Geochemical study of soil salinity in a toposequence near Riebeeck West, South Africa

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DEDICATION

To my loving Wife Theresia and Daughter Lara-Christie

Abstract

A geochemical investigation of salt distribution in soils of the semi-arid of Western Cape, South Africa, was carried out following a pilot study which revealed widespread soil salinity in the Berg River catchment. The present study looks at the distribution of the salts along a toposequence in a subcatchment of the Berg River underlain by Malmesbury Group shale. The objectives were: to investigate salt distribution in relation to landscape topography; to identify potentially harmful trace elements associated with the salinity; and to determine the processes responsible for salt distribution.

Ten soil profiles were dug to a depth of 200 cm at points along a slope of angle 10.2° along and 367 m long. The profiles at the crest of the toposequence are underlain by silcrete and alluvium while Malmesbury shale parent material underlies the rest of the profiles. Contour drains disrupt the natural shape of the slope. The soil texture is loamy sand to clay loam at the crest and loamy to sandy-clay loam in the midslope. Mineralogy at the crest is quartz dominated and kaolinite occurs in the mid and lower slope.

The $pH_{(H_2O\ \&\ KCl)}$ were measured in a 1:2.5 soil:water/1M KCl suspension and it was found that the soils were acidic at the crest ($pH_{(KCl)} < 4.5$) ; alkaline ($pH_{(KCl)} > 8$) in the midslope and moderately acidic to neutral ($pH_{(KCl)}$ 5.4-6.9) at the footslope and valley bottom. The saturated paste extract (SPE) results indicated highest ECe of 10.97dS/m at the midslope while the crest and valley bottom segments had highest ECe of 0.54 and 3.75 dS/m respectively. In general the order of dominance for soluble cations was $Na^+>Ca^{2+}>Mg^{2+}>K^+$ and anions $Cl^->SO_4^{2-}>NO_3^->F^-$, although samples from the footslope and valley bottom were dominated by Ca^{2+} and SO_4^{2-}. NH_4OAc extractable cations had highest concentrations in order of dominance $Ca^{2+}>Mg^{2+}>Na^+>K^+$. The midslope had highest concentrations of soluble and exchangeable ions. Trace elements (Se, B & As) were determined by ICP-MS and were found to concentrate within the salts in the midslope but not to detrimental levels. Eluviation, leaching at the crest and footslope, and evaporation are responsible for the observed salt distribution in this study.

Most soils in this study are salt-affected although those at the crest are categorized as normal (ECe < 4dS/m; ESP < 15%). Soils in the mid and lower segments of the toposequence are either saline-sodic or sodic (ECe < 4dS/m, ESP > 15%). There is need for immediate reclamation and preventive measures to be put in place if agricultural activities are to be continued in a sustainable manner.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

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1. 1 Introduction

Salinisation, the accumulation of soluble salts in soils, occurs widely in arid and semi-arid regions (Szabolcs, 1992), and is a serious land degradation issue threatening the health and productivity of many catchments. Worldwide salinisation of soils is a subject of concern because the problem begins unnoticed, the effects are not immediately apparent, and the resultant deterioration in environmental quality is long lasting, costing the affected nations and individuals huge amounts of money in research efforts to combat and control it.

The mechanism of salinisation has been the subject of much debate (Acworth and Jankowski, 2001). In some instances, salinity may be considered a natural phenomenon but in others, increasing salinity is often the result of land use practices, such as clearing of indigenous trees for crop cultivation and urbanization or developing irrigation schemes for agricultural activities. These land use practices result in what is termed dryland salinity (Cartwright et al., 2004). Dryland salinity was first reported in Australia by Wood (1924) and later studied intensively after yield losses from farm lands were reported from Australia (Peck, 1978). Dryland salinity has also been reported from Argentina (Lavado and Taboada, 1987); India (Chouhari and Sharma, 1984); North America (Miller et al., 1981) and South Africa (Flügel, 1987, 1995). Dryland salinity phenomenon also exist in the South Western Cape province of South Africa which strikingly has a similar climate, soils, natural salt levels in the regolith, topography and land use practices to many parts of Australia (Prof. M.V. Fey, personal communication).

The Department of Waters Affairs and Forestry (DWAF) has monitored Berg River water quality since the mid 1970s. Natural soil salinity has already been identified as the source of some of the salts affecting the water quality of the Berg River (Fourie and Steer, 1971; Fourie and Gorgens, 1977). Few scientific studies have yet looked at the detailed distribution of salts within the soils of the Berg River catchment or any other river basins in South Africa. The Berg River is known for its strategic importance to rural and industrial development in the Western Cape. An increase in the salt content of the river would adversely affect its use for domestic, industrial, agricultural or environmental purposes.

This study forms part of the pilot studies (Water Research Commission (WRC) project No. K5-1342) of a specifically selected sub catchment of the Berg River and will look at a toposequence within the sub catchment (Fey and de Clercq, 2003).

1.2 Aims and Objectives

The aim of this study was to carry out a geochemical study of the distribution of salts along a toposequence in a sub catchment of the Berg River basin. The following key questions were addressed:

- What is the salt distribution in relation to landscape topography?
- Are there potentially harmful trace elements associated with soluble salts?
- What are the potential consequences of the salt accumulation?
- Which processes are responsible for the observed distribution of salts?

1.3 Previous research.

Much of South African research on salinity in the past decades has been related to irrigation agriculture where drainage water dissolves salts from the irrigated lands and then flows back into the river (Flugel, 1989). Fourie (1976) assessed the salinity of the Berg River in 1976 by focusing on certain Berg River tributaries in the west bank as well as on the east bank below Voëlvlei and indicated them to be naturally quite saline (Figure 1.1). More recently, Fey and de Clercq (2003) from the University of Stellenbosch undertook a pilot study of the salinity of the Berg River to determine whether there is a dryland (non-irrigated) agricultural impact on the river salinity similar to those being studied intensively in Australia. The project objectives were to make a preliminary estimate of salts stored in the regolith, calculate the current decantation of these salts into the river, and to determine the rate of change of the salts discharged in response to changes in land use practices. The geographical distribution of salts in key areas was determined using an electromagnetic induction device (EM38) as well as carrying out laboratory analyses of soils sampled from bare patches in wheat fields identifies by remote sensing.

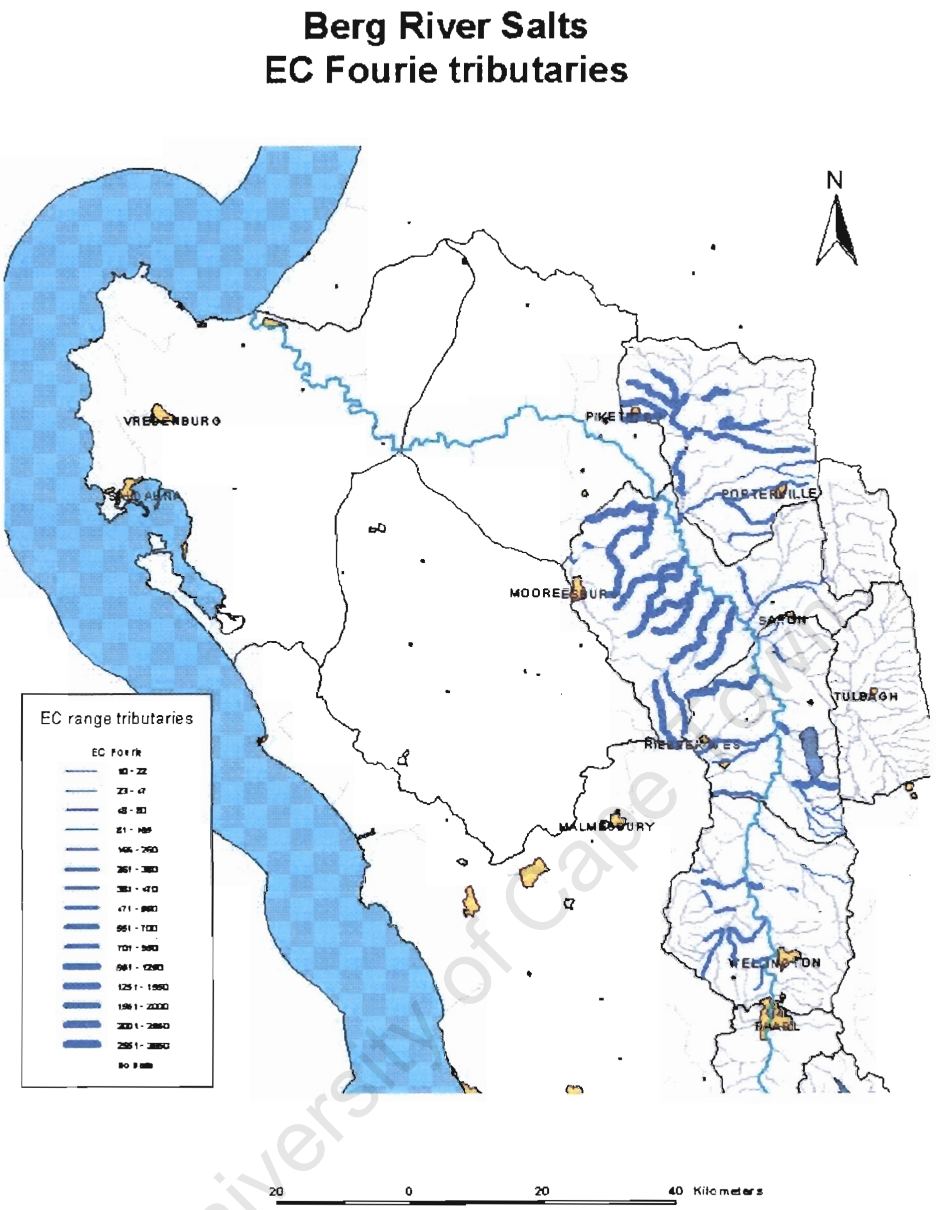

Figure 1.1 ArcView image of the Berg River catchment showing salinity classes (in mS/m) of tributary segments based on data of Fourie (1976)

The study revealed a widespread patchiness in wheat fields confirmed to be associated with soil salinity. Significantly saline sections of the Berg River catchment were identified and found to be situated in the Swartland, a fertile undulating region formed from Malmesbury Group Rocks. Modelling of runoff under different vegetation scenarios (winter wheat and renosterveld) suggested that land use changes have a potential impact on salt release from the regolith into surface water. The soils were found to be sufficiently saline to affect wheat growth. The findings of this study suggested the need for a more detailed survey of salt distribution in the soils, regolith, and ground- and surface waters coupled with a fundamental study of salt mobilization in response to climate, topography and land use practice in a small scale catchment.

- ***Why a toposequence?***

Topography is among the five factors controlling the formation of soil and previous studies have shown that various soil properties are related to the position of a soil along the slope as well as to the slope gradient (Yair, 1990). Generally the toposequence provides a reasonably sound basis for describing the distribution of both salinity and soil types (Prof. M.V. Fey, personal communication). Geochemical studies of soil toposequence in South Africa are scarce. However, a South African granite landscape was studied by Munnik *et al.* (1992). These authors sampled soil profiles along nine hillslopes and found that coarse sand proportions increased and clay proportions decreased down the toposequence suggesting possible deposition of material at the footslope by soil creep. In Australia, Conacher (1975) identified throughflow (lateral subsurface flow of infiltrated water through the soil) and sheet floods to be important in the transportation of soluble salts and clay particles down toposequences. A geochemical study of soils associated with Malmesbury Group rocks along a toposequence by Schloemann (1994), found high sodium chloride precipitation at the bottom of the slope. He ascribed this to possible evaporation of throughflow water and capillary uplifted groundwater as suggested in Conacher (1975) and Buol *et al.* (1980).

1.3 Study Area Description

The study area is located 3km to the NE of the town of Riebeeck West (33° 21' 07" S & 18° 52' 03" E), approximately 70 km north of Cape Town in the Western Cape Province, South Africa. Riebeeck West is 56.6 km from the coast and 8.5 km from Berg River.

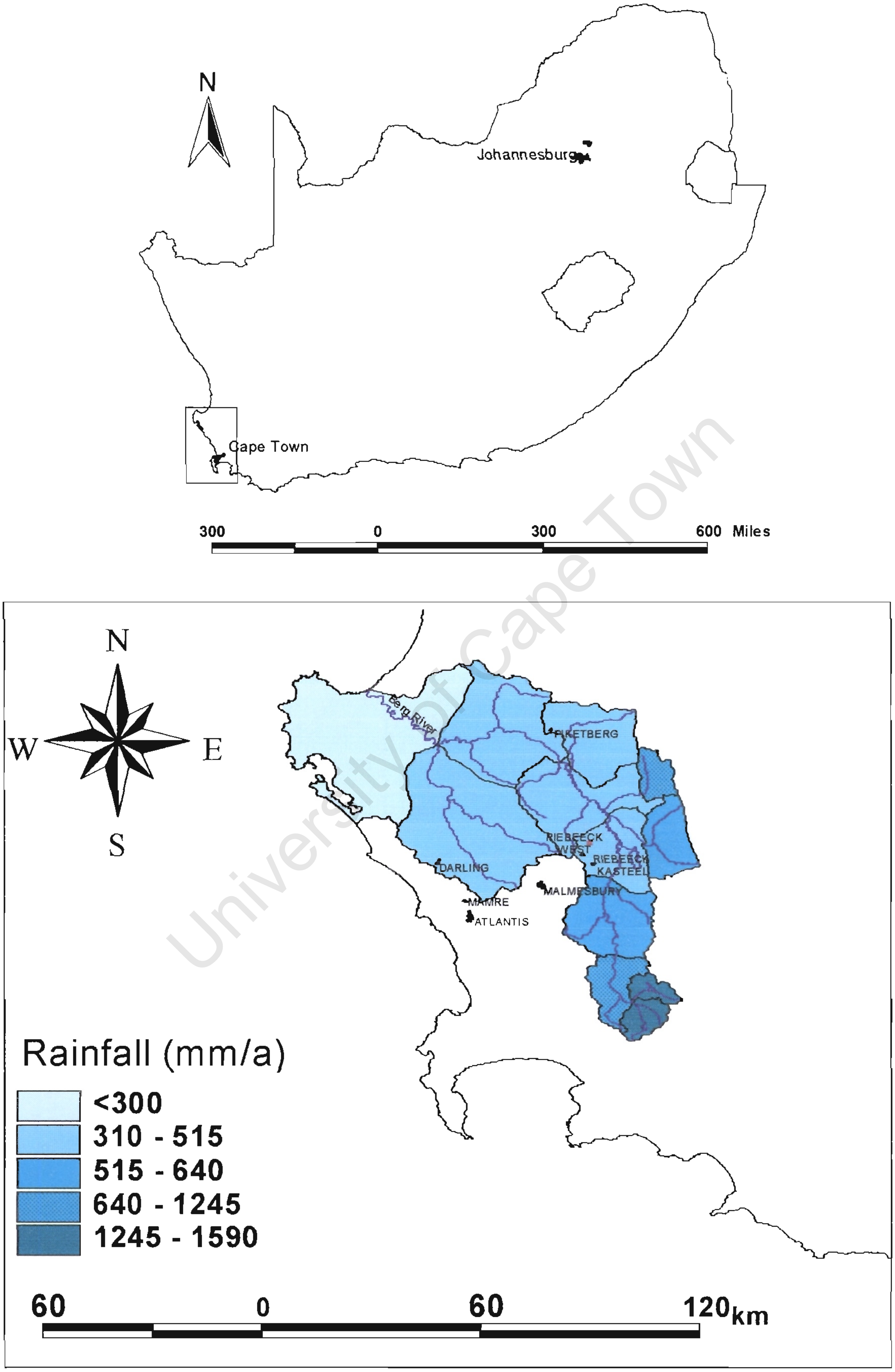

Figure 1.2: a) Map of South Africa; **b)** Locating map of study area shown in red.

1.3.1 Topography and Drainage

Riebeek West is situated at the eastern foot of the 974 m high Kasteelberg Mountain. The Swartland, a wide fertile undulating plain cultivated with wheat, vineyards, fruits and vegetables, is found to the east of Riebeeck West, and has an average elevation of 200 metres. The Berg River and its tributaries form the most important drainage system in the area. The Berg River rises at approximately 1500 m AMSL in the Groot Drakenstein Mountains, and flows northwards through the swartland draining agricultural lands before reaching the Atlantic Ocean at Velddrif in St Helena Bay (Snaddon, 1998).

1.3.2 Climate

The climate of the west coast of South Africa is predominantly Mediterranean with hot, dry and windy summers (October to March) and cool, wet winters (April and September) (Visser and Schochs, 1973). The windy summer months are conducive to evaporation. Mean annual precipitation within the Berg River basin ranges from 2600 mm in the mountainous region to 400 mm on the coastal plain. The cold Benguela current which flows up the west coast moderates the temperature which increases inland causing abrupt changes in climatic conditions a short distance away from the sea. Warm dry Berg winds, generated in autumn and spring when hot air is drawn off the plateau into a southwards moving offshore low pressure cell, are responsible for high transpiration and evaporation (Nieman, 1981). Potential evaporation rates vary from 1800 mm/a in the south to 2100 mm/a in the north with the lowest being in June, (50-90 mm) and the highest in December (280-300 mm) (Nieman, 1981).

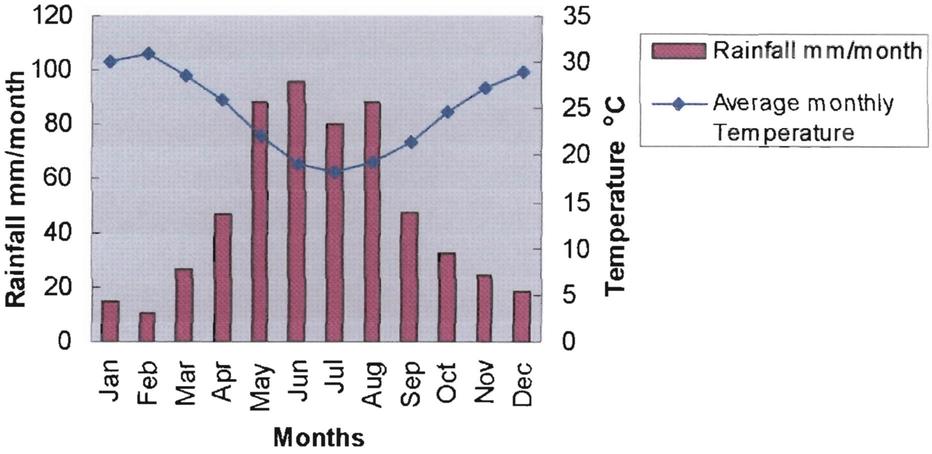

Figure1.3 Long term data for average monthly rainfall and temperature ***(Adapted from climate statistics for the winter rainfall region (1989) and compiled by Agrometerology section, Elsenburg; Soil and Irrigation Research Institute and the Department of Agriculture and Water Supply)***

1.3.3 Geology and Soils

The major geological units in the area of interest are the metasediments of the Malmesbury Group consisting of fine-grained greywacke, schists, phyllites, quartzitic sandstones, limestone beds, chlorite lenses, feldspathic grits and conglomerate beds; and the Table Mountain Group (TMG) consisting of conglomerates, sandstone, greywacke, shale and tillite. The Table Mountain Group rocks unconformably overlie the Malmesbury Group. The Malmesbury Group underlies the low lying undulating Swartland whereas the steep relief of the region where the Berg River originates is due to the resistant TMG.

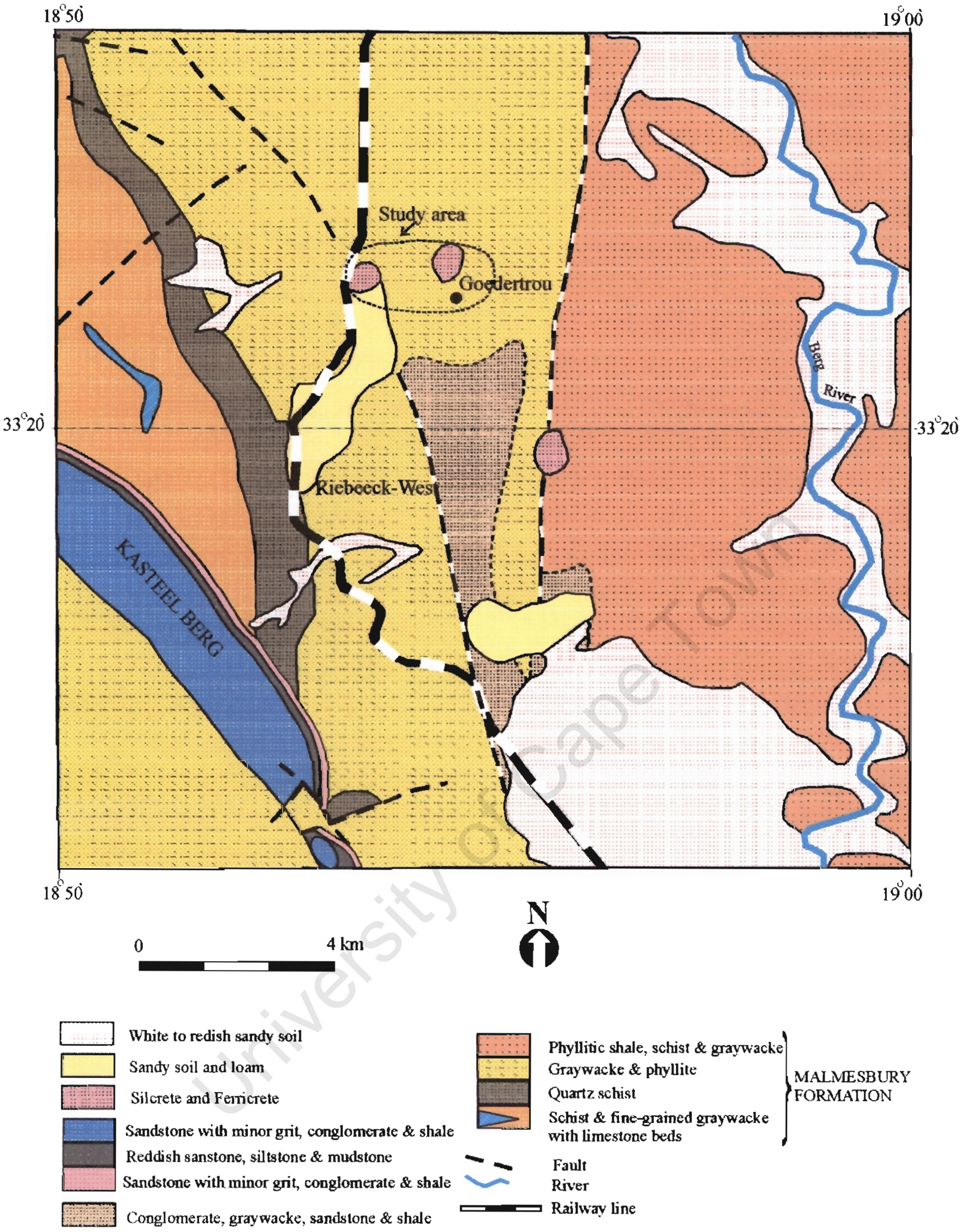

Figure 1.4 Geology, topography and drainage of the study area

The Tertiary and Quaternary sub-eras are represented by alluvium, sandy and loamy soils, and silcrete and ferricrete deposits. These younger deposits overlie the Malmesbury Group rocks in many places and form the parent material to the investigated soils.

1.3.4 Vegetation and land use

The study area is situated in the Swartland, an undulating fertile land cultivated predominantly for wheat production. In addition to wheat, viticulture, fruit and vegetables are common crops grown under dryland conditions with minimal or no irrigation. The original vegetation was Renosterveld shrubland which was generally associated with the nutrient–rich Malmesbury sediments. Most of the original vegetation has been cleared to exploit the soil nutrients for wheat farming (Meadows, 1998). The sampling site for this study had vineyards planted at the crest, with the midslope and valley bottom currently under pasture rotation.

Figure 1.5 Vineyards and pasture as land use practice.

1.4 Literature.

1.4.1 Definition of soil salinity

A soil is saline when it contains sufficient neutral soluble salts in the crop root zone to a concentration which results in yield reductions (Ayers and Westcot, 1985). Such soils do have an electrolytic conductivity (ECe) > 4.0 Sm^{-1} at 25°C obtained from a saturated paste extract (Sposito, 1989). The major constituents of soluble salts of major concern in saline soils include the cations Ca^{2+}, Mg^{2+}, K^{+} and anions Cl^{-}, SO_4^{2-}, and CO_3^{2-} or HCO_3^- with sodium and Chloride being by far the most dominant ions particularly in highly saline soils (Pitty, 1978). However, Ca and Mg are usually present in sufficient quantities to meet the nutritional needs of the crops. The pH value of the saturated paste extract is generally less than 8.5, and more often near neutrality.

Irrigated lands are often altered by salts from a saline water table or from salts in the applied water. Arid and semi-arid regions are most affected by salinity problems because of insufficient annual rainfall to flush out the accumulated soluble salts. Based on work done in different parts of the world, saline soils are known to form under different environmental conditions, and have diverse morphological, chemical, physical and biological properties (Northcote and Skene 1972; Mitchell et al., 1978). Salinity can also be "transient" (salinity not associated with a permanent saline groundwater), (Fitzpatrick *et al.* 2003). Acid saline soils do occur when the pH of the soil is < 3.5 with the presence of sulphur and high EC values (Fitzpatrick *et al*, 1996).

1.4.2 Sources of salts

Sources of salts in arid and semi-arid regions include rainfall, mineral weathering, and "fossil" salts (Bresler *et al.* 1982). Surface runoff and groundwater flow can redistribute the accumulated salts, and thereby affect farming activities. These sources are briefly explained below:

- ***Deposition of salts by rainfall***

Rainfall can transport salts of marine origin and deposit them on land and in surface waters. According to Malherbe (1953), sea winds carry fine salt particles to land, some of which get deposited in water or may be brought to the soil by rain or mist.
The annual accretion rate of salt by rainfall deposition in the wheat belts of Western Australia has been recorded as 100-250 kg/ha in high rainfall coastal areas, decreasing to 10-20 kg/ha 300 km inland (Hingston and Gailitis, 1976). Atmospheric salt composition changes as air masses move inland from the coast. Absolute Cl^- and Na^+ concentrations and the ratio of Cl^- and Na^+ in the rainfall are predominant at the coast while Ca^{2+} and SO_4^{2-} concentrations dominate as air moves inland because of salt additions from terrestrial sources (Bresler *et al.*, 1982). Bresler *et al.*, (1982) estimated the atmospheric contribution to salt load of arid lands at 10-25 % of the total yearly contribution due to weathering.

- ***Fossil salts***

Fossil salts can be considered as a primary source for soluble salts derived from prior salt deposits or from entrapped solutions in marine sediments of ancient seas (Sparks, 1995). These sediments are buried, lithified, then uplifted and become parent material for the soil. . Evaporation of groundwater can concentrate these salts at the surface thereby degrading the soil (Figure 1.5). The combined effects of cyclic and fossil salts can be deduced from the chloride (Cl^-) contents of local waters because this ion is almost exclusively of marine or former lacustrine origine. Excessive salinity in 10% - 12% of the total exploitable waters of Israel was reported by Yaalon (1963) being derived from residual brines, connate sea water, and fossil salts. The present hard pans and soils of the North- western coastal area of Western Cape developed as a result of sea water intrusion to the dryland (Malherbe 1953).

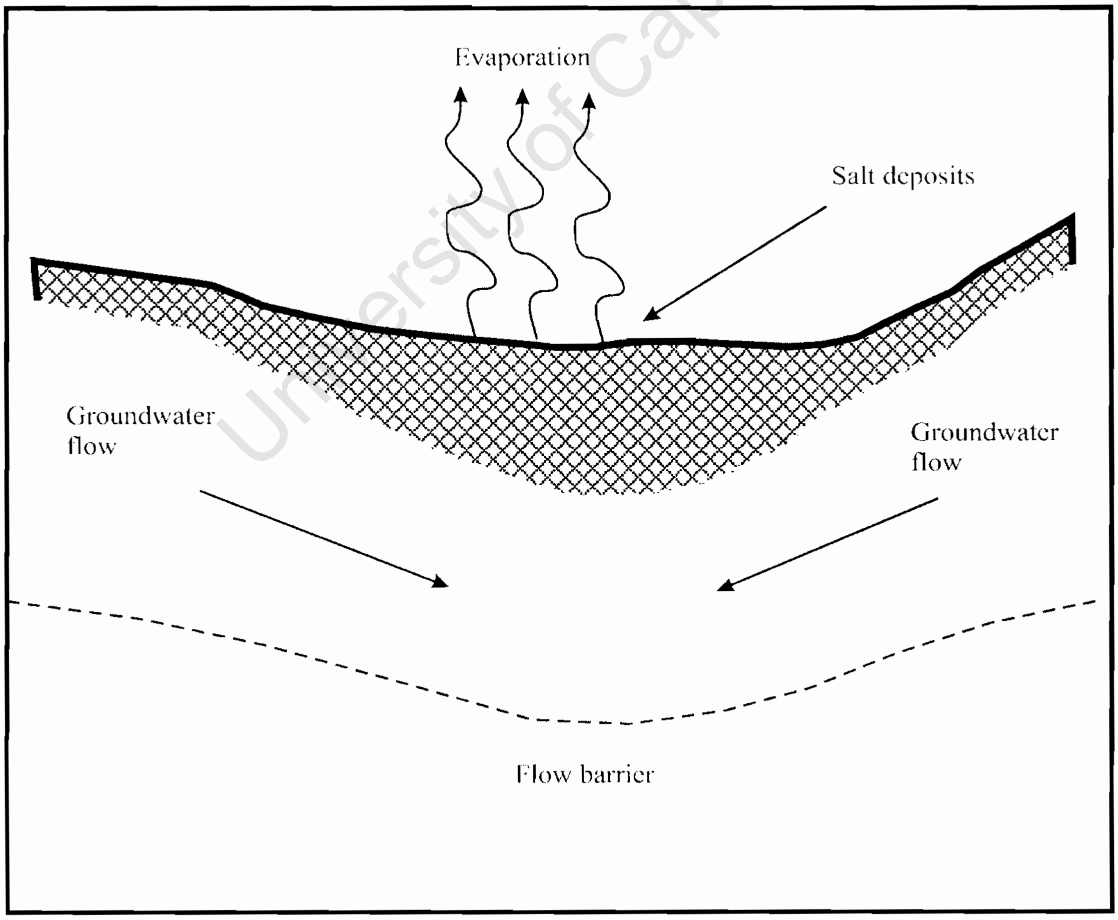

Figure 1.6 Typical situations conducive to the accumulation of salt in a semi-arid climate (Adapted from McBride, 1994).

- ***Mineral weathering***

Primary minerals constitute a source from which salts may be released and adversely affect plant growth (Bresler *et al.* 1982). During the process of chemical weathering, which involves hydrolysis, hydration, oxidation and carbonation; salts are gradually released and made soluble. Examples of weathering reactions to release soluble salts include:

$$\underset{\text{Olivine}}{Mg_2SiO_4} + 4\,H_2O \rightarrow 2\,Mg^{2+} + Si\,(OH)_4^0 + 4\,OH^- \qquad (1)$$

$$\underset{\text{Feldspar}}{2\,NaAlSi_3O_8} + 11\,H_2O \rightarrow \underset{\text{Kaolinite}}{Al_2O_5\,(OH)_4} + 4\,Si\,(OH)_4^0 + Na^+ + OH^- \qquad (2)$$

Geologic formations through which drainage water passes may significantly influence the composition and total concentration of salts. This is because geologic materials have highly variable elemental composition. Some materials tend to have higher contents of salts than others. Certain sedimentary rocks in South Africa (Dwyka Series, the Malmesbury shale and the Enon conglomerate) are rich in soluble salts that on weathering to soil material may cause an accumulation of salts under low rainfall conditions (Malherbe, 1953). During the wet winter, flood and seepage water transport salts from the higher- to lower-lying areas where the water evaporates and the salts are left to concentrate on the soil surface. The salts in the districts of Malmesbury and Picketberg in the Western Cape are thought to originate from the sea as well as from the weathering of the underlying bed rock (Malherbe, 1953). Studies to estimate salt contributions from mineral weathering have revealed salts concentrations of 3-5 mEq/L after solutions had been in contact with the unweathered minerals in arid-land soils for substantial periods of time (Rhoades *et al.* 1968 as stated in Bresler *et al.* 1982).

- *Anthropogenic sources*

Anthropogenic sources of salinity are dominated by land use activity, mainly irrigated agriculture and mining. Application of fertilizers and poor quality irrigation water to lands can increase salt release in a landscape (McBride, 1994). Geological formations such as the Dwyka, the Bokkeveld shale and the Enon conglomerate contain saline groundwater (Malherbe (1953). If groundwater from these formations is used for irrigation, the soils may become saline.

1.4.3 Processes of salinisation

- *Primary and Secondary Salinity*

Saline soils are categorized as primary or secondary by the source of salts and process of accumulation (George *et al.* 1997). Primary soil salinity is one which naturally occurs in the landscape and affects the development of the landscape over time. Examples are marine plains, coastland regions, salt lakes and pans. Salinity is accumulated through deposition of oceanic salts, rain and wind (Hingston and Gailitis, 1976; Evans, 1998; and Summerell *et al.* 2000). In a primary soil salinisation process, salt stored in the soils or groundwater is concentrated through evaporation and transpiration by plants.

- *Secondary soil salinity*

Secondary soil salinity is the salinisation of land due to land use practices, and interference with the hydrological cycle. This category of soil salinity emanates from irrigation and dryland management systems which result in rising water tables mobilizing salt in the soil (Cartwright *et al.*, 2004). Dryland salinisation is induced by extensive changes in the vegetation cover in a catchment such as clearing the native vegetation. Most of the salinity cases reported in Australia resulted when deep-rooted tree species were supplanted by shallow-rooted grasses (Hutton, 1958 in Bresler *et al.*, 1982). The effect of this land use practice caused water table levels to rise with a subsequent increase in soil salinity. Salts that might have accumulated over decades or centuries were removed by deep percolation due to the original vegetation. Another form of secondary salinisation is irrigation salinity, caused by artificial water importation into a region in excess of crop demand. This process leads to increased recharge to the groundwater. Where groundwater drainage is limited, the water table rises, mobilizing salts and redistributing them into the root zone of surface water causing soil and stream salinity (Greiner, 1998).

Fitzpatrick *et al.*, (2003) defined a secondary type of salinity that manifests both on the surface and subsurface of soils termed "dry saline land salinity". The main difference from dryland salinity is that it is not often related to a saline ground water table, and mostly occurs in upland winter zones. "Surface expressed" salinity is concentrated at the soil surface and "subsurface expressed" salinity occurs at the root zone or the subsoil (Fitzpatrick et al., 2003). Dry saline land salinity occurs extensively in many sodic soil landscapes in Australia. Salt accumulations in the soil surface ranging from 4 - 60 dS/m, and 2-8 dS/m in the subsoil in Australia have been attributed to dry saline land salinity (Rengasamy, 2002). Such degraded soils portray the characteristics of sodic soils with slow water infiltration in the upper layers of the soils because the soil pores are clogged by dispersed clay which often results in temporary water logging of the subsoil, and perched water tables. Salts accumulate during evapotranspiration as the perched water dries off. This subsoil salinity fluctuates with depth and also with season as the balance between downward and upward fluxes change. While about 16% of the dryland cropping area in Australia can be affected by dryland salinity, 67% of similar area has the potential for induced dry saline land salinity, costing the Australian farming economy approximately $1330 million per year (Rengasamy, 2002).

The chemistry of soil water during a salinisation process can be illustrated using the Hardie and Eugster model (Drever, 1997). Precipitation of salts during the evaporation of soil water according to this model can be explained in terms of successive chemical divides. Of the two ions involved in the precipitation of a salt during soil water evaporation, the concentration of one of the ions may build up in solution while the concentration of the other diminishes. Calcite is always the first mineral to precipitate causing a first chemical divide. If the concentration of calcium is less than that of alkalinity, calcium will be removed from solution during evaporation thereby forming an alkaline carbonate solution. On the other hand, if the concentration of calcium is greater than that of alkalinity, all carbonate species will be removed from the solution resulting in a nearly neutral sulphate or chloride solution.

1.4.4 Consequences of salinisation

Salt accumulation in soils has serious consequences for the soils, plants and the environment. Three potential hazards of salt- degraded soils to plants are salinity, sodicity and alkalinity. Salinisation leads to the accumulation of soluble salts in soils while sodication and alkalinization processes have been found to saturate the exchange complex of the soils with sodium. The first two hazards are used to classify soils as saline or sodic, or both (Table 1.1).

Table 1.1 Characterization of saline and sodic soils and their potential to degrade soil properties (Adapted from McBride, 1994)

Soil Properties	**ECe(mS/cm)**	**ESP (%)**	**Typical pH**	**Structure**
Saline	> 4	< 15	< 8.5	Good
Sodic	< 4	> 15	> 9.0	Poor
Saline-Sodic	> 4	> 15	< 8.5	fairly good

Solution Properties

Hazard	**Salinity (EC)**	**Sodicity (SAR)**	**Alkalinity**
Low (safe)	< 0.25	< 7	<1.25
Medium (marginal)	0.25 – 0.75	7 – 13	1.25 – 2.5
High (Unsuitable)	0.75 – 2.25	13 – 20	< 2.5
Very High	> > 2.25	> 20	> 2.5

- *Sodicity*

A soil is considered sodic when it has higher than normal levels of exchangeable Na^+. The proportion of sodium on its exchange sites is termed ESP while the ratio of sodium to other divalent cations is sodicity (equations 3 & 4). A widely used criterion to describe the proportions of major cations on soil exchange sites is the U.S. Salinity Laboratory's Exchangeable Sodium percentage, (ESP) where

$$ESP = \frac{Exchangeable - Na}{Exchangeable(Ca + Mg)} \times \frac{100}{1} \text{-------} (3)$$

The classification above Table 1.1 suggests that sodic soils are likely to be associated with high alkalinity due to high pH values. The exchangeable sodium percentage is a soil property while sodium adsorption ratio is a solution property. According to McBride (1994), SAR can be calculated using the equation:

$$SAR = \frac{[Na^{+}]}{\left\{([Ca^{2+}] + [Mg^{2+}]) \div 2\right\}^{1/2}} \text{------}(4)$$

where all solution concentrations are expressed in units of millimoles of cationic charge per litre. SAR is a useful index for predicting the tendency for irrigation water to produce excessive exchangeable sodium in the soil it is being used to irrigate. An empirical relationship between ESP and SAR (Equation 5) has been established which can be used to predict the composition of the exchange sites of the soil based on soil solution composition (McBride, 1994).

$$\frac{ESP}{(100 - ESP)} = 0.015SAR \text{----------}(5)$$

K^{+} has not been included in the sodicity definition because it dissolves in soils very slowly and rarely occupies a significant fraction of the exchange sites and thus has little effect on the level of exchangeable Na^{+}. Sodic soils usually have an ECe < 4 dS/m, and a lower limit of the sodium adsorption ratio of 13 (Sparks 1995). Sodicity is a problem when the soil's ESP value is above 15% (Tan, 1993). At this ESP cut-off value, marked clay swelling and dispersion is likely to occur (Oster *et al.*, 1980). Sodicity is therefore a major hazard as it results in soil structural damage due to the presence of high exchangeable Na^{+}. Sodicity problems can be extensive as the resulting clay dispersion and soil aggregate structure deterioration may in turn reduce the permeability and drainage of the soil, resulting in poor aeration, and enhanced surface crusting and shrink-swell behaviour under cycles of wetting and drying (McBride, 1994). The reduced permeability and drainage leads to insufficient water supply to plants with yield reduction as crop water demand is not met.

- *Alkalinity*

Alkalinity is a further problem that may arise if the solute concentration of irrigation water has high concentrations of Ca^{2+} and CO_3^{2-} + HCO_3^- The effect will be that calcium carbonate may precipitate blocking soil pores, and causing an increase in the SAR through the reduced Ca^{2+} concentration (Ayers and Westcot, 1985).

- *Osmotic effects*

Salinity can affect plant growth and often cause death by lowering the free energy of water in solution, thereby reducing the ability of plant roots to extract water from the soil (Fitter and Hay, 1987). Dissolved salts cause plant cell dehydration where water instead flows from the high osmotic potential (low salts in plant cells) to low osmotic potential (high salts in soils).

- *Ion toxicities*

In addition to the osmotic hazards, direct toxicities of sodium, chloride and boron to plants also arise (Bresler *et al*, 1982). The effect of these toxicities depends on crop sensitivity. The toxicities of sodium depend on the ratio of Na^+ to Ca^{2+} plus Mg^{2+} in the soil. Nutritional imbalance in plants can be a result of salinity e.g excessive Na^+ or K^+ uptake relative to Ca^{2+} and Mg^{2+} (McBride, 1994). Boron is an additional specific ion which is seriously considered in salinity appraisals. Boron is common in active fault zones or former marine sediments and the range between deficiency and toxicity concentrations for many crops is narrow. In contrast to soils of humid regions, boron toxicity is most commonly found in alkaline soils of arid regions; which have high levels of Na^+ which form quite soluble borate salts (McBride, 1994). Boron also has the tendency to be weakly absorbed by soils so that its actual root-zone concentration may not vary in strict proportion to the degree to which the irrigation water has been concentrated during plant growth.

1.5 Summary of Literature Review

The study area is in a semi-arid region where precipitation is usually insufficient to meet the evapotranspiration (ET) needs of plants. Essentially, no water percolates through the soil under natural conditions since ET greatly exceeds precipitation over most of the year. This results in salts not leaching through the soils but tending to accumulate on the surface in amounts or types detrimental to plant growth. The review of geochemical studies of soils in the Western Cape attributes the presence of salts to evaporation of throughflow water and capillary uplifted groundwater.

Different modes and origin of salts have been identified and salinity types for example primary and secondary salinity mostly experienced in Australia is equally explained. The physico-chemical properties are highlighted in order to understand the diverse nature of salt affected soils and to develop appropriate approaches for their successful reclamation and management.

CHAPTER 2

MATERIALS AND METHODS

2.1 Soil sampling, classification and pre-treatment of soil samples

This section involves the description of soil sample collection, preparation, classification and analytical methods used.

2.1.1 Soil Sampling

Sampling was completed on the 26th and 27th July 2004, towards the end of the winter season. There was some minor rainfall a week before sampling, but no rain fell within the sampling period. The toposequence selected for this study appears on the 1:10 000 orthophoto map series 3318 Riebeeck West (Director General of Surveys, 1975). At the crest of the slope are vineyards, while the middle of the slope and valley bottom part is planted with shrubs for pasture. A small dam marks the end of the subcatchment. The toposequence is underlain by silcrete and alluvial material at the top, Malmesbury shale in the middle and alluvium at the valley bottom (Figure 2.1). The area of the selected catchment for this study is about 5ha. The length of the sampled slope is approximately 367 m long and it has an average slope angle of 10.2°. Numerous contour drains occupy the midslope controlling soil erosion and channelling water away from the stream catchment. The stream draining the catchment is ephemeral and was not flowing at the time of sampling. A small shallow well was present at the valley bottom.

Fourteen 200 cm deep pits were dug along the toposequence using an excavator. Ten of the pits were selected based on five different terrain units, namely crest, scarp, midslope, footslope and valley bottom (Figure 2.2). Soil samples were collected from a clean face in the pit. All recognisable horizons within the pits were sampled and labelled with the pit number, followed by a letter indicating the soil horizon, e.g. "1B1" refers to pit 1, sample from the B1 horizon. Because elements are unevenly distributed within a horizon, soil samples were collected from the vertical range of each horizon and mixed thoroughly in a plastic dish before bagging. In total thirty-one 2.5 kg samples were collected from 10 soil pits.

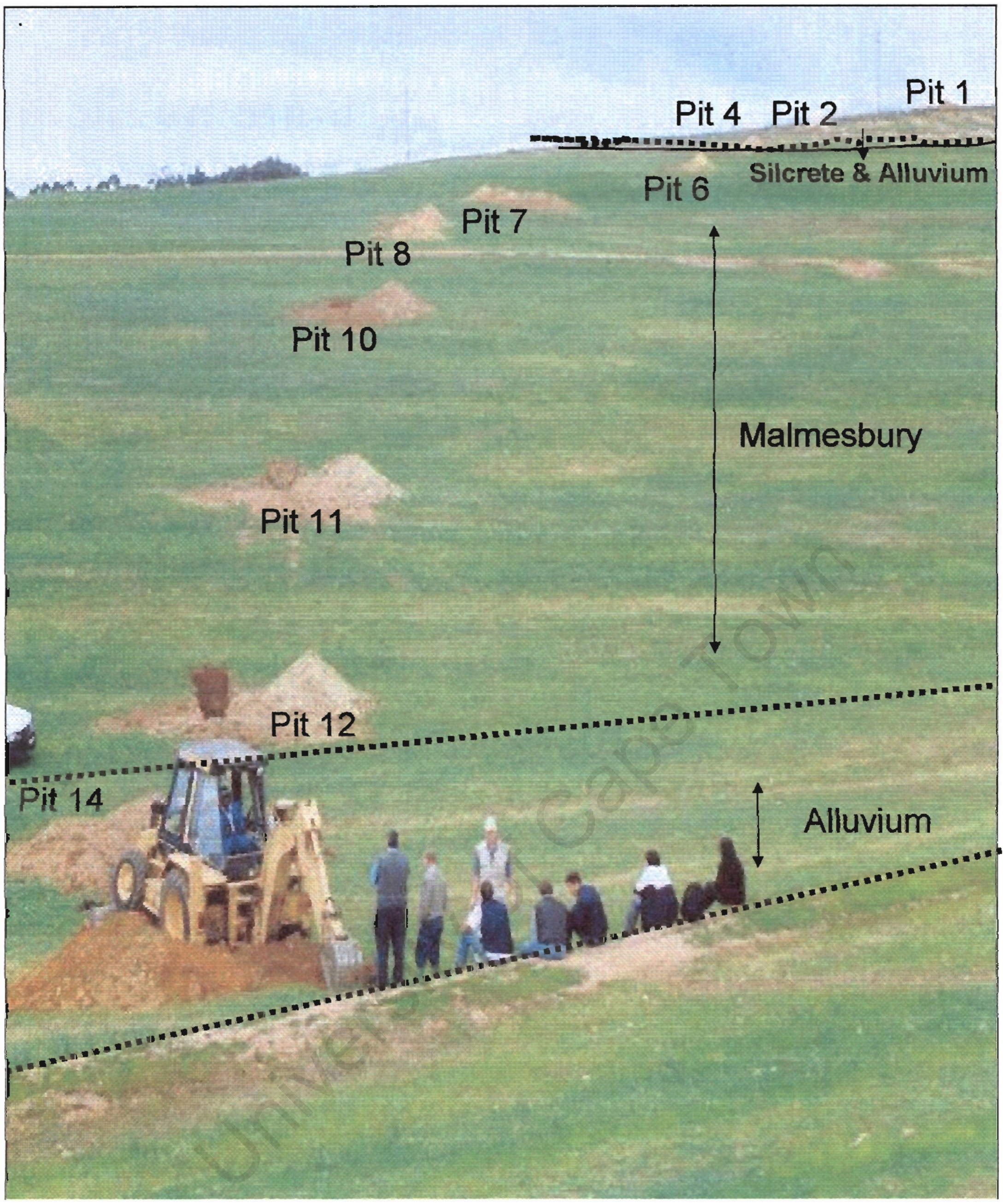

Figure 2.1a Excavation of soil pits

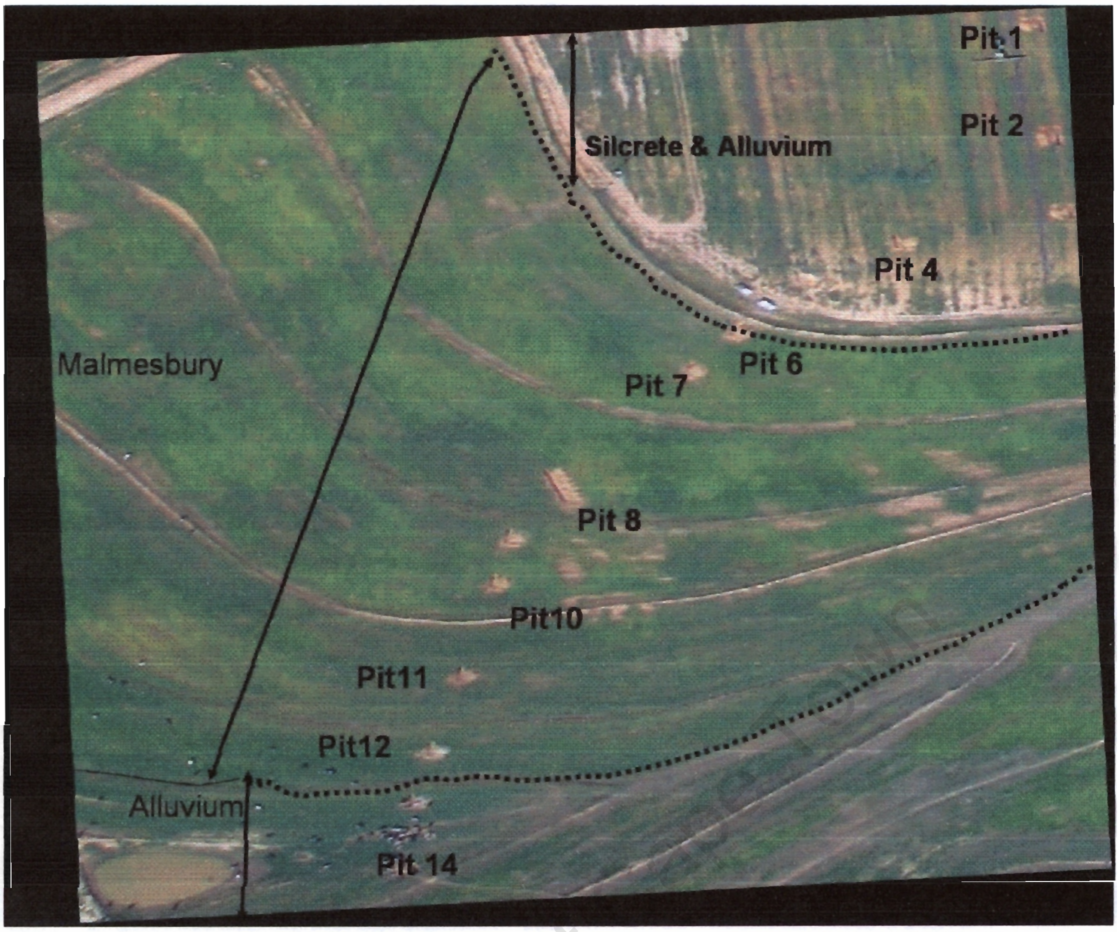

Figure 2.1b Aerial photograph showing layout of the soil pits on the toposequence.

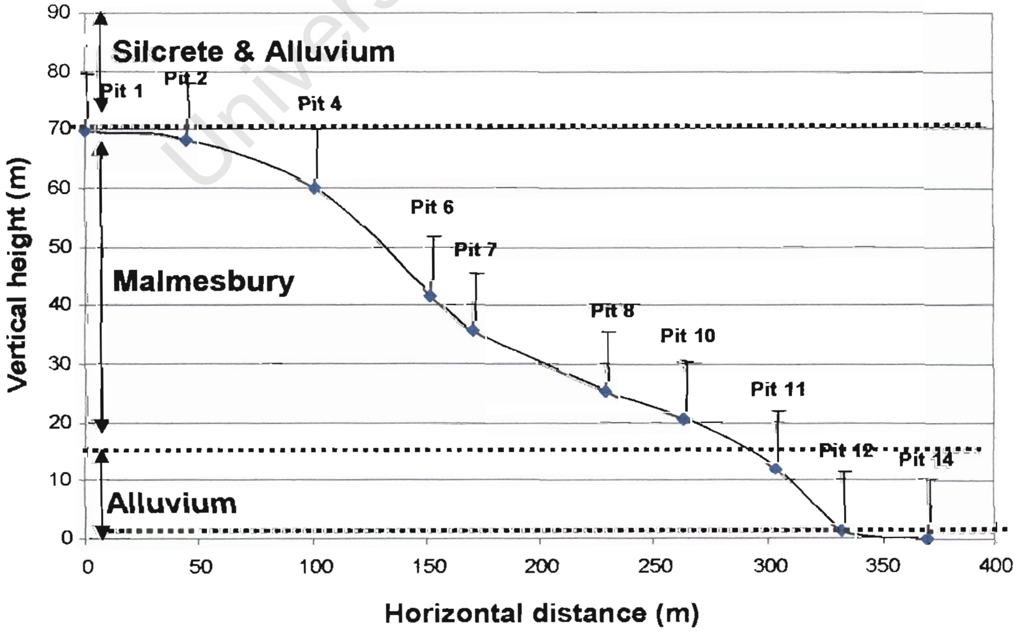

Figure 2.2 A simplified soil profile showing sampled soil pits along the toposequence. Vertical exaggeration (VE) = 2.94)

2.2 Soil Description and Classification

The sampled soil profiles were described and classified by Heinrich Schlom (University of Stellenbosch) and the author using "Soil Classification: A Taxonomic System for South Africa" (Soil Classification Working Group, 1991). The colours were described by the author using a Munsell Soil Colour Chart (1992) (Table 2.1)

Table 2.1 Summary of soil sampling data

Pit No.	Slope position	Slope angle	GPS Coordinates (WGS.84) South	East	Sample I.D	Depth (cm)	Colour dry	moist
1	Crest	2°	33° 18' 45.7"	018° 53' 38.2'	1A	0-20	Dark brown	Brown
					1B1	20-100	Dark brown	Yellowish red
					1B2	100-200	Reddish yellow	Yellowish red
2	Crest	2°	33° 18' 44.3"	018° 53' 37.6'	2A	0-50	Dark brown	Reddish brown
					2B1	50-100	Dark Red	Dusky red
					2B2	100-200	Strong brown	Dark brown
4	Scarp	8°	33° 18' 42.6"	018° 53' 38.4	4A	0-20	Reddish brown	Dark reddish brown
					4B1	20-100	Dark Red	Weak red
					4B2	100-200	Reddish yellow	Reddish yellow
6	Midslope	20o	33° 18' 41.1"	018° 53' 39.2'	6A	0-20	Reddish yellow	Dark reddish gray
					6B1	20-100	Reddish brown	Yellowish red
					6B2	100-200	Reddish yellow	Reddish yellow
7	Midslope	18°	33° 18' 40.5"	018° 53' 39.2'	7A	0-30	Dark reddish gray	Dark reddish brown
					7B1	30-70	Reddish brown	Yellowish red
					7B2	70-200	Reddish yellow	Olive yellow
8	Midslope	10°	33° 18' 38.6"	018° 53' 39.5'	8A	0-20	Brownish yellow	Yellowish
					8B1	20-100	Yellow	Yellow
					8B2	100-200	Dark yellowish brown	Dark brown
10	Midslope	8°	33° 18' 37.5"	018° 53' 39.6'	10A	0-20	Strong brown	Strong brown
					10B1	20-80	Reddish yellow	Reddish yellow
					10B2	80-200	Reddish yellow	Reddish yellow
11	Midslope	12°	33° 18' 36.2"	018° 53' 39.3'	11A	0-50	Reddish brown	Yellowish red
					11B1	50-100	Reddish yellow	Yellowish red
					11B2	100-200	Reddish yellow	Reddish yellow
12	Footslope	20°	33° 18' 35.1"	018° 53' 39.0'	12A	0-40	Strong brown	Brown
					12B1	40-100	Reddish yellow	Reddish yellow
					12B2	100-200	Pale yellow	Grayish brown
14	Valley bottom	2°	33° 18' 34.1"	018° 53' 38.6'	14A	0-10	Grayish brown	Dark grayish brown
					14B1	10-40	Yellowish brown	Dark Yellowish bron
					14B2	40-90	light yellowish brown	Yellowish brown
					14B3	90-200	Yellowish brown	Yellowish brown

Details of soil profiles are provided in the Appendix A, as well as photographs of the soil pits and their surroundings.

2.1.3 Pre-treatment of soil samples

Prior to analysis the samples were air-dried for 72 hours in a clean environment to avoid contamination. Large rocks (> 1cm diameter) were removed from the bulk soil before drying. Once dry, the soil samples were gently ground using a mortar and pestle to break down aggregates and sieved through a 2 mm sieve. A representative sample attained by coning and quartering, was weighed before and after sieving to determine the approximate proportion of < 2 mm material. The fine earth fraction (< 2 mm diameter) was stored in plastic bags for further physical and chemical analyses.

2.3 Soil analysis

2.3.1 Particle size analysis:

Particle size distribution was determined according to the general principles of the Soil Classification Working Group (1991). 20 g of < 2mm air-dry soil was pre-treated with H_2O_2 to remove organic matter and the suspension dispersed with Calgon.

The clay and silt contents were determined by pipette sampling (Gee and Bauder, 1986) and the sand fraction by dry sieving. The soil textural classification was determined using a soil textural triangle (Soil Classification Working Group, 1991)

2.3.2 Mineralogical composition of bulk samples:

The bulk samples were ground to fine powder using an agate mortar and pestle. In order to investigate the mineralogy in the soil samples, this analysis was performed on the bulk samples without separation of any fractions. The samples were prepared for XRD by pressing ground samples into an XRD sample holder using a hand-held press consisted of a flat, polished steel surface and wooden handle with which pressure was applied to the powder sample in the holder. To prevent preferential orientation of minerals at the surfaces, the sample surface was pressed against whatman No. 1 filter paper. The samples were analysed using a Philips PW 1390 X-ray diffractometer (XRD). The samples were irradiated with monochromatic X-rays emitted by a copper K-α X-ray tube (λ (K-α) = 1.542 Å). The X-ray generator was operated at 40 kV and 25 mA. The samples were scanned between 5° and 70°, analysing each 0.03° increment for 0.5s, resulting in an approximately 15 minute long scan.

2.3.3 Soil pH:

Soil pH was measured in a 1:2.5 suspension of soil in both distilled water and in 1M KCl solution McBride 1994). It is necessary to measure soil pH in neutral salt solution to compensate for the dilution effect. Measurements were made with a PHM 290 pH meter calibrated with standard buffers of 7.0 and 4.0 (± 0.02 pH units at 25°C) before use. Duplicate analyses were done in both cases.

2.3.4 Electrical Conductivity (EC):

Electrical conductivity is the ability of the solution to conduct electrical current and is dependent on the number of ions in solution. It is commonly used to estimate the amount of soluble salts in solution. This has been found to be a convenient way to approximate the salinity of a solution (Drever, 1997). The EC was measured in a 1:5 soil: water extract using a WTW Multi 340i pH meter and EC values are reported at a reference temperature of 20° C. The EC of the saturated paste extract was measured at the University of Stellenbosch (SUN) using an EDT RE 387 Tx Microprocessor

Conductivity meter at a reference temperature of 25° C. Duplicate analyses were done for both cases of EC determination. Because of the differences of reference temperature in the measurements, the two readings are not directly comparable.

2.3.5 Carbon and Nitrogen.

Total carbon and total nitrogen were determined at the Department of Soil Science laboratory, SUN, using a EURO EA Elemental Analyzer. Total carbon was analysed by dry combustion using a medium-temperature resistance furnace as described by Allison *et al.,* (1965). The samples were prepared by grinding in a ball grinder using agate containers and balls to pass through a 0.15 mm sieve. Inorganic carbon as carbonate was determined by means of the Karbonat Bombe Muller and Gastner, (1971), as described by Birch, (1981). This test was carried out on three samples from pits 10 and 11 which were the only ones which produced effervescence with 10% hydrochloric acid. The Karbonat Bombe is a simple device for the determination of calcium carbonate in sediments, soils and other materials by measuring the amount of CO_2 produced on reaction of sample with an acid (Muller and Gastner, 1971):

$$\text{e.g. } CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \text{ ------------------ } (7)$$

The reaction of $CaCO_3$ with HCl produces CO_2. The volume of CO_2 gas measured as a pressure guage fitted to the bombe. The instriument was calibrated using known massed of pure $CaCO_3$

2.3.6 Preparation of aqueous extracts

It is desirable to know solute concentrations in the soil solution at field water contents because the absolute and relative amounts of the various solutes are influenced by water content. Aqueous extracts of soil samples were used to estimate soluble salts in soils. Concentrations of major solutes (Ca^{2+}, Mg^{2+}, Na^+, K^+, CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-, and NO_3^-) are needed to quantify the salinity status in the study area. This can be done in two ways: i) Using constant soil: water ratio i.e. 1:5; ii) Making a saturated paste extract. Standardization of the soil:water ratio is required so that results can be applied and interpreted universally.

- *1:5 aqueous extract.*

This method may be advantageous for monitoring purposes especially when relative rather than absolute changes of solute concentration are required. It is easier to prepare than the saturated paste method but is less well-related to soil properties and errors from peptization, hydrolysis, cation exchange, and mineral dissolution are greater (Hesse, 1971). The 1:5 soil:water ratio was prepared according to the method described by Hesse (1971). 10 g of <2mm air-dried soil were added to 50 mL of deionised water, shaken in a horizontal mechanical shaker for 30 minutes, and then allowed to stand for 15 minutes to let the bulk of the soil settle. The mixture was centrifuged at 2000 rpm for 5 minutes and filtered through a 0.45μm membrane filter. The filtrates were stored in a refrigerator for subsequent analyses.

- *Saturated paste extract*

Soil salinity is conventionally defined and measured on aqueous extracts of soil saturated pastes (U.S. Salinity Laboratory Staff, 1954). The soil:water ratio obtained from this method is useful as it is the lowest, reproducible soil-to water ratio for which sufficient extract can be readily removed from the soil with suction and because it is related to field soil water properties. The saturated paste extract (SPE) was prepared using 400g of < 2mm air-dry soil. Distilled water was added gently to the soils to reach saturation and was allowed to equilibrate over night. At saturation the soil paste glistens as it reflects light, flows slightly when the container is tipped, slides freely and cleanly off the spatula, and consolidates easily when the container is tapped after a trench is formed in the paste with the side of the spatula (Rhoades, 1982). The extraction was done on a vacuum line using Whatman 50 filter paper on a Buchner funnel. The EC of the extracts was measured and the extract filtered through a 0.45μm Millipore filter before diluting for use in various analyses. The saturated paste extracts of sodic soils (pH > 8.5 and ECe < 4.0 dS/m) are usually dark in colour due to suspended organic matter, which interferes with most analytical procedures.

2.3.6 Extractable base cations (Ca, Mg, K, and Na)

Cations were extracted with neutral 1M ammonium acetate according to the method of Thomas (1982). 25 mL of 1M neutral ammonium acetate solution was added to 5g of < 2 mm air-dried soil in 100 ml centrifuge tubes and shaken on a reciprocal shaker for about 30 minutes. The mixture was centrifuged at 2000 rpm for about 5 minutes and filtered through a 120 mm filter paper. The process was repeated to generate 50

mL NH_4OAc extract. Atomic Absorption Spectroscopy (AAS) was used to determine the concentrations of Ca Mg, Na and K in the ammonium acetate extract. AAS determines the amount of radiation from a light source that is absorbed by an element. The degree of absorption is specific to the element being analysed. The sample is aspirated and mixed with nitrous oxide and combusted, resulting in atomisation (Potts, 1987). A Flame Varian Spectra AA-250 plus was used for the analysis. The spectrometer was calibrated and samples diluted to fall within the calibration range.
Effective cation exchange capacity (ECEC) was calculated as the sum of all the exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+).

2.3.7 Extractable acidity:

Extractable acidity was measured on samples with pH (KCl) < 4.5 according to the method described by (Thomas 1982). 50 mL of 1M KCl was added to 5g of < 2mm air-dried soil in 100 mL centrifuge tubes and shaken on a reciprocal shaker for about 30 minutes. 10 mL aliquots of 1M KCl extract were titrated against 0.01M NaOH to a phenolphthalein end point of pH 8.3.

2.3.8 Alkalinity

Alkalinity was determined by potentiometric titration of 1:5 extracts 1 M KCl extracts to a pH of 4.5 with 0.02 N HCl. Alkalinity was calculated from the volume of acid needed to reduce the pH of sample to 4.5. Due to insufficient extract, alkalinity in the SPE was not determined.

2.3.9 Major ions

Major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anions (F^-, Cl^-, NO_3^-, SO_4^{2-} and $PO_4^{3-)}$ were determined in the 1:5 extract and SPE. The anions were measured with Dionex DX-120 Ion Chromatograph. Ion chromatography (IC) relies on the variable adsorption of ions to separate them on an exchange separator column. Peak areas for each ion are calibrated using solutions of known concentrations. Prior to analysis, samples were filtered through a 0.22 μm Millipore filter membrane to remove suspended solids and diluted with distilled water to within calibration range. The Dionex DX-120 software integrates the area under each conductivity peak, subtracts the background and then calculates the concentrations of the anions based on the calibrations. Major and extractable cations were analysed by AAS at SUN Soil Science Department.

2.3.10 Trace metals

Trace metals were analysed in the SPE using the Inductively Coupled Plasma Mass Spectrometer (ICP-MS) in the Department of Geological Sciences at UCT. ICP-MS is a fast, precise, and accurate multi-element analytical technique for the determination of trace element abundances (< 0.1 wt. %) and isotopic ratios in liquid and solid samples. The concentrations of the following elements were determined: Li, B, Al, Si, P, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Ba, Pb, and U. ICP-MS operates by ionising a liquid or solid sample in argon plasma at high temperature and separating the ions by mass for measurement (Potts, 1987). Filtered samples were prepared at two dilutions (100 and 1000 times) using 2% HNO_3. Each sample received an internal standard containing elements not being analysed. The samples were loaded into the auto sampler programmed to analyse each sample twice, interspersed with analyses of certified NIST standards and blank samples. Internal standards were used to correct for drift and matrix effects. However, this technique has some limitations mainly due to interferences by argon ions produced in the plasma. A well-known interference is between ^{56}Fe and $^{40}Ar^{16}O$ (Potts, 1987).

CHAPTER 3

RESULTS

The physico-chemical properties of soils in this study were determined by analysing air-dried <2 mm soil samples and the results obtained are presented in this chapter. The results have been grouped into five sections including: the general parameters, soil solution chemistry, derived parameters, Phreeqc modeling and bulk samples determination.

3.1 General parameters

3.1.1 Soil pH

Results of soil pH in distilled water and 1 M KCl are presented in Table 3.1. The pH $_{(kcl)}$ varied greatly along the toposequence being acidic in the crest (< 4.5); alkaline (8.7-9.5) in the midslope; and moderately acidic to neutral in the lower parts of the slope (4.5- 7.5). pH $_{(KCl)}$ was on average 2 pH units lower than pH $_{(H2O)}$.

3.1.2 Electrical conductivity

Electrical conductivity (EC) values for both 1:5 water extract and the SPE show a maximum value of 10.97 dS/m (in SPE) at the midslope (Table 3.1). Soil salinity also varies with depth of soil pits with pits in the midslope and at the bottom of the slope having higher EC values in the surface soil compared to those at the crest and scarp positions which have much higher EC values in sub soils.

3.1.3. Total carbon

Total carbon in all pits ranged from 0.10 % to 4.11 % with the midslope and crest having approximately the same percentage (Table 3.1). The footslope and the bottom of the slope had much higher percentage total carbon with the valley bottom topsoil registering an extremely high percentage relative to all physiographic positions. This is due to much smaller depth of sampling of sample 14A, resulting in less dilution of surface organic carbon compared to the rest of the samples. Mean concentrations in the top soil and sub soil samples were 1.2% and 0.85% respectively (n=10). Total carbon in the subsoils of pits 10 & 11 is higher because of the presence of calcium carbonate. Organic carbon was calculated by subtracting inorganic carbon from total carbon percentage

Table 3.1 General physico-chemical parameters

								Particle size distribution				
Sample I.D	pH (H_2O)	pH (KCl)	EC(1-5) dS/m	EC(SPE) dS/m	TC (%)	IC (%)	OC (%)	< 2 mm (%)	Sand (%)	Silt (%)	Clay (%)	Class[a]
1A	6.6	5.3	0.05	0.45	1.11			61.6	80.8	12.9	6.3	ls
1B1	6.8	5.8	0.05	0.25	0.51			54.5	84.7	7.2	8.1	ls
1B2	7.4	6.7	0.05	0.54	0.26			43.4	71.2	7.2	21.5	sl
2A	6.0	4.7	0.031	1.93	0.88			54.2	75.6	14.5	9.9	sl
2B1	5.6	4.1	0.03	2.46	0.47			49.3	84.3	9.0	6.7	ls
2B2	4.6	3.7	0.05	7.38	0.40			43.8	80.2	11.6	8.2	ls
4A	5.8	4.5	0.05	10.97	1.42			47.7	83.2	8.5	8.3	ls
4B1	4.9	4.0	0.04	1.88	0.79			58.4	69.4	7.2	23.4	scl
4B2	4.8	3.9	0.06	2.52	0.35			39.1	58.0	4.8	37.2	scl
6A	5.3	4.4	0.20	3.73	0.98			49.3	75.4	10.1	14.6	sl
6B1	5.9	4.0	0.24	0.41	0.62			69.7	42.7	12.1	45.2	cl
6B2	6.4	4.0	0.90	0.20	0.21			43.6	49.2	25.5	25.3	cl
7A	5.8	5.0	0.30	0.23	0.10			65.9	48.7	27.8	23.5	scl
7B1	6.3	4.4	0.37	1.63	1.15			33.4	65.0	18.1	16.9	sl
7B2	7.8	6.3	0.57	3.03	0.12			29.4	41.8	33.0	25.2	l
8A	7.9	7.3	1.04	2.62	0.89			62.2	49.4	19.4	31.1	scl
8B1	9.3	8.0	0.48	5.16	0.58			52.3	51.5	24.6	24.0	scl
8B2	9.0	7.7	0.32	1.67	0.10			42.5	49.0	26.2	24.8	l
10A	8.1	7.3	1.52	1.78	0.80			31.6	51.2	27.8	21.0	scl
10B1	9.3	8.1	0.82	1.77	1.97	1.92	0.05	68.0	48.1	27.8	24.1	scl
10B2	9.1	8.2	1.10	0.44	0.09			51.2	47.2	31.3	21.5	scl
11A	6.7	5.6	0.24	0.43	0.67			34.4	69.7	13.7	16.6	sl
11B1	8.8	5.9	0.29	0.30	1.71	1.44	0.27	62.7	62.7	10.1	27.2	scl
11B2	9.5	7.5	0.26	5.78	1.91	2.00	<0.1	53.4	61.7	18.3	20.0	sl
12A	7.5	6.7	0.32	4.82	1.30			53.0	52.9	28.0	19.1	sl
12B1	8.8	6.8	0.20	2.40	0.19			54.2	77.4	13.7	8.9	sl
12B2	8.9	6.9	0.13	8.18	0.11			43.8	64.8	29.7	5.5	sl
14A	6.5	6.0	0.60	1.10	4.11			11.9	49.6	25.1	25.3	cl
14B1	6.5	5.3	0.18	1.45	0.80			26.9	71.0	9.5	19.5	sl
14B2	6.5	5.4	0.17	2.20	0.54			30.3	70.2	16.8	13.1	sl
14B3	7.0	5.4	0.09	1.76	0.13			41.2	81.3	11.2	7.5	ls
MIN. Value:	**4.6**	**3.7**	**0.03**	**0.20**	**0.09**	**1.71**	**0.05**	**11.9**	**41.8**	**4.8**	**5.5**	
MAX. Value:	**9.5**	**8.2**	**1.52**	**10.97**	**4.11**	**1.92**	**2.00**	**69.7**	**84.7**	**33.0**	**45.2**	
Average:	**7.1**	**5.8**	**0.35**	**2.56**	**0.82**	**1.85**	**0.77**	**47.2**	**63.5**	**17.5**	**19.0**	

[a] ls = loamy sand; sl = sandy loam ; scl = sandy clay loam; cl = clay loam ; l = loam
bdl * = below detection limit; IC = Inorganic carbon; OC = Organic carbon

3.1.4 Particle size distribution

There is some variation in the distribution of soil particle size along the toposequence and with depth of soil pits. The midslope is observed to contain the lowest sand content and highest silt and clay content with respect to other terrain units along the toposequence. The bottom of the slope has equal proportions of clay and silt. Generally the clay fraction is high in nearly all the subsoils in the toposequence except at the valley bottom where sample 14B3 has the lowest clay content of 7.5% (Table 3.1).

3.2 Soil solution chemistry

3.2.1 Major elements

The dominant major cation in the 1:5 soil:water extract is sodium, with highest concentration in the middle part of the toposequence and lowest concentration at the crest. Chloride is the dominant anion in the 1:5 soil:water extract, followed by sulphate and bicarbonate ions. These anions were found concentrated in the midslope as in the case of the cations, and tend to decrease with depth of soil pits in most cases.

Table 3.2 Major in 1:5 water extracts (concentrations measured in $mmol_c/L$)

Sample	Ca^{2+}	Mg^{2+}	Na^+	K^+	F^-	Cl^-	NO_3^-	$H_2PO_4^-$	SO_4^{2-}	HCO_3^-
1A	0.08	0.03	0.15	0.25	0.01	0.07	0.05	0.04	0.05	0.28
1B1	0.17	0.07	0.22	0.07	0.01	0.09	0.05	bdl	0.10	0.38
1B2	0.15	0.08	0.31	0.02	0.02	0.04	0.01	bdl	0.08	0.58
2A	0.06	0.02	0.11	0.14	bdl	0.03	0.02	0.07	0.04	0.18
2B1	0.08	0.02	0.08	0.13	bdl	0.03	0.01	0.02	0.10	0.08
2B2	0.12	0.10	0.13	0.02	bdl	0.05	0.01	0.03	0.04	0.18
4A	0.13	0.08	0.15	0.15	bdl	0.09	0.12	0.01	0.07	0.08
4B1	0.10	0.05	0.09	0.09	bdl	0.05	0.06	0.00	0.15	0.03
4B2	0.13	0.11	0.13	0.09	bdl	0.15	0.03	bdl	0.24	0.03
6A	0.72	0.23	0.63	0.07	0.01	0.74	0.01	0.01	0.54	0.08
6B1	0.04	0.23	2.01	0.34	0.01	1.22	0.00	bdl	0.54	0.03
6B2	0.01	0.06	7.17	0.02	0.04	3.75	0.01	bdl	0.85	0.38
7A	0.35	0.13	1.94	0.03	0.02	1.20	bdl	0.00	1.02	0.38
7B1	0.05	0.32	3.11	1.08	0.04	1.84	0.03	bdl	0.78	0.37
7B2	0.01	0.07	4.42	0.19	0.11	4.77	0.01	bdl	0.31	0.18
8A	1.64	0.94	6.37	0.12	0.05	4.36	0.21	0.01	3.99	0.73
8B1	0.07	0.23	4.08	0.16	0.12	1.75	0.10	bdl	0.61	2.58
8B2	0.02	0.02	2.54	0.03	0.11	1.57	0.08	bdl	0.42	2.48
10A	1.23	1.00	11.51	0.10	0.04	9.09	0.11	bdl	3.89	0.88
10B1	0.05	0.14	7.28	0.08	0.11	4.35	0.10	0.01	1.02	2.68
10B2	0.02	0.19	9.67	0.03	0.12	7.62	0.02	bdl	1.46	0.98
11A	0.81	0.41	0.60	0.09	0.02	0.24	0.07	bdl	1.38	0.28
11B1	0.21	0.26	2.09	0.06	0.07	0.23	0.10	bdl	1.02	2.08
11B2	0.08	0.11	1.85	0.04	0.05	0.17	0.05	bdl	0.31	2.28
12A	1.03	0.59	0.91	0.23	0.01	0.23	0.06	0.01	0.09	1.58
12B1	0.15	0.72	1.82	1.31	0.13	0.54	0.11	0.00	0.33	1.78
12B2	0.01	0.16	1.11	0.16	0.09	0.43	0.04	bdl	0.11	0.78
14A	2.06	1.69	1.44	0.77	0.02	1.21	0.37	0.11	3.06	0.53
14B1	0.25	0.26	0.83	0.29	0.01	0.53	0.14	0.01	0.63	0.18
14B2	0.13	0.21	1.00	0.18	0.01	0.49	0.25	bdl	0.48	0.23
14B3	0.02	0.04	0.75	0.02	0.01	0.34	0.10	bdl	0.15	0.38

bdl = Below detection limit(<0.1 mg/L in solution)

3.2.2 Major ions in saturated paste extract (SPE).

Major cations and anions order of dominance in the SPE are as follows: Cations: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and anions: $Cl^- > SO_4^{2-} > NO_3^- > F^- > H_2PO_4^- > NO_2^-$. The distribution of these ions follow the same pattern as in 1:5 soil:water extract.

Table 3.3 Major cations and anions from SPE (Concentrations measured in $mmol_c/L$).

(bdl = Below detection limit (<0.1 mg/L in solution)

Sample I.D	Ca^{2+}	Mg^{2+}	Na^+	K^-	F^-	Cl^-	NO_2^-	NO_3^-	$H_2PO_4^-$	SO_4^{2-}
1A	1.12	0.44	1.28	1.22	bdl	1.55	bdl	0.85	bdl	0.84
1B1	1.60	0.66	1.24	0.16	bdl	1.50	bdl	0.10	bdl	0.64
1B2	1.10	0.58	2.08	0.05	bdl	1.42	bdl	bdl	bdl	1.80
2A	0.73	0.29	0.79	0.59	bdl	0.74	bdl	0.04	0.14	0.62
2B1	0.56	0.19	0.56	0.54	bdl	0.57	bdl	0.20	0.05	0.51
2B2	1.12	0.71	1.47	0.09	bdl	0.97	bdl	0.38	0.10	1.44
4A	1.80	1.05	1.23	0.70	bdl	1.61	0.36	1.19	bdl	0.92
4B1	0.87	0.35	0.54	0.31	bdl	0.55	bdl	0.65	bdl	0.59
4B2	0.78	0.54	0.76	0.28	bdl	1.42	bdl	0.30	bdl	0.82
6A	9.22	3.05	5.68	0.15	bdl	9.94	bdl	bdl	bdl	10.05
6B1	0.34	0.82	13.19	0.03	bdl	11.57	bdl	0.08	bdl	3.77
6B2	0.43	2.50	55.62	0.11	bdl	64.84	bdl	bdl	bdl	8.52
7A	0.23	0.91	23.31	0.14	0.43	19.57	bdl	0.58	bdl	4.71
7B1	8.23	3.24	20.28	0.16	bdl	19.25	bdl	bdl	bdl	15.59
7B2	0.26	1.51	43.35	0.06	0.07	53.99	bdl	0.11	bdl	3.83
8A	22.31	12.49	49.89	0.53	bdl	52.68	1.78	0.43	bdl	44.08
8B1	0.55	1.42	25.49	0.11	0.21	17.86	bdl	1.00	bdl	6.70
8B2	0.25	0.86	23.10	0.14	0.56	19.24	bdl	0.63	bdl	4.59
10A	17.69	13.70	96.09	0.23	bdl	111.13	bdl	0.08	bdl	41.65
10B1	0.68	2.28	47.67	0.14	0.72	45.89	bdl	0.98	bdl	9.97
10B2	0.47	4.83	83.86	0.17	0.16	88.98	bdl	0.26	bdl	16.25
11A	9.53	4.90	4.88	0.07	0.00	3.69	0.44	bdl	0.02	16.55
11B1	1.97	2.58	11.81	0.04	0.04	2.94	bdl	1.17	bdl	9.65
11B2	0.54	0.77	8.82	0.14	0.06	2.72	bdl	0.81	bdl	3.79
12A	12.24	7.65	8.56	0.55	bdl	7.47	bdl	1.57	bdl	18.18
12B1	0.66	1.61	14.07	0.04	0.10	7.47	bdl	1.26	0.05	4.32
12B2	0.19	0.28	12.09	0.03	0.30	7.47	bdl	bdl	bdl	2.61
14A	23.90	10.08	9.93	2.08	bdl	10.72	bdl	bdl	bdl	36.02
14B1	4.17	3.78	7.66	0.58	bdl	7.54	0.93	0.28	0.65	7.99
14B2	3.30	4.58	13.30	0.19	bdl	10.41	0.72	4.01	0.16	7.51
14B3	0.71	2.04	12.09	0.04	bdl	8.93	bdl	2.89	0.28	3.64

3.2.3 Exchangeable cations

Exchangeable cations were determined in SPE with neutral NH_4OAc and the results given in Table 3.4 Since the soils were saline with excess amounts of soluble ions, exchangeable cations were corrected by subtracting the soluble ions determined in 1:5 soil:water extracts.

Table 3.4 Ammonium acetate exchangeable cations

Sample	Ca^{2+} (mmol$_c$/kg)	Mg^{2+} mmol$_c$/kg	Na^{+} (mmol$_c$/kg)	K^{+} (mmol$_c$/kg)
1A	41.44	10.37	2.24	6.80
1B1	57.98	16.13	3.83	5.58
1B2	38.27	17.86	3.72	1.88
2A	25.70	7.53	2.70	5.17
2B1	21.68	6.87	2.63	6.32
2B2	4.17	2.63	2.46	1.33
4A	26.82	9.38	1.89	3.34
4B1	9.96	4.28	2.28	2.62
4B2	8.98	6.54	2.37	2.01
6A	30.32	7.49	2.04	1.27
6B1	19.46	42.80	23.34	<0.1
6B2	6.54	34.12	36.82	1.60
7A	4.32	22.06	12.79	1.32
7B1	38.87	9.59	<0.1	<0.1
7B2	2.12	17.37	16.57	<0.1
8A	60.91	26.09	5.79	3.03
8B1	81.14	71.61	15.20	2.15
8B2	6.34	22.02	9.85	1.30
10A	49.06	23.99	2.24	1.64
10B1	78.42	81.44	19.01	2.62
10B2	7.14	21.03	<0.1	0.69
11A	56.86	24.03	3.87	1.39
11B1	160.75	73.09	9.81	1.44
11B2	156.16	70.41	11.90	2.44
12A	119.34	26.59	4.55	3.17
12B1	26.30	73.71	14.20	<0.1
12B2	11.03	70.95	41.65	0.93
14A	20.27	11.53	1.13	<0.1
14B1	97.56	25.93	7.50	8.00
14B2	18.91	18.81	4.72	0.60
14B3	5.94	17.33	5.92	0.37

3.2.3 Trace elements

Trace element chemistry were determined by ICP- MS from saturated paste extract and the results is given in Table 3.5 All concentrations were measured in ppb and Selenium, Arsenic and Boron were the key elements of interest in this study.

Table 3. 5. Trace element chemistry of saturated paste extracts (Concentrations in ppb)

Sample I.D	Li	B	Al	Si	P	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Rb	Sr	Ba	Pb	U
A	13.9	398.0	488.5	9241.9	3862.5	59.2	224.1	1476.3	2.2	8.7	35.3	48.6	5.8	2.1	18.1	165.5	42.4	0.5	0.2
1B1	19.1	237.1	188.0	9210.3	4405.0	42.4	16.7	2529.3	1.2	3.3	13.1	24.2	3.1	13.4	4.1	349.3	24.4	0.5	0.1
1B2	20.6	427.4	187.2	3442.8	2709.9	62.0	5.0	1693.7	1.0	3.5	11.9	51.9	2.1	45.4	2.0	271.6	1.1	58.2	1.6
2A	18.4	358.8	742.6	8024.3	8332.1	67.9	154.0	1680.6	0.9	6.7	32.3	31.3	5.7	25.7	8.1	65.2	11.4	0.7	0.1
2B1	90.2	73.5	690.0	5465.2	*n.d.*	6.9	96.4	237.6	0.6	3.5	60.8	75.9	1.5	11.8	4.8	66.1	64.4	0.9	0.1
2B2	9.4	143.9	348.5	8717.3	1635.5	13.3	109.2	998.7	3.4	9.2	14.8	36.7	1.7	*0.0*	1.8	164.7	10.1	0.2	0.0
4A	8.6	77.9	615.3	6956.5	838.3	38.8	282.4	473.8	1.4	5.8	35.8	61.2	3.7	11.0	13.3	225.3	47.4	6.9	0.4
4B1	5.8	45.8	2504.0	3369.5	*n.d.*	24.3	103.7	147.9	1.8	11.2	6.9	75.9	3.0	*0.0*	11.0	112.3	64.6	1.8	0.2
4B2	8.9	111.1	272.5	2362.9	2161.1	33.7	46.5	12.9	1.7	4.5	16.3	7.2	0.4	0.2	6.8	101.1	31.9	1.5	0.1
6A	7.4	92.2	556.6	5051.4	3117.6	1.5	982.2	513.2	10.2	12.9	18.8	67.1	3.3	15.3	3.5	1259.1	71.9	2.3	0.3
6B1	3.5	214.3	183.7	4128.4	5740.6	31.8	35.2	534.7	0.9	16.9	13.5	59.7	2.3	11.9	1.0	70.0	12.2	0.2	0.1
6B2	87.1	150.5	187.6	4342.3	3838.9	39.9	20.7	1143.5	0.2	2.3	13.2	65.9	12.4	36.0	1.1	99.6	27.8	1.8	0.1
7A	6.8	1349.0	240.1	2207.7	7371.8	30.1	9.3	520.6	1.0	3.3	12.8	33.4	4.5	21.7	1.8	43.2	6.4	0.9	0.1
7B1	58.0	308.0	306.8	5284.4	*n.d.*	*n.d.*	3094.3	947.7	19.7	18.7	33.5	75.7	4.5	24.0	4.1	1090.9	147.0	4.1	1.0
7B2	69.1	13.0	358.4	2334.5	*n.d.*	54.2	7.5	2308.3	0.4	1.0	8.7	33.2	10.1	35.0	1.7	62.2	28.5	*n.d.*	0.0
8A	64.7	655.2	144.6	4384.6	*n.d.*	14.5	45.1	393.8	5.4	21.2	217.3	68.4	12.3	54.9	14.1	2883.5	94.0	1.1	26.5
8B1	16.0	911.4	153.8	3489.7	4190.8	34.1	12.2	1065.1	1.1	11.4	9.1	27.3	5.0	13.7	2.0	117.9	12.1	0.1	1.5
B2	47.2	1322.2	154.6	1899.1	4404.1	17.1	7.9	2437.6	0.6	1.2	7.4	311.7	5.0	26.2	2.2	48.9	137.8	*n.d.*	0.2
10A	49.6	453.9	16356.3	4725.9	*n.d.*	*n.d.*	73.3	349.4	5.9	24.3	36.9	93.1	21.0	56.8	9.3	3034.7	72.5	*n.d.*	7.6
10B1	34.4	287.1	194.8	2497.9	*n.d.*	4.1	7.0	2174.8	0.8	4.0	16.6	47.7	9.2	34.7	1.7	211.3	20.4	0.4	1.4
10B2	28.1	147.0	138.6	1301.7	833.4	*n.d.*	10.6	767.5	0.0	1.5	17.2	63.7	14.2	54.2	2.1	114.5	20.0	0.3	1.5
11A	7.0	140.6	211.4	8442.3	*n.d.*	12.0	108.7	242.9	2.5	18.4	26.2	62.0	1.8	5.4	2.6	1361.7	23.3	*n.d.*	0.1
11B1	17.9	536.8	150.5	4509.7	4732.5	14.9	4.8	122.6	0.5	3.0	21.5	39.3	2.2	16.7	1.6	535.1	10.2	0.2	1.8
11B2	17.1	438.9	258.3	9715.0	3734.9	15.2	110.7	34.4	0.6	4.0	17.3	58.1	3.5	15.0	2.1	162.2	8.7	1.9	3.3
12A	3.1	78.6	89.2	2798.3	678.4	36.5	5.1	186.0	6.8	20.0	50.0	44.3	6.2	7.3	7.2	1496.3	67.8	*n.d.*	10.2
12B1	8.2	278.4	133.2	2430.0	2149.0	20.2	14.6	552.2	0.5	3.2	9.7	54.5	3.0	11.1	1.4	168.3	14.1	0.1	2.3
12B2	23.8	59.0	4329.0	9790.4	4829.4	17.6	28.7	2856.0	1.6	5.6	21.4	35.0	3.8	11.2	8.6	21.2	16.5	3.3	0.5
14A	14.4	184.5	115.2	12521.9	7228.4	21.0	2471.5	675.9	19.1	29.8	56.2	93.8	9.1	7.7	27.4	3189.9	83.1	0.6	0.9
14B1	25.3	285.4	222.6	7832.7	8368.8	21.4	527.3	74.2	4.6	18.5	43.6	91.0	2.9	1.2	7.3	644.7	45.5	7.1	0.3
14B2	22.0	223.5	169.5	7547.3	6023.4	51.0	505.0	2145.3	2.7	19.0	26.7	47.6	4.8	12.1	5.3	622.2	34.3	0.5	0.1
14B3	20.2	136.8	155.5	4957.1	1738.2	33.0	155.0	29.5	3.3	4.4	4.4	32.3	3.3	0.5	2.4	120.7	17.8	*n.d.*	0.0

3.3 Derived parameters

3.3.1 Extractable acidity

Extractable acidity was determined only for samples with pH (KCl) ≤ 4.5. (Table 3.5) The acidity concentrations ranged from 2 - 35 mmol$_c$/kg. There was an increase in acidity with depth in the selected pits (pits 2, 4, and 6) which were all located in the crest and scarp respectively on the toposequence.

3.3.2 Effective cation exchange capacity

Base saturation and effective cation exchange capacity (ECEC) were calculated from NH_4AOc extractable cations (Ca, Mg Na, and K) and KCl extractable acidity (Table 3.5). The details of the calculations are presented in the Appendix B. Effective cation exchange capacity (ECEC) was found to be very high (52.58 – 245.09 mmol$_c$/kg) for samples in the midslope compared to other parts of the toposequence. There were decreases of ECEC with depth at the bottom of the slope and footslope.

3.3.3 Exchangeable sodium percentage

Exchangeable sodium percentage (ESP) was calculated from saturated paste extract cations (Table 3.5). ESP is not uniformly distributed along the toposequence as highest ESP values are found at the midslope ranging from 52.23 – 46.34. 24 %. There were decreases with depth at the bottom of the slope. ESP at the footslope ranged from 2.96- 34.8 % while the crest and scarp registered relatively lower values (3.68 – 4.32%). ESP was found to increase generally with depth of the soil pits.

3.3.4 Sodium adsorption ratio

Sodium adsorption ratio (SAR) was calculated from the concentrations of Na^+, Ca^{2+}, and Mg^{2+} obtained from AA analysis of major cations in the SPE (Table 3.3). SAR was found to follow the same pattern of variation along the toposequence as ESP. At the crest and scarp, SAR ranged from 0.69 – 2.27 compared to the midslope where the ratio varied from 8.47 – 51.49. The footslope and bottom of the slope had SAR ratios of 2.71-24.95 and 2.41-10.31 respectively

Table 3.6 Derived parameters from SPE and ammonium acetate extract

Sample I.D	ECEC (mmolc/Kg)	Base saturation (%)	Acidity (%)	ESP (%)	SAR $mmol_c/L^{1/2}$
1A	60.86	nd*	nd	3.68	1.45
1B1	83.52	nd	nd	4.58	1.16
1B2	61.73	nd	nd	6.02	2.27
2A	46.09	89.15	10.47	5.85	1.11
2B1	48.50	77.32	21.94	5.43	0.91
2B2	34.59	30.61	65.83	7.11	1.53
4A	45.43	91.20	8.33	4.16	1.03
4B1	54.14	35.35	62.68	4.22	0.69
4B2	54.90	36.25	61.23	4.32	0.93
6A	60.12	68.40	27.79	3.40	2.29
6B1	105.49	81.04	16.87	22.12	17.26
6B2	81.07	97.53	1.70	45.42	45.91
7A	40.48	nd	nd	31.59	30.88
7B1	47.23	93.65	4.28	1.47	8.47
7B2	35.77	nd	nd	46.34	46.14
8A	95.82	nd	nd	6.04	11.96
8B1	170.09	nd	nd	8.94	25.68
8B2	39.51	nd	nd	24.94	31.00
10A	76.93	nd	nd	2.91	24.25
10B1	181.49	nd	nd	10.47	39.16
10B2	26.46	nd	nd	9.04	51.49
11A	86.16	nd	nd	4.49	1.82
11B1	245.09	nd	nd	4.00	7.83
11B2	240.91	nd	nd	4.94	10.87
12A	153.64	nd	nd	2.96	2.71
12B1	108.86	nd	nd	13.05	13.18
12B2	124.56	nd	nd	33.44	24.95
14A	32.80	nd	nd	3.45	2.41
14B1	138.99	nd	nd	5.40	3.84
14B2	43.04	nd	nd	10.97	6.70
14B3	29.55	nd	nd	20.02	10.31
nd* =	not determined				
Minimum	**26.46**	**30.61**	**1.70**	**1.5**	**0.69**
Maximum	**245.09**	**97.53**	**65.83**	**46.3**	**51.49**
Average	**85.61**	**70.05**	**28.11**	**21.0**	**13.88**

3.4 Phreeqc modelling

Saturation indices indicate the saturation state of a mineral with respect to solution composition. The saturation index (SI) is defined as:

$$SI = \log_{10}(\frac{IAP}{K_{sp}})$$

where IAP is the ion activity product as defined by mass equation and K_{sp} is the solubility-product constant for the mineral. Phreeqc modelling was done on SPE with samples with charge balance difference less than 10%. Phreeqc results are given in Table 3.7

Table 3.7 Saturation indices for SPE

Sampe ID	Calcite	pH	Fluorit	Gypsum	Halite	Quartz	Kaolinite	SiO_2 (a)
2B2	-6.09	4.55	-	-2.29	-7.53	0.22	0.59	-1.08
4A	-3.49	5.79	-	-2.46	-7.44	0.12	6.67	-1.18
4B1	-5.60	4.86	-	-2.85	-7.82	-0.19	3.26	-1.49
4B2	-5.68	4.82	-	-2.55	-7.61	-0.35	0.95	-1.65
6A	-3.78	5.33	-	-0.88	-6.00	-0.01	4.07	-1.32
6B1	-3.98	5.92	-	-2.58	-5.55	-0.10	5.49	-1.40
7A	-4.40	5.81	-0.66	-2.78	-5.11	-0.37	-4.83	-1.67
7B1	-1.97	6.31	0.73	-0.90	-5.21	0.01	-0.73	-1.29
8A	0.66	7.49	-	-0.42	-4.49	-0.04	4.54	-1.34
8B1	-0.83	7.47	-1.03	-2.49	-5.17	-0.16	4.34	-1.47
8B2	-1.19	7.45	-0.48	-2.95	-5.18	-0.43	3.25	-1.73
10A	0.78	7.61	-	-0.64	-3.90	0.03	8.56	-1.28
10B1	-0.56	7.60	0.03	-2.40	-4.54	-0.30	3.70	-1.60
10B2	-0.62	7.67	-1.44	-2.47	-4.04	-0.56	3.10	-1.86
11A	-1.27	6.60	-	-0.72	-6.51	0.21	6.87	-1.09
11B1	-0.89	7.28	-2.04	-2.32	-6.42	0.27	5.82	-1.03
12A	-0.01	7.23	-	-0.82	-6.04	-0.26	4.18	-1.56
12B2	-1.39	7.40	-1.30	-3.24	-5.84	0.28	8.19	-1.02
14A	-1.35	6.44	-	-0.33	-5.83	0.40	6.69	-0.90
14B1	-1.76	6.53	-	-1.36	-6.01	0.18	6.89	-1.12
14B2	-1.91	6.52	-	-1.58	-5.66	0.17	6.61	-1.13
14B3	-1.71	6.94	-	-2.48	-5.75	-0.02	5.69	-1.32

3.5 Data quality

Charge balance

According to fundamental principles, a solution is expected to maintain the electrical neutrality of the compounds it dissolves. The total number of positive charges carried by the cations must therefore equal the total number of negative charges carried by the anions (Drever, 1997). The charge balance of a solution is the percentage difference between the sum of the cations and anions (in $mmol_c/l$), and it gives an indication of the quality of the data (Clescerri *et al.* 1998)

$$\%difference = \frac{\sum Cations - \sum anions}{\sum Cations + \sum anions} * \frac{100}{1} \text{-----------------} (8)$$

Charge balance calculations were performed on the 1:5 soil water extract and on the SPE (Table 3.7). Although the percentage difference according to Clescerri *et al.* (1998) should be ± 5%, percentage differences of ± 10% are acceptable for the purpose of this study (M.V. Fey, personal communication). Out of 31 samples analysed from 1-5 water extracts, 45% of the samples analysed had a charge balance within the 5% limit and 12% within the 10% limits. The inaccurate charge balances calculated were those with high EC values. Errors on these analyses may have been exacerbated by extreme dilution required to achieve concentrations within the calibration range of the IC. For the SPE samples analysed by IC, about 74 % of the charge balances are within the 10% limits. Some anions could not be determined (e.g., bicarbonate anions) due to insufficient sample.

The relationship between ECe and sum of major cations and anions content is given in figure 4.6 & 4.7. Strong relationships were found which are important for confident interpretation of electrical conductivity measurements.

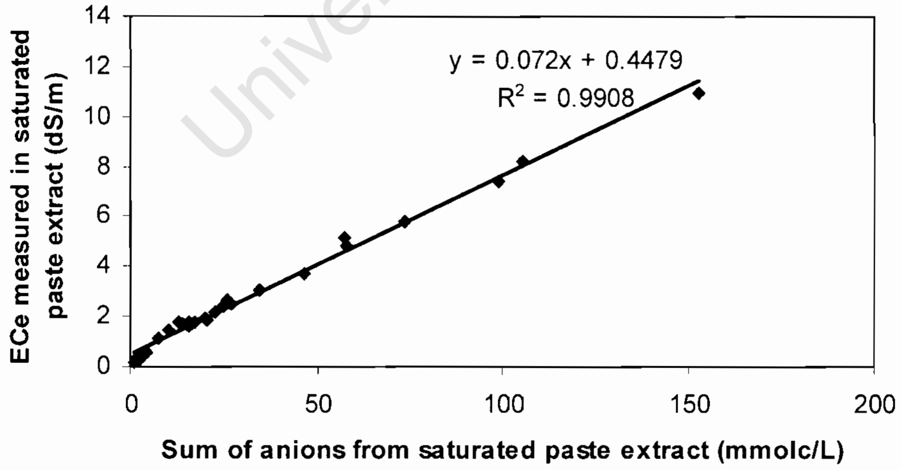

Figure 3.1 Relationship between total anions content from saturated paste extract and EC from saturated paste extract.

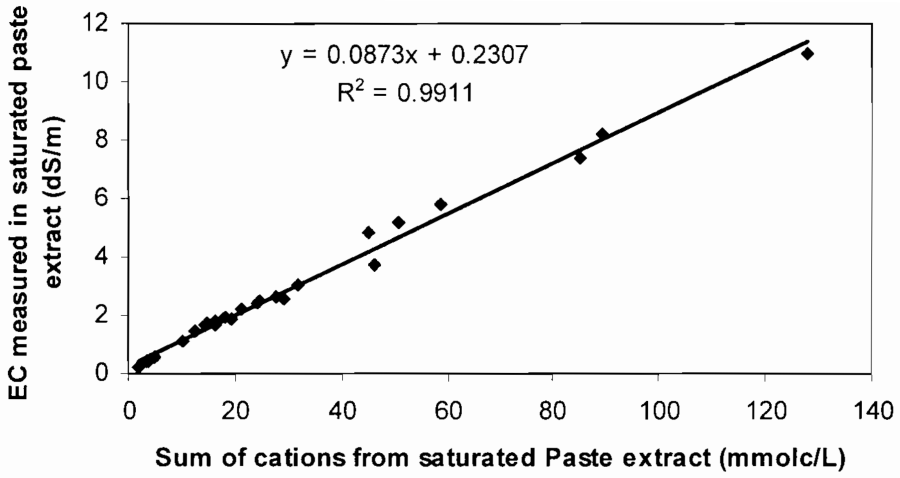

Figure 3.2 Relationship between total cation content from saturated paste extract and EC from saturated paste extracts

Duplicate analyses were performed on pH (H_2O); pH (KCl); EC (1-5 water extract); EC (SPE) and in calcium carbonate determination. These were done to estimate the precision of the analytical methods used in the analyses. These calculations are presented in Table 3.7. Precision is a measure of the random error of a method, often calculated as the percentage of the measurement that encompasses 2 standard deviations from the mean (Ramsey, 2000). An estimate of precision was done by completing duplicate analyses of samples. Percentage estimates of precision and accuracy (bias) are calculated as follows:

$$\mathrm{Pr}\,ecision = \frac{Std}{Mean} \times \frac{100}{1} ----------- (9)$$

where Std is standard deviation

$$Accuracy = \frac{Av.Meas.Conc. - Cert.Value}{Cert.Value} \times \frac{100}{1} -------- (10)$$

where Av.Meas. is average measured value and Cert.Value is certified value.

The systematic error of the ICP-MS was measured and is known as bias. Bias is estimated by calculating the difference between the measured value of a known standard and its reference value, as a percentage of the reference value. A summary of some of the precision and bias of some analytes are presented in Table 3.9.

Table 3.8 Analytical appraisal by charge balance of the saturated paste extract and 1:5 soil:water extract.

Sample	Saturated paste extract (mmolc/L)			1-5 water extract (mmolc/L)		
I.D	Cations	Anions	%difference	Cations	anions	%differnce
2B2	3.39	2.89	7.90	0.37	0.30	11.41
4A	4.78	4.08	7.87	0.52	0.37	17.51
4B1	2.06	1.79	7.01	0.34	0.28	10.11
4B2	2.36	2.54	-3.55	0.45	0.45	0.70
6A	18.10	19.98	-4.94	1.65	1.37	9.18
6B1	14.38	15.41	-3.47	2.62	1.81	18.37
7A	24.59	25.29	-1.40	2.45	2.61	-3.07
7B1	31.92	34.83	-4.37	4.56	3.06	19.68
8A	85.22	98.96	-7.46	9.06	9.35	-1.58
8B1	27.57	25.76	3.40	4.55	5.16	-6.29
8B2	24.35	25.02	-1.36	2.61	4.65	-28.05
10A	127.71	152.86	-8.96	13.82	14.01	-0.68
10B1	50.78	57.56	-6.26	7.56	8.26	-4.43
10B2	89.34	105.66	-8.37	9.90	10.19	-1.43
11A	19.38	20.70	-3.30	1.92	1.99	-1.82
11B1	16.39	13.80	8.57	2.63	3.50	-14.20
12A	29.00	27.21	3.17	2.76	1.98	16.51
12B2	12.59	10.38	9.63	1.44	1.46	-0.43
14A	45.99	46.74	-0.81	5.96	5.29	5.99
14B1	16.20	17.40	-3.58	1.63	1.49	4.57
14B2	21.38	22.81	-3.25	1.51	1.45	2.16
14B3	14.88	15.73	-2.80	0.83	0.97	-7.85

Table 3.9. ICP-MS and Kabonate Bombe data quality

Method (standard)	Analyte	Unit	Precision %	Number Duplicates	Bias %	repeats
ICP-MS (NIST-1640)	Li	µmol/kg	49	31	58.1	3
	B	µmol/kg	55	32	71.9	3
	Al	µmol/kg	57	32	78.1	3
	Si	µmol/kg	11.3	32	-64.7	3
	P	µmol/kg	50.6	17	n.d	
	Cr	µmol/kg	66.6	26	156.2	2
	Mn	µmol/kg	16.6	32	-48.1	3
	Fe	µmol/kg	58.6	23	154.8	1
	Co	µmol/kg	43	31	38.7	3
	Ni	µmol/kg	26	32	-18.8	3
	Cu	µmol/kg	13.6	32	-57.5	2
	Zn	µmol/kg	23.3	32	-27.2	3
	As	µmol/kg	45.3	32	41.6	3
	Se	µmol/kg	34.3	25	37.2	3
	Rb	µmol/kg	11.8	32	-63.1	3
	Sr	µmol/kg	5.1	32	-84.1	3
	Ba	µmol/kg	12.6	32	-60.6	3
	Pb	µmol/kg	32	17	88.2	3
	U	µmol/kg	9.8	32	n.d	4
	$pH_{(H2O)}$		1.5	8		
	$pH_{(KCl)}$		1.7	8		
	$EC_{(1:5)}$	dS/m	5.8	8		
	$EC_{(SPE)}$	dS/m	0.4	8		
Karbonat Bombe	$CaCO_3$	%	1.2	3		

(n.d = not determined)

3.6 Bulk Mineralogy

X-ray diffractometry of bulk samples reveals the presence of quartz, kaolinite, feldspar, calcite and goethite (Table 3.10 with d-spacings in Å units given in parenthesis). The diffractograms of the top and subsoil samples are all very similar, and contain common peaks (Figure 3.9). The scans also showed peaks which were closed to interstratified 2:1 silicate.. Based on the qualitative interpretation of the relative intensities of the peaks, the bulk mineralogy of top and subsoil samples may be described as follows:

Dominant minerals: Quartz

Sub dominant minerals: Kaolinite

Minor minerals: Goethite, hematite and calcite

Table 3.10. Mineralogy of bulk samples

Pit No	Terrain uni	Mineral	d-spacing of characteristic peak in Å)
1	Crest	Quartz (3.34, 4.25, 1.81); Kaolinite (3.56, 7.1, 4.41, 2.23, 1.48); Hematite (2.70); Goethite (4.18).	
2	Crest	Quartz (3.34, 4.25, 1.81); Kaolinite (3.56, 7.1, 4.41, 2.23, 1.48); Hematite (2.70); Goethite (4.18).	
4	Scarp	Quartz (3.34, 4.25, 1.81); Kaolinite (3.56, 7.1, 4.41, 2.23, 1.48); Hematite (2.70); Goethite (4.18).	
6	Midslope	Quartz (3.34, 4.25, 1.81); Kaolinite (3.56, 7.1, 4.41, 2.23, 1.48); Hematite (2.70); Goethite (4.18); calcite(3.03.	
7	Midslope	Quartz (3.34, 4.25, 1.81); Kaolinite (3.56, 7.1, 4.41, 2.23, 1.48); Hematite (2.70); Goethite (4.18); calcite(3.03.	
8	Midslope	Quartz (3.34, 4.25, 1.81); Kaolinite (3.56, 7.1, 4.41, 2.23, 1.48); Hematite (2.70); Goethite (4.18); calcite(3.03.	
10	Midslope	Quartz (3.34, 4.25, 1.81); Kaolinite (3.56, 7.1, 4.41, 2.23, 1.48); Hematite (2.70); Goethite (4.18); calcite(3.03.	
11	Midslope	Quartz (3.34, 4.25, 1.81); Kaolinite (3.56, 7.1, 4.41, 2.23, 1.48); Hematite (2.70); Goethite (4.18); calcite(3.03.	
12	Footslope	Quartz (3.34, 4.25, 1.81); Kaolinite (3.56, 7.1, 4.41, 2.23, 1.48); Hematite (2.70); Goethite (4.18); calcite(3.03.	
14	Valley bott	Quartz (3.34, 4.25, 1.81); Kaolinite (3.56, 7.1, 4.41, 2.23, 1.48); Hematite (2.70); Goethite (4.18); calcite(3.03.	

CHAPTER 4

DISCUSSION

This chapter will include the discussion of soil analyses results with emphasis on the behaviour of major ions down the toposequence and will include an investigation of the relationship of soluble and extractable ions with clay, total carbon and salinity. The agricultural implications of the soil salinity will be mentioned, as well as the mineral saturation indices in the study and the distribution and concentration of potentially harmful trace elements along the toposequence. Finally, a proposed model will be developed to explain salt behaviour in the study and a section on the consequences of salt accumulation will be included.

4.1 Particle size distribution

The results for particle size analysis reveal that the percentage of sand is generally higher in the A and B1 than the B2 horizons (Table 3.2). The results show the order of sand fraction dominance as: Crest > Scarp > Valley bottom > Footslope > Midslope (Figure 4.1 a, b, & c). At the crest, the sand fraction makes up 71.2-84.7% of the soil. The clay and silt fractions dominate the soils in the midslope segment of the toposequence. The crest is underlain by silcretes and alluvium in contrast to the midslope which is underlain by clay rich Malmesbury shales. The increase in proportion of finer earth particles from the top- to the subsoil and, within the subsoil, from the top to the lower segments of the toposequence, may be due to eluviation i.e. the movement of water and fine earth particles vertically into the subsoils. Soil textures from the pits at the top of the toposequence are sandy to loamy sand with single grain and medium crumb structures while the midslope and valley bottom soils have loamy to clay loam soil textures. Soils at the crest therefore have greater permeability and inherently higher hydraulic conductivity compared to the clay-rich midslope, footslope and valley bottom. The high proportion of sand in the B-horizons of nearly all pits (except at the valley bottom) would likely facilitate eluviation in the toposequence.

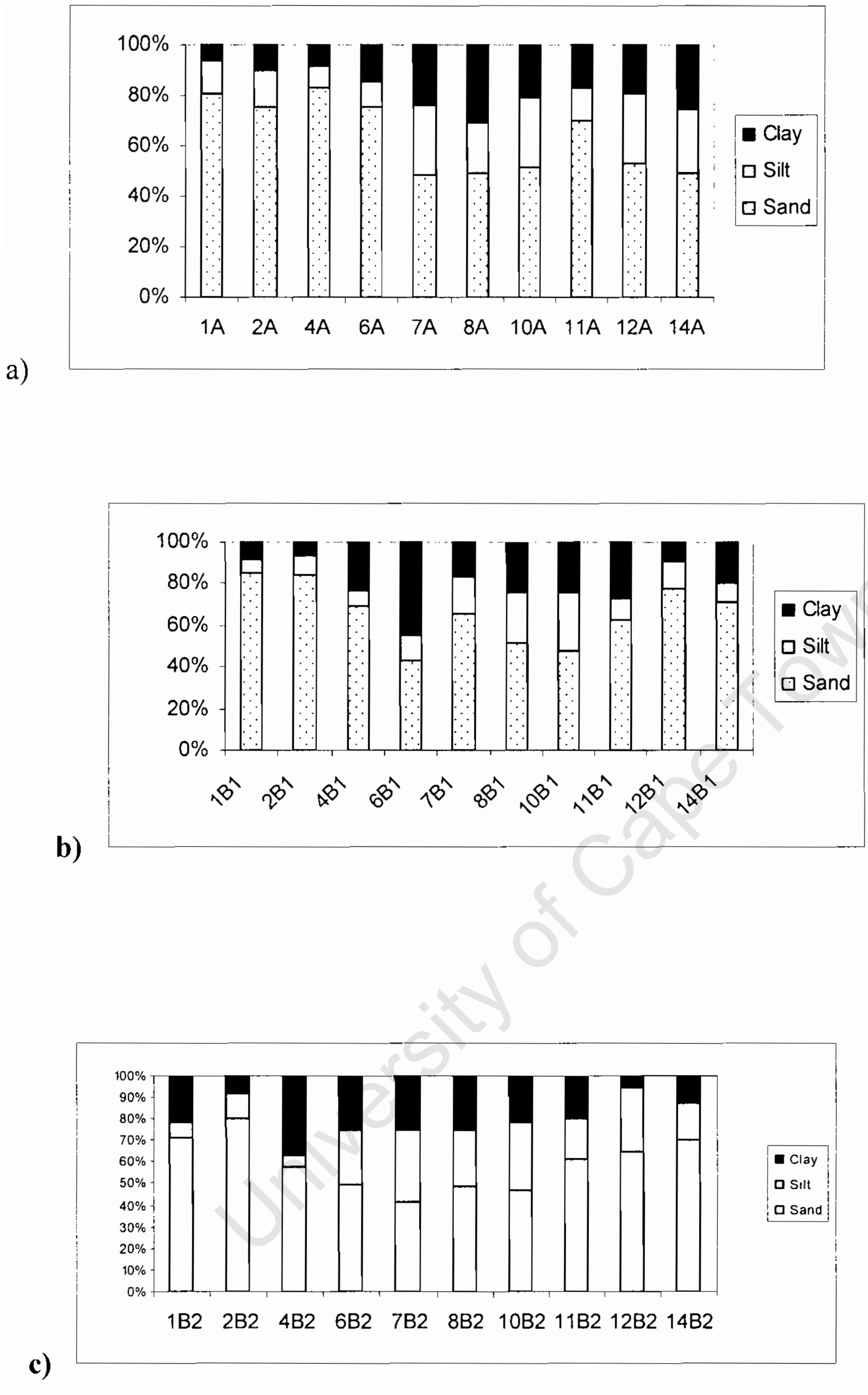

Figure 4.1 Distribution of particle size by depth of soil profile and down the slope a) A-horizon; b) B1- horizon; c) B2-horizon

4.2 pH and extractable acidity

Soil pH (KCl) values indicate some variation in soil acidity along the toposequence. The strong acidity at the top of the toposequence might be due to leaching and possibly due to the type of fertilizer being applied to the vineyards planted at the crest as reflected in the site for pits 1, 2, & 3 (McBride, 1994). It is very likely that the farmer has applied some lime to reduce soil acidity in the vineyards because the acidity % as well as the pH of A- horizons at the crest is higher than the B horizons.

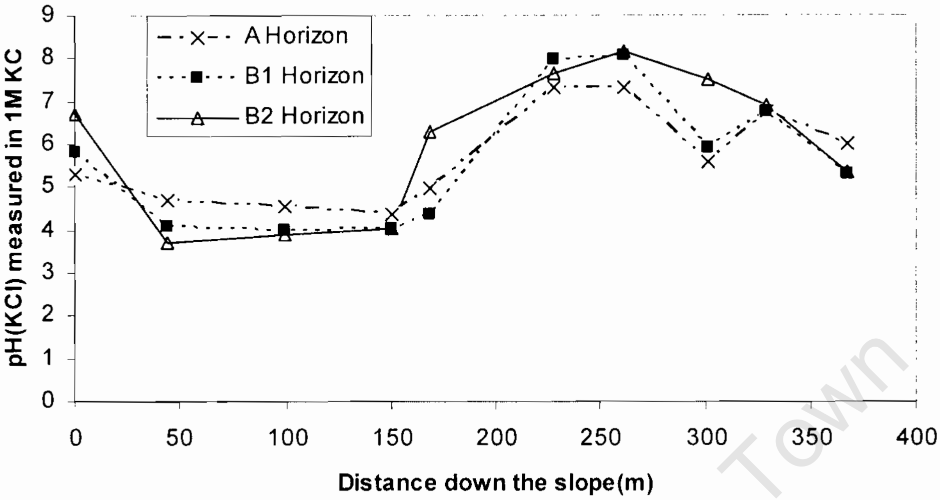

Figure 4.2a Variation of soil pH measured in 1 M KCl in the soil pits and along the toposequence.

The pH of the supernatant of a soil/water mixture is usually 1 to 1.5 units higher than that of soil solution near solid surfaces (Alloway, 1995). The lower pH is because K^+ ions are capable of replacing other cations on exchange surfaces, reducing the activity of H^+ in the supernatant and concentrating the protons in a diffuse layer near the solid surfaces. From this argument, it would be expected that a sample with a higher cation exchange capacity will have a greater ΔpH_{KCl} (where ΔpH refers to the difference between pH_{H2O} and pH_{KCl}) because there are more exchange sites on which the H^+ ions can be replaced by other cations. The relationship between soil pH (KCl) and pH $_{(H2O)}$ in this study gives a good correlation with an average ΔpH_{KCl} of -0.76. (Figure 4.2b)

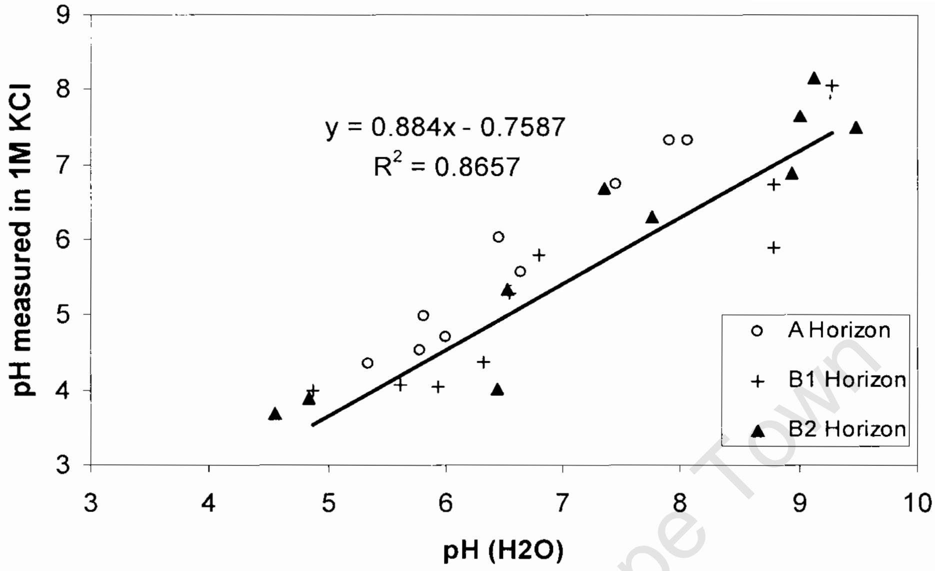

Figure 4.2b Relationship between soil pH (KCl) and Soil pH (H_2O)

Extractable acidity is the acidity associated with the solid phase of soils that can be displaced with a concentrated neutral salt. This acidity indicates the amount of reserve acidity in the soil. It consists of bound H^+ associated with easily dissociating carboxylic acid groups as well as phenolic groups on humus, organically bound Al^{3+}, and H^+ and Al^{3+} occupying cation exchange sites (Sposito, 1989; McBride, 1994). Extractable acidity was determined only in samples with pH (KCl) ≤ 4.5. The values obtained were found to increase with depth, correlating negatively with soil pH measured in 1M KCl (Figure 4.2c). High concentrations of extractable acidity occur in samples 2B2 (24 $mmol_c$/kg) and 4B1 & 4B2 (33 $mmol_c$/kg each) which registered low pH (3.6 - 4.1).

The ratio of extractable acidity to effective cation exchange capacity plotted against soil pH in 1M KCl (Figure 4.2d) agrees with the classical relationship between acid saturation of the exchange sites and the pH (Sposito, 1989). The ratio of extractable acidity to ECEC declines sharply to nearly zero as the pH value increases from 3.9 to 5.2. This particular trend is typical for acid soils.

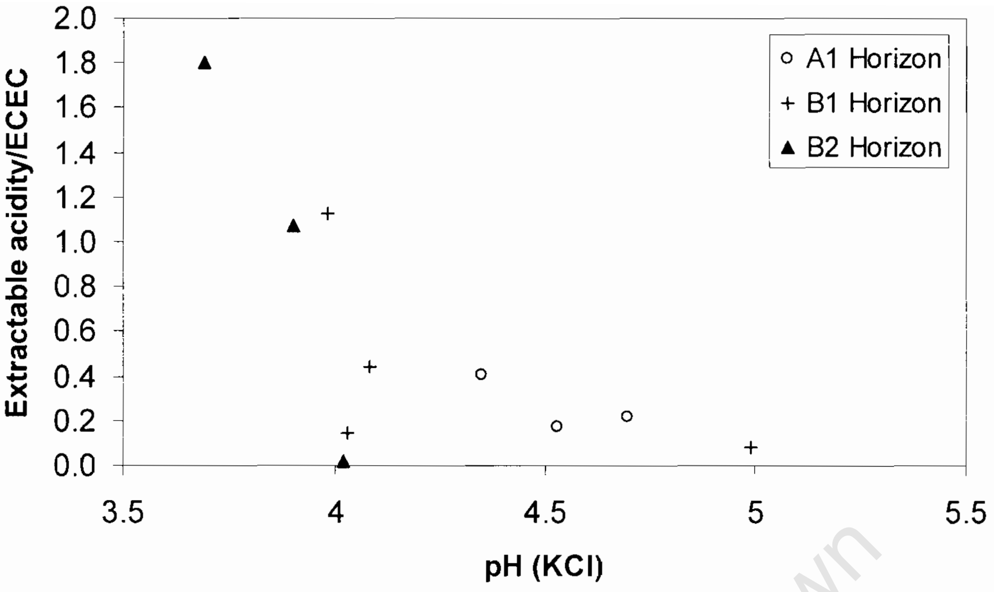

Figure 4. 2c The relationship between the ratio of exchangeable acidity to the ECEC and the pH measured in 1M KCl.

4.3 Major ion behaviour

4.3.1 General observation

Sodium and chloride are the dominant ions in nearly all samples of this study, except in samples 11A, 12A and 14A where Ca^{2+}, Mg^{2+}, SO_4^{2-} dominate. In these pits Ca^{2+} dominates the surface soils compared to Na^+ while SO_4^{2-} dominates Cl^- in the top soils. The mean relative abundance of the major dominant ion concentrations for all samples in the toposequence was calculated and found that Na^+ represents 72% of total soluble cations while Ca^{2+} and Mg^{2+} represent 15 and 10 % respectively. Similarly, Cl^- represents a relative abundance of 65% of all the anions while sulphate represents 31%. The contribution of F^-, $H_2PO_4^-$ and NO_2^- (obtained from SPE) to total concentrations of anions is negligible as most of these ions are below detection limits. F^- is not detectable in the upper and lower parts of the toposequence and tends to accumulate in the middle part coinciding with high clay content (Table 3.3).

The dominance of Na^+ and Cl^- in most samples in this study can be explained by the proximity of the study site to the sea. Related studies have revealed dominance of Na^+ and Cl^- ions in water bodies close to the coast in the Western Cape, while bicarbonates dominate further inland (Silberbauer and King, 1991). Sodium can be contributed from aerial deposition especially as the study site is relatively close to the sea (Scheffer and Schachtschabel, 1989). Ca, Na and K could be released by chemical alteration of K, Ca, and Na feldspars in parent material to kaolinite, (Hamblin and Christiansen, 1995; Tan 1993):

$$4NaAl_3Si_3O_8 + 4H_2CO_3 + 18H_2O \rightarrow 4Na^+ + 4HCO_3^- + 8H_4SiO_4 + Al_4Si_4\,O_{10}(OH)_8 \quad \textbf{(11)}$$

(Na-plagioclase) (Kaolinite)

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow H_4Al_2Si_2O_9 + 4H_4SiO_4 + 2K^+ \quad \textbf{-- (12)}$$

(Orthoclase)

Feldspars minerals and kaolinite are commonly distributed in all the soil pits, especially at the crest where alluvium and silcretes form the main parent material.

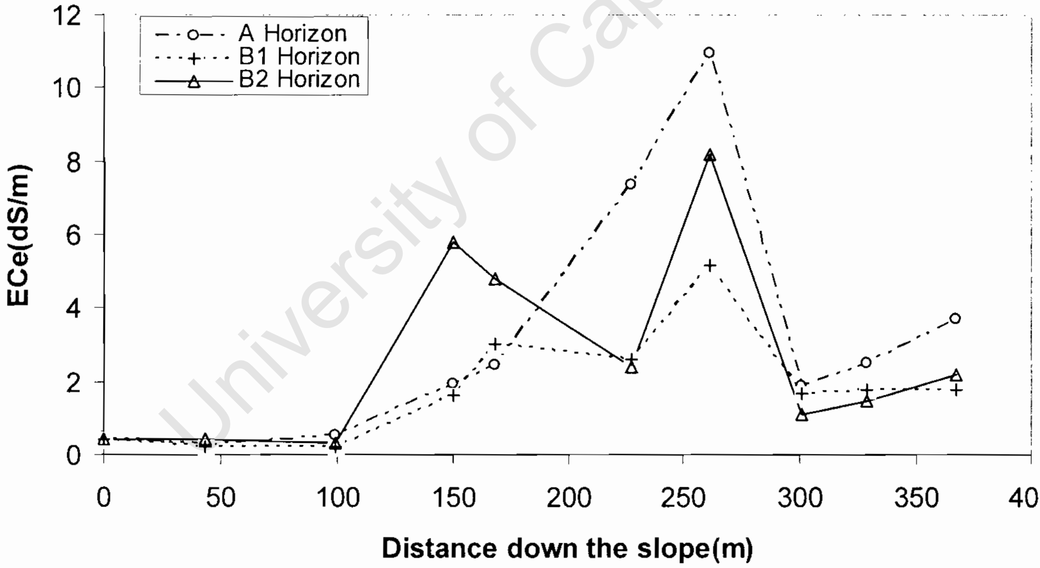

Figure 4.3a Variation of ECe down the toposequence

4.3.2 Behaviour of soluble ions down the toposequence

Soluble ion concentrations were plotted with distance down the slope to illustrate their variation in the toposequence (Figure 4.3 (a – f)). The samples from the upper parts of the toposequence i.e. the crest and scarp have generally low concentrations of cations and anions. The parent materials (silcrete and alluvium) in this segment of the toposequence have a sandy texture and are not enriched in clay compared to the midslope. The subsoils at the top of the slope have generally higher salt concentrations than the topsoils, supporting the hypothesis of leaching. The higher pH in the midslope is associated with higher salt content. Calcite was identified in the sub soils of pits 10 & 11. An increase in pH will cause precipitation of carbonates and generation of H^+ while a decrease in pH will result in dissolution of carbonates and removal of H^+ from solution (McBride, 1994).

Soluble sodium ion concentrations dominate in the midslope where the highest concentration occurs in pit 10 (Figure 4.3a) coinciding with the highest EC and relatively high clay content. Samples from the lower slope have relatively high Na^+ concentrations compared to the crest where average Na^+ concentrations is only 0.44mmol$_c$/L. Soluble Na concentrations decrease with soil depth in the midslope and increase with depth in the footslope and valley bottom. Processes responsible for this behaviour might be high leaching at the crest, evaporation of soil water in the midslope and a combination of evaporation and leaching in the lower slope where groundwater would be closer to the soil surface. At slope breaks especially around pit 8 the water table is closer to the soil surface since that area is less steep compared to locations where pits 4 & 6 are situated. Capillary water then moves from the lower horizons to the A horizons concentrating the salts through evaporation.

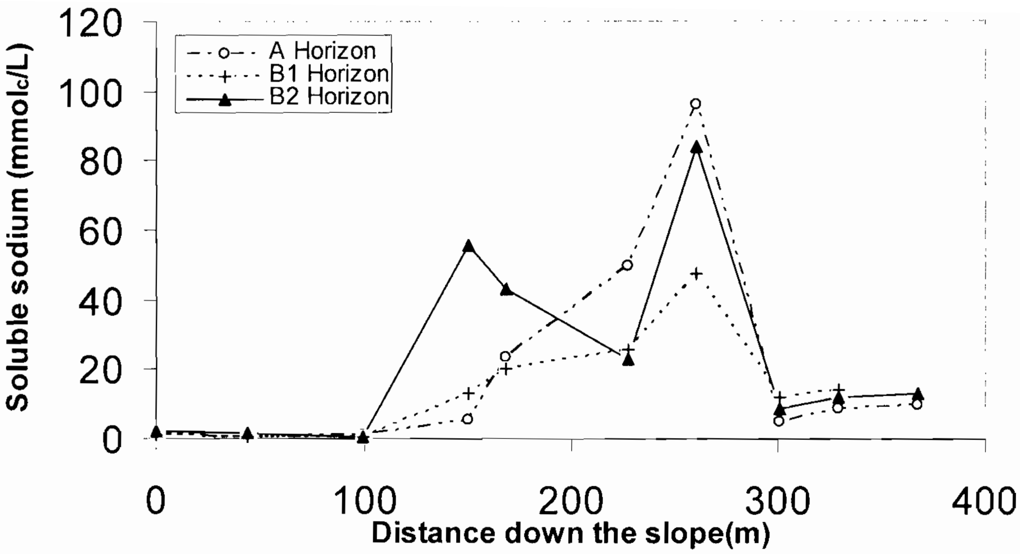

Figure 4.3b Variation of soluble Na in the toposequence

Thin A horizons were common in most profiles around the midslope compared to profiles at the base of the toposequence. This explains why Na concentrated more in the midslope where capillary groundwater moved upwards to concentrate salts on the surface instead of leaching out to the lower horizons and concentrating at the base of the toposequence. The slope gets flatter in the midslope bringing the bedrock closer to the surface thereby impeding leaching. Soluble Mg^{2+} and Ca^{2+} behave similarly to Na^{+} down the toposequence but have much lower concentrations in the sub soils as opposed to the top soil. The likely processes controlling soluble Mg^{2+} and Ca^{2+} are leaching at the top of the slope and concentration of the ions by evaporation at the middle of the slope. Processes at the valley bottom would likely be a combination of both leaching and evaporation since the water table at this point is closer to the soil surface.

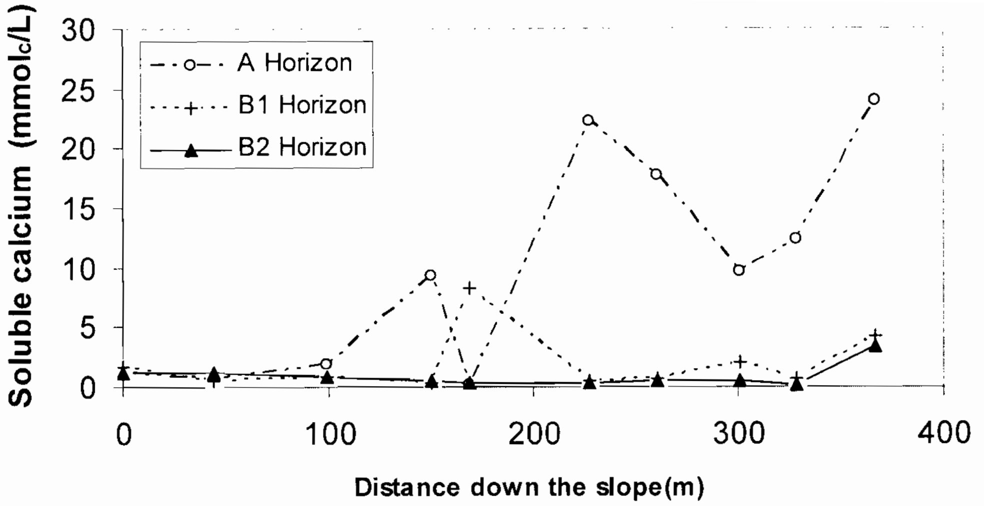

Figure 4.3c Variation of soluble calcium in the toposequence

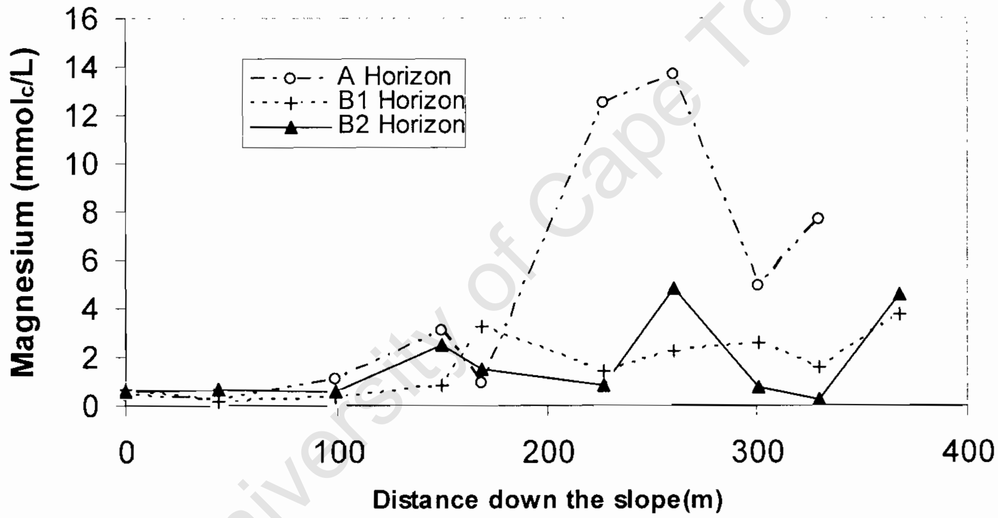

Figure4.3d Variation of soluble magnesium in the toposequence

Soluble potassium has quite a different pattern of distribution compared to the rest of the soluble cations. It has highest concentration at the crest and valley bottom and not in the midslope (Figure 4.3e). K^+ concentration systematically increases with depth of soil with the highest concentration occurring in the pit 14 at the valley bottom and lowest concentrations in sample 6B1. The highest value in 14A coincides with highest total carbon suggesting a relationship of potassium with carbon content. High values in the crest suggest application of inorganic fertilizer or manure to the vineyard.

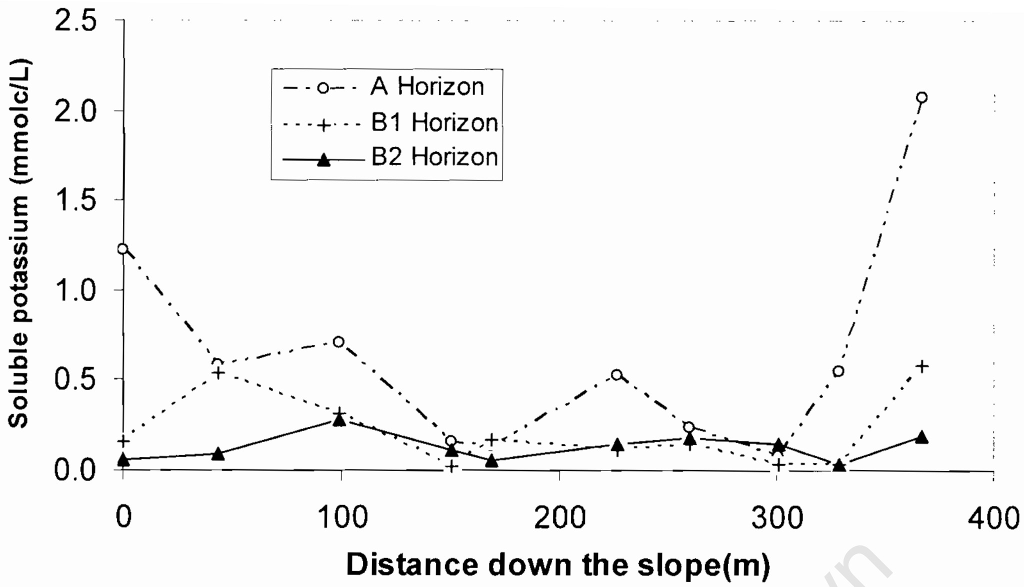

Figure 4.3e Variation of soluble potassium in the toposequence

Soluble chloride in soils may result from mineral weathering but the source of chloride is more commonly atmospheric deposition (Scheffer and Schactschabel, 1989). The highest Cl concentration (45.89-111.13 mmol$_c$/L) occurs in pit 10 in the midslope (Figure 4.3f). This soil profile has relatively high organic matter and clay contents which have the ability to adsorb water that can be evaporated. The highest concentration of soluble Cl$^-$ corresponds to the highest ECe value (10.97dS/m) and Na concentration in sample 10A of this study indicating that Cl$^-$ behaves very similarly to soluble Na.

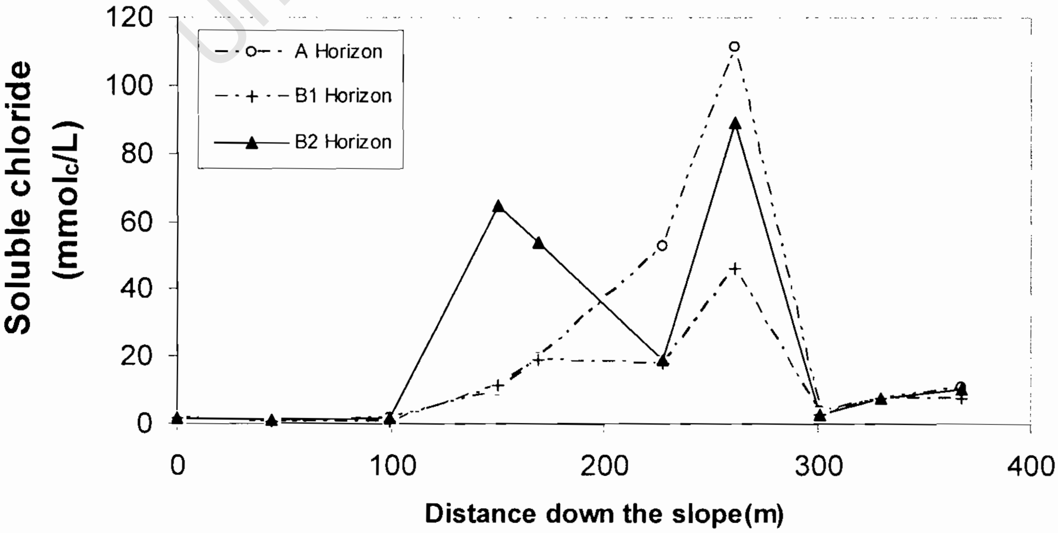

Figure4.3f Variation of soluble chloride in the toposequence

The highest concentration of sulphates occurs in pit 8 at the middle of the toposequence and it is found to be decreasing with soil depth except at the crest where higher concentrations exist in B2 horizon relative to top soil (Figure 4.3 g). SO_4^{2-} behaves similarly to Mg^{2+} and Ca^{2+}

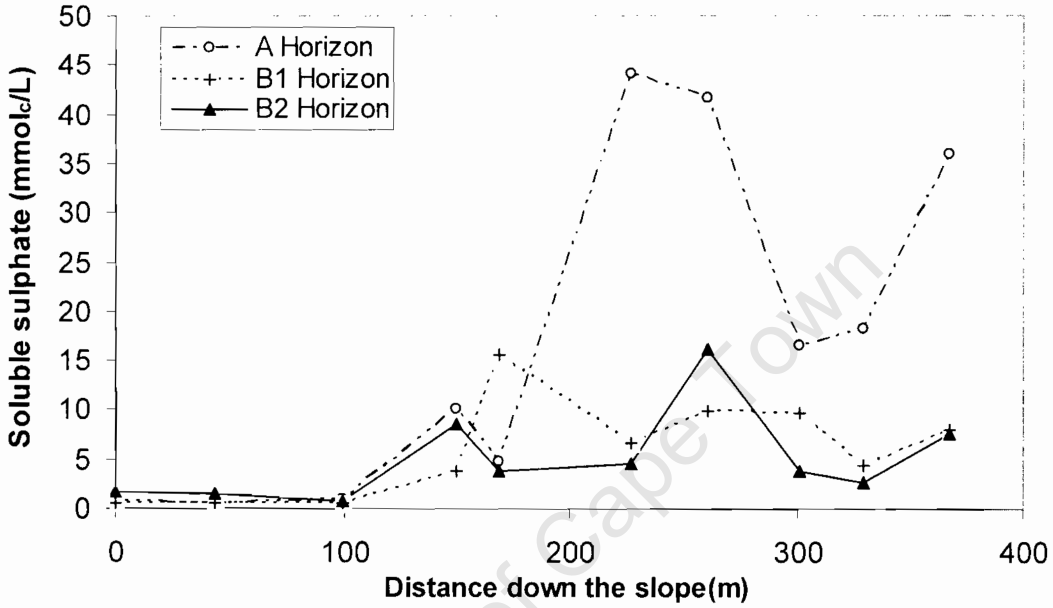

Figure4.3g Variation of soluble sulphate in the toposequence

4.3.3. Relationship of ion concentrations to salinity

A strong correlation between SPE conductivity and Cl concentration (Figure 4.3j) indicates that Cl makes up a major proportion of total dissolved solids. This relationship shows that Cl content in soils increases with increasing EC. A better correlation is observed between the two variables in the subsoils than the top soil suggesting that ions other than Cl dominate in the top soil and have more influence in the EC.

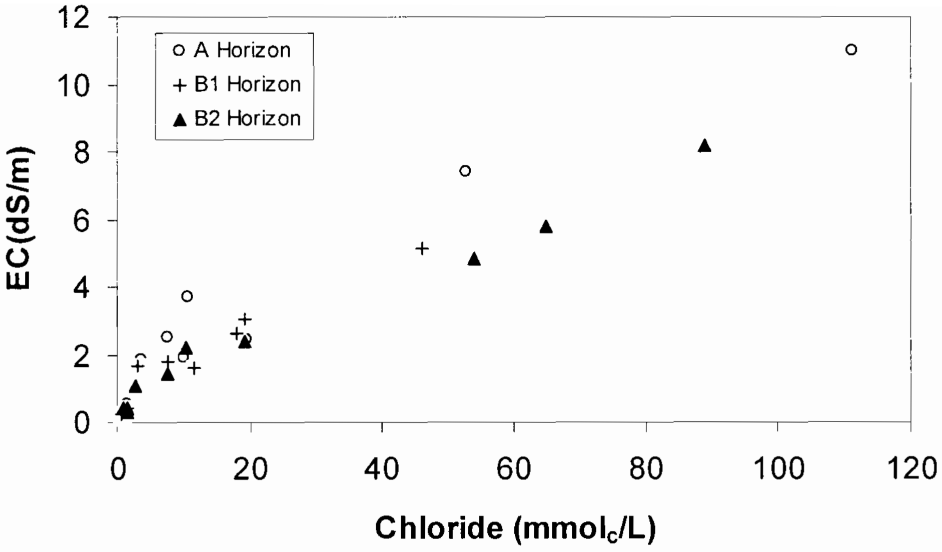

Figure4.3h Variation of $EC_{(SPE)}$ with chloride concentration

In an evaporative environment, all ion concentrations should increase with increasing amount of evaporation until they begin to precipitate, resulting in relatively straight line relationships against a conservative element, in this case Cl^- (Drever, 1997).

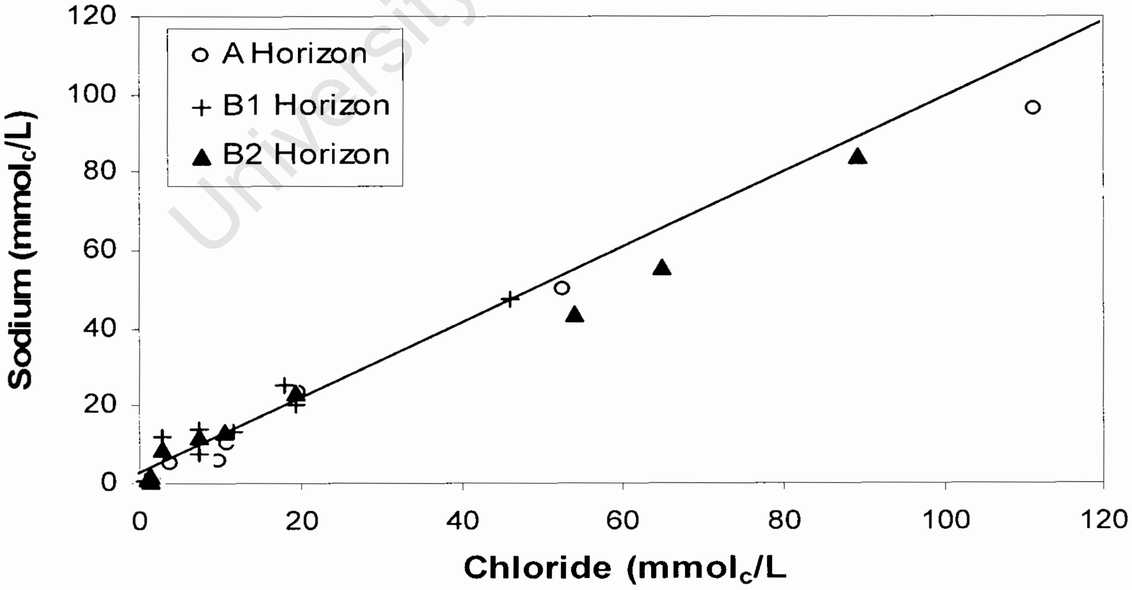

Figure 4.3 i Relationship between Na and Cl.

Na and Cl behave similarly and generate a straight line relationship (Figure 4.3h)

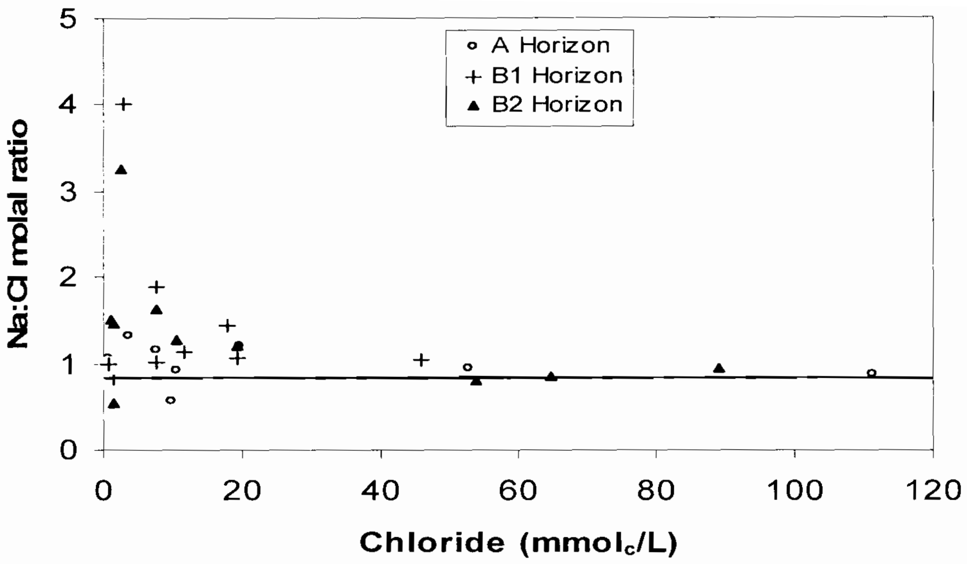

Figure 4.3j Variation of the Na:Cl ratio with increasing salinity. The horizontal line represents the Na:Cl ratio in sea water of 0.86.

The ratio of Na:Cl is 0.86 at high salinities. This is the ratio of Na:Cl in sea water and suggest a sea water source (Figure 4.3i). However, at low salinities, the ratio is variable but generally greater than 0.86 suggesting an additional input of sodium. This could be weathering of feldspars. Only Na and Cl show a linear relationship. For all other ions, the highest concentrations tend to be at lowest Cl^- concentration (Figure 4.3. k, l, and m). General behaviour shows that Mg, Ca and K concentrations are high at low Cl concentrations in the A-horizon but low at high Cl concentration in the B2-horizon. This suggests leaching of Cl from A to accumulate in B2 (except in pit 10 & 11).

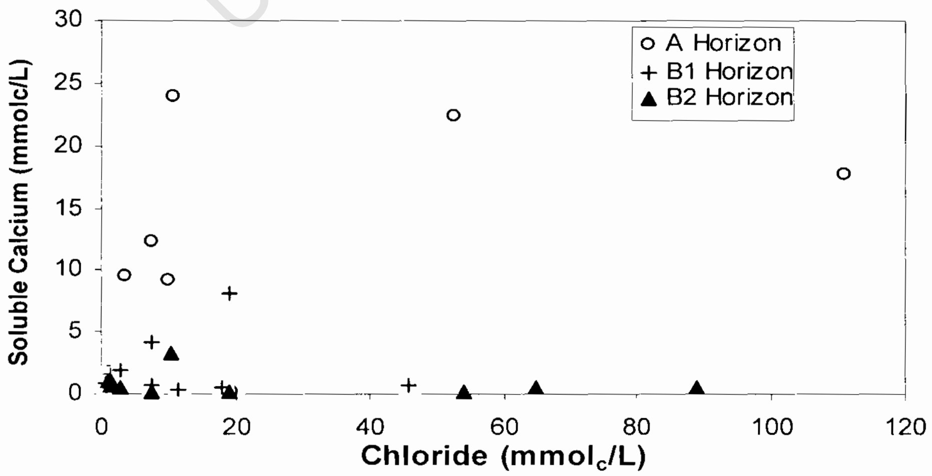

Figure 4.3k Relationship between Calcium and chloride

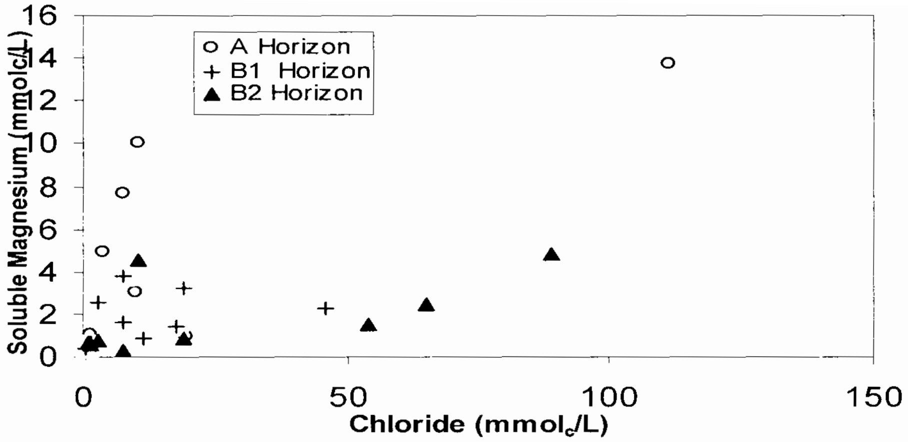

Figure 4.3l Relationship between Magnesium and chloride

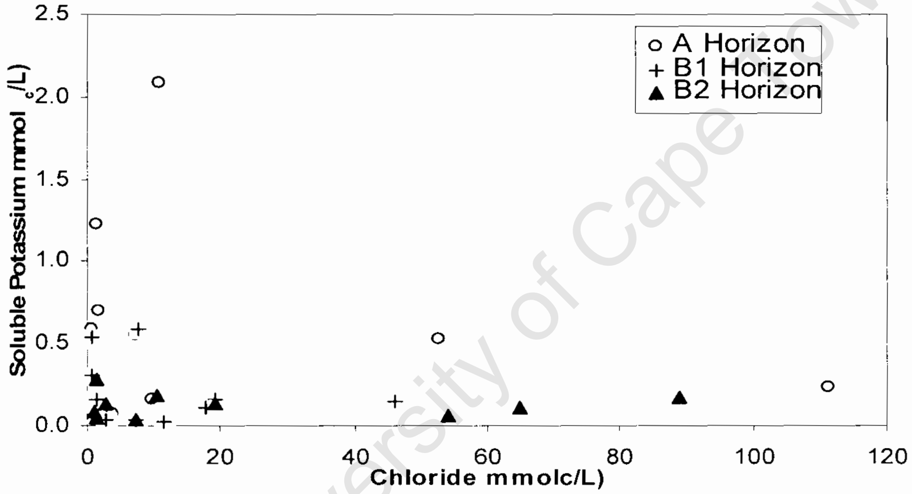

Figure 4.3m Relationship between potassium and chloride

4.3.4 Relationship of soluble ions to clay content

The presence of contour drains in the midslope coupled with the low permeability clay-rich soils is an impediment to drainage. Rain water accumulating in these parts of the toposequence may evaporate or transpire leaving behind salts to accumulate. The groundwater table becomes shallower as one moves down the slope and could be evaporated at the bottom of the toposequence. Evaporation of groundwater often results in increasing salt concentrations observed in the footslope and valley bottom (Conacher, 1975). However, the contour drains created artificially to control soil erosion at this site modify the slope angle and affects this basic rule.

Soluble Ca^{2+}, Mg^{2+} and SO_4^{2-} concentrations are highest in the A- horizon forming a nearly linear relationship with clay content. (Figures 4.3.4 a, b and & e) The high concentration values correspond to high clay content suggesting a preferential adsorption of divalent cations on to clay colloids compared to mono-valent ions such as K^+ & Na^+ (Tan, 1993). Increased concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-} in the A-horizon may also be as a result of soil- water evaporation or residual concentration by leaching of sodium. There is no apparent relationship between clay content and soluble Ca^{2+}, Mg^{2+} and SO_4^{2-} concentrations in the B1 and B2 horizons.

No significant relationship exists between the concentrations of soluble Na^+, Cl^- and K^+ and clay content (Figure 4.3.4d). The outlier identified as sample 14A in the plot of soluble potassium with clay (Figure 4.3.4c) shows the highest potassium concentration corresponding to high clay content. This sample was collected over a relatively small sampling depth compared to samples from all other pits. K^+ appears to be concentrated in this sample suggesting that K is concentrated in the upper parts of the A-horizon.

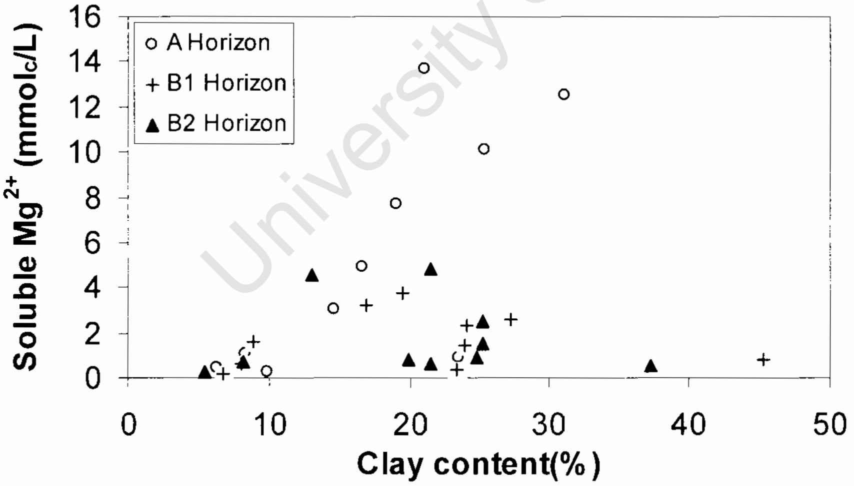

Figure 4.3.4a) Relationship between soluble magnesium and clay content

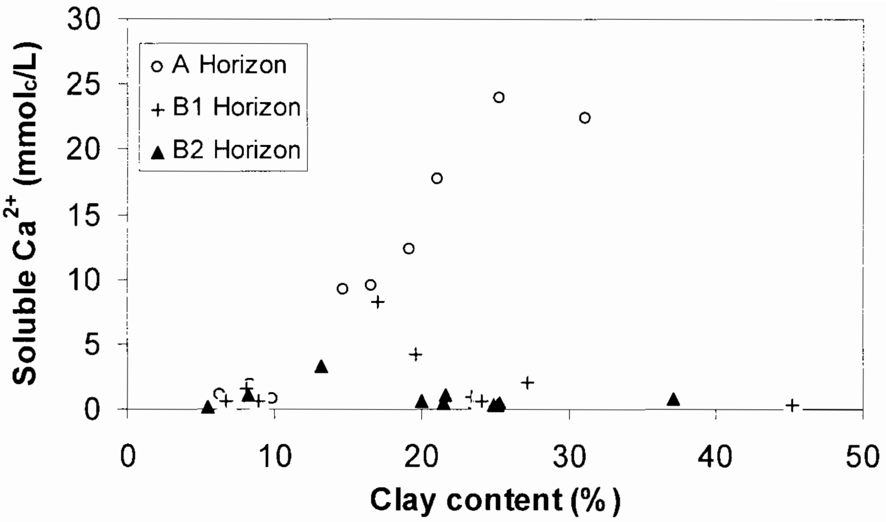

Figure4.3.4b) Relationship between soluble calcium and clay content

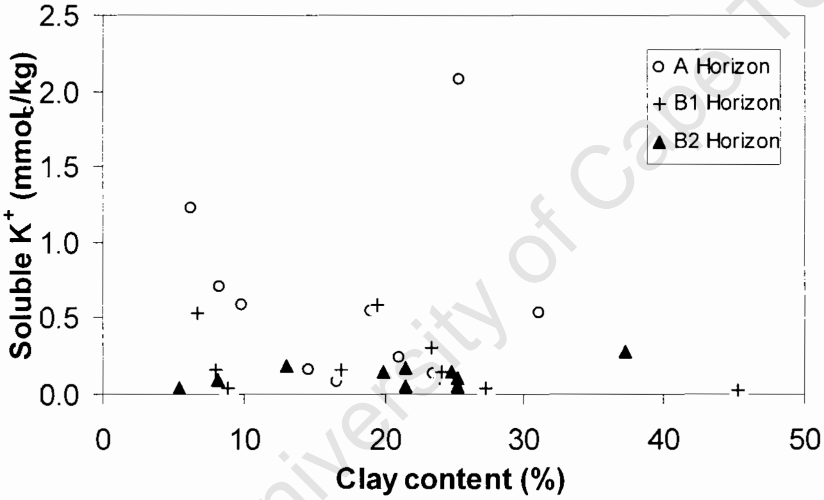

Figure4.3.4c) Relationship between soluble potassium and clay content

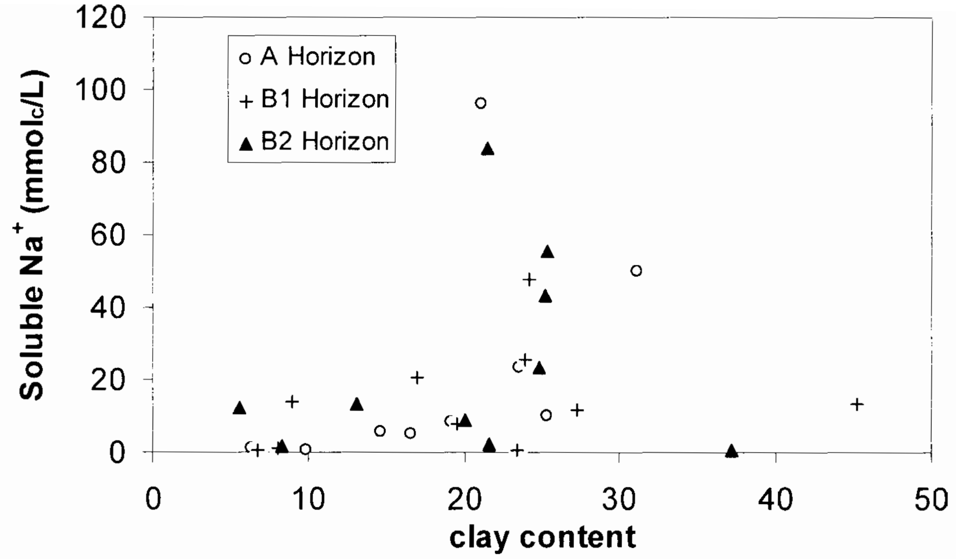

Figure 4.3.4d) Relationship between soluble sodium and clay content

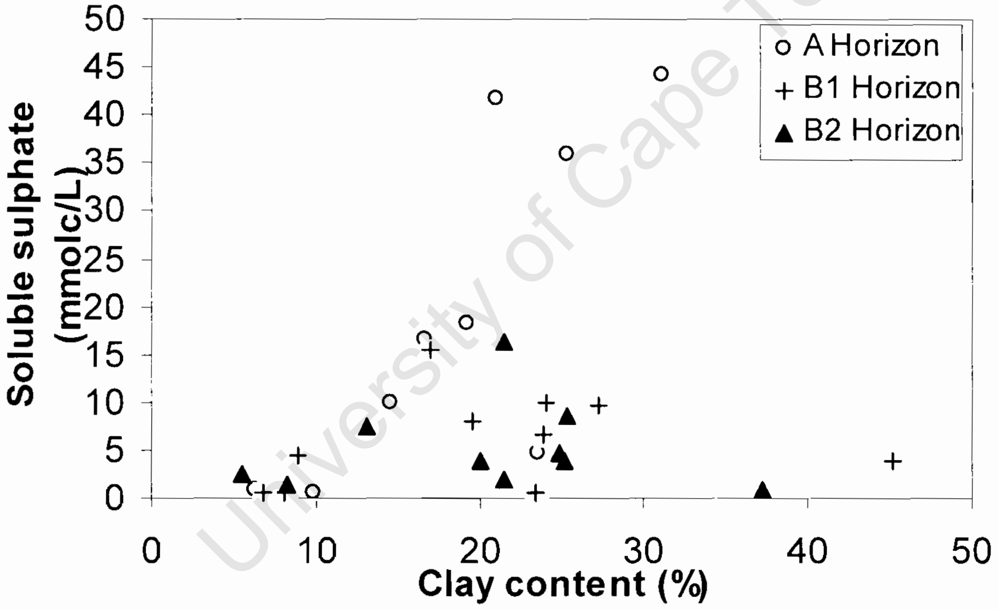

Figure 4.3.4e) Relationship between soluble sulphate and clay content

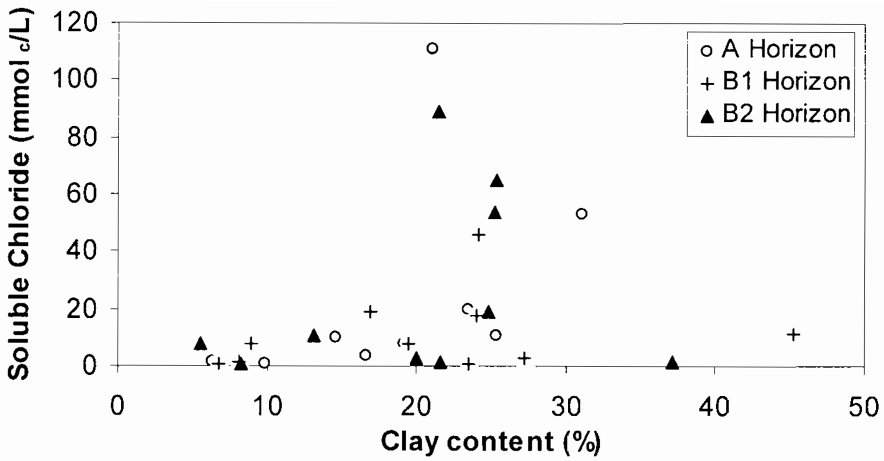

Figure 4.3.4f) Relationship between soluble chloride and clay content

4.3.5 Relationship between of soluble ions and total carbon content

Plotting soluble Mg^{2+}, Ca^{2+} and K^{+} against total carbon makes it clear that these ions are concentrated in the A- horizon compared to the B1 & B2 horizons (Figure 4.3.5 a, b & c). The concentrations of Mg^{2+} and Ca^{2+} are however not strongly related to total carbon content but strongly controlled by clay (McBride, 1994). This suggests that the ions might have been concentrated on the soil surface through evaporation. The subsoils are generally low in soluble ion concentrations at lower clay content.

The highest concentration of soluble Ca corresponds with the highest total carbon concentration, but this is due to the presence of inorganic carbon in the form of calcium carbonate (Figure 4.3.5a). Soluble Mg^{2+} concentration is highest in the A-horizon. No meaningful relationships exist within the sub soils (Figure 4.3.5b).

Soluble K^{+} correlates with total carbon content in the A- horizon where K^{+} increases with increasing total carbon. The highest soluble K^{+} occurs in the valley bottom (sample14A) corresponding to the highest total carbon concentration (Figure 4.3.5c).

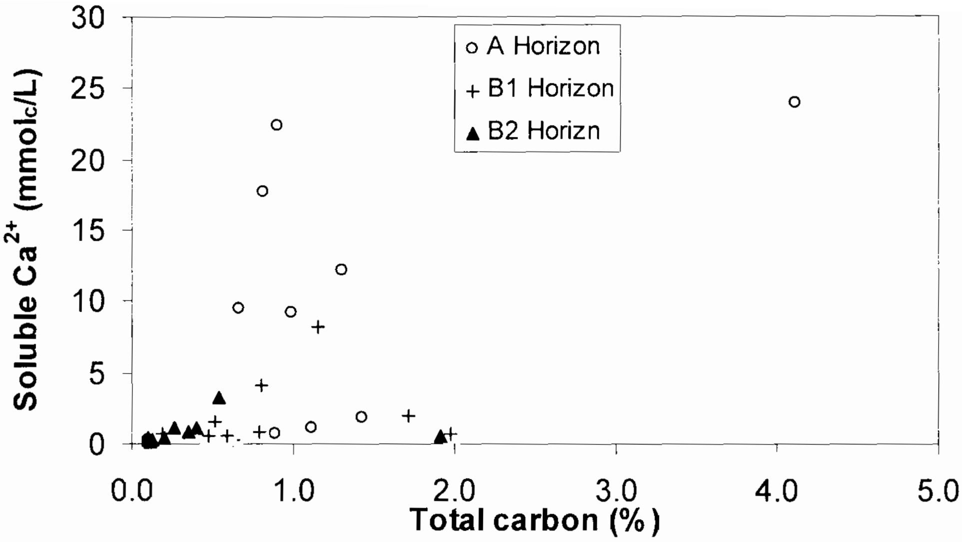

Figure 4.3.5a) Relationship between soluble calcium and total carbon

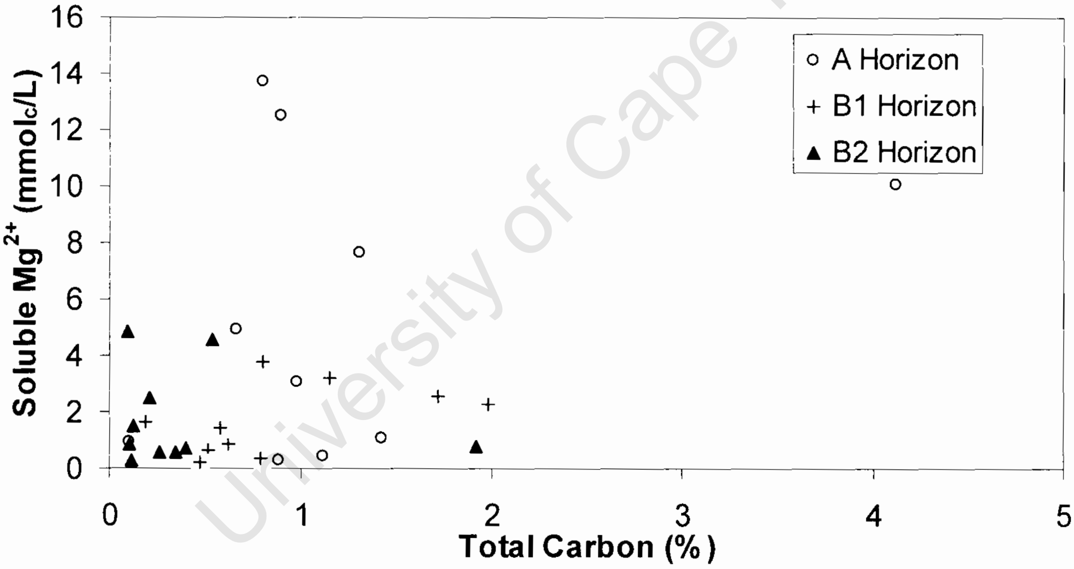

Figure 4.3.5b) Relationship between soluble magnesium and total carbon

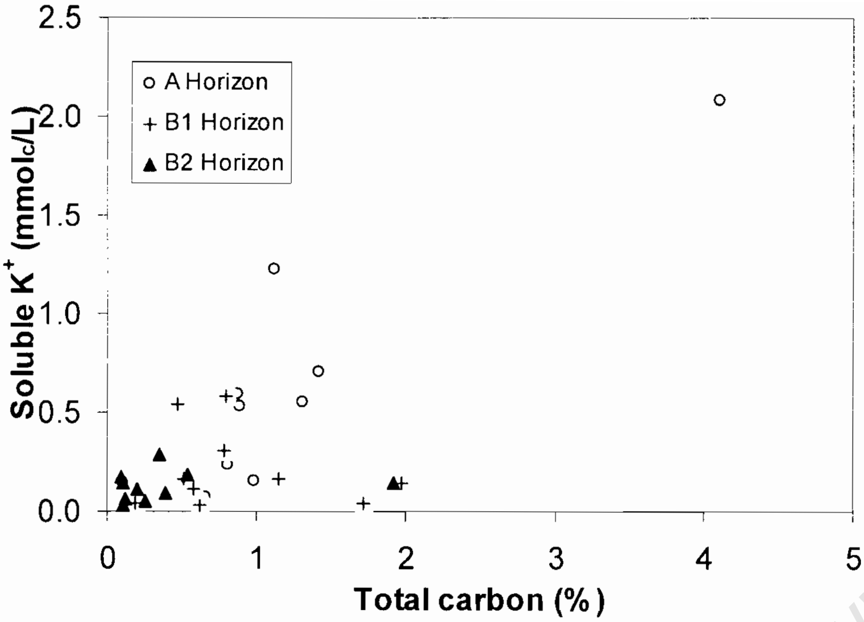

Figure 4.3.5c) Relationship between soluble potassium and total carbon

Soluble Na$^+$ concentrations in the B2 horizon correspond to low total carbon content except in sample 11B2 where calcite precipitates. Leaching must have been responsible for the low soluble Na$^+$ concentration corresponding to the highest total carbon content registered in sample 14A compared to Mg^{2+}, Ca^{2+} and K$^+$ (Figure 4.3.5d).

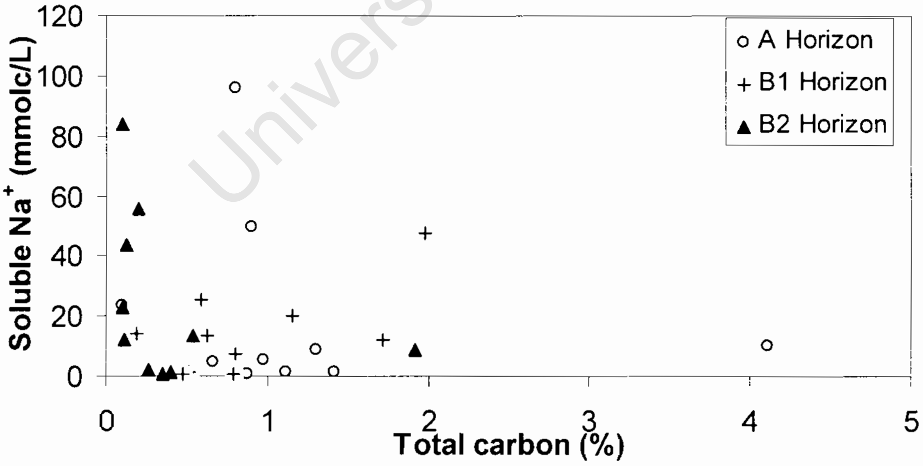

Figure 4.3.5d) Relationship between soluble sodium and total carbon

The relationship of sulphate to total carbon resembles that of Na$^+$ with respect to samples from the B2 horizon. However, a relatively high sulphate concentration in the A- horizon corresponds to the highest total carbon content (Figure 4.3.5e) suggesting some affinity of sulphate for organic matter.

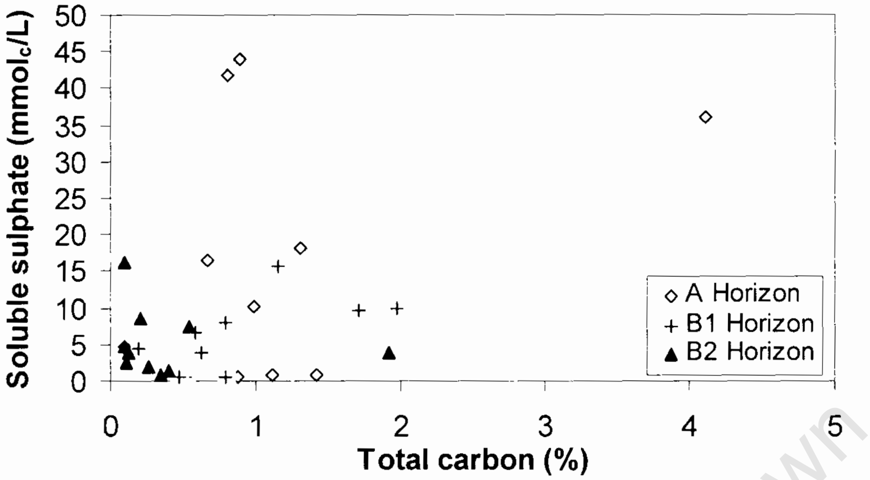

Figure 4.3.5e) Relationship between soluble sulphate and total carbon

The relationship of chloride with total carbon is insignificant for samples from A, B1 and B2 horizons. The samples from the B1 horizon show a weak linear relationship where Cl$^-$ increases slowly with increasing total carbon.

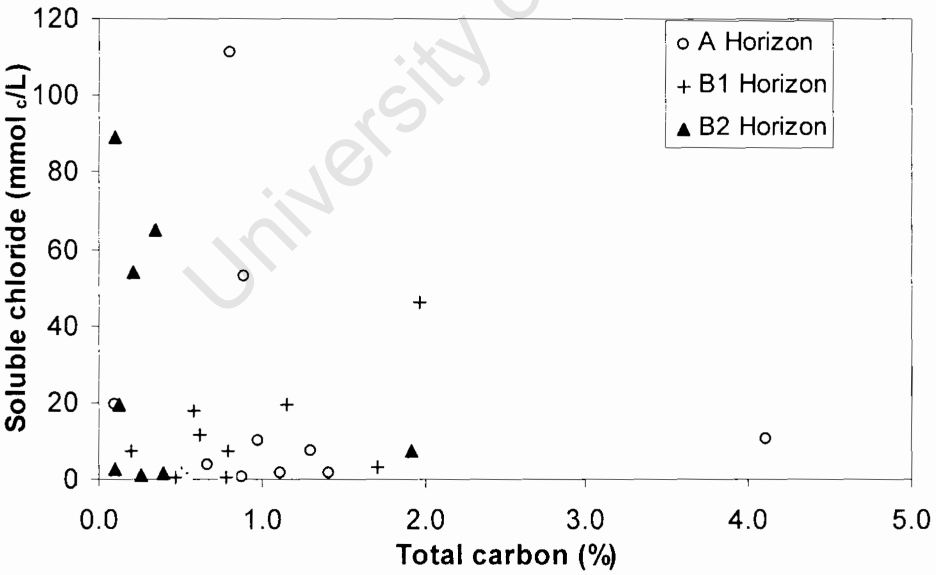

Figure 4.3.5f) Relationship between soluble chloride and total carbon

Summary of major ions behaviour in soil

The correlation matrix in Table4.1 was made from 1:5 soil:water extract and it shows the poor relationship of major ions with organic carbon discussed in section 4.3.5.

Only Ca and Mg showed a weak correlation ($r^2 = 0.66$) with clay content meanwhile Na and Cl has a strong correlation ($r^2 = 0.96$). All major cations except K correlate weakly with SO_4 ($r^2 = 0.65$).

Table 4.1 Correlation matrix between dissolved ions, and other factors

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Clay	0C	Cl	SO_4	HCO_3
Ca^{2+}	1.00								
Mg^{2+}	**0.90**	1.00							
Na^+	0.19	0.28	1.00						
K^+	0.15	0.48	-0.07	1.00					
Clay	0.20	0.20	0.34	-0.08	1.00				
OC	**0.65**	**0.66**	-0.17	0.33	0.03	1.00			
Cl	0.23	0.29	**0.96**	-0.15	0.31	-0.15	1.00		
SO_4	**0.79**	**0.78**	**0.65**	0.08	0.36	0.00	**0.66**	1.00	
HCO_3	-0.04	0.09	0.33	0.03	0.15	-0.08	0.17	0.08	1.00

4.3.6 Extractable ions and their distribution in the toposequence

The plot of extractable Na^+ with distance down the slope (Figure 4.3.6a) reveals high concentrations of Na in the footslope (Pit 12: 41.65 mmol$_c$/kg) and lowest concentrations at the crest and scarp (Pits 1, 2 & 4: 2.24-3.72 mmol$_c$/kg), coinciding with the decreasing pH values observed which reduces the ability of ions to adsorb on to clay surfaces. Extractable Na is made up of both exchangeable and soluble fractions, with the greater proportion probably consisting of the soluble fraction. At 7B1 and 10B2 horizons in the midslope, Na occurs entirely in the soluble form with a <0.1 mmol$_c$/kg in the extractable form suggesting evaporation of salts in these parts of the toposequence. Soluble Na^+ distribution differs from extractable Na^+ distribution in that the highest soluble Na^+ content occurs in pit 10, and relatively lower concentrations found in the valley bottom. This suggests that soluble Na^+ is more leached in the valley bottom and concentrated through soil water evaporation in the midslope. Both the extractable and soluble Na^+ leached at the crest and scarp positions. Extractable Na^+ ion concentrations were found to increase with soil depth between 100-200 m and 300-400 m but between 200 and 300 m they decrease with depth. This again reflects the different zones of leaching and concentration. At the leached zones (i.e. crest & valley bottom) salt concentrations will increase with depth, but in evaporation zones (midslope), salt will concentrate at the surface.

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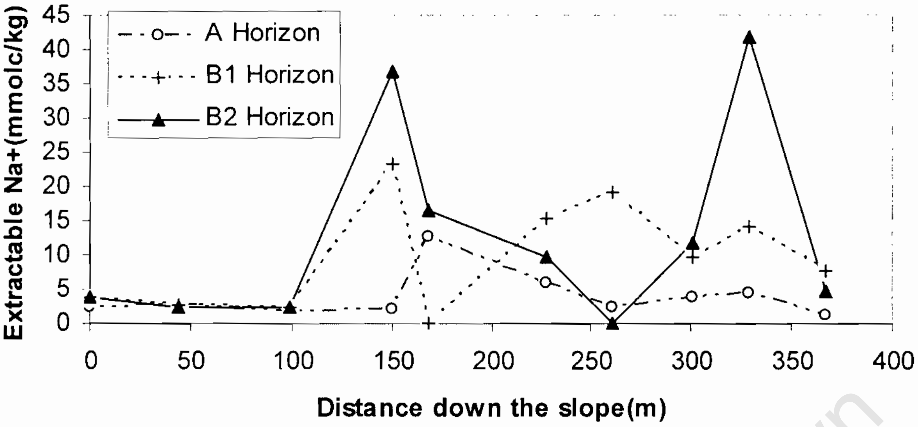

Figure 4.3.6a) Variation of extractable Na^+ in the toposequence

In a plot of extractable Ca versus distance down the slope (Figure 4.3.6b), extractable Ca concentrations are highest at the midslope (161.83 $mmol_c/kg$). The high extractable Ca concentration coincides with the clay rich parent material present in this segment of the toposequence. The low concentration of Ca at the top of the slope is probably due to the lack of source minerals in the alluvial parent material, but low extractable Ca in the upper slope suggests possible leaching of salts. The spike in horizon B2 of pit 11 is anomalous due to the presence of calcite in the sample.

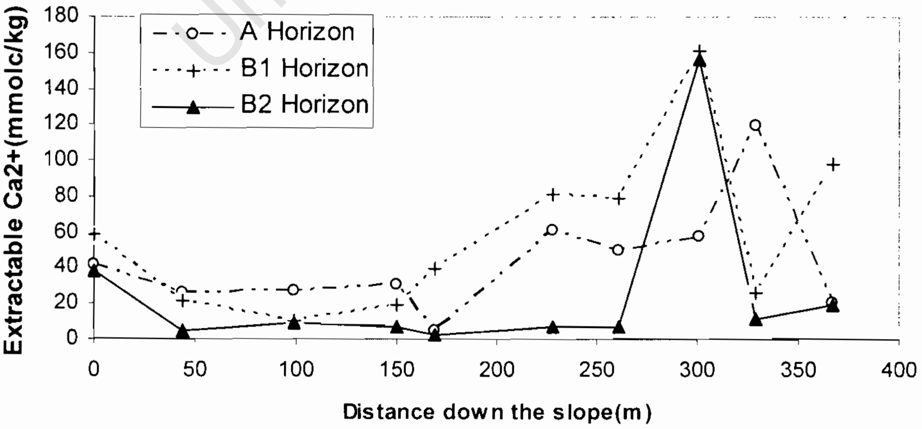

Figure 4.3.6b) Variation of extractable Ca^{2+} in toposequence

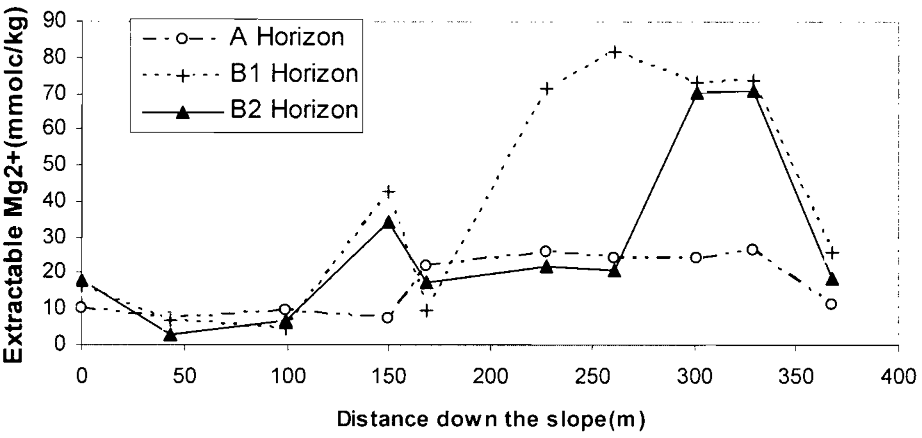

Figure 4.3.6c) Variation of extractable Mg^{2+} in the toposequence

Mg in the SPE is found to accumulate in the midslope along with the clays. The behaviour of Mg^{2+} in the extractable fraction is quite similar to soluble Mg^{2+} except that extractable Mg^{2+} concentrations are relatively higher in pits 11 and 12. In these pits the highest extractable Mg^{2+} concentrations are in the subsoil, as apposed to soluble Mg^{2+} which is highest in the topsoil. This data suggests leaching of soluble Mg^{2+} from the subsoil.

The distribution of extractable K^+ in the toposequence is different from other cations discussed above (Figure 4.3.6d). High concentrations of K^+ occur at the crest (1.41-8.03 $mmol_c$/kg) and at the valley bottom (0.46-9.44 mmolc/kg) with low concentration in the midslope. The K concentrations at the crest may be attributed to agro-chemical inputs (e.g. potassic fertilizers) in the vineyards present on this part of the toposequence.

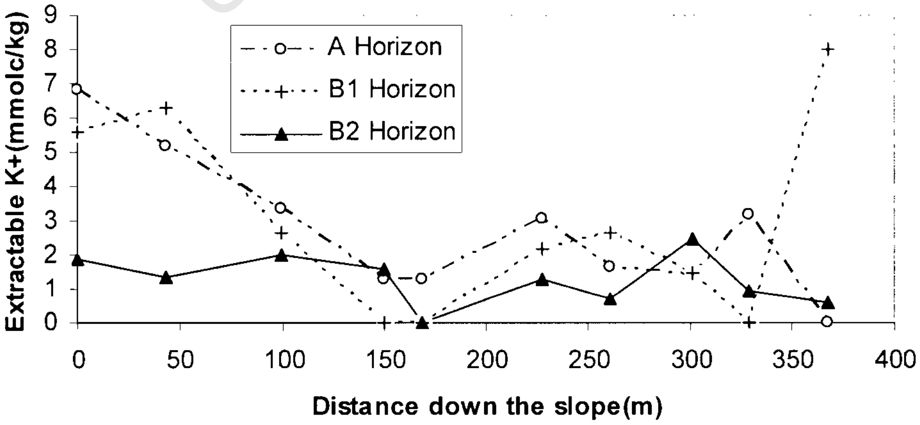

Figure 4.3.6d Variation of extractable K^+ in the toposequence

4.3.7. Relationship between ECEC and total carbon and / or clay content

There is no meaningful relationship between ECEC and clay content as expected (Figure 4.3.7a) perhaps due to the fact that the clay fraction is dominated by kaolinite which has a relatively low CEC (McBride, 1994). On the other hand, ECEC seems to be related to total carbon content as there is an increase in ECEC concentration with increase in carbon content especially with samples from the midslope (Figure 4.3.7b). Sample 14A with the highest carbon concentration is an outlier and cannot be used to assess this relationship. The poor relationship of ECEC with total carbon and clay content could also be explained from the fact that saline soils influence total exchangeable ions the presence of excess soluble salts (Rhoades, 1982).

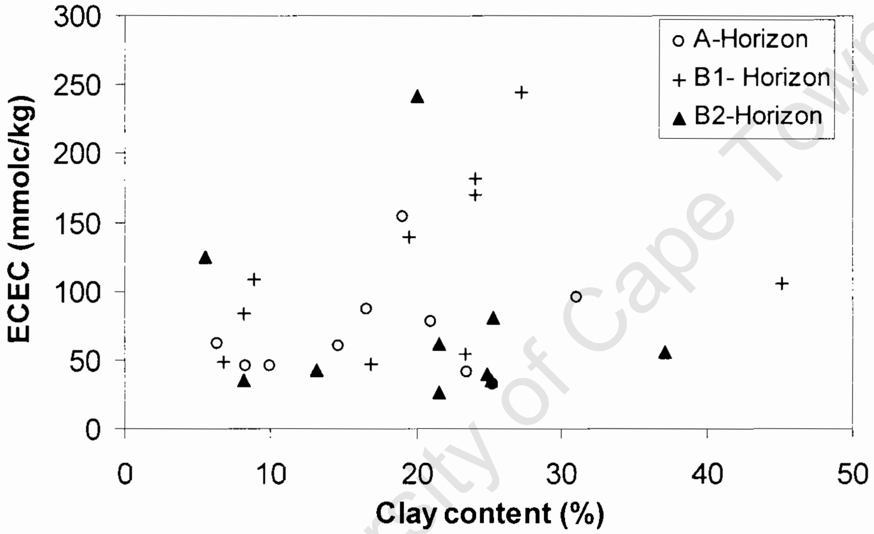

Figure 4.3.7a Relationship between ECEC and Clay content

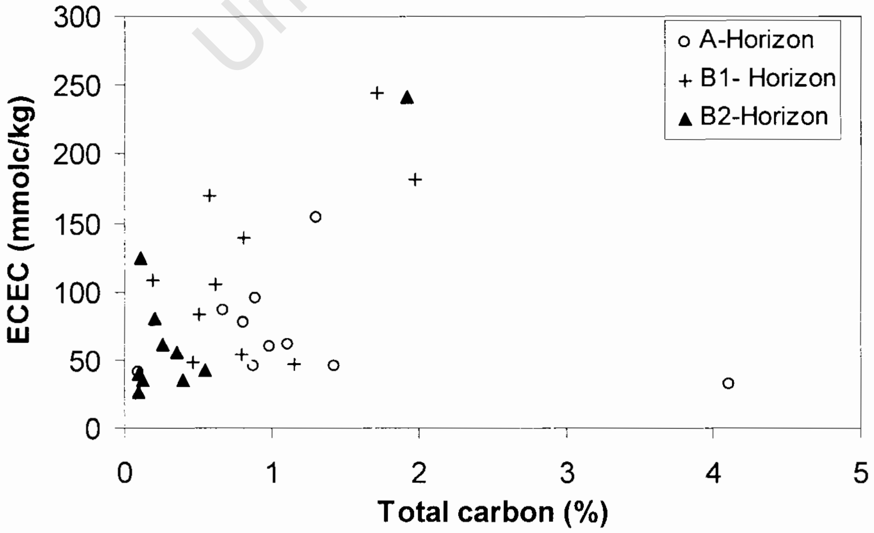

Figure 4.3.7b Relationship between ECEC and Total carbon

4.3.8 Mineral saturation indices.

The mineral saturation index is a useful concept in interpreting soil-water solution geochemistry (Parkhurst and Appelo, 1999). A mineral saturation index (SI) is calculated using the formula

$$SI = \log_{10}\{\frac{IAP}{K_{sp}}\} \text{----------------------------------} \textbf{(13)}$$

where IAP is the ion activity product as defined by the mass action equation, and K_{sp} is the solubility product constant for the mineral.

A mineral saturation index indicates the extent to which mineral dissolution and /or precipitation reactions are likely to influence the composition of a soil-water solution. A positive saturation index indicates that the water will be supersaturated with respect to a particular mineral phase, and therefore, that the mineral could be expected to precipitate out of solution. A saturation index of zero implies that the soil water solution has a composition in equilibrium with a particular mineral phase and that the mineral should neither precipitate nor dissolve in it. A negative saturation index implies that the soil-water is under-saturated with respect to a particular mineral phase and that the mineral will dissolve if brought into contact with water of that composition (Drever, 1997).

The results of Phreeqc modelling indicate that kaolinite, calcite (samples 8A & 10A) and quartz particularly at the valley bottom and at the crest are slightly super saturated with respect to the soil water solution obtained from SPE (Table 3.4). This implies these minerals are likely to precipitate. Calcite, fluorite, gypsum, halite, silica and quartz (particularly in the midslope) were under saturated (Table 3.4) and are likely to dissolve in the soil water solution. In a plot of calcite saturation index with distance down the slope the slope (Figure 4.3.9a), it was found that calcite is supersaturated in the topsoils of two samples (8A & 10A) in the midslope of the toposequence. It is also observed that calcite is mostly under saturated in the subsoils at the crest of the toposequence. The saturation of calcite in pits 10 & 11 coincides with the results obtained during XRD scans and the inorganic carbon found using the karbonat bomb.

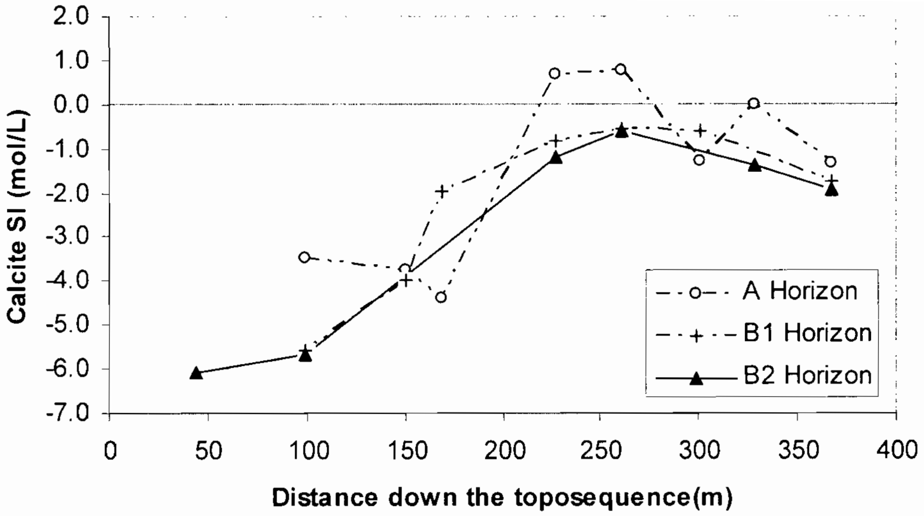

Figure 4.3.8a) Distribution of calcite saturation index in the toposequence

In the relationship between mineral saturation indexes and chloride concentration (Figure 4.3.9d), kaolinite is supersaturated while quartz and calcite are nearly at equilibrium with the solution. Silica, halite, gypsum and fluorite are under saturated. The halite saturation index increases in soil-water solution as the chloride concentration increases (Figure 4.3.9e).

Na and Cl concentrations are likely to be controlled by halite. However, halite saturation has not yet been attained. Calcite is probably the mineral controlling Ca solubility.

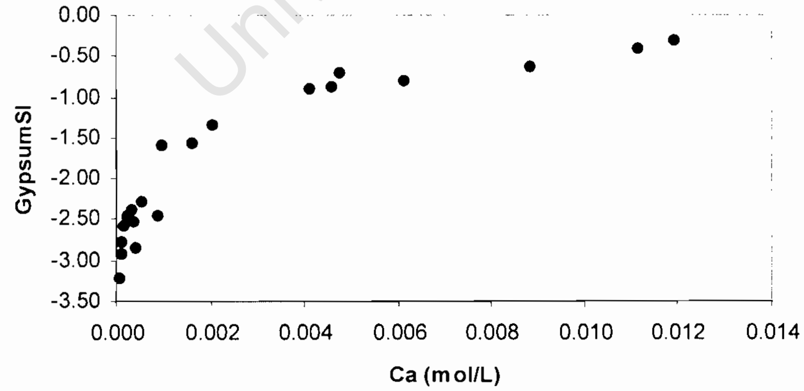

Figure 4.3.8b Relationship between gypsum saturation index and calcium concentration

Gypsum is the least soluble among common sulphate minerals and as such will easily reach saturation, precipitate and control solubility. According to Phreeqc modelling results of SPE in this study (Table3.6), gypsum is much closer to saturation than halite, and may be the mineral observed forming a slight crust on the surface of the soils in parts of the field area. A correlation exists between Ca^{2+} and SO_4^{2-} (Figure 4.3.9c) suggesting gypsum solubility controls Ca and SO_4^{2-} concentrations

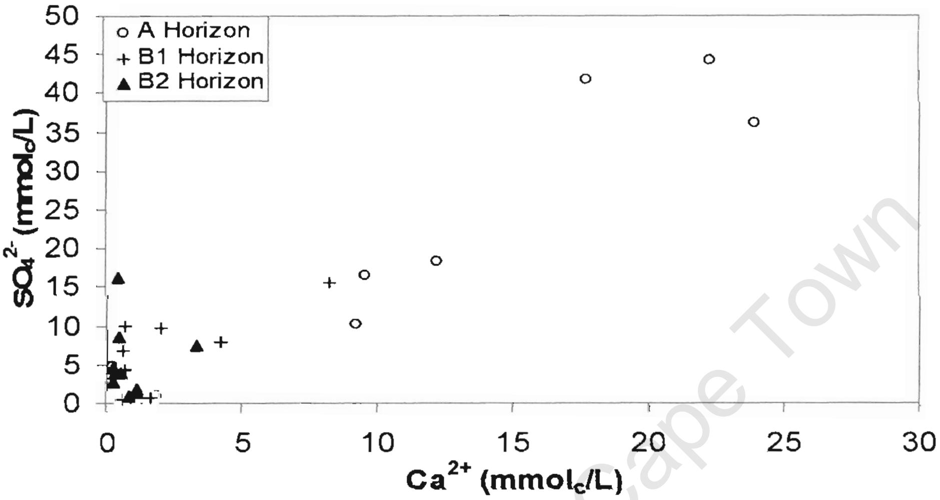

Figure 4.3.8c Relationship between Calcium and sulphate in the saturated paste extracts

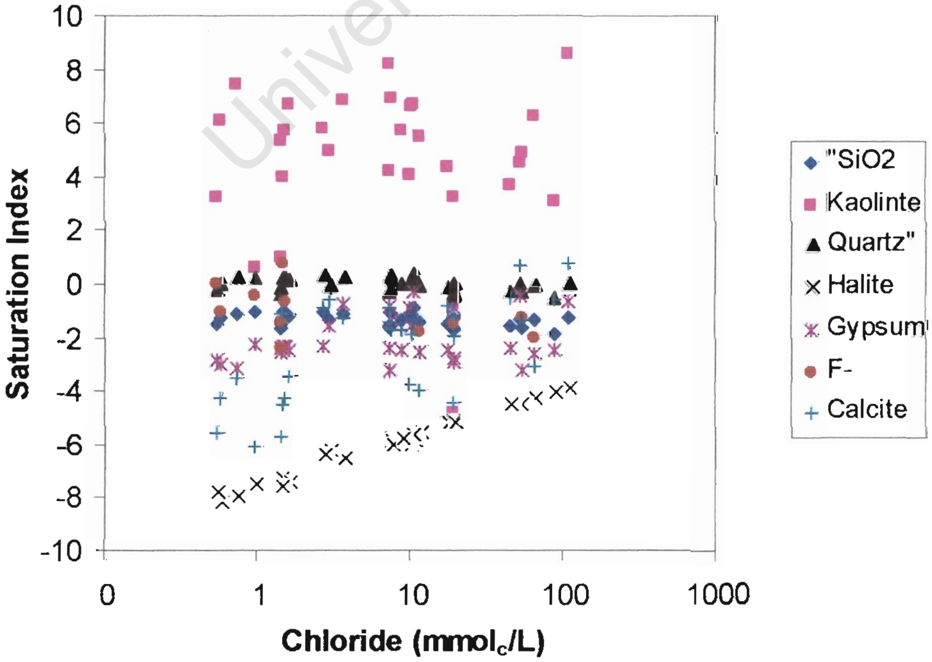

Figure 4.3.8d Relationship between mineral saturation index with chloride concentration

Nearly all samples including the less saline ones appear to be in equilibrium with quartz while kaolinite is supersaturated in all samples except samples 7A & 7B1 which are under saturated (Figure 4.3.8d).

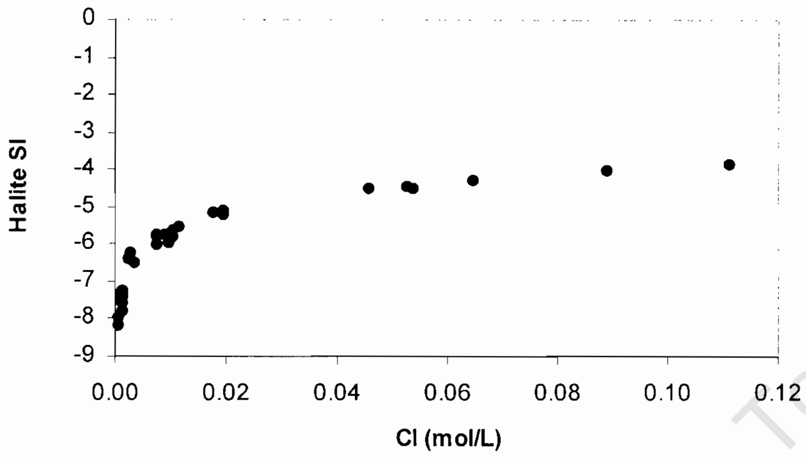

Figure 4.3.8e Relationship between Halite saturation index and chloride concentration

4.3.9 Variation of selected trace elements in the toposequence

Selenium

Selenium is an essential trace element but can be toxic to both plants and humans. It is widely studied because of the narrow range between toxic and sub-optimal concentrations in humans (Davies, 1980). Se occurs in igneous rocks but at higher concentrations in sedimentary rocks such as shales and sandstones (NAS-NRC, 1983). Weathering oxidises insoluble reduced selenides to more soluble selenites and selenates (McBride, 1994). The behaviour of Se in soils is determined by the redox potential of that environment since it exists in numerous oxidation states. Selenate (SeO_4^{2-}) is an inorganic mobile form of Se and is predominant in semi-arid regions while selenite (SeO_3^{2-}) is found in soils of humid regions (Adriano, 1986). Se in most surface soils varies between 0.1 and 2.0 mg/kg (NAS-NRC, 1983, Girling, 1984). Soils contaminated by selenium at a concentration up to 3 mg/kg are said to be polluted (Kelly, 1980). It is likely that most of the Se in this study is incorporated into iron oxide concretions Schloemann (1994) and therefore immobile with no likely toxic implications. The XRD scans showed the presence of haematite and Goethite which have the characteristic deep red and yellowish brown colours respectively in soils. Se occurs in higher concentrations in the midslope (sample 10A: 56.8 ppb in the SPE). This occurrence is associated with the enriched Malmesbury shales at the midslope with moderate to high pH, and corresponds to the high concentrations of other ions in this region. The crest has very low Se concentrations coinciding with the soil acidity that prevails in this part of the toposequence. The concentration of Se in some samples is also found to decrease with soil depth.

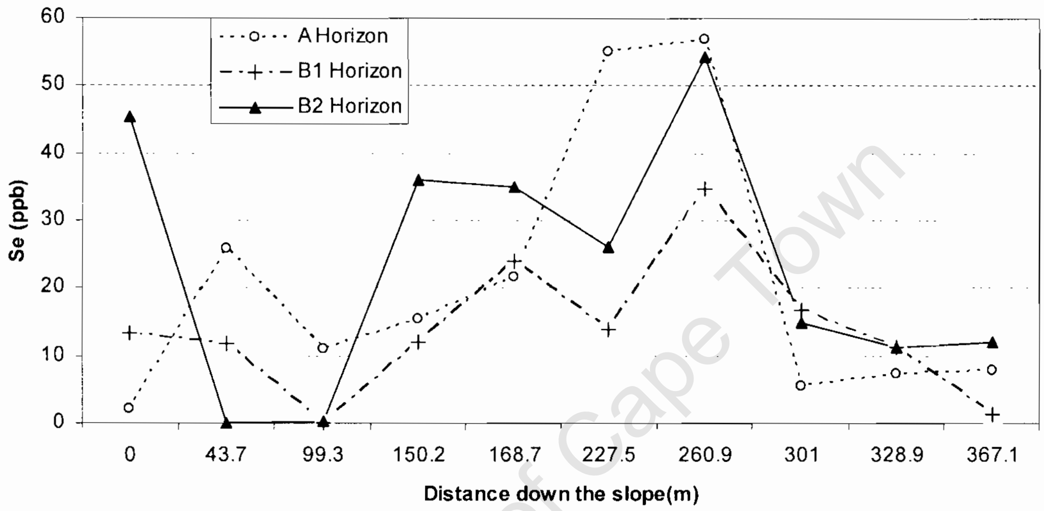

Figure 4.3.9a Variation of selenium concentration in the toposequence

Arsenic

Arsenic is an essential trace element but can be toxic to plants, animals and humans if concentrations in soil and water are too high. Arsenic has an affinity for clay minerals and Fe-oxides adsorbing effectively at pH range between 7 and 9 (McBride, 1994). Soils and sediments analysed in related studies in the same area were enriched in As compared to igneous rocks (Schloemann, 1994). Arsenic exists in reduced (arsenite) and oxidised (arsenate) states depending on the redox potential of the environment In oxidising environments As is virtually immobile. The oxidised arsenate may be transported by movement of iron oxide to which h arsenate is adsorbed. As the particles get into a reducing environment, arsenic is reduced and immobilized (O'Neil, 1995). Arsenic can be concentrated by evaporative concentration which seems to be a most likely mechanism for increasing As concentrations with increasing salinity. The highest concentration of As was found at the midslope of the toposequence (sample 10A: 21.0 ppb) and the lowest concentrations at the top and lower sections of the toposequence (Figure 4.3.9b). This trend coincides with the lower pH and clay content at the crest and valley bottom resulting in As being adsorbed to clay and iron oxides, and reducing their mobility in soils. Arsenic is unlikely to be toxic in these soils considering that the highest concentration registered in the soils of this study is below the 50ppm concentration considered to have toxic implications (Kelly, 1980).

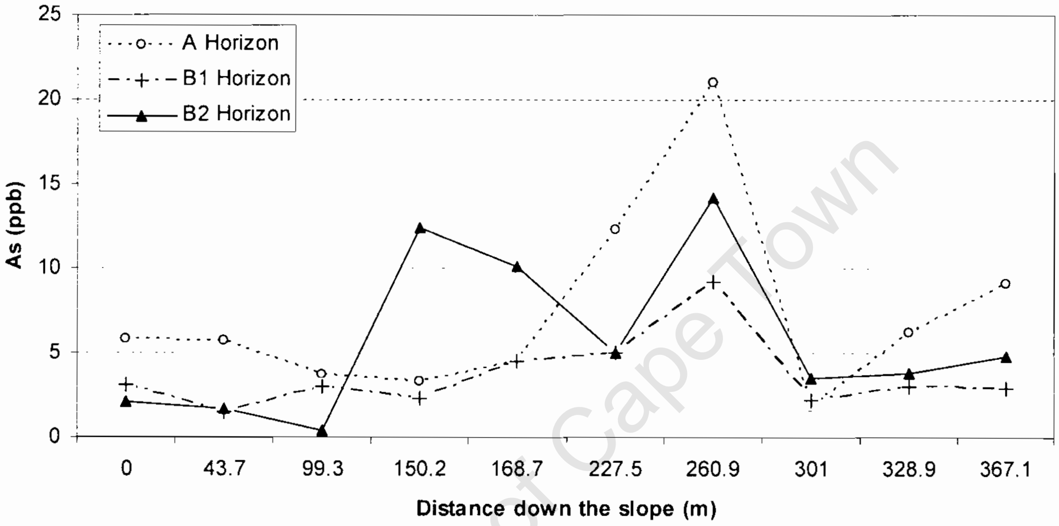

Figure 4.3.9b Variation of arsenic concentration in the toposequence

Boron

Boron results from weathering of boron - containing minerals such as tourmaline (Richards, 1954). It occurs in soils co-precipitated in secondary metal oxides, clay minerals and mica. Soluble borate salts are found in alkaline soils in arid regions where B toxicities are common (McBride, 1994). According to McBride, (1994), boron is effectively adsorbed on to oxides and silicate minerals at pH 8 to 9 range with its availability generally reduced in coarse-textured, calcareous and acid-leached soils. The B concentration in this study is highest (1322.2-1349 ppb) in the midslope with pH $_{(KCl)}$ of 7 to 8 range (Figure 4.3.9c). Boron adsorption in the midslope coincides with the high clay content in this segment of the toposequence compared to the top and lower part of the toposequence where much of the B has been leached out of the soils.

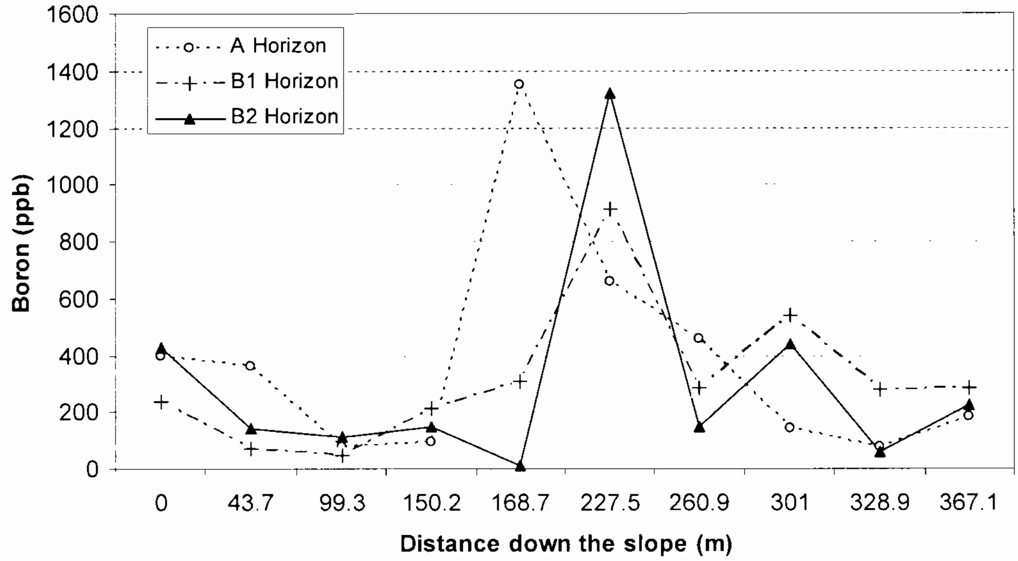

Figure 4.3.9c Variation of boron concentration in the toposequence

Silicon

The distribution of silicon in the toposequence was quite different in that silicon was found concentrated more at the valley bottom and crest. Si concentrations decrease down the soil profile. The distribution of silicon could be linked to the silcrete and alluvium parent material at the crest and valley bottoms which are likely to be responsible for the observed higher quartz concentrations.

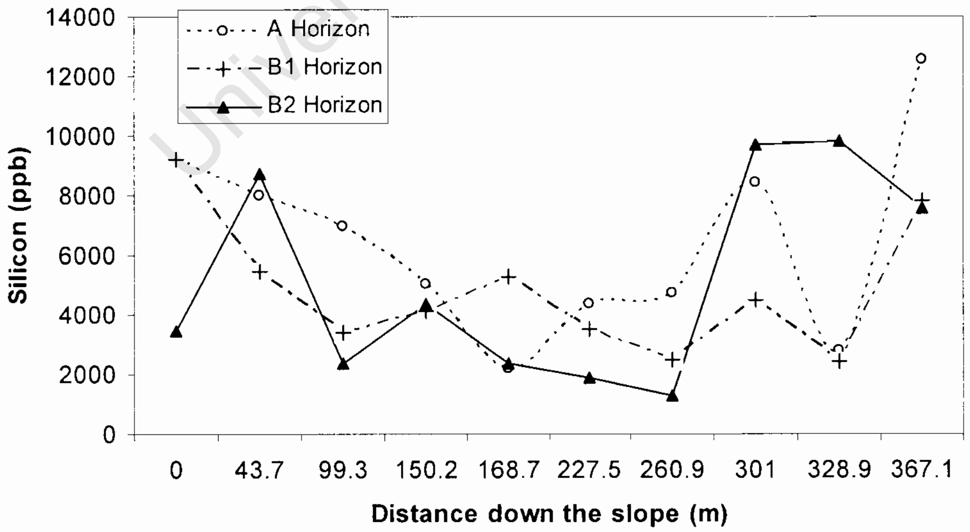

Figure 4.3.9d) Variation of silicon concentration in the toposequence

4.3.10 Proposed model of salt behaviour in this study

Processes occurring in the toposequence and responsible for transport of salts are leaching, resulting in low concentrations of base cations and high acidity, while concentration, results in high concentrations of soluble salts, base cation saturation, calcite precipitation and higher pH. The process of leaching starts by the removal of the most soluble and mobile ions e.g. Na, Cl, followed by the base cations e.g. Ca, Mg, K, leaving behind acidity and immobile ions like Fe, Al and Si. A slightly leached soil may well have Mg and/or Ca in excess of Na and SO_4 in excess of Cl as it is seen in samples 11A, 12A, and 14A. Continued leaching of Mg, Ca and SO_4 (i.e. the soluble fractions) will result in lower overall ion concentrations, but will still have high ECEC and perhaps slightly lower pH than before e.g. 11B1, 12B1, and 14B1. Finally the base cations and alkalinity begin to leach leading to significantly lowered pH and the appearance of extractable acidity e.g. profiles 2, 4 and 6.

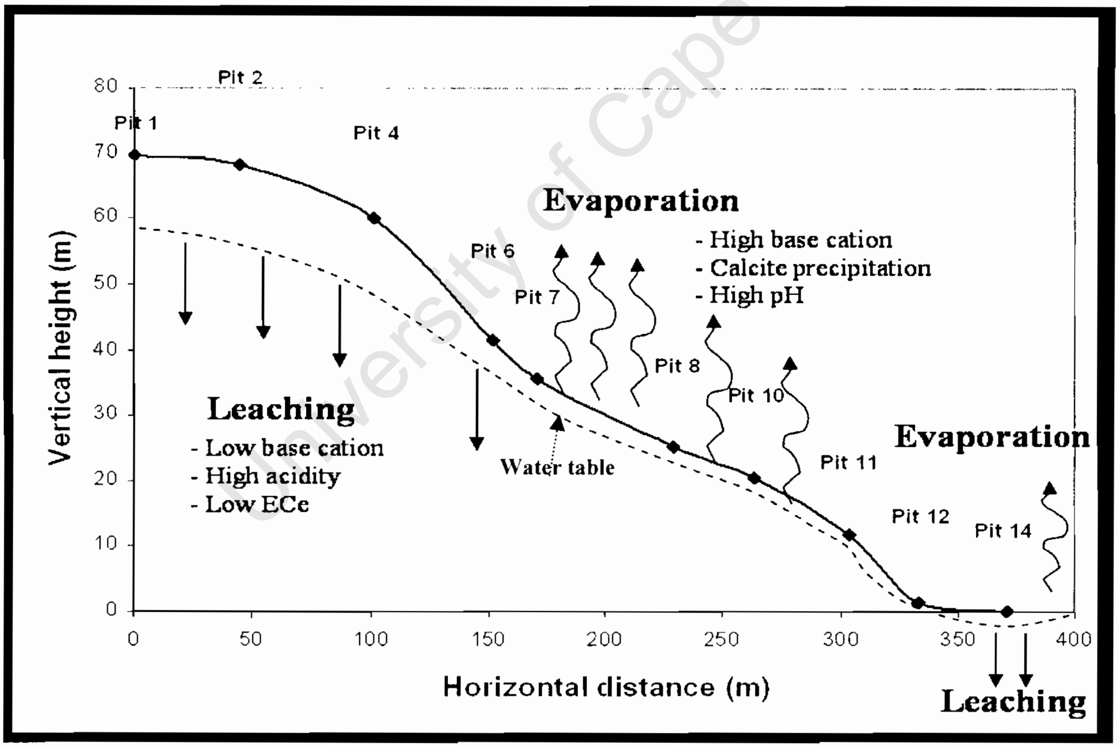

Figure 4.3.10 Simplified profile diagram to illustrate processes influencing salt distribution in the toposequence

The process of concentration starts with the available ions and concentrates them in solution until they begin to precipitate. Sodium is easily leached into groundwater and would concentrate in soils when capillary uplifted groundwater is evaporated, resulting in accumulation of soluble salts on the surface of the soil (McBride, 1994) During concentration, all ions will concentrate until the solution reaches saturation with respect to minerals e.g. calcite. The pH will also increase because of accumulation of bicarbonate. Sites like the midslope of this study at which evaporation dominates can be identified by high pH, high EC, 100% base cation saturation and presence of calcite (Figure 4.3.8)

4.3.11 Consequences of salt accumulation

Salt accumulation in soils can be a potential hazard to soils and plants. The soils in the toposequence under study vary from normal (i.e. non-saline and non-sodic), to saline-sodic and sodic (McBride, (1994); Table 4.1)

Normal soils occur in pits 1, 2 & 4 at the crest and pit 11 towards the footslope where the ECe and ESP values are less than 4d S/m and 15% respectively. Although soils from these pits are considered normal in terms of salinity and sodicity, they are still problematic to plant growth due to acidity, especially soils from pits 2 & 4 with 3.7-4.5 soil pH $_{(KCl)}$ range. Such low pH range enhances the solubility of Al, Fe and Mn which may become toxic to plants (Sparks, 1995). Soils from pit 11 are considered normal and are not acidic in nature but their SAR is high ($10.87 mmol_c/L^{1/2}$) especially in sample 11B2 compared to soils from pits 1, 2 & 4 with SAR < 2 $mmol_c/L^{1/2}$ and ECe< 1dS/m.

Saline-sodic top soils with sodic subsoils are common (samples 8A & 10A). Soils classified as saline-sodic are characterised by their appreciable contents of soluble salts (> 4 dS/m) and exchangeable sodium (>15%) (Sparks, 1995; McBride, 1994). In pit 6 for example, only the B2 horizon is saline-sodic while B1 is sodic and A horizon is considered normal but strongly to moderately acidic. Similarly, in pit 7 the A and B1 horizons are sodic while the B2 horizon is saline-sodic. All horizons in pit 10 are saline – sodic. However, as long as this category of soils has excess salts, the soil is still in a flocculated state.

Table 4.2 Soil salinity appraisal (explanation of terms is given in Chapter 1, Table1.)

Sample I.D	ESP (%)	SAR $mmol_c/L^{1/2}$	pH (H2O)	pH (KCl)	EC(SPE) dS/m	Nature of soil
1A	4.73	1.45	6.6	5.3	0.45	Normal
1B1	5.71	1.16	6.8	5.8	0.41	Normal
1B2	8.15	2.27	7.4	6.7	0.44	Normal
2A	6.83	1.11	6.0	4.7	0.25	Normal
2B1	6.07	0.91	5.6	4.1	0.20	Normal
2B2	8.59	1.53	4.6	3.7	0.43	Normal
4A	5.52	1.03	5.8	4.5	0.54	Normal
4B1	4.91	0.69	4.9	4.0	0.23	Normal
4B2	5.25	0.93	4.8	3.9	0.30	Normal
6A	7.57	2.29	5.3	4.4	1.93	Normal
6B1	28.13	17.26	5.9	4.0	1.63	Sodic
6B2	61.92	45.91	6.4	4.0	5.78	Saline-sodic
7A	42.63	30.88	5.8	5.0	2.46	Sodic
7B1	21.18	8.47	6.3	4.4	3.03	Sodic
7B2	65.29	46.14	7.8	6.3	4.82	Saline-sodic
8A	26.66	11.96	7.9	7.3	7.38	Saline-sodic
8B1	18.47	25.68	9.3	8.0	2.62	sodic
8B2	42.93	31.00	9.0	7.7	2.40	Sodic
10A	40.92	24.25	8.1	7.3	10.97	Saline-sodic
10B1	25.27	39.16	9.3	8.1	5.16	Saline-sodic
10B2	60.45	51.49	9.1	8.2	8.18	Saline-sodic
11A	7.18	1.82	6.7	5.6	1.88	Normal
11B1	7.85	7.83	8.8	5.9	1.67	Normal
11B2	8.41	10.87	9.5	7.5	1.10	Normal
12A	5.43	2.71	7.5	6.7	2.52	Normal
12B1	18.09	13.18	8.8	6.8	1.78	Sodic
12B2	35.81	24.95	8.9	6.9	1.45	Sodic
14A	13.27	2.41	6.5	6.0	3.73	Normal
14B1	7.92	3.84	6.5	5.3	1.77	Normal
14B2	19.17	6.70	6.5	5.4	2.20	Sodic
14B3	28.67	10.31	7.0	5.4	1.76.	Sodic

The structure of the A- horizon is massive to weak, platy to blocky, and that of the B-horizon is prismatic, columnar or course blocky with very hard consistency when dry in the saline-sodic and sodic samples. These soils are not yet problematic in terms of soil dispersion but if irrigated or leached, swelling and dispersion will cause degrading of soil structures (Sparks 1995). The pH would also become strongly alkaline (> 8.5) if the soluble salt content is decreased either by leaching or irrigating the soils. The presence of excess soluble salts will inhibit plant growth by lowering the free energy of water in soil, thereby reducing the osmotic potential of the soil solution and the ability of plant roots to extract water from the soil (Tan, 1993). The osmotic pressure generated by salts can be estimated using the empirical equation (McBride, 1994):

$$\textit{Osmotic potential} = EC\ (mS/cm) \times 0.36 \text{ --------------------------------- } \mathbf{(14)}$$

Soils considered saline can be reclaimed by adequately draining the soil profiles with good quality water that is low in salinity; has a low Na^+ to Ca^{2+} and Mg^{2+} ratio to prevent the development of sodicity, and a low concentrations of ions (Na^+, Cl^- & B) that may have specific toxic effects to plants (Ayers and Westcot, 1985).

Typically sodic soils occur in pits 12 & 14 occupying the footslope and valley bottom positions in the toposequence (Table 3.5). In these pits, the highest ECe value was 3.75 dS/m and occurred in sample 14A, while the pH for all samples in the pits ranged from moderately acidic to strongly alkaline (6.5-8.9 pH $_{(H2O)}$). The high pH values are due to hydrolysis of Na_2CO_3 as indicated in the equation below

$$Na_2CO_3 + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2CO_3 \text{ -------------------- } \mathbf{(15)}$$

Apart from samples 12A, 14A & 14B1, the threshold levels of ESP for the rest of the samples in these pits exceed the 15% borderline for soil to be considered sodic (McBride, 1994). The main problem is that the presence of large amounts of exchangeable sodium ions along with the low ECe values causes clay dispersion in the soils. The clay is dispersed because the electrolytic concentration of the soils decreases below the flocculation value of the clay (Keren and Miyamoto, 1990). The dispersive effect of the exchangeable sodium should result in poor soil structures, restricting permeability. As these soils are dispersed, the soil colloids migrate, clogging soil pores. This situation drastically reduces the rate at which water percolates through the soil, resulting in poor soil structure often leading to surface crusting, cementation, and soil erosion (McBride, 1994). Surface crusts produced as a result of dispersion will reduce seedling emergence and water penetration thereby enhancing soil erosion.

The structures of sodic soils are similar to those of saline-sodic soils, which are prismatic and columnar in the top and subsurface soils. Poor vegetation growth and bare spots were observed in the field during soil sampling. These sites were identified as saline-sodic and non- saline sodic after soil analyses were performed on samples collected from the spots (i.e. in pits 6, 7, 8, 10, 12 & 14). A typical saline bare patch is shown in (Figure 4.3.9) and occurred near pit 10.

Figure 4.3.11 Typical bare saline patches associated with poor vegetation growth

The profiles considered sodic in this study can be ameliorated with the application of gypsum ($CaSO_4$. $2H_2O$) either directly to the profiles or added to irrigation water to provide a soluble source of calcium. Calcium prevents the soil structure from deteriorating, and also defends plants against the toxic effects of sodium. The resultant effect will be to reduce the SAR and ESP at the soil exchange sites, with a consequent reduction of sodicity hazard (Shainberg *et al.*, 1989).

4.3.12 Agricultural implications

The two farms in this study are the vineyard found at the crest while the midslope and base of the slope are occupied with halophytes serving for cattle rearing. The farmer implements supplementary irrigation to the vineyards and applies fertilizers to supplement soil nutrients. Soils in the crest are acidic, lower in clay content with sandy to loamy sand textures and having single grained structures. The implications of these physical properties are that base cations are easily leached out costing the farmer extra funds to acquire inorganic fertilizers. The sand content, > 80 % with moderate silt and clay content makes this portion of the field a better agricultural soil compared to the rest of the field where loam and clayey soils exist. The second farm used for cattle rearing has saline, saline-sodic and sodic soils with its attendant disadvantages mentioned in chapter one.

CHAPTER 5

CONCLUSION

A pilot study (Water Research Commission (WRC) project no. K5-1342) of salinity in the Berg River catchment revealed a widespread patchiness in wheat fields confirmed to be associated with soil salinity and suggested the need for a more detailed survey of salt distribution in a selected sub catchment of the Berg River basin. This study forms part of the more detailed project currently being undertaken. and looked at salt distribution along a selected toposequence in a small subcatchment of the Berg River. This chapter summarises the main findings of the investigation, and will attempt to answer the key questions posed in the introduction, namely:

- What is the salt distribution in relation to landscape topography?
- Are there potentially harmful trace elements associated with soluble salts?
- What are the potential consequences of the salt accumulation?
- What processes are responsible for the observed distribution of salts?

The soils for the most part are developed from highly weathered Malmesbury shales, although the top of the toposequence is underlain by alluvial material and silcrete. The physical and chemical properties vary widely down the toposequence The sand fraction dominates the upper part of the slope associated with the silcrete and alluvium parent material, while the clay and silt fractions are concentrated in the midslope and lower parts of the toposequence coinciding with the Malmesbury shale parent material. The soil textures are generally loamy to sandy-clay loam and their structures vary from single grain through angular to prismatic and columnar reflecting the effects of salts. Weathering of feldspar minerals to kaolinite occurs in the toposequence. The upper slope is mainly dominated by quartz while the mid and lower slopes are composed also of quartz, but with feldspar, kaolinite, calcite, hematite and goethite.

Soil chemistry also varies along the toposequence in relation to the processes controlling the distribution of ions. The upper slope (pits 2, 4 and 6) is generally acidic with $pH_{(KCl)}$ 3.7- 4.7 reflecting the degree of leaching, nature of parent material and possibly fertilization. The midslope soils are slightly acidic to alkaline ($pH_{(KCl)}$ 6.3 - 8.2) coinciding with increasing salt content. The clay rich nature of parent material and presence of contour drains result in waterlogging, and salts concentrate through evaporation. The lower slope soils are moderately acidic to neutral as leaching becomes more important again. Acidity decreases with soil depth while salinity generally increases with soil depth in the valley bottom indicating leaching and eluviation of salts from the surface vertically into the subsoils.

The soils are marine influenced either from source of parent material or marine aerosols brought in by precipitation or prevailing winds as Riebeeck West is relatively close to the sea. This is reflected by the dominance of Na^+ and Cl^- as major cation and anion. The presence of other important ions like Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-} indicate an additional salt source, most likely weathering of silicate minerals like feldspar. Human influence is seen to have a role in concentrating the ions because poor drainage due to contour drains allows the salts to accumulate through evapotranspiration. High K concentrations appear to be due to some form of fertilization. The absence of deep rooted plants to consume rainwater during the wet winter period might have led to the groundwater table rising close to the surface bringing salts to the surface soil.

The local relief or topography was expected to influence the distribution of salts in this landscape. However, due to the modification of the slope by contour drains, salt distribution in this study varies with slope gradient, the affinity of the ions with respect to the nature of parent material and drainage conditions. The samples from the upper parts of the toposequence i.e. the crest and scarp have generally low concentrations of cations and anions being influenced by the silcrete and alluvium parent material in this segment of the toposequence. The sandy texture allows leaching of the ions and the low clay content reduces the retention ability of ions on to soil colloids. Most of the salts in this study are concentrated in the midslope (where highest EC occurs), where the enriched clay parent material and contour drains result in accumulation of salts. The distribution of the salts is similar for most of the ions except K^+ which concentrates mostly at the crest and valley bottom. The concentration of the salts varies with soil depth with most of the soluble salts concentrating in the top soil of the midslope.

The distribution pattern of trace elements in the toposequence varies with different topographic positions. Selenium, boron and arsenic occur in low concentrations in the crest and at the lower slope, but in higher concentrations in the midslope. The increased concentrations in the midslope are associated with increased clay content, increased salinity and Malmesbury shale parent material. Silicon was found to occur mostly in the crest and valley bottom as opposed to the midslope. The concentrations of selected trace elements discussed in the text were below the recommended maximum levels for soils to be considered polluted.

Soils in most part of this study are salt-affected with inherent soil structure deterioration. The soils in the crest are classified as normal but the mid and lower segments of the toposequence are saline-sodic and sodic. There is need for immediate reclamation and preventive measures to be put in place if meaningful agricultural activities need to be carried out.

The variation in salt concentration along the toposequence is governed by a) leaching and eluviation of ions, where soils are very acidic b) the retention of water and dissolved solids by clay especially in the mid and lower slope positions and c) the evaporation of soil-water where groundwater table is closer to the soil surface. Eluviation, leaching and evaporation processes influence the distribution of salts in this study.

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Appendix

Appendix A: Soil Profile Description

Pit no: 1
Location: Goedertrou - Riebeek West
Date of sampling: 2004 / 07 / 27
Latitude: 33°18′45.7″
Longitude: 18° 53′38.2″
Slope: 2°
Parent material: Silcrete and alluvial material
Vegetation/Land use: Vineyard farm
Diagnostic horizons: Orthic A; Neocutanic B1; Neocutanic B2.
Soil form: Sweet water
Soil family: Fielden
Water table: None
Terrain unit: Crest
Described by: Daniel Folefoc

Figure A-1.Showing the soil profile 1.

Horizon	Depth (cm)	Description
1A	0-20	dry, dark brown (5YR 3/3, 5YR 4/4 when moist); Very stony loamy sand; medium to coarse crumb; loose; clear boundary

1B1	20-105	dry, dark reddish brown (5YR 3/3, 5YR 4/6 when moist); stony loamy sand; medium angular; loose; wavy boundary
1B2	105-200	dry, reddish yellow (5YR 6/6, 5YR 5/8 when moist); stony sandy loam; sub angular blocky, loose
Remarks		Borehole containing fresh water located near this pit.

Pit no: 2
Location: Goedertrou - Riebeek West
Date of sampling: 2004 / 07 / 27
Latitude: 33°18′44.3″
Longitude: 18° 53′37.6″
Slope: 2°
Parent material: Silcrete and alluvial material
Vegetation/Land use: Vineyard farm
Diagnostic horizons: Orthic A; Neocutanic B1; Neocutanic B2.
Soil form: Sweet water
Soil family: Fielden
Water table: None
Terrain unit: Crest
Described by: Daniel Folefoc

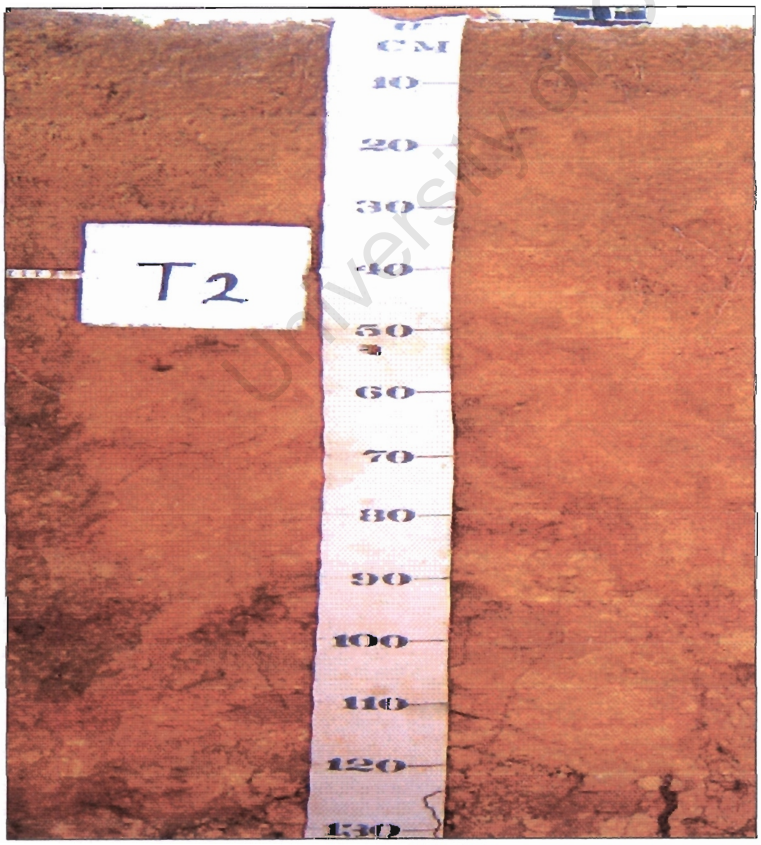

Figure A-2: Showing the soil profile 2.

Sample ID	Depth (cm)	Description
2A	0-45	dry, dark brown (5YR 4/3, 5YR 4/4 when moist); stony sandy loam; fine to medium crumb; loose; many fine roots; wavy boundary
2B1	45-90	dry, dark red (2.5YR 3/6, 2.5YR ¾ when moist); stony loamy sand; medium angular blocky; loose, few roots; dark cutans, wavy boundary
2B2	90-200	dry, strong brown (7.5YR 5/6, 7.5YR ¾ when moist); loamy sand; subangular blocky; hard

Pit no: 4

Location: Goedertrou - Riebeek West
Date of sampling: 2004 / 07 / 27
Latitude: 33°18′42.6″
Longitude: 18° 53′38.4″
Slope: 8°
Parent material: Malmesbury shale
Vegetation/Land use: Cultivated pastures
Diagnostic horizons: Orthic A; Neocutanic B1; Neocutanic B2.
Soil form: Sweet water
Soil family: Fielden
Water table: None
Terrain unit: Scarp
Described by: Daniel Folefoc

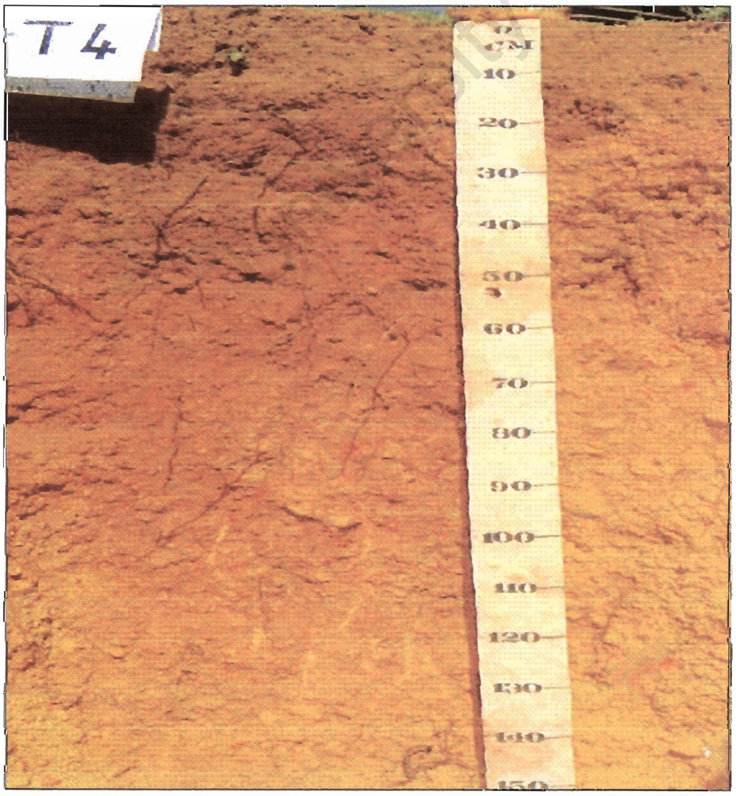

Figure A-3: Showing the soil profile 4

Sample ID	Depth (cm)	Description
4A	0-20	dry, reddish brown (5YR 4/3, 5YR 3/3 when moist); sandy clay loam; coarse angular; hard; clear boundary
4B1	20-100	dry, dark red (2.5YR 3/6, 2.5YR 3/3 when moist); sandy clay loam; subangular blocky; many medium roots; dark brown cutans; wavy boundary
4B2	100-200	dry, reddish yellow (7.5YR 6/6, 7.5YR 6/6 when moist); sandy clay loam; very hard

Pit no: 6

Location: Goedertrou - Riebeek West
Date of sampling: 2004 / 07 / 27
Latitude: 33°18′41.1″
Longitude: 18° 53′39.2″
Slope: 20°
Parent material: Malmesbury shale
Vegetation/Land use: Cultivated pastures.
Diagnostic horizons: Orthic A; Pedocutanic B; Saprolite
Soil form: Lusiki
Soil family: Dubana
Water table: None
Terrain unit: Midslope
Described by: Daniel Folefoc

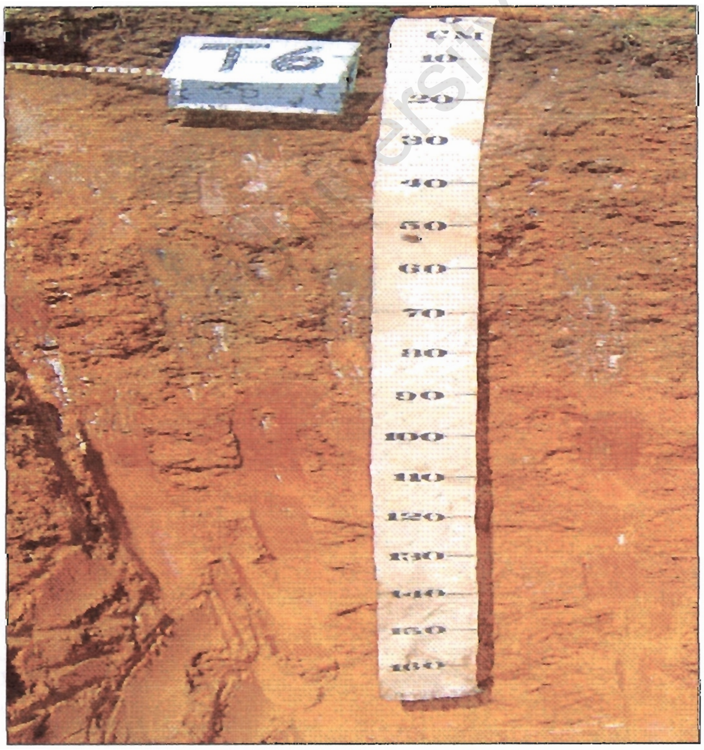

Figure A-4: **Showing the soil profile 6**

Sample ID	Depth (cm)	Description
6A	0-25	dry, reddish yellow (5YR 4/3, 5YR 4/2 when moist); sandy loam; coarse crumb; loose; fine roots; clear boundary
6B1	25-90	dry, reddish brown (5YR 5/4, 5YR 4/6 when moist); clay loam; prismatic; very hard; clear boundary
6B2	90-200	dry, reddish yellow (5YR 7/6, 5YR 6/8 when moist); clay loam; subangular blocky; very hard; ant hills and termitaria

Pit no: 7

Location:	Goedertrou - Riebeek West
Date of sampling:	2004 / 07 / 27
Latitude:	33°18′40.5″
Longitude:	18° 53′39.2″
Slope:	18°
Parent material:	Malmesbury shale
Vegetation/Land use:	Cultivated pastures
Diagnostic horizons:	Orthic A; Pedocutanic B; Saprolite.
Soil form:	Lusiki
Soil family:	Dubana
Water table:	None
Terrain unit:	Midslope
Described by:	Daniel Folefoc

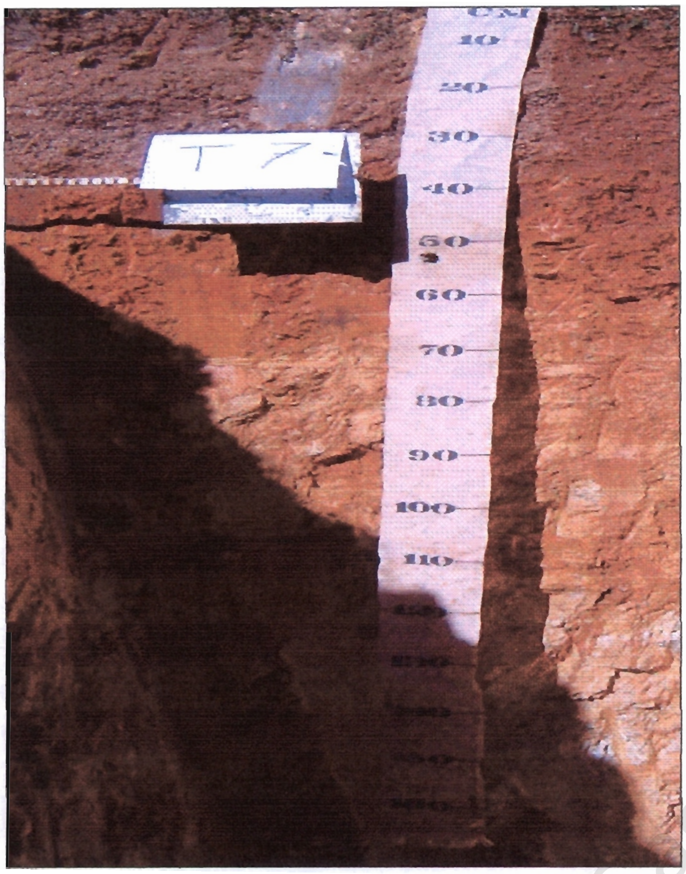

Figure A-5: **Showing a soil profile 7**

Sample ID	Depth (cm)	Description
7A	0-40	dry, reddish gray (5YR 4/2, 5YR 3/3 when moist); sandy clay loam; subangular blocky; hard; clear boundary
7B1	40-70	dry, reddish brown (5YR 4/4, 5YR 5/8 when moist); sandy loam; medium columnar; hard; clear boundary
7B2	70-200	dry, reddish yellow (5YR 7/8, 2.5YR 6/8 when moist); loam; prismatic; very hard

Pit no: 8

Location:	Goedertrou - Riebeek West
Date of sampling:	2004 / 07 / 27
Latitude:	33°18′38.6″
Longitude:	18° 53′39.5″
Slope:	10°
Parent material:	Malmebury shale
Vegetation/Land use:	Cultivated pasture
Diagnostic horizons:	Orthic A; Pedocutanic/Lithocutanic B; Saprolite.
Soil form:	Glenrosa
Soil family:	Dumisa
Water table:	None
Terrain unit:	Midslope

Described by:	Daniel Folefoc

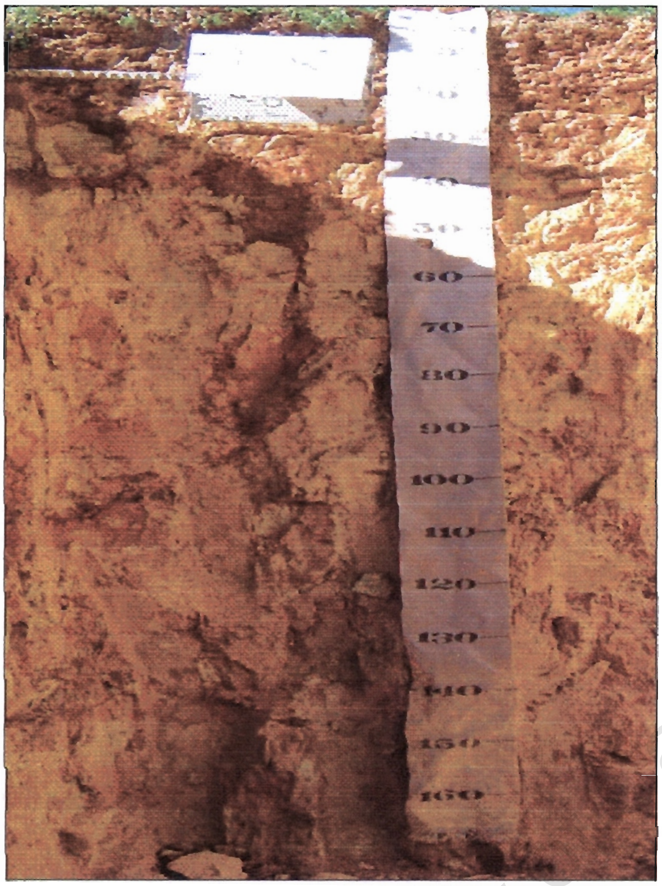

Figure A-6: Showing a soil profile 8.

Sample ID	Depth (cm)	Description
8A	0-20	dry, brownish yellow (10YR 6/6, 10YR 8/8 when moist); sandy clay loam; platy to massive; hard; wavy boundary
8B1	20-100	dry, yellow (10YR 8/6, 10YR 7/6 when moist); sandy clay loam; prismatic; very hard; dark brown cutans; diffuse boundary
8B2	100-200+	dry, yellowish brown (10YR 3/6, 10YR 3/3 when moist); loam; platy to massive; hard

Pit no: 10

Location:	Goedertrou - Riebeek West
Date of sampling:	2004 / 07 / 27
Latitude:	33°18′37.5″
Longitude:	18° 53′39.6″
Slope:	8°
Parent material:	Malmesbury shale

Vegetation/Land use: Cultivated pasture
Diagnostic horizons: Orthic A; Pedocutanic/Lithocutanic B; Saprolite.
Soil form: Swartland
Soil family: Burgersdorp
Water table: None
Terrain unit: Midslope
Described by: Daniel Folefoc

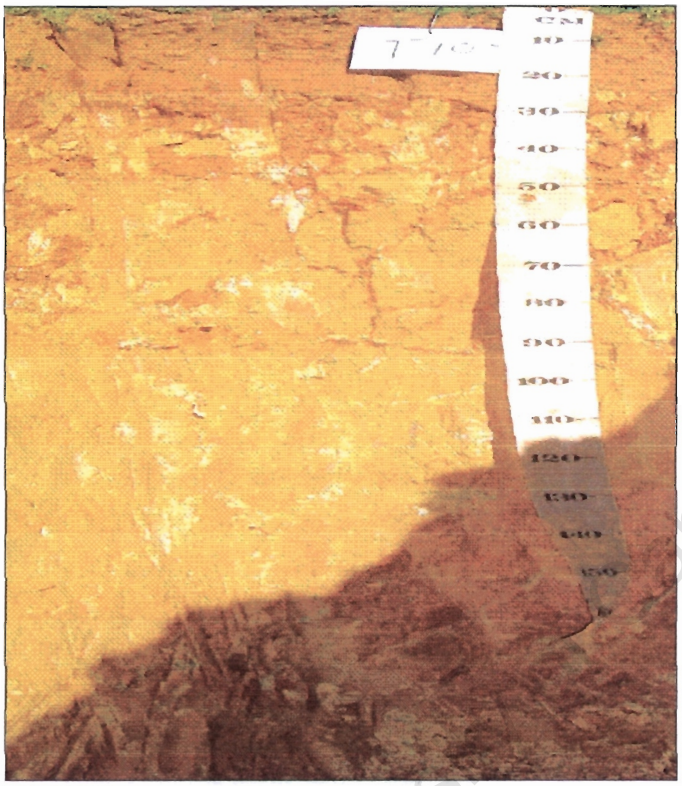

Figure A-7: Showing a soil profile 10

Sample ID	Depth (cm)	Description
10A	0-30	dry, strong brown (7.5YR 5/6, 7.5YR 5/6 when moist); sandy clay loam; platy to massive; very hard; clear boundary
10B1	30-90	dry, reddish yellow (7.5YR 7/6, 7.5YR 6/8 when moist); sandy clay loam; medium columnar; hard; reddish yellow cutans; wavy boundary
10B2	90-200+	dry, reddish yellow (7.5YR 7/8, 7.5YR 7/8 when moist); sandy clay loam; platy to massive; hard

Remarks: Calcite tested positive in both 10B1 & 10B2 with 10 % HCl

Pit no: 11

Location:	Goedertrou - Riebeek West
Date of sampling:	2004 / 07 / 27
Longitude:	33°18′44.3″
Latitude:	18° 53′37.6″
Slope:	12°
Parent material:	Malmesbury shale
Vegetation/Land use:	Cultivated pasture
Diagnostic horizon:	Orthic A; Pedocutanic/Lithocutanic B; Saprolite.
Soil form:	Swartland
Soil family:	Burgersdorp
Water table:	None
Terrain unit:	Midslope
Described by:	Daniel Folefoc

Figure A-8: Showing the soil profile 11

Sample ID	**Depth (cm)**	**Description**
11A	0-20	dry, reddish brown (5YR 5/4, 5YR 4/6 when moist); sandy loam; medium granular; loose; many fine roots; clear boundary
11B1	20-100	dry, reddish yellow (5YR 4/4, 5YR 5/6 when moist); sandy clay loam; subangular blocky; hard; clear boundary
11B2	100-200+	dry, reddish yellow (5YR 6/8, 5YR 5/6 when moist); sandy loam; subangular blocky; hard
Remarks:		Calcite tested positive in both 11B1 & 11B2 with 10 % HCl

Pit no: 12

Location:	Goedertrou - Riebeek West
Date of sampling:	2004 / 07 / 27
Latitude:	33°18′35.1″
Longitude:	18° 53′39.0″
Slope:	20°
Parent material:	Malmesbury shale
Vegetation/Land use:	Cultivated pasture
Diagnostic horizon:	Orthic A; Pedocutanic B; Soft phlinthic.
Soil form:	Swartland
Soil family:	Riebeek
Water table:	None
Terrain unit:	Footslope
Described by:	Daniel Folefoc

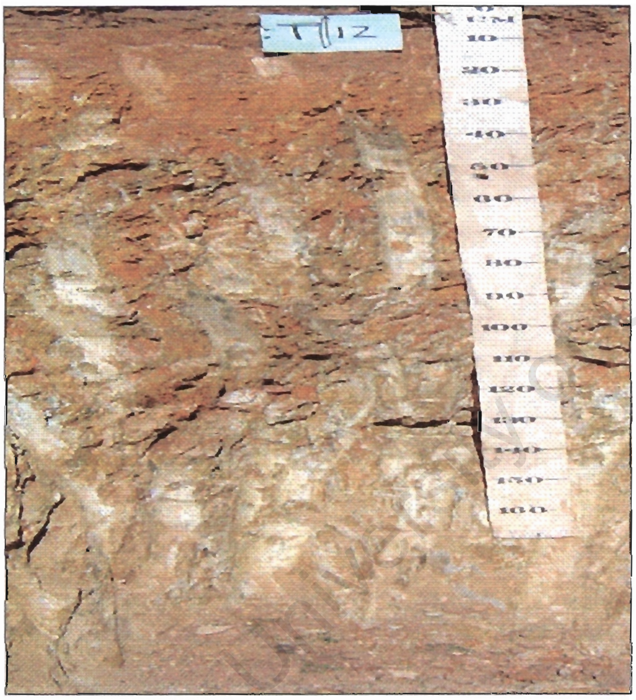

Figure A-9: Showing the soil profile 12

Sample ID	Depth (cm)	Description
12A	0-10	dry, strong brown (7.5YR 4/6, 7.5YR4/4 when moist); sandy loam; medium granular; hard; reddish brown cutans; clear boundary
12B1	10-100	dry, reddish yellow (7.5YR 6/6, 7.5YR 7/8 when moist); sandy loam; prismatic; hard; wavy boundary
12B2	100-200+	dry, pale yellow (2.5YR 7/3, 2.5YR 5/2 when moist); sandy loam; platy to prismatic; very hard; grayish cutans

Pit no: 14
Location: Goedertrou - Riebeek West
Date of sampling: 2004/07/27
Latitude: 33°18′34.1″
Longitude: 18° 53′39.0″
Slope: 2°
Parent material: Malmesbury shale
Vegetation/Land use: Cultivated pasture
Diagnostic horizon: Neocutanic B
Soil form: Longlands
Soil family: Sherbrook
Water table: None
Terrain unit: Valley bottom
Described by: Daniel Folefoc

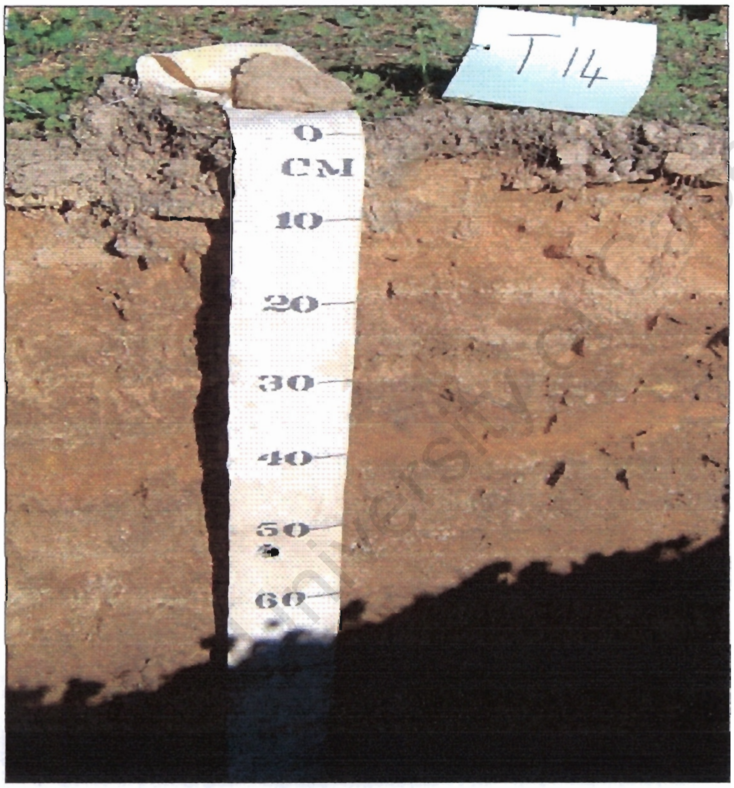

Figure A-10: Showing the soil profile14

Sample ID	**Depth (cm)**	**Description**
14A	0-10	dry, grayish brown (10YR 5/2, 10YR 4/2 when moist); clay loam; medium crumb; hard; organic matter with fine roots; clear boundary
14B1	10-35	dry, yellowish brown (10YR 5/4, 10YR 4/3when moist); sandy loam; subangular blocky; quartz gravel; very hard; diffuse boundary

14B2	35-90	dry, light yellowish brown (10YR 4/4, 10YR 5/4 when moist); sandy loam; prismatic; very hard; wet mottled; diffuse boundary
14B3	90-200+	dry, yellowish brown (10YR 5/6, 10YR 5/8 when moist); loamy sand; subangular blocky; very hard; black manganese nodules
Remarks:		Presence of cow dung and bract shallow well close to the soil pit

Appendix B: Analytical methods

B-1 Soil Analysis

B-1.1 Particle size determination

Particle size distribution was determined according to the general principles of Soil Classification Working Group, 1991. 20 g of < 2mm air-dry was pre-treated with H_2O_2 to remove organic matter and the suspension dispersed with Calgon. The clay and silt were determined by pipette sampling Gee and Bauder, (1986) and the sand fraction by dry sieving. The individual soil textures were then determined by constituting the silt, clay and sand class limits using soil textural triangle (Soil Classification Working Group, 1991)

Apparatus/reagent:

1 litre glass sedimentation cylinders, hand stirrer(metal rod joined to a metal plate roughly the diameter of the cylinders), an electric mixer, lowry pipette (10 cm^3) and stand, constant room temperature, 53µm sieve with receiving pan, drying oven, evaporating dishes; and for reagent Calgon cm^3 (sodium hexametaphosphate).

Procedure

Soil samples was pre-treated as mentioned above, and calgon dispersing solution (10 mls) was added to 20g < 2 mm air-dried soil samples and shook in an electric mixer for 3 minutes.

Separation of clay & silt fractions from sand:

The silt and clay were washed through a 0.053 sieve into the cylinder. The samples were washed until the percolates were clear, where upon the sand fractions were dried in an oven (105° C) and their weights taken before, the cylinders were made up to I litre capacity using distilled water. The cylinders were left to stay in a room with two measurements were performed for each sample and the average taken as EC of the SPE. Duplicate analysis was made for eight samples to check precision.

B-1.4 Procedure for the determination of Calcium carbonates using the karbonat Bombe

Five to six grams of ground-up soil samplewas placed in the cylinder and spread evenly. A plastic container containing 5 mL of concentrated hydrochloric acid was inserted to stand on the sample with care taken not to allow spillage of the acid on the sample. After this, the cap (inserted with a gasket) upon which the manometer and thumbscrew are mounted was tightened and the thumbscrew closed to allow for equalization of the interior and exterior pressure. By tipping the entire" Bombe" the acid in the plastic container came in contact with the sample powder whereby calcite and aragonite contained in the sample reacted within 10-15 seconds effervescing strongly. The pressure of carbon dioxide gas produced was measured by the manometer and calibrated in order to know the true value of the calcium carbonate. The calibration was based on the general formula proposed by (Muller and Gastner, 1971).

$$\% \text{ CaCO}_3 \text{ (unknown sample)} = \text{CaCO}_3 \text{ manometer value x } 100/ \text{ CaCO}_3 \text{ (Manometer value of the standard sample)} \ldots\ldots\ldots \quad \textbf{(6)}$$

Measurements were performed thrice and their mean value used to ensure accuracy.

B-1.5 Determination of KCl extractable acidity determination

KCl extractable acidity was determined according to method described by Thomas, (1982). 50 mL of KCl was added to 5g of air-dried soil in 100 ml centrifuge tubes and shaken on a reciprocating shaker for about 30 minutes. The mixture was centrifuged at 2000 rpm for 5 minutes and filtered through a 120mm filter membrane. A few drops of phenolthalein was added to a blank of 10 ml I M KCl solution and the in the supernatant of the KCL extract. These were titrated against standard 0.01 M NaOH solution. Phenolphthalein was as an indicator whose with a pink end point. The volume of the NaOH needed to neutralise the acidity was recorded and the number of moles of NaOH was calculated. The following formula was used to calculate the acidity in $\text{mmoles}_c/\text{Kg}$:

$$\text{Conc. of acidity} = \frac{(C_{NaOH})(V_{NaOH}) - V_{blank})\ \text{ml}}{V\text{sample (ml)}} \times \frac{V_{KCl(ml)}}{M_{(sample)}} \times \frac{1000}{1} \qquad (7)$$

Where $C_{NaOH\,)}$ = sodium Hydroxide concentration

V_{blank} = volume of blank

Vsample = Volume of sample

$M_{(sample}$ = Mass of sample

$V_{KCl(ml}$ = Volume of KCl

B-1.6 Determination exchangeable cations using ammonium acetate

Exchangeable cations were determined according to method described by Thomas, (1982). Five grams of air-dried and sieved (< 2 mm) soil was placed in a 100 mL centrifuge tube, stoppered and weighed. To this 25 mL of 1M ammonium acetate adjusted to a pH 7 was added and the solution shaken on a horizontal shaker for 30 minutes. The mixture was centrifuged at 2000 rpm for about 5 minutes and filtered through a 120mm filter membrane. Atomic Absorption Spectroscopy (AAS) was used to determine the concentrations of Ca Mg, Na and K from the supernatant solution obtained from the ammonium acetate extract. The liquid samples were nebulised, aspirated into the flame, (temperature 2000-3000 K), and atomised. Ground state atoms absorb energy in the form of light of a specific wavelength and are elevated to an excited state. The amount of light energy absorbed at this wavelength will increase as the number of atoms of the selected element in the light path increases. The concentration of an element in the original sample can be determined by relating the amount of the light absorbed to that of the element in a standard of known concentration.

Appendix C : XRD Bulk Mineralogy Scans

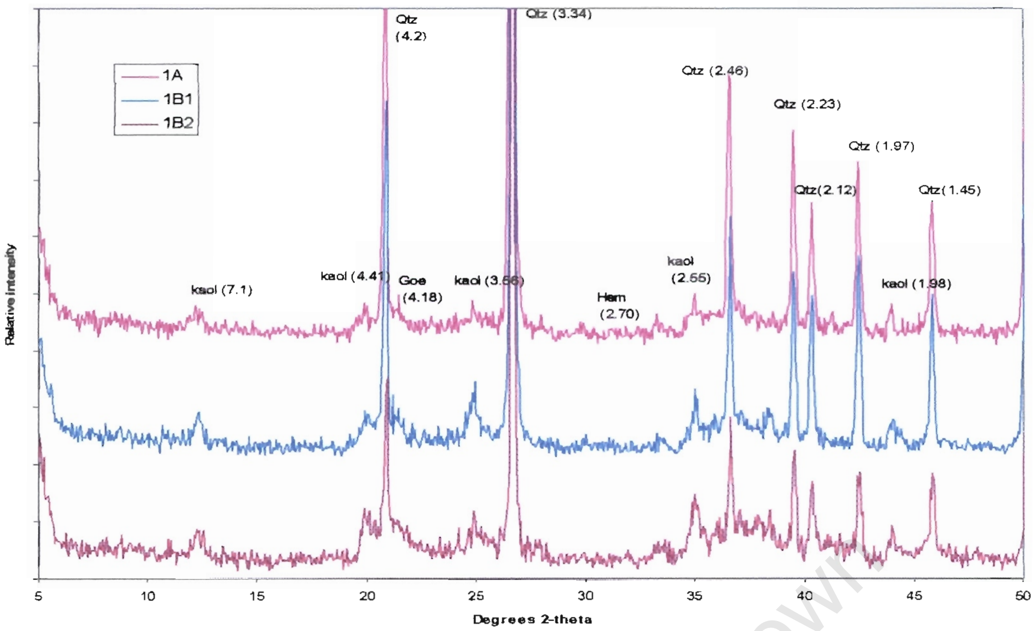

Figure C-1 Bulk Mineralogy XRD Scan of samples from Pit 1. (Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

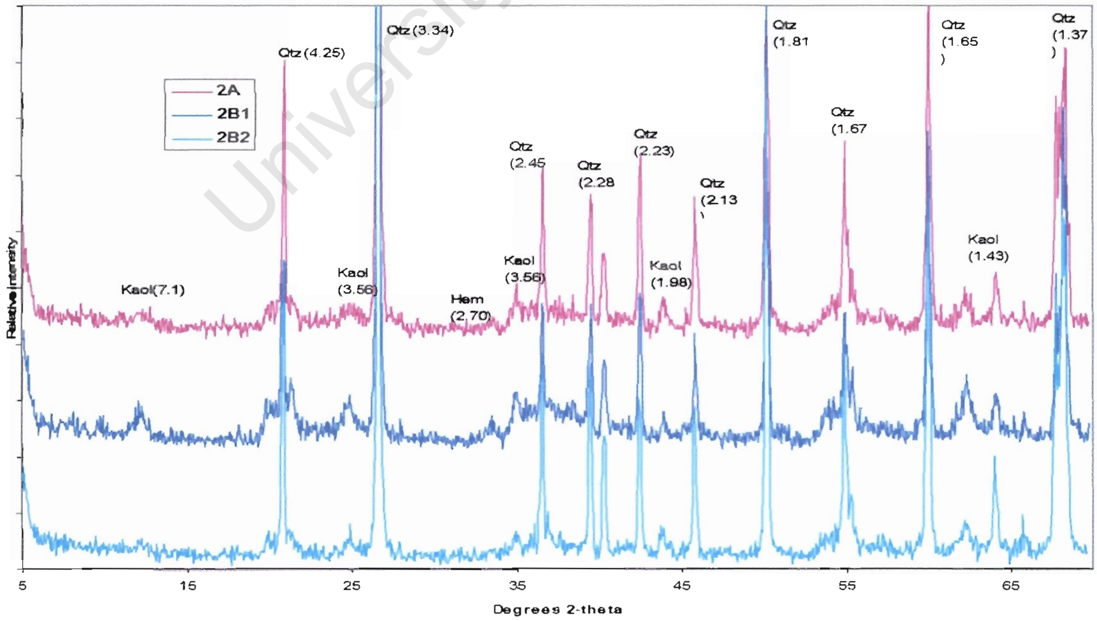

Figure C-2 Bulk Mineralogy XRD Scan of samples from Pit 2. (Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

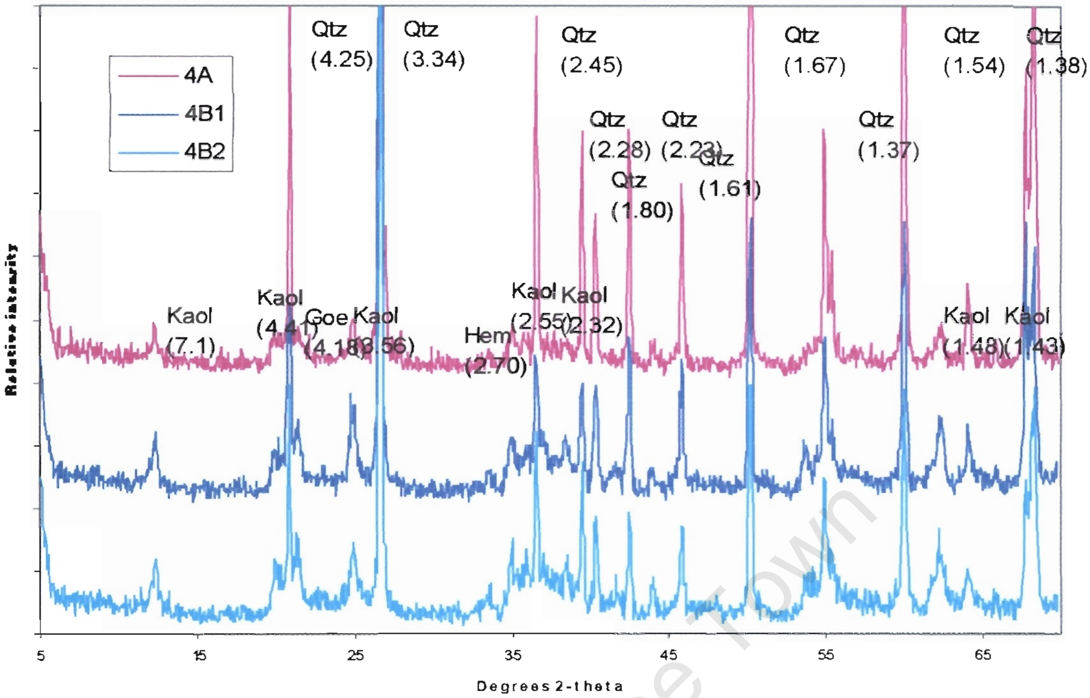

Figure C-4 Bulk Mineralogy XRD Scan of samples from Pit 4.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

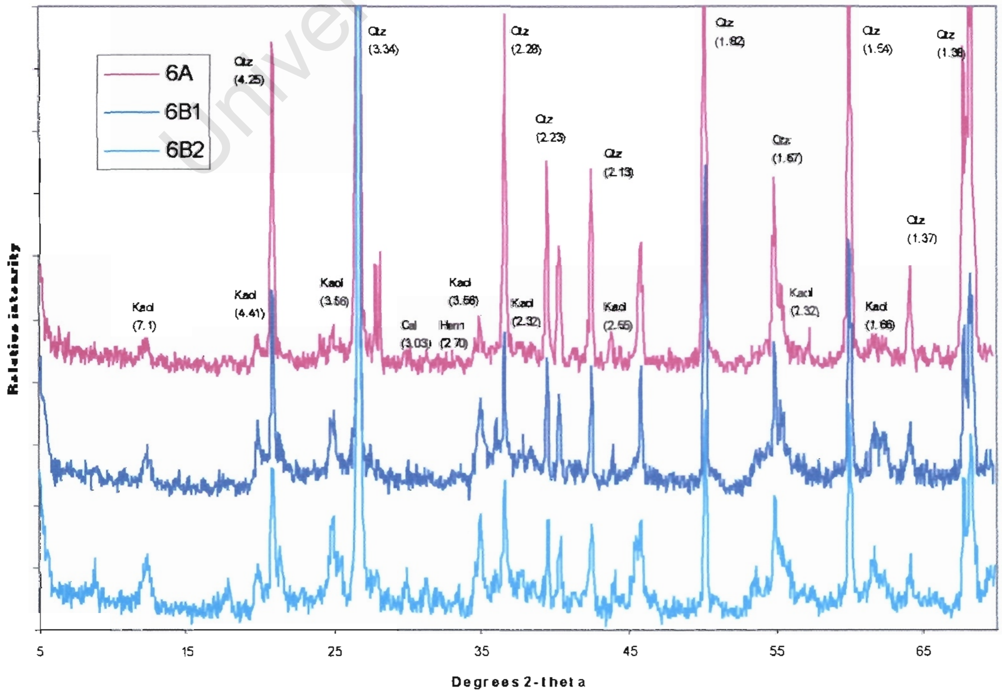

Figure C-6 Bulk Mineralogy XRD Scan of samples from Pit 6.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

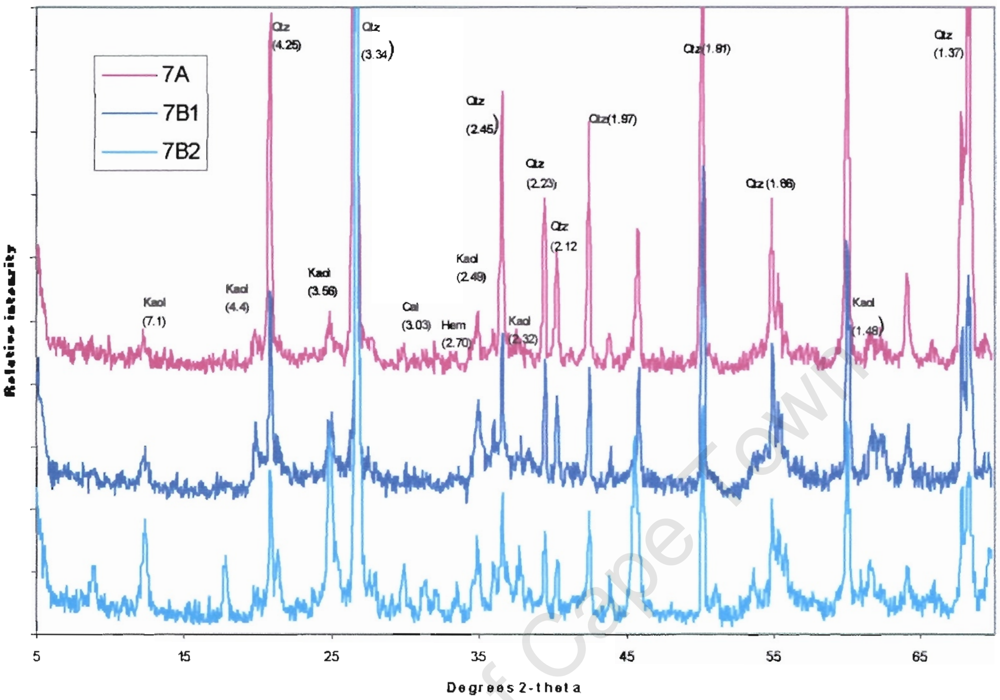

Figure C-7 Bulk Mineralogy XRD Scan of samples from Pit 7.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

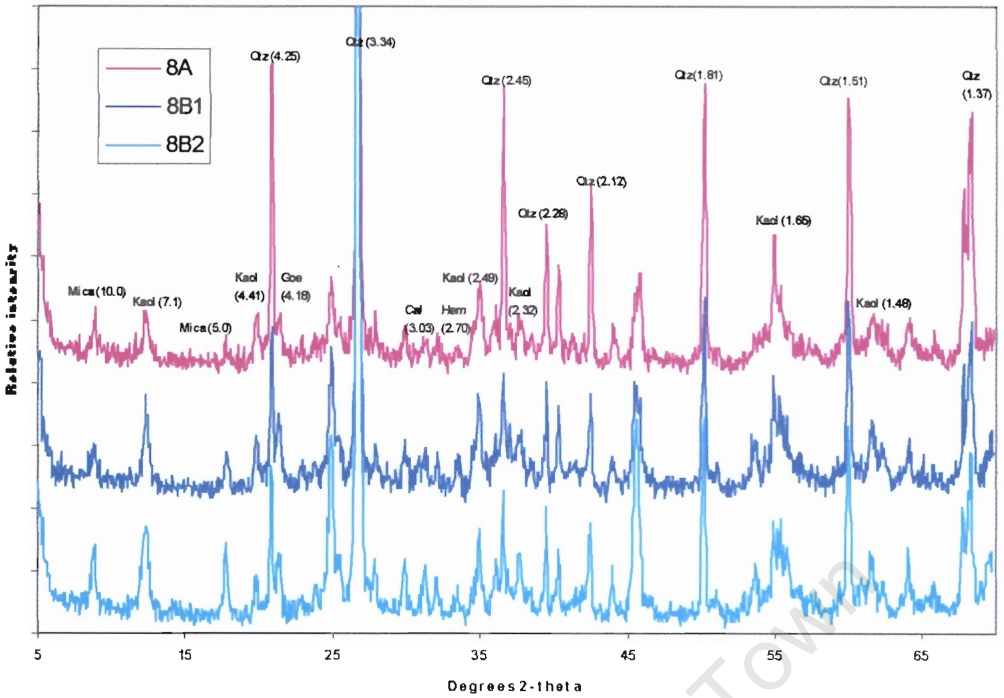

Figure C-8 Bulk Mineralogy XRD Scan of samples from Pit 8.
(Qtz =Quartz; Kaol =kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

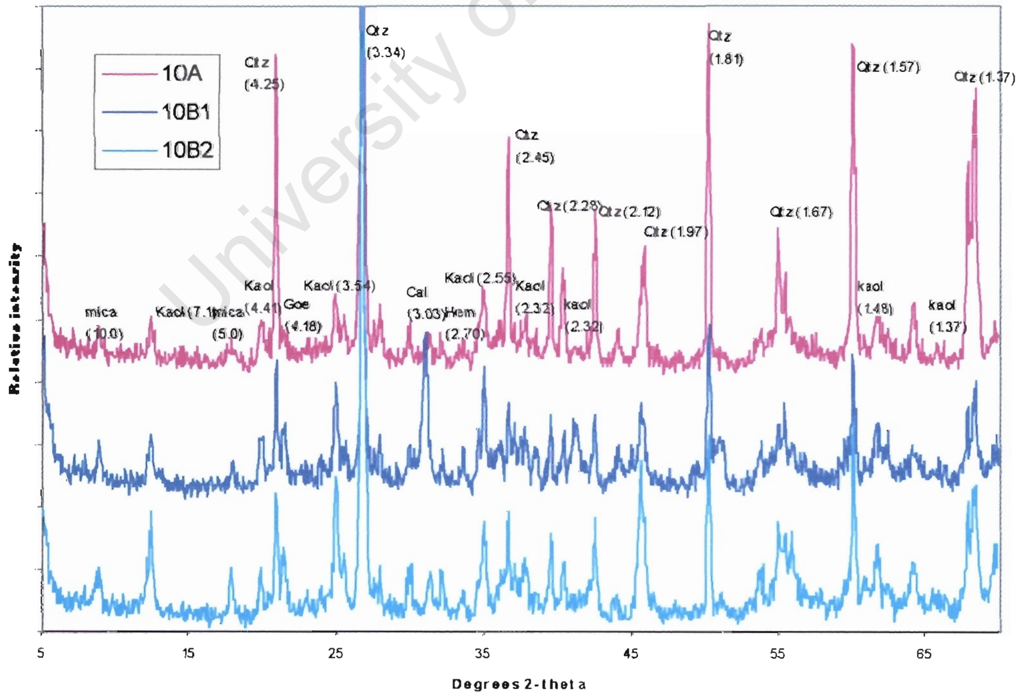

Figure C-10 Bulk Mineralogy XRD Scan of samples from Pit 10.
(Qtz =Quartz; kaol =kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

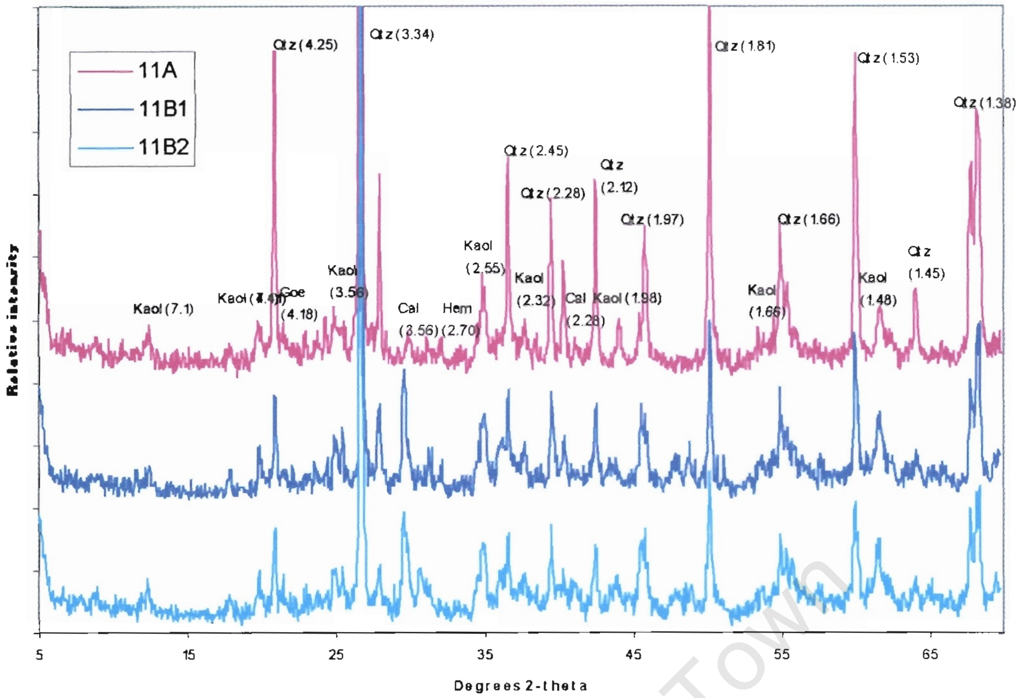

Figure C-11 Bulk Mineralogy XRD Scan of samples from Pit 11.
(Qtz =Quartz; kaol =kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

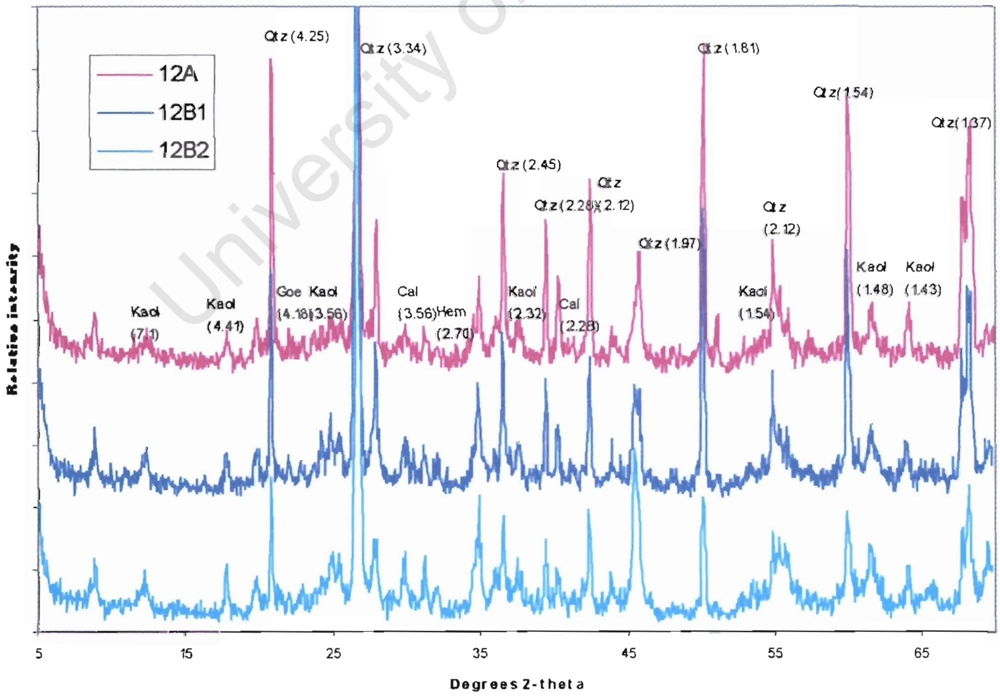

Figure C-12 Bulk Mineralogy XRD Scan of samples from Pit 12.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

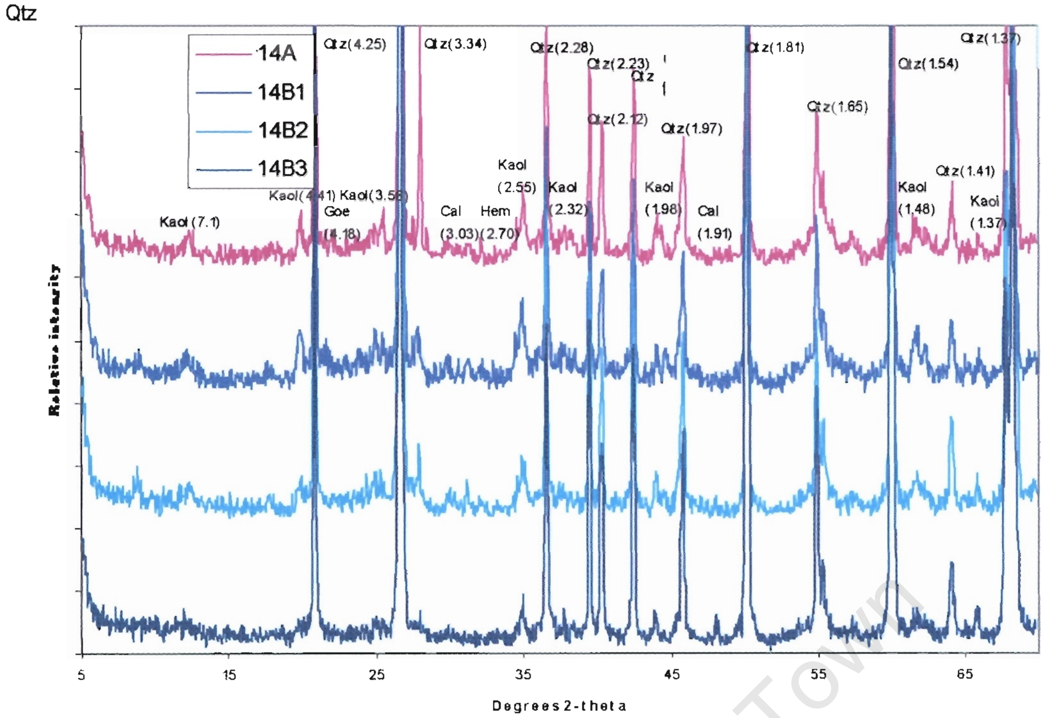

Figure C-14 Bulk Mineralogy XRD Scan of samples from Pit 14.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe. = Goethite)

Appendix D: Data quality for duplicate analysis

To ensure the accuracy and precision of the laboratory analysis, certain samples and analytes were analysed in duplicates. Some of these details are reflected in appendix D, Tables D1-4.

Table D-1. **Results for duplicate analysis for pH (H_2O)**

Sample I.D	**pH(H2O) 1**	**pH(H2O) 2**	**mean**	**Difference**
2A	6	6.21	6.105	-0.21
4B1	4.87	4.88	4.875	-0.01
6B2	6.44	6.44	6.44	0
8A	7.9	7.7	7.8	0.2
10B1	9.27	9.3	9.285	-0.03
11B2	9.48	9.5	9.49	-0.02
14A	6.45	6.5	6.475	-0.05
14B3	7.04	7.07	7.055	-0.03
			Stdev	0.11
			Mean	7.19
			Precision	1.54

Table D-2 Results for duplicate analysis for pH(KCl)

Sample I.D	**pH(KCL) 1**	**pH(KCL) 2**	**mean**	**Difference**
2A	4.7	4.9	4.8	-0.2
4B1	3.98	3.85	3.915	0.13
6B2	4.02	4	4.01	0.02
8A	7.33	7.45	7.39	-0.12
10B1	8.06	8.06	8.06	0
11B2	7.49	7.46	7.475	0.03
14A	6.02	6.01	6.015	0.01
14B3	5.41	5.4	5.405	0.01
			Stdev	0.10
			Mean	5.88
			Precision	1.71

Table D-3. Results for duplicate analysis for EC(1-5) water extract

Sample I.D	**EC(1-5) 1**	**EC(1-5) 2**	**mean**	**Difference**
2A	0.031	0.042	0.04	-0.011
4B1	0.04	0.06	0.05	-0.018
6B2	0.90	0.94	0.92	-0.043
8A	1.04	1.07	1.05	-0.034
10B1	0.82	0.81	0.82	0.014
11B2	0.26	0.24	0.25	0.020
14A	0.60	0.66	0.63	-0.064
14B3	0.09	0.12	0.11	-0.026
			Stdev	0.03
			Mean	0.48
			Precision	5.83

Table D-4 Results for duplicate analysis forEce (SPE)

Sample I	EC(SPE)	EC(SPE) 2	mean	Difference
2A	25.4	25.71	25.56	-0.31
4B1	23	22	22.5	1
6B2	578	579	578.5	-1
8A	738	736	737	2
10B1	516	518	517	-2
11B2	110	110	110	0
14A	373	374	373.5	-1
14B3	175.8	175.5	175.65	0.3
			Stdev.	1.26
			Mean	317.46
			Precision	0.40

Table D-5. Results for duplicate analysis for calcium carbonate in three samples

Sample I.D	**1st reading (Kpa)**	**2nd**	**3rd**	**4th**	**mean**	**stdev**	**%RSC**	**Precision**
Standards	149	149	150	150	149.5	0.35	0.24	0.24
10B1	15.39	16.05	16.26	16.26	15.99	0.41	2.58	2.58
11B1	12.75	12.75	12.8	12.8	12.775	0.03	0.23	0.23
11B2	16.77	16.71	16.5	16.8	16.695	0.14	0.81	0.81

Appendix E: Data for simplified soil profile

	Horizontal Diff	Height	Horizontal Diff	Vertical Diff	Cumulative Height
1	0	69.66	44.52	1.55	69.66
2	44.52	68.11	56.76	7.98	68.11
4	101.28	60.13	50.75	18.47	60.13
6	152.03	41.66	18.78	6.1	41.66
7	170.81	35.56	58.17	10.25	35.56
8	228.98	25.31	34.47	4.84	25.31
10	263.45	20.47	40.41	8.59	20.47
11	303.86	11.88	28.98		11.88
12	332.84	1.33	38.21	1.33	1.33
14	371.05	0	0	0	0

Appendix C : XRD Bulk Mineralogy Scans

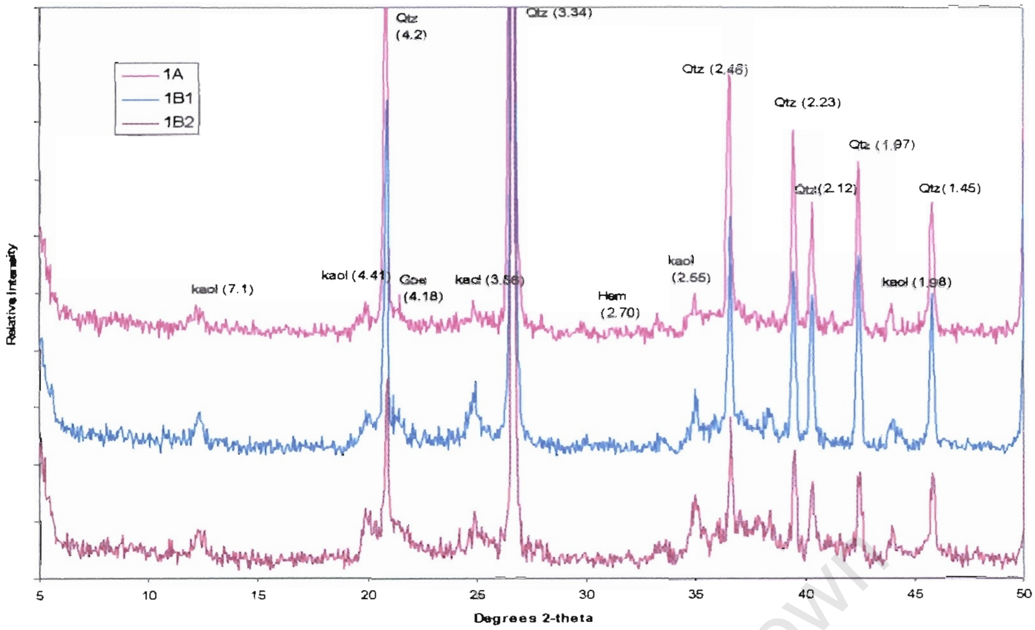

Figure C-1 Bulk Mineralogy XRD Scan of samples from Pit 1.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

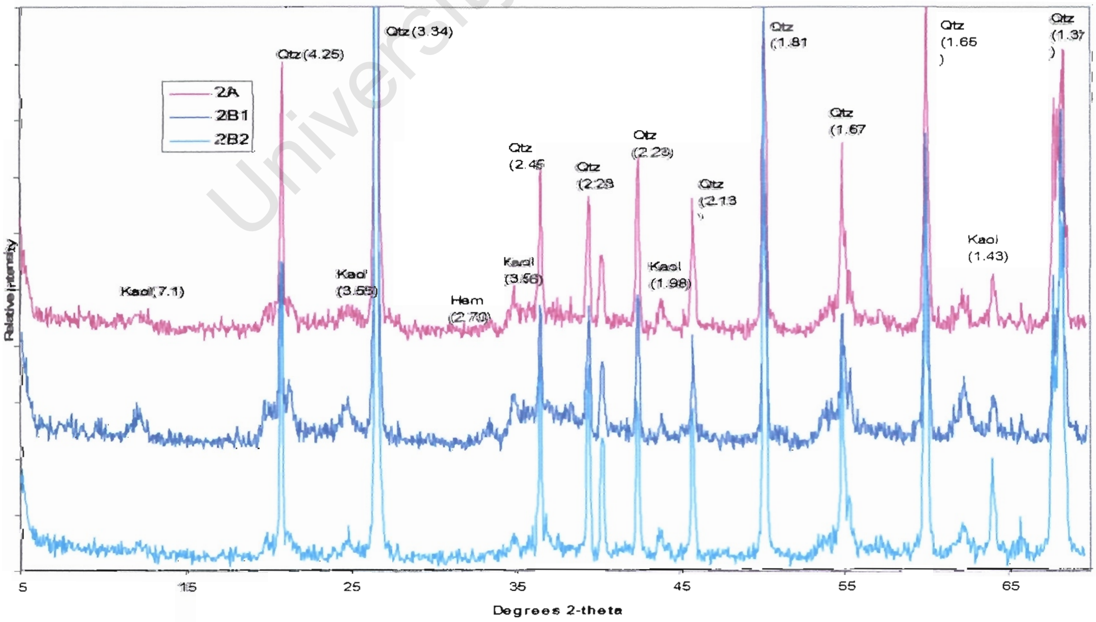

Figure C-2 Bulk Mineralogy XRD Scan of samples from Pit 2.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

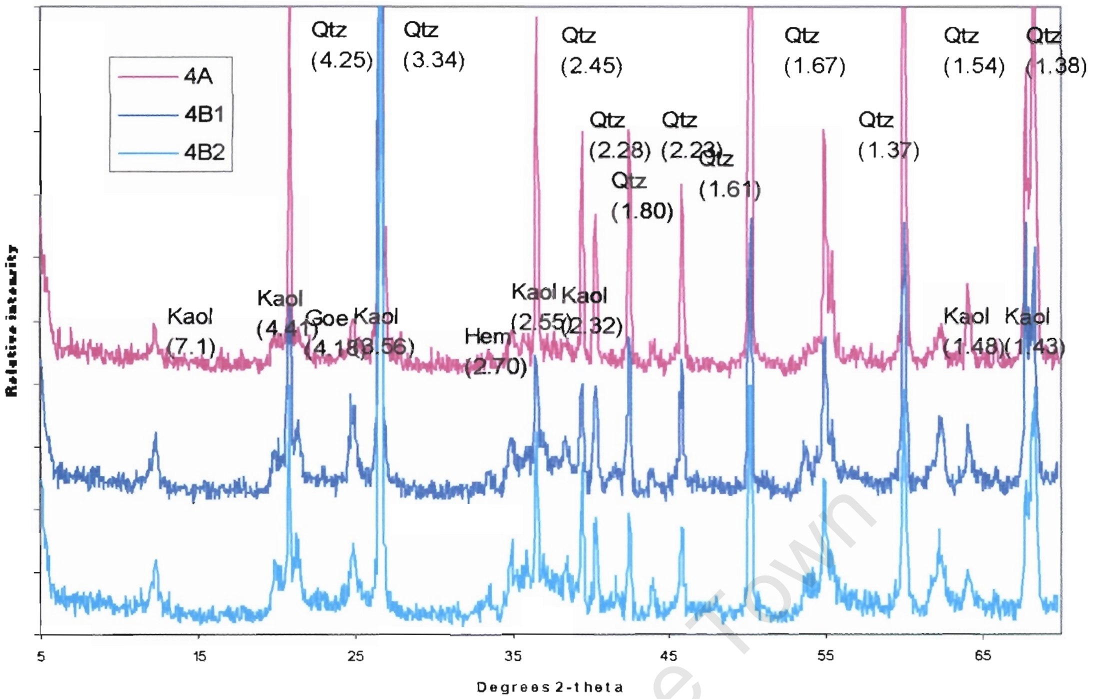

Figure C-4 Bulk Mineralogy XRD Scan of samples from Pit 4.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

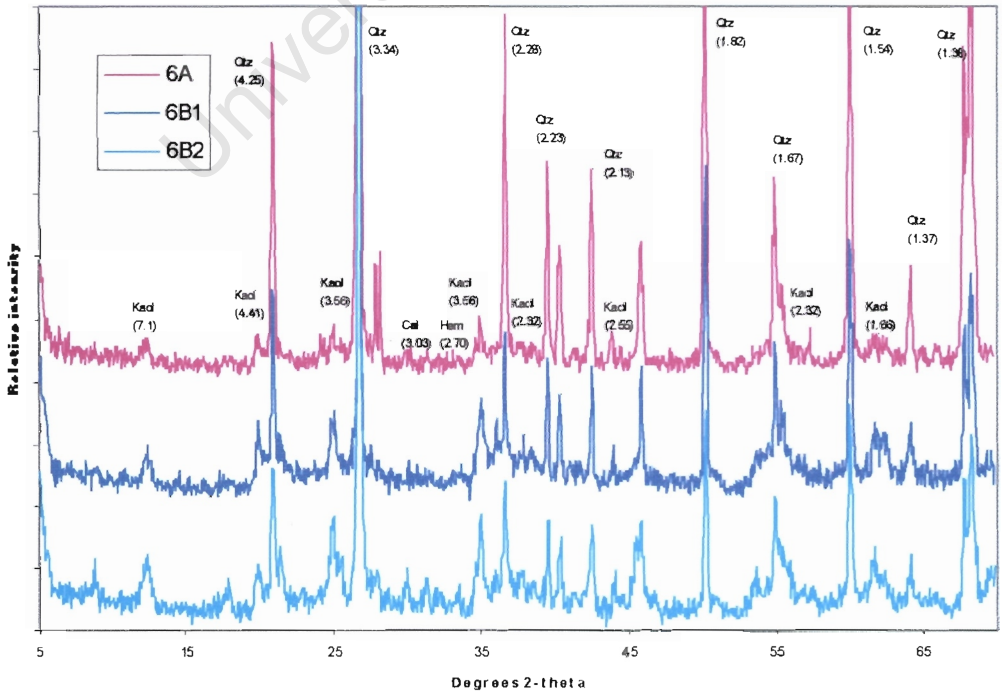

Figure C-6 Bulk Mineralogy XRD Scan of samples from Pit 6.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

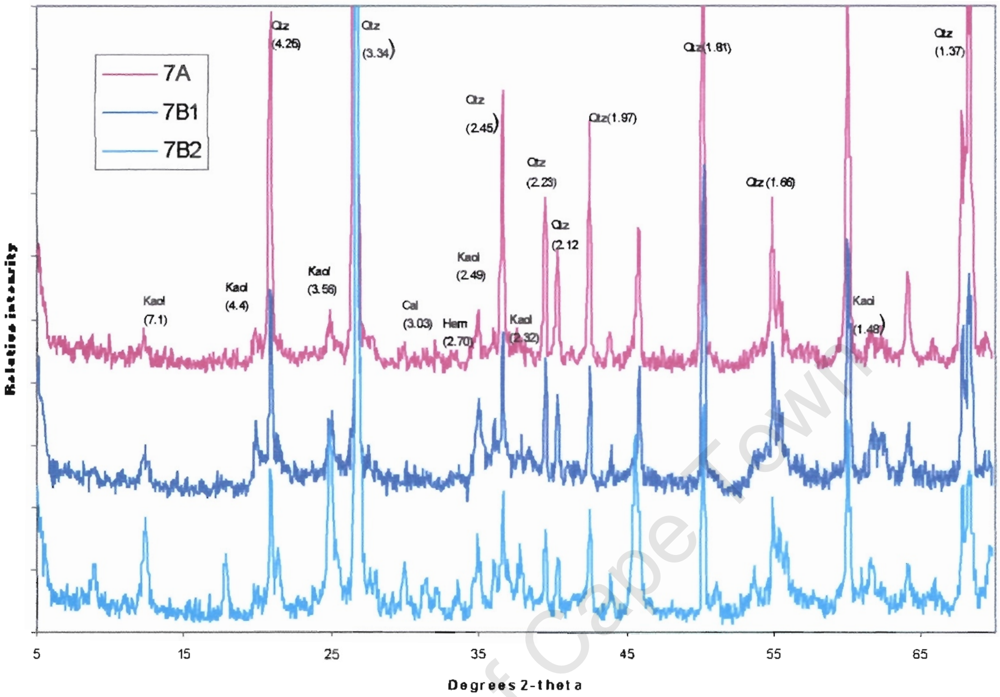

Figure C-7 Bulk Mineralogy XRD Scan of samples from Pit 7.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

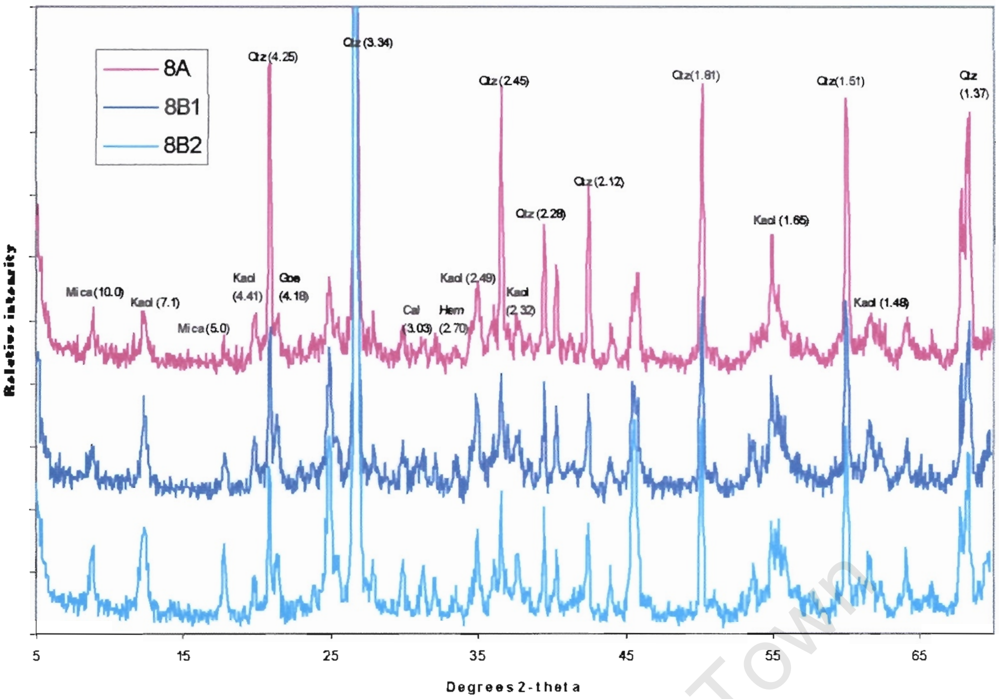

Figure C-8 Bulk Mineralogy XRD Scan of samples from Pit 8.
(Qtz =Quartz; Kaol =kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

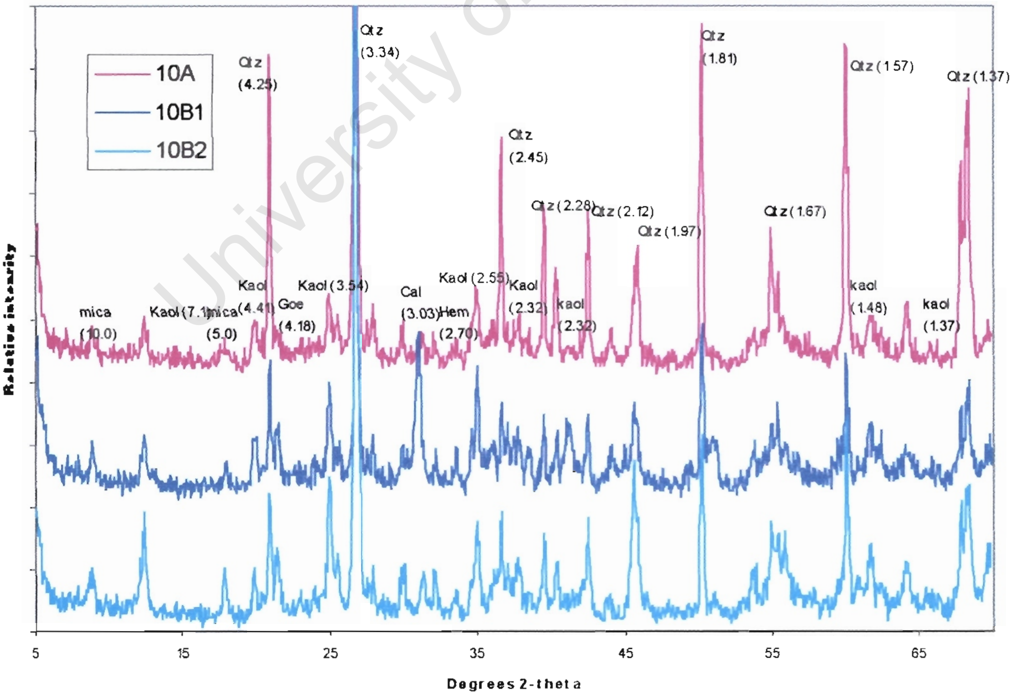

Figure C-10 Bulk Mineralogy XRD Scan of samples from Pit 10.
(Qtz =Quartz; kaol =kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

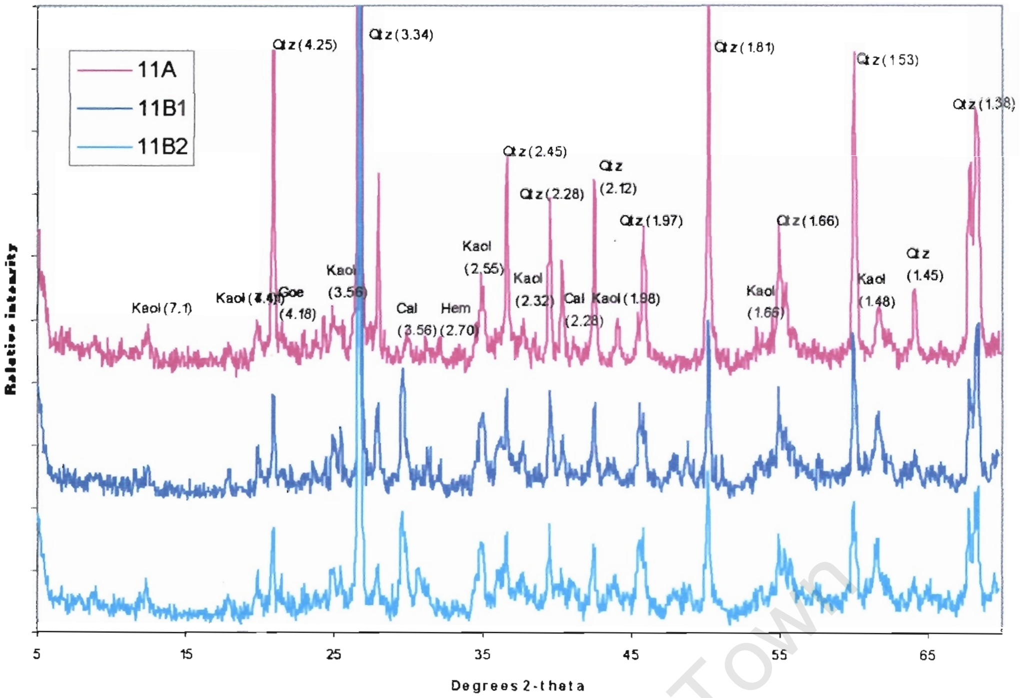

Figure C-11 Bulk Mineralogy XRD Scan of samples from Pit 11.
(Qtz =Quartz; kaol =kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

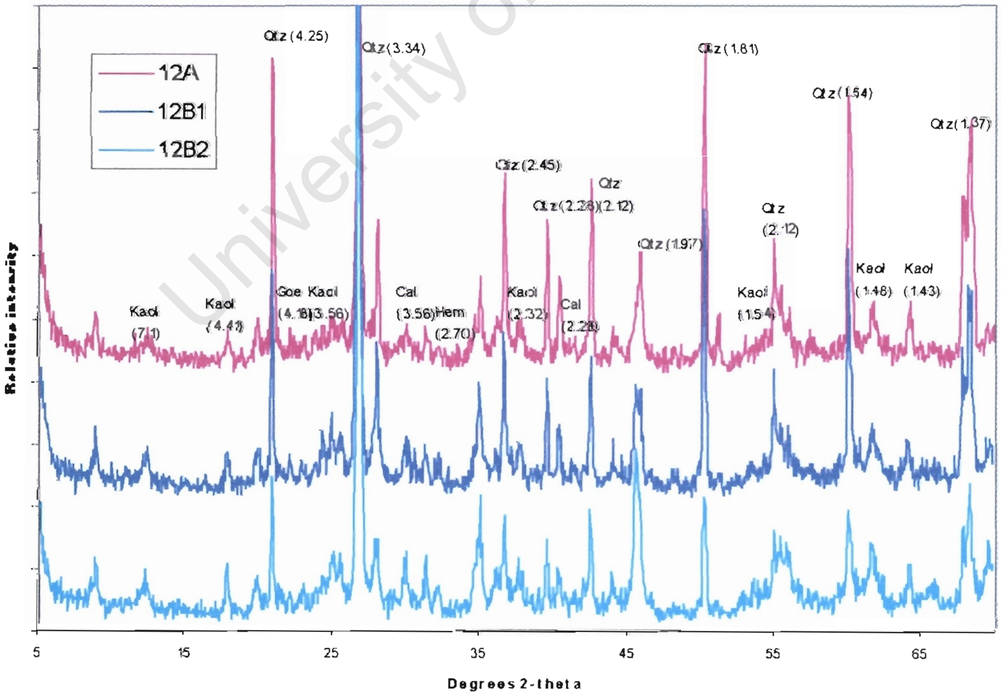

Figure C-12 Bulk Mineralogy XRD Scan of samples from Pit 12.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe = Goethite)

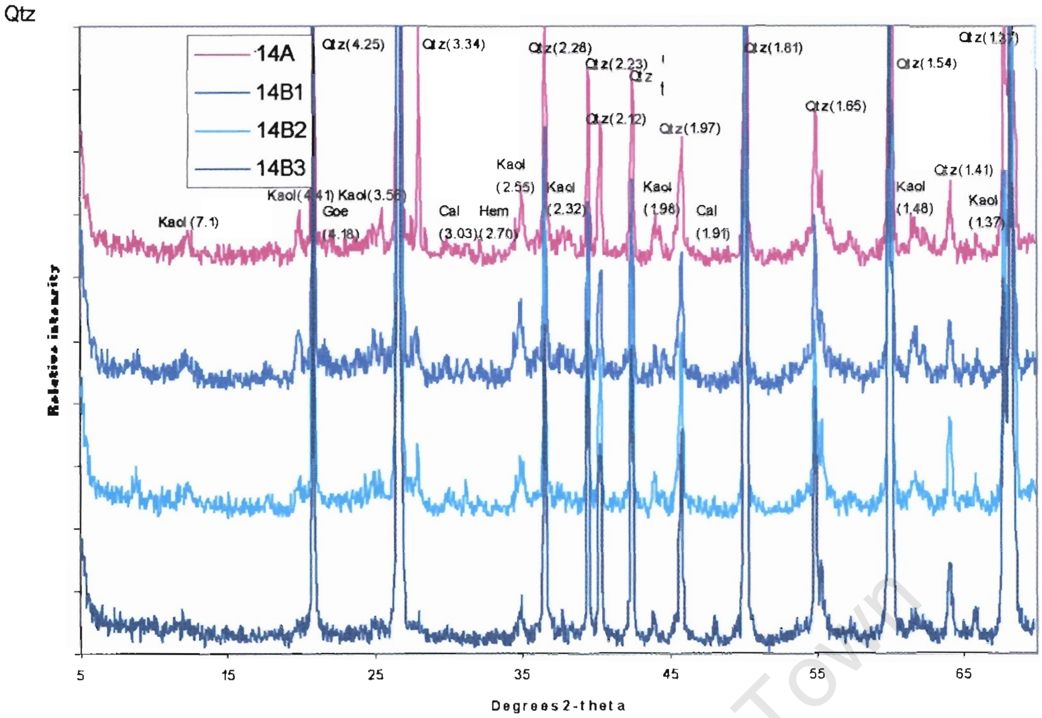

Figure C-14 Bulk Mineralogy XRD Scan of samples from Pit 14.
(Qtz =Quartz; Kaol =Kaolinite; Hem = Hematite; Cal = Calcite; Goe. = Goethite)

Appendix D: Data quality for duplicate analysis

To ensure the accuracy and precision of the laboratory analysis, certain samples and analytes were analysed in duplicates. Some of these details are reflected in appendix D, Tables D1-4.

Table D-1. **Results for duplicate analysis for pH (H_2O)**

Sample I.D	**pH(H2O) 1**	**pH(H2O) 2**	**mean**	**Difference**
2A	6	6.21	6.105	-0.21
4B1	4.87	4.88	4.875	-0.01
6B2	6.44	6.44	6.44	0
8A	7.9	7.7	7.8	0.2
10B1	9.27	9.3	9.285	-0.03
11B2	9.48	9.5	9.49	-0.02
14A	6.45	6.5	6.475	-0.05
14B3	7.04	7.07	7.055	-0.03
			Stdev	0.11
			Mean	7.19
			Precision	1.54

Table D-2 Results for duplicate analysis for pH(KCl)

Sample I.D	**pH(KCL) 1**	**pH(KCL) 2**	**mean**	**Difference**
2A	4.7	4.9	4.8	-0.2
4B1	3.98	3.85	3.915	0.13
6B2	4.02	4	4.01	0.02
8A	7.33	7.45	7.39	-0.12
10B1	8.06	8.06	8.06	0
11B2	7.49	7.46	7.475	0.03
14A	6.02	6.01	6.015	0.01
14B3	5.41	5.4	5.405	0.01
			Stdev	0.10
			Mean	5.88
			Precision	1.71

Table D-3. Results for duplicate analysis for EC(1-5) water extract

Sample I.D	**EC(1-5) 1**	**EC(1-5) 2**	**mean**	**Difference**
2A	0.031	0.042	0.04	-0.011
4B1	0.04	0.06	0.05	-0.018
6B2	0.90	0.94	0.92	-0.043
8A	1.04	1.07	1.05	-0.034
10B1	0.82	0.81	0.82	0.014
11B2	0.26	0.24	0.25	0.020
14A	0.60	0.66	0.63	-0.064
14B3	0.09	0.12	0.11	-0.026
			Stdev	0.03
			Mean	0.48
			Precision	5.83

Table D-4 Results for duplicate analysis forEce (SPE)

Sample I	EC(SPE)	EC(SPE) 2	mean	Difference
2A	25.4	25.71	25.56	-0.31
4B1	23	22	22.5	1
6B2	578	579	578.5	-1
8A	738	736	737	2
10B1	516	518	517	-2
11B2	110	110	110	0
14A	373	374	373.5	-1
14B3	175.8	175.5	175.65	0.3
			Stdev.	1.26
			Mean	317.46
			Precision	0.40

Table D-5. Results for duplicate analysis for calcium carbonate in three samples

Sample I.D	**1st reading (Kpa)**	**2nd**	**3rd**	**4th**	**mean**	**stdev**	**%RSC**	**Precision**
Standards	149	149	150	150	149.5	0.35	0.24	0.24
10B1	15.39	16.05	16.26	16.26	15.99	0.41	2.58	2.58
11B1	12.75	12.75	12.8	12.8	12.775	0.03	0.23	0.23
11B2	16.77	16.71	16.5	16.8	16.695	0.14	0.81	0.81

Appendix E: Data for simplified soil profile

	Horizontal Diff	Height	Horizontal Diff	Vertical Diff	Cumulative Height
1	0	69.66	44.52	1.55	69.66
2	44.52	68.11	56.76	7.98	68.11
4	101.28	60.13	50.75	18.47	60.13
6	152.03	41.66	18.78	6.1	41.66
7	170.81	35.56	58.17	10.25	35.56
8	228.98	25.31	34.47	4.84	25.31
10	263.45	20.47	40.41	8.59	20.47
11	303.86	11.88	28.98		11.88
12	332.84	1.33	38.21	1.33	1.33
14	371.05	0	0	0	0