taken below dripper at OnderHexrivier site

Distance from dripper	Depth (cm)	pH$_{KCl}$	1 M KCl extractable				1 M NH$_4$OAc (pH 7) extractable				Bray-2	1 M KCl extratable		0.3 M NH$_4$F extractable			
			Ca	Mg	H/Al	Al	Ca	Mg	K	Na	P	NO$_3$-N	NH$_4$-N	Cl	NO$_3$	SO$_4$	PO$_4$
			(mmol$_c$/kg)				(mmol$_c$/kg)				(mg/kg)	(mg/kg)		(mg/kg)			
-60cm	0-20	5.82	15.0	8.8	<0.1	0.2	16.4	9.5	1.7	2.0	70.5	18.7	3.0	92.2	72.3	<0.1	66.9
	20-40	3.60	3.8	2.5	10.5	8.4	3.3	2.4	1.0	0.5	87.0	4.6	5.9	17.7	<0.1	<0.1	332.8
	40-60	3.54	3.7	2.7	15.0	13.0	3.4	2.5	1.2	0.5	102.0	5.1	3.7	19.1	15.6	<0.1	645.3
	60-80	3.55	2.2	2.0	16.0	13.6	1.8	2.2	1.4	0.3	72.0	2.9	4.7	11.3	<0.1	<0.1	224.2
	80-100	3.55	3.4	3.8	14.0	11.6	3.2	3.8	1.5	0.4	55.5	2.9	7.2	11.6	<0.1	<0.1	112.0
-40cm	0-20	4.74	11.3	6.8	1.0	0.9	11.0	6.5	1.8	1.1	61.5	42.0	5.9	40.7	216.3	<0.1	108.2
	20-40	3.58	4.3	2.7	8.0	6.7	4.0	2.7	1.0	0.6	60.0	15.4	3.7	20.0	56.0	<0.1	207.8
	40-60	3.42	1.9	1.4	18.0	14.6	1.9	1.5	1.2	0.3	93.8	7.1	3.4	11.3	22.8	<0.1	428.7
	60-80	3.83	5.8	3.3	12.0	10.5	6.0	3.5	1.5	0.6	66.8	18.0	5.0	23.2	67.4	<0.1	150.6
	80-100	3.50	2.1	1.5	19.3	16.1	1.7	1.4	1.1	0.3	41.3	6.0	3.6	11.0	18.1	11.7	64.7
-20cm	0-20	3.98	9.5	2.9	2.5	1.4	8.0	2.8	1.2	0.6	62.3	12.2	7.7	9.0	41.2	<0.1	128.9
	20-40	3.30	1.3	0.9	10.5	7.9	1.0	0.9	0.8	0.3	66.8	2.4	3.3	6.9	<0.1	<0.1	142.9
	40-60	3.31	1.2	0.8	18.3	15.1	0.7	0.9	0.9	0.3	86.3	3.0	4.3	5.1	<0.1	<0.1	314.8
	60-80	3.40	0.8	0.7	20.0	17.0	0.3	0.7	0.9	0.3	90.0	2.1	3.0	3.6	<0.1	<0.1	323.0
	80-100	3.45	0.9	0.7	19.8	17.0	0.6	0.8	0.9	0.3	70.5	1.6	3.3	9.1	<0.1	<0.1	200.2
0cm	0-20	3.17	1.7	1.6	6.5	3.2	0.8	1.6	0.6	0.5	17.3	2.4	5.3	7.7	<0.1	<0.1	0.0
	20-40	3.25	1.1	1.0	8.8	5.7	0.4	1.1	0.7	0.4	26.3	1.9	2.9	5.9	<0.1	<0.1	40.0
	40-60	3.17	0.7	0.7	19.0	15.0	0.3	0.8	0.9	0.4	54.8	1.1	3.0	8.0	<0.1	<0.1	110.0
	60-80	3.26	0.9	0.7	22.3	18.2	0.3	0.7	0.9	0.3	69.0	1.2	2.7	8.0	<0.1	<0.1	152.1
	80-100	3.32	0.8	0.7	23.8	20.6	0.3	0.7	0.9	0.3	90.8	1.6	5.1	4.4	<0.1	<0.1	327.0
20cm	0-20	3.50	2.6	3.1	4.8	2.4	2.1	3.1	0.7	0.5	15.0	2.1	5.0	14.0	<0.1	<0.1	0.0
	20-40	3.12	1.0	1.0	10.5	7.1	0.7	1.2	0.7	0.5	24.0	1.6	2.2	6.0	<0.1	<0.1	0.0
	40-60	3.10	1.0	0.8	18.0	14.0	0.6	0.9	1.0	0.5	44.3	1.5	2.4	7.8	<0.1	<0.1	54.8
	60-80	3.22	1.0	0.8	22.0	18.5	0.6	0.8	1.0	0.4	60.0	2.5	2.8	11.5	<0.1	<0.1	106.8
	80-100	3.35	0.8	0.6	23.0	19.3	0.5	0.7	0.9	0.3	92.3	1.3	7.3	6.1	<0.1	<0.1	296.1
40cm	0-20	4.02	4.9	2.7	2.8	2.0	4.3	2.6	0.7	0.4	27.8	1.8	5.3	12.0	<0.1	<0.1	0.0
	20-40	3.32	1.5	1.2	11.3	8.2	1.2	2.4	0.8	0.4	39.8	1.6	2.6	11.3	<0.1	<0.1	70.9
	40-60	3.36	1.0	0.8	17.3	13.8	0.5	0.8	0.9	0.3	75.8	2.5	2.9	9.3	<0.1	<0.1	172.9
	60-80	3.36	0.9	0.8	21.3	18.3	0.6	0.8	1.0	0.3	91.5	2.5	2.6	7.5	<0.1	<0.1	325.1
	80-100	3.39	0.9	0.8	22.5	19.7	0.7	0.8	0.9	0.3	100.0	2.2	6.1	11.7	<0.1	<0.1	409.6
60cm	0-20	3.98	4.1	3.4	2.8	2.1	3.6	3.3	0.9	0.5	53.3	2.6	3.4	12.6	<0.1	<0.1	92.3
	20-40	3.54	1.7	1.3	9.8	7.5	1.3	1.2	0.8	0.3	72.0	2.0	4.4	10.3	<0.1	<0.1	202.4
	40-60	3.49	1.2	0.9	18.0	14.7	0.8	0.9	0.9	0.3	93.0	1.3	6.1	5.1	<0.1	<0.1	402.2
	60-80	3.50	1.2	1.0	17.5	16.0	1.0	1.1	1.1	0.3	77.3	1.8	3.6	8.8	<0.1	<0.1	203.3
	80-100	3.47	1.4	1.1	19.0	15.6	1.1	1.1	1.2	0.3	48.8	1.3	2.9	8.1	<0.1	<0.1	81.3

Table B.5. Soil chemical data for samples taken below dripper at Swartvlei site.

Distance from dripper	Depth (cm)	pH_{KCl}	1 M KCl extractable Ca	Mg	H/Al	Al	1 M NH₄OAc (pH 7) extractable Ca	Mg	K	Na	Bray-2 P (mg/kg)	1 M KCl extractable NO₃-N	NH₄-N	0.3 M NH₄F extractable Cl	NO₃	SO₄	PO₄
			(mmol_c/kg)				(mmol_c/kg)					(mg/kg)		(mg/kg)			
-60cm	0-20	4.99	6.3	2.1	0.0	0.2	6.4	2.1	0.2	0.2	50.3	23.8	14.8	2.9	89.0	<0.1	0.0
	20-40	4.77	6.1	1.8	0.3	0.2	6.8	1.9	0.2	0.2	51.8	18.4	32.6	1.5	65.7	<0.1	52.9
	40-60	4.89	5.6	2.4	0.3	0.2	6.0	2.4	0.2	0.5	45.0	26.4	13.5	21.7	107.4	<0.1	47.0
	60-80	4.93	3.6	1.8	0.3	0.4	3.5	1.7	0.2	0.4	27.8	9.6	29.6	3.7	30.3	<0.1	25.5
	80-100	4.8	3.4	1.6	0.3	0.3	3.0	1.5	0.2	0.3	27.8	8.5	4.4	1.4	20.7	<0.1	14.9
-40cm	0-20	4.8	6.2	1.6	0.3	0.3	6.3	1.6	0.3	0.4	50.3	24.2	4.8	11.8	89.8	<0.1	43.7
	20-40	4.93	5.1	1.3	0.3	0.3	5.0	1.3	0.3	0.5	37.5	11.9	3.4	10.9	34.4	<0.1	13.8
	40-60	4.8	4.1	1.1	0.3	0.3	3.6	1.0	0.4	0.8	30.0	11.2	4.9	13.2	37.1	<0.1	24.5
	60-80	4.57	3.2	1.1	0.5	0.3	3.0	1.1	0.3	0.5	25.5	7.7	5.2	13.9	26.7	<0.1	28.2
	80-100	4.58	2.6	1.0	0.5	0.4	2.6	1.0	0.4	0.4	22.5	6.6	13.2	5.3	22.8	<0.1	0.0
-20cm	0-20	3.94	2.6	1.1	1.3	0.9	2.8	1.1	0.5	0.4	33.8	8.3	4.2	2.9	27.8	<0.1	23.3
	20-40	3.79	1.5	0.8	1.8	1.5	1.3	0.8	0.3	0.4	26.3	6.3	3.8	9.8	15.7	<0.1	46.1
	40-60	3.84	1.3	0.8	1.8	1.5	1.0	0.7	0.3	0.3	26.3	5.6	5.7	1.4	8.7	<0.1	40.3
	60-80	3.87	1.1	0.7	2.0	1.7	0.9	0.6	0.3	0.3	34.5	3.5	4.9	3.2	<0.1	<0.1	55.1
	80-100	4.11	1.4	0.8	1.3	1.5	1.1	0.8	0.4	0.3	21.0	3.0	14.0	3.3	<0.1	<0.1	0.0
0cm	0-20	4.21	2.5	1.3	0.8	0.6	2.2	1.2	0.4	0.4	19.5	4.1	4.1	5.4	<0.1	<0.1	0.0
	20-40	3.77	1.5	1.0	1.8	1.6	1.2	0.9	0.3	0.2	16.5	5.0	4.2	6.6	<0.1	<0.1	0.0
	40-60	3.72	1.5	0.9	2.0	1.6	0.9	0.7	0.3	0.3	21.0	9.8	4.3	7.9	20.4	<0.1	18.6
	60-80	3.75	1.4	0.7	2.5	2.0	0.7	0.6	0.3	0.3	21.8	6.9	6.4	7.4	23.3	<0.1	0.0
	80-100	3.9	1.0	0.7	2.3	2.0	0.6	0.6	0.3	0.3	12.0	5.9	9.0	7.0	15.8	<0.1	0.0
20cm	0-20	4.41	4.5	1.4	0.5	0.4	4.5	1.2	0.4	0.3	53.3	5.4	3.4	9.6	11.8	<0.1	52.8
	20-40	4.05	2.9	1.0	1.0	0.6	2.9	0.9	0.3	0.3	37.5	4.1	3.0	8.6	<0.1	<0.1	32.2
	40-60	3.76	1.9	0.8	1.5	1.2	1.7	0.7	0.3	0.2	24.8	4.4	4.7	7.3	<0.1	<0.1	32.5
	60-80	3.87	2.1	0.9	1.5	1.5	2.0	0.7	0.3	0.2	37.5	5.0	13.0	7.7	19.5	<0.1	57.9
	80-100	3.96	2.0	0.8	1.5	1.4	1.8	0.8	0.3	0.5	33.8	7.3	8.5	11.8	23.4	<0.1	31.8
40cm	0-20	5.7	12.7	3.9	0.0	0.4	27.2	3.8	2.6	2.1	48.8	46.5	22.2	71.6	662.1	86.0	82.7
	20-40	4.71	5.3	2.1	0.5	0.5	6.3	1.9	0.9	0.7	31.5	36.1	10.0	16.2	147.8	12.5	47.6
	40-60	3.81	3.0	1.1	1.5	1.2	2.6	0.9	0.5	0.4	32.3	15.1	5.5	10.7	48.3	<0.1	38.8
	60-80	3.86	2.7	1.2	1.5	1.3	2.6	1.0	0.5	0.5	32.3	16.6	6.0	9.6	62.6	<0.1	37.0
	80-100	3.96	2.5	1.1	1.5	1.4	2.2	0.9	0.4	0.3	31.5	13.9	7.9	10.4	43.2	<0.1	27.4
60cm	0-20	6.1	6.8	2.5	0.0	0.4	16.6	2.6	0.9	0.2	42.0	13.9	9.9	7.9	46.6	43.8	46.5
	20-40	5.02	5.1	2.5	0.3	0.3	6.4	2.3	0.9	0.3	35.3	10.6	5.8	14.1	34.0	6.8	63.0
	40-60	3.98	2.4	1.4	1.0	1.8	2.7	1.2	0.4	0.3	34.5	8.2	4.4	10.8	28.6	<0.1	52.6
	60-80	3.94	2.0	1.2	1.5	1.6	<0.1	0.3	0.3	0.2	36.8	7.3	7.8	10.3	25.3	<0.1	55.0
	80-100	4	1.7	1.0	1.5	1.5	1.5	0.8	0.3	0.2	40.5	6.6	7.9	7.3	19.5	<0.1	57.4

B.3. Soil buffering data

Table B.6(a). Soil chemical data for buffering experiments on Brakfontein and BoHexrivier orchard soils.

Sample	H⁺/OH⁻ Added (mmol₍c₎/kg)	pH	Supernatant EC (mS/m)	I (M)	KCl extract pH	Ca	Mg	H/Al	Al (NaF)	Al (CAS)	ECEC (mmol₍c₎/kg)	Base Saturation (%)
BFA	24H	3.12	211.0	0.023	4.19	2.1	0.7	4.0	<0.1	1.1	6.8	41.5
[Brakfontein	16H	4.25	191.6	0.021	4.69	3.3	0.9	2.2	<0.1	0.0	6.4	65.6
topsoil]	8H	5.49	184.2	0.020	5.52	5.4	0.8	0.8	<0.1	0.0	7.0	88.5
	4H	6.04	178.2	0.019	5.84	7.3	0.9	<0.1	<0.1	0.0	8.2	100.0
	0	6.64	178.4	0.019	5.73	10.1	0.8	<0.1	<0.1	0.0	10.9	100.0
	4OH	7.43	165.8	0.018	6.14	8.7	1.0	<0.1	<0.1	0.0	9.7	100.0
	8OH	8.26	156.0	0.017	6.50	11.6	1.1	<0.1	<0.1	0.0	12.7	100.0
	16OH	10.03	131.0	0.014	6.97	11.2	0.8	<0.1	<0.1	0.0	12.1	100.0
	24OH	11.07	122.1	0.013	8.57	15.8	0.7	<0.1	<0.1	0.0	16.5	100.0
BFE	24H	2.16	294.0	0.032	4.00	1.0	0.5	4.4	0.8	1.7	6.0	26.3
[Brakfontein	16H	2.42	238.0	0.026	4.18	1.3	0.6	2.6	0.3	1.1	4.6	43.0
subsoil]	8H	2.96	181.6	0.020	4.27	1.8	0.6	2.8	<0.1	0.6	5.1	45.3
	4H	3.55	163.8	0.018	4.35	2.8	0.6	2.6	<0.1	0.6	6.0	56.6
	0	4.75	154.8	0.017	4.93	3.2	0.6	1.0	<0.1	<0.1	4.8	79.1
	4OH	6.65	146.6	0.016	6.18	4.8	0.6	<0.1	<0.1	<0.1	5.4	100.0
	8OH	7.89	136.2	0.015	6.13	8.4	0.7	<0.1	<0.1	<0.1	9.0	100.0
	16OH	10.04	112.4	0.012	7.53	9.3	0.5	<0.1	<0.1	<0.1	9.8	100.0
	24OH	11.16	111.4	0.012	8.76	12.1	0.5	<0.1	<0.1	<0.1	12.6	100.0
BHA	24H	3.12	211.0	0.023	3.81	4.0	1.4	9.8	5.6	5.0	15.2	35.5
[BoHexrivier	16H	3.8	195.0	0.021	4.12	6.3	2.1	5.5	2.6	2.2	13.9	60.4
topsoil]	8H	4.48	185.7	0.020	4.55	8.6	2.1	2.8	0.8	1.1	13.6	79.3
	4H	5.1	181.8	0.020	4.93	11.5	2.2	1.3	<0.1	<0.1	15.0	91.3
	0	5.61	179.3	0.019	5.26	10.7	2.2	1.0	<0.1	<0.1	13.9	92.8
	4OH	5.96	169.8	0.018	5.53	11.7	2.1	<0.1	<0.1	<0.1	13.7	100.0
	8OH	6.24	159.7	0.017	5.61	14.4	1.9	<0.1	<0.1	<0.1	16.3	100.0
	16OH	6.95	145.8	0.016	5.74	13.6	2.3	<0.1	<0.1	<0.1	15.8	100.0
	24OH	7.53	123.8	0.013	6.07	21.0	2.0	<0.1	<0.1	<0.1	22.9	100.0
BHB	24H	2.34	233.0	0.025	3.63	2.7	0.8	16.8	11.6	12.8	20.3	17.1
[BoHexrivier	16H	2.67	202.0	0.022	3.70	3.3	0.9	17.2	11.6	12.2	21.4	19.7
subsoil]	8H	3.18	175.0	0.019	3.85	4.3	1.0	14.4	9.8	10.0	19.7	26.9
	4H	3.52	162.7	0.018	3.95	6.0	1.1	12.8	7.8	8.3	19.9	35.6
	0	3.83	160.7	0.017	4.03	6.8	1.3	10.8	7.0	7.2	18.9	43.0
	4OH	4.15	148.7	0.016	4.25	8.7	1.2	7.4	3.8	3.9	17.3	57.3
	8OH	4.62	137.1	0.015	4.47	12.9	1.3	2.6	1.6	2.2	16.8	84.5
	16OH	6.02	117.2	0.013	5.39	20.4	1.7	1.6	<0.1	<0.1	23.7	93.2
	24OH	6.98	100.8	0.011	5.76	21.3	1.6	0.4	<0.1	<0.1	23.3	98.3

Note: The "1 M KCl exchangeable cations" columns (Ca, Mg, H/Al, Al (NaF), Al (CAS)) are given in mmol₍c₎/kg.

Table B.6(b). Soil chemical data for buffering experiments on OnderHexrivier and Swartvlei orchard soils.

Sample	H⁺/OH⁻ Added (mmol_c/kg)	pH	Supernatant EC (mS/m)	I (M)	KCl extract pH	Ca	Mg	H/Al	Al (NaF)	Al (CAS)	ECEC (mmol_c/kg)	Base Saturation (%)
OHA	24H	5.78	180.5	0.019	6.40	19.0	4.4	0.8	<0.1	<0.1	24.2	96.7
[OnderHexrivier	16H	5.86	172.3	0.019	5.86	19.5	3.2	0.8	<0.1	<0.1	23.4	96.6
topsoil]	8H	5.95	164.2	0.018	5.86	16.9	2.7	0.8	<0.1	<0.1	20.4	96.1
	4H	6.06	161.4	0.017	6.15	19.9	2.6	0.6	<0.1	<0.1	23.1	97.4
	0	6.29	158.1	0.017	6.01	23.9	0.9	0.4	<0.1	<0.1	25.2	98.4
	4OH	6.68	152.1	0.016	6.00	24.0	2.2	<0.1	<0.1	<0.1	26.2	100.0
	8OH	7.13	144.3	0.016	5.98	22.5	2.3	<0.1	<0.1	<0.1	24.8	100.0
	16OH	7.88	128.1	0.014	6.31	22.7	2.7	<0.1	<0.1	<0.1	25.4	100.0
	24OH	8.4	106.7	0.011	6.37	26.9	2.0	<0.1	<0.1	<0.1	28.9	100.0
OHB	24H	2.57	224.0	0.024	3.70	2.8	0.9	20.0	14.6	14.4	23.7	15.5
[OnderHexrivier	16H	2.88	194.7	0.021	3.82	3.4	0.9	18.4	13.0	13.3	22.7	19.0
subsoil]	8H	3.23	166.5	0.018	3.88	3.8	1.0	17.2	12.2	12.8	21.9	21.5
	4H	3.5	161.1	0.017	3.94	5.5	1.1	15.8	10.6	11.7	22.4	29.6
	0	3.83	153.2	0.016	4.02	7.4	1.2	14.0	9.2	10.0	22.6	38.0
	4OH	4.21	141.0	0.015	4.37	9.4	1.2	10.6	7.0	8.3	21.2	50.0
	8OH	4.5	128.0	0.014	4.66	10.9	1.4	7.4	3.4	5.6	19.6	62.3
	16OH	5.56	106.3	0.011	5.19	17.0	1.6	3.0	<0.1	1.7	21.6	86.1
	24OH	6.52	88.9	0.009	5.51	20.5	1.7	0.8	<0.1	<0.1	22.9	96.5
SVA	24H	2.25	275.0	0.030	3.99	1.3	0.6	3.0	<0.1	0.6	4.9	38.7
[Swartvlei	16H	2.78	202.0	0.022	4.17	1.8	0.5	2.4	<0.1	0.6	4.7	49.0
topsoil]	8H	3.32	175.2	0.019	4.42	1.9	0.5	2.0	<0.1	<0.1	4.5	55.2
	4H	3.66	166.7	0.018	4.52	3.1	0.6	1.6	<0.1	<0.1	5.3	69.6
	0	4.71	158.0	0.017	5.03	3.9	0.6	1.2	<0.1	<0.1	5.8	79.1
	4OH	6.06	149.0	0.016	5.61	4.4	0.5	0.8	<0.1	<0.1	5.7	85.9
	8OH	6.8	142.3	0.015	6.02	6.9	0.5	0.8	<0.1	<0.1	8.2	90.3
	16OH	8.39	119.5	0.013	6.38	9.8	0.5	<0.1	<0.1	<0.1	10.4	100.0
	24OH	10.49	98.6	0.011	8.15	12.7	0.5	<0.1	<0.1	<0.1	13.3	100.0
SVE	24H	2.06	303.0	0.033	3.94	0.8	0.4	2.6	<0.1	1.7	3.8	31.3
[Swartvlei	16H	2.35	237.0	0.026	4.00	1.0	0.4	2.6	<0.1	1.1	4.1	36.3
subsoil]	8H	2.76	190.1	0.021	4.20	1.0	0.5	2.8	<0.1	1.1	4.3	35.5
	4H	3.2	170.4	0.018	4.27	1.4	0.5	2.8	<0.1	1.1	4.7	40.7
	0	4.17	159.0	0.017	4.57	2.6	0.5	2.2	<0.1	1.1	5.3	58.3
	4OH	5.74	146.7	0.016	5.66	4.2	0.5	0.6	<0.1	<0.1	5.3	88.7
	8OH	6.75	138.9	0.015	5.72	5.3	0.5	<0.1	<0.1	<0.1	5.8	100.0
	16OH	8.47	115.3	0.012	6.54	9.6	0.4	<0.1	<0.1	<0.1	10.0	100.0
	24OH	10.56	97.4	0.010	7.57	11.8	0.4	<0.1	<0.1	<0.1	12.2	100.0

C. CALCULATIONS

C.1. Lime requirement

(from Table 3.2)

Lime Requirement per hectare per pH unit for a soil depth of 20 cm and bulk density of 1333 kg.m^{-3}

Neutralization: 1 mmol H$^+$/kg requires 0.5 mmol Ca^{2+}/kg (as CaCO$_3$)

Thus, LR   = 0.5 mmol/kg x (0.2 m x10000 m^2 x1333 kg/m^3) x 100mg/mmol

=133300000 mg of lime

=0.1333 tonnes of lime for each mmol H$^+$/kg

C.2. Cost price ratio of commercial calcium nitrate : ammonium nitrate

(From General discussion and Conclusions)

1. Commercial Ca(NO$_3$)$_2$ (50% solution) contains 8.5% N and costs R3052/tonne

    For a 200 kg N/ha/year, the cost is therefore R7181 (R36 per kg of N)

2. Commercial ammonium nitrate contains 19% N and costs R1370/tonne

    For a 200 kg N/ha/year, the cost is therefore R1440 (R7.20 per kg of N)

    This would need a maximum of 720 kg of CaCO$_3$ to neutralize acidity formed by

    nitrification (3.6 kg CaCO$_3$/ kg of N). At R200/tonne, this lime would cost R144/ha.

    Thus, total cost   = R1440 + R144

    = R1584/ha

    = R7.92/ kg of N

This would imply that calcium nitrate use to avoid acidification is 4.53 times more expensive than ammonium nitrate, even when lime needs associated with the latter are considered.

Bless the Lord, O my soul;

and all that is within me,

bless His holy name!

Bless the Lord, O my soul,

and forget not all His benefits:

Who forgives all your iniquities,

Who heals all your diseases,

Who redeems your life from destruction,

Who crowns you with lovingkindness

and tender mercies,

Who satisfies your mouth with good

things,

so that your youth is renewed like the

eagle's.

Psalm 103:1-5