LAND TREATMENT OF GRAPE-PROCESSING EFFLUENTS NEAR ROBERTSON, WESTERN CAPE

A G PAPINI

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I declare that this research is my own and that it was conducted under the supervision of Associate Professors M.V. Fey and J.P. Willis. No part of this research has been submitted in the past, or is being submitted, for a degree at another university.

Signature removed

A G PAPINI

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ABSTRACT

Land treatment is the predominant disposal method of effluents generated by distilling, wine making and grape juice production in the Western Cape. Primary settling and treatment in aerobic and anaerobic lagoons typically precede disposal to land. Land treatment can effectively remove COD and may also benefit the soil by increasing organic matter, cation exchange capacity and moisture retention capacity. Adverse effects can include salinisation of soils and groundwater, soil structural degradation and odours generated by anaerobic conditions.

The Robertson effluent irrigation site is 35 ha and effluent is spray irrigated at rate of 6mm/day. The climate is semi-arid with maximum temperatures often exceeding 30°C in summer and evaporation rates of up to 9mm/day. The Robertson area receives most of its rainfall in winter, when effluent volumes are at a maximum and average evaporation rates are less than 3mm/day. The site has a westerly aspect and has thin cover of sandy loam on steeper slopes and coarse textured colluvium, up to 2m thick, on the more gentle slopes. Contour ridges with intervening paddocks have been constructed across the extent of the site and in some cases expose underlying shale.

Effluent, surface and groundwater samples were collected on and downstream of the site between August and November of 1999. The effluent composition had a pH range of 4.5 to 5.5; COD from 2.5 to 3.3 g/l, EC of 140 to 200 mS/m and an SAR of 7 to 17 $\text{mmol}_c/\text{l}^{0.5}$. Land treatment results in a 90 to 95% reduction in COD, neutralization of effluent acidity, up to 10 fold increase in salinity and doubling of the SAR. Groundwater leaving the site, primarily through the shale saprolite, rises to surface at a seepage zone 400m from the site. Evaporation results in a salt efflorescence and prevalence of halophytes in the seepage zone. Shallow groundwater may result in increased salinity and sodicity levels in soils of downstream irrigation schemes. A salt load of approximately 400 kg/day is estimated

to leave the site and is expected will ultimately reach the Breede river, some 2.5 km away. The high salinity (~ 1000 mS/m) and potential Na and Cl toxicity of the groundwater places a constraint on its re-use for irrigation. The moist and wet soil samples, which had similar salinity levels to that of ponded effluent support vigorous and varied grass species. The occurrence of dry soils that were saline (EC > 400 mS/m) and did not support grasses, may indicate that irrigation coverage of the site is incomplete. The SAR of the effluent and that of soil solutions does not appear to have had a deleterious effect on soil physical properties as Ca and Mg are the dominant exchangeable cations. However, a high particulate concentration in the effluent and precipitation of salts on the site may reduce soil permeability.

Application of the Hardy-Eugster model of brine evolution provides a framework for understanding some of the compositional changes observed in treated effluent but does not account for all the observed changes. Geochemical processes that may also significantly affect composition include ion exchange, adsorption and reduction. The behaviour of major ions during evaporative concentration was compared against Cl concentration and indicated non-conservative behaviour for Ca, Mg, K, HCO_3 and SO_4. Initially Ca, Mg and HCO_3 are removed as carbonates although precipitation of Mg silicate (sepiolite) and $CaSO_4$ (gypsum) is possible as indicated by a positive saturation index for these minerals in some samples. Ion exchange and sorption remove K while SO_4 losses are attributed to biogenic reduction.

The sustainability of the irrigation scheme appears assured provided salts are continuously flushed. The hydroleogical conditions may place a constraint on continued use of the site because of salinisation of adjacent land. The successful treatment of grape-processing effluents at the Robertson site cannot be assumed for other wastewater irrigation schemes since site specific factors (such as climate, soil type and hydrogeological regime) may play a more important role than effluent composition in determining treatment efficiency and potential environmental impacts.

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CHAPTER 1

INTRODUCTION

1.1 Background

The disposal of wastewater generated by the grape-processing industry, which includes juice and wine producers as well as distilling operations, has long evaded the scrutiny of the regulatory authorities. This situation appears to be changing with both wine producers and government initiating research into the impact of current disposal practices and alternative treatment methods. The promulgation of the New Water Act (1998) has brought pressure on the 'polluter' to demonstrate compliance through a licensing system that requires monitoring and assessment of environmental impacts. The export orientation of the wine industry has brought pressure to bear on wine producers and distillers, as it demands adherence to internationally accepted standards (e.g. ISO14000) in demonstrating environmental performance.

Irrigation of effluent or direct discharge into streams and rivers has been common practice and is still the norm. Deterioration of the aquatic ecosystem is inevitable where organic-rich, saline effluent is disposed of close to drainage channels. Increased salinity in irrigation water can have serious implications for the crops of down-stream farmers. The impact on soil from grape-processing effluent and implication for sustainability is less well documented. Although guidelines for the disposal of effluent and land have been published (Thompson, 1985) there are no South African guidelines specific to the irrigation of grape-processing effluents. The Australian and New Zealand governments have recently published best practice guidelines for winery effluent disposal.

The grape-processing industry in South Africa primarily disposes of its effluents by irrigation on pastures. The opportunities for land disposal are constrained by the vintage period (when the largest volumes of wastewater are generated) coinciding with the rainy season and cooler temperatures.

This dissertation is based on an investigation of a site near Robertson that is irrigated with grape-processing effluents. The site is a good example of land treatment of grape-processing effluents as it has been utilised for almost 25 years. Application of distillery effluent has been taking place since 1975 with grape-concentrate effluent added in 1984; the site area doubled to 35 hectares at this time. Effluent was flood-irrigated up until 1995 when a 44-gun spray irrigation system was installed. The site is approximately 4 km south of the Breede River, a vital regional water resource.

1.2 Focus and value of the study

The aim of this study was to carry out an investigation of the changes in composition of the grape-processing effluent resulting from irrigation (land treatment). These include effluents generated from a grape-juice concentrating plant and a distillery in Robertson in the Western Cape. The study also addresses pathways of effluent migration and the potential impact on the surrounding environment arising from the irrigated site. Evolution in the effluents chemistry is compared with that predicted by geochemical models in the literature.

Comparison between irrigated and adjacent non-irrigated soil is undertaken in order to assess whether there have been changes in soil properties brought about by effluent irrigation. The twin problems of soil salinity and sodicity commonly associated with irrigation in semi-arid regions are addressed with regard to the sustainability of the current scheme.

The investigation also aims to provide recommendations on how to better manage the effluent disposal.

In summary, the key objectives of the study are:

1) To characterise the effluent chemistry and that of water and soils from the site and immediately down-stream of the site and to compare with adjacent non-irrigated land.

2) To assess the degree and extent of pollution leaving the site and the nature of impact to the receiving environment.

3) To evaluate whether the current irrigation practice is sustainable.

4) To make recommendations for improving management of the site and/or further research efforts.

1.3 Limitations

The organic load and salinity of grape-processing effluents are seasonally controlled because of the vintage season that runs from February to approximately June in the Robertson area. The sampling period extended from late August to early November, a non-vintage period. Data were not available on temporal changes in effluent composition. Not being able to sample for a full year limited observation of the variability associated with climate and the vintage season.

The soils were sampled on 25th August, several days after rain and when the soil moisture conditions were at a maximum. It is assumed that in the summer months the site would have less effluent ponding in the furrows.

The non-irrigated (control) soil was sampled from several sites approximately 50m north of the irrigation site. This soil is a sandy colluvium and cannot be considered as representative of the whole site as there are other soil types present in the area. In addition, the irrigated soils have been highly disturbed and mixed with underlying weathered rock (shale).

1.4 Structure of the Dissertation

A review of pertinent literature and principles of land treatment is presented in Chapter 2. This chapter will also include details on the nature of grape-processing effluents and the beneficial and adverse aspects of their disposal on land. Chapter 3 will commence with details of the site including locality, climate, geology and soils. The bulk of this chapter describes how the sampling was done and the analytical methods that were employed. Chapter 4 summarises, in figures, the data with a view to evaluating the performance of the site and in assessing potential environmental impacts. The raw data are presented in Appendices A to D. In Chapter 5, the changes in effluent composition will be evaluated to the geochemical processes that may be occurring. This will be compared with some of the models from the literature that describe the evolution of natural waters by evaporative concentration. Finally, Chapter 6 will conclude with a general discussion and comment on the sustainable use of the site, recommendations to improve current performance and areas warranting further research.

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CHAPTER 2

LAND TREATMENT - A LITERATURE REVIEW

2.1 Introduction

This literature review covers the topics believed to be of relevance in the land treatment of grape-processing effluents. It is not intended to be an all-inclusive review of research in this field but rather covers issues pertinent to the Robertson site.

Land treatment has been defined by Overcash & Pal (1979 in Ginster, 1993) as *"the intimate mixing or dispersion of wastes into the upper zone of the soil-plant system, with the objective of microbial stabilization, adsorption, immobilization, selective dispersion or crop recovery, leading to environmentally acceptable assimilation of the waste".* This definition emphasises the treatment role of application of waste to land as opposed to mere disposal. Application of sewage effluent and solids to soils is commonplace and seen as a beneficial soil conditioner adding nutrients and improving structure. However, Cook et al., (1994) found that the permeability of a highly permeable soil was reduced by 50% after 32 months of irrigation with sewage effluent. The use of treated or partially treated effluent for irrigating productive agricultural or forest crops can be a better alternative than discharge to rivers, particularly in dry countries (Bond, 1998, p.545).

At the outset it must be stated that rarely can pollution be eliminated entirely. Most mineral salts not taken up by plants and later removed from the land, will merely be transferred to soil or drainage water. The aim of land treatment is to minimise the effects of pollution usually by retaining, at least in the short term, the undesirable salts in the soil in a way that they eventually reach groundwater and/or streams at a reduced rate, thereby minimising their influence on water quality. At the same time every effort should be made to prevent serious soil damage not only to promote sustainability, but also, in the event of disposal being terminated, to enable the land to be re-used for other purposes (Thompson, 1985).

Aerobic digestion of grape-processing effluents produces innocuous waste products: primarily carbon dioxide and water. Anaerobic treatment is much slower and produces odorous by-products. The objective of land treating grape-processing effluents should therefore be to maximize the rate of organic matter mineralization. This requires that all the factors that govern microbial activity (temperature, pH, moisture content, oxygen availability, inorganic nutrients, accessibility, etc.), and therefore influence the rate of mineralisation and humification of newly added organic matter, be optimized.

Wastewater ideally suited for land treatment include, inter alia, effluents from sewage treatment plant, liquid animal wastes and wastewater from fruit and vegetable processing. These wastes are characterised by their high organic content. Thompson (1985) defined four categories of wastewater in relation to their suitability for application onto different soil types. These categories are (1) sewage wastewaters, (2) ammoniacal and ammonium-rich wastewaters, (3) wastewaters with high organic matter but a low sodium adsorption ratio (SAR), and (4) alkaline wastewaters with a high SAR. Wineries and distilleries are generally classified as category 3 although distilleries can produce alkaline and high SAR effluents.

A wide variety of land treatment systems exist but three broad categories are recognised. These are (1) rapid infiltration where wastewater is applied to permeable soils (sand and loamy sands) at rates of up to 150m per year (King, 1986). The high loading rate makes evaporative losses insignificant and most of the wastewater eventually reaches the groundwater. On low permeability soils, overland flow systems, with application rates of 1.5 – 7.5m/year are employed. Most of the wastewater leaves the site as run-off. Irrigation systems use the same techniques as conventional irrigation schemes with application rates of 0.3 to 3m/year (King, 1986). In these slow rate systems, high levels of waste treatment are achieved and most of the applied wastewater is lost through evaporation with a small amount entering groundwater. It is this type of treatment system that is in operation at the Robertson site.

The final fate of waste constituents applied to soil can be either through (1) aerial removal, (2) in situ treatment and storage and (3) removal from the site by drainage (Thomas, 1986 in Ginster, 1993). Aerial removal includes uptake by crops, gaseous release from organic degradation, denitrification and volatilization reactions and loss of water through evaporation. In-situ treatment and storage encompasses organic matter decomposition (including humification) and inorganic element attenuation (e.g. through adsorption) by soil organic matter and clay minerals. Some waste leaves the site by drainage into groundwater and, unless sufficiently dilute, can lead to groundwater contamination. The extent to which these 3 pathways contribute to treatment of the wastewater depends on the site characteristics and waste type.

Soil-plant systems have a specific assimilative capacity beyond which release of harmful constituents and soil degradation can occur. Overcash and Pal (1979) define a land-limiting constituent as a particular constituent in the wastewater which controls the land area required for safe disposal of the applied waste. In the case of grape-processing effluents, the organic content is the land-limiting constituent.

Site criteria determining environmental acceptability of land treatment include high net evaporation; soil with sufficient infiltration capacity but also importantly, water holding capacity and adequate vegetation cover to stabilize the soil surface and increase evapotranspiration. The suitability of vegetation cover often depends on its tolerance to salinity; specific toxic ions and ability to withstand waterlogged conditions. Thompson (1985) evaluated the suitability of different soil types for receiving wastes based on the wastewater composition. For the disposal of high organic matter, low SAR effluents, the most suitable land was determined as having moderately shallow reddish brown, medium textured and calcareous soils (other than sands) underlain by relatively impermeable rock on relatively steep slopes. He specified, however, that drains and catchment dams would have to be installed at the lower end of the site.

2.2 The Nature of Grape Processing Effluents

The land treatment of grape-processing effluents encompasses harnessing the metabolic utilization of organic compounds by micro-organisms. Treatment is challenging because wastewaters have high organic loads, are acidic and often saline with a high Na content (relative to Ca and Mg). The effluents originate primarily from cleaning water and from distillery still wash, the residue left after the recovery, by distillation of alcohol from lees or defective wine (Chapman, 1995). About 90% of the lees wine distilled for alcohol spirit remains as residual stillwash. Distillery effluent also contains a 5% 'bleed-off' from cooling tower wastewater.

Simple carboxylic acids, sugars and alcohols dominate the organic carbon content of grape distilling effluents. Chapman (1995, p.40) determined that distillery wastewater has significantly higher biological oxygen demand (BOD)(up to 16 g/l) than winery wastewater (8 g/l in vintage and 3g/l in non-vintage seasons). The organic content is both soluble (< 0.45 µm) and particulate (>0.45 µm). In winery wastewater the BOD is largely made up of dissolved organic compounds whereas in stillage, soluble components accounted for only 30 – 40% of the BOD. The dissolved organic matter in stillage from the Barossa winelands in South Australia is made up primarily of organic acids with lesser but equal amounts of alcohol and sugar. The organic acids are tartaric acid, lactic acid and acetic acid whilst glycerol comprise the main alcohol (Chapman, 1995). Grape juice consists primarily of glucose and fructose. These sugars are present in much greater concentrations than the organic acids which are predominantly tartaric and malic acid (Chapman, 1995 p.38).

The low pH of grape-processing effluents results from dissociation of organic acids. Carboxylic acids are moderately strong acids (Mc Bride, 1994), releasing protons to form carboxylate anions:

$$\text{R-COOH} = \text{R-COO}^- + \text{H}^+ \quad (K_a \approx 10^{-3} - 10^{-6})$$

The negative log of the dissociation constant, pK_a, is numerically equal to the pH at which half of the acid is dissociated and half undissociated (Mc Bride, 1994).

Distillation of lees produces a wastewater with the consistency of thick soup. Suspended solids concentrations can be as high as 20 g/l and originate from bacteria, yeast and grape residues. Best practice guidelines require filtering or settling before irrigation as excessive particulate levels can contribute to soil clogging (Chapman, 1995 p.160).

Seasonal variability in the composition of grape-processing effluents is reportedly high (personal communication: E. Oliver, Technical Manager, KWV). In the vintage period (February to May in the Southern Hemisphere) higher organic load effluents are produced. Averaged analyses of wastewater originating from distilleries in the Barossa Valley of South Australia (Chapman, 1995), data from the KWV distillery at Robertson (Tarras-Wahlberg, 1993) and recent analyses (May 99) from the distillery are presented in Table 2.1. Data were not available for grape-juice effluents.

Table 2.1: Analyses (averages) of distillery wastewater

Analysis	**Australia**[1] (1998)	**KWV**[2] (1993)	**KWV**[3] (1999)
pH	3 – 5	5.0	3.6
EC (mS/m)	175-700	1 700	469
BOD (mg/l)	13 000-35 000	5 270	17 700
Suspended Solids	5 000-30 000	500	4 100
SAR	8	n/a	<1
Na (mg/l)	260-540	350	31
K (mg/l)	1 300-2 100	n/a	1 628
Ca (mg/l)	90-140	16	72
Mg (mg/l)	70-100	n/a	109
Total Organic Carbon (g/l)	1-15	n/a	n/a
Kjeldahl Nitrogen (mg/l)	500-1 700	n/a	504
Phosphorus (mg/l)	100-400	7	190
C : N : P	10-50:4:1	n/a	40-50:3:1

n/a = not available. [1]: Effluent Management Guidelines for Australian Wineries and Distilleries, 1998, p.12. [2]: Tarras-Wahlberg, 1993, p.9 - 80% grape-juice effluent and 20% distillery effluent. [3]: Averaged analyses from May 1999 supplied by E. Oliver (Technical Manager, KWV).

The pH of the effluents depends on the relative concentration of organic acids to alkali (used as cleaning agent) but is usually acidic in the vintage season. The distillation of wine lees concentrates the residual stillwash, which therefore becomes saline. Salinity (EC) of grape-processing effluent is highly variable and depends on the amount of alkali used for cleansing and the degree of recycling. Average BOD for stillwash can range from 13 – 35 g/l with BOD/COD ratio ranging from 0.4 – 0.7. A BOD/COD > 0.5 indicates a readily biodegradable substance (Chapman, 1995, p.48). Under ambient conditions, the BOD of wastewater measures the total molecular oxygen utilized (over a specified incubation period) for the biochemical degradation of organic matter. The COD is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant and is invariably greater than the BOD. In winery wastewater the BOD is almost entirely due to the decomposition of dissolved organic compounds (carboxylic acids and sugars) whereas in stillage, the BOD of soluble compounds accounted for only 30-40% of the total BOD. A BOD/COD ratio > 0.5 generally indicates readily degradable organic matter (Chapman, 1995).

Chapman (1995, p.51) observed that concentrations of soluble Na, K, Ca and Mg in stillwash are similar to their concentrations in grape juice. Sulphur is added as SO_2 gas, which is passed through distilling wine to prevent growth of harmful fungi. The high K originates from potassium bi-tartrate, a major constituent in grapes.

The carbon to nitrogen ratio (C:N), is a measure of the biodegradability of organic matter and is generally high for grape-processing effluents. For Barossa distillery effluents a C:N ratio of 13:1 is reported (Chapman, 1995), which is within the typical C:N ratio of 10-14 for soil organic matter (Jenkinson, 1988).

2.3 Benefits of Disposal on Soil

Direct land application of stillage as irrigation water and as fetilizer has been cited as having the following effects: increase in soil pH, increase in water and mineral salt retaining characteristics, restoration and maintenance of soil fertility and increase in soil microflora (Almeida et al., 1950 in Sheehan and Greenfield, 1979). When soluble and particulate organic matter is applied onto soil it can be respired as CO_2, converted into humic substances, incorporated into the soil biomass or leached from the soil horizon. Humification and increased biomass are beneficial to soils whereas leaching can result in pollution of groundwater.

Humification of grape-processing effluent may be impeded in the soil because of the acidity of the wastewater and nutrient imbalance. To understand the biodegradation potential of the soil ecosystem, one can refer to the following organic matter indicators for normal aerobic arable soil (Verstraete et al., 1996):

- Contains about 0.5% organic C of which some 1% is microbial biomass
- Per hectare, a normal soil microbial biomass (approximately 2 000 kg wet weight) metabolizes every year some 5 000 – 10 000 kg organic matter to CO_2. Approximately 1/3 represents mineralization of microbial biomass.
- As long as the input of fresh organic matter is below 30 tons dry matter per ha per year, relatively rapid conversion without adverse effects on plant growth can be expected.

The addition of organic rich effluents may benefit soils. This could be particularly beneficial to soils in the Western Cape which are typically of low organic content.

2.3.1 Reduction of Organic Content

Heterotrophic bacteria require organic matter as a source of combined carbon from which they can derive energy by respiration and carbon for cell synthesis. They also require nitrogen and various other nutrients. The chemical composition of a typical cell is C~50%; N~14%; P~3%; K~2%; Fe~0.2%; Ca, Mg and Cl~0.5% (Lerner, 1996).

The simple organic chemistry of grape-processing effluents suggests they should be extensively and rapidly removed from the soil solution by processes of microbial metabolism in the soil. Microbial activity can account for the metabolism up to 95% of the soluble concentration of organic carbon in wastewater, mainly into carbon dioxide and assimilation into the microbial biomass (Chapman, 1995). However, Chapman (1995) states that distillery wastewater requires pre-treatment to reduce the total organic carbon content (TOC) and BOD to levels similar to those of winery wastewater to achieve these rates.

Incubation studies (Chapman, 1995) have demonstrated that the solution concentration of ^{14}C-labelled lactic acid and glycerol, compounds found in distillery effluents, could be rapidly reduced to <5% of ^{14}C-input by adsorption and microbial metabolism. The use of ^{14}C allows determination of the partitioning of organic matter into CO_2, biomass ^{14}C and non-biomass ^{14}C. The addition of grape-processing effluents is likely to increase the capacity of the soil to support larger populations of micro-organisms which reduces the time for removal of the soluble organic matter in subsequent irrigations. There is a significant body of evidence indicating that an acclimatized soil microbial population usually increases the rate of BOD removal (Chapman, 1995; Pearce et al., 1995).

Van Veen et al. (1985) indicated the rate of CO_2 evolution and N immobilization is more rapid in sandy loam soil than in clay soils. Ladd et al. (1991) found that in a Vertisol and an Alfisol amended with glucose and $(NH_4)_2SO_4$, the extent of decomposition of ^{14}C-labelled residues was greater, and the accumulation of residual ^{14}C as microbial biomass ^{14}C was less, in the lighter textured, weakly aggregated Alfisol than in the heavily-textured, strongly aggregated Vertisol.

Tare and Bokil (1982) found that most COD removal occurred in the top 15cm of the soil profile. These researchers recommended that a dry period (recovery period) should follow irrigation, the duration of which depends on soil type, wastewater characteristics and prevailing environmental conditions. Chapman (1995) found that adsorption and microbial uptake are responsible for initial decrease in the solution concentration of organic carbon immediately after irrigation. Jones and Edwards (1998) showed that citrate degradation was greatly reduced over short periods (6 – 22 h) in the presence of kaolinite, illite and smectite and almost completely inhibited by the presence of ferric hydroxide. It appears that sorption of organic molecules on the soil's solid phase could provide an important mechanism by which the bioavailability and capacity for biodegradation by the soil's microbial biomass is reduced (Jones and Edwards, 1998). The rate of turnover of organic matter is generally retarded by adsorption on mineral surfaces by making the organic molecule less available to the soil population (Oades, 1989).

Numerous studies have indicated that maximum degradation of hydrocarbons in soils occurs between 20 and 30° C and that the rate becomes insignificant below 5° C (Verstraete et al., 1995). The moisture content influences the availability of the compound and thus the rate of biodegradation, which is greatest when the moisture content of the soil is 50 to 70% of the soil water holding capacity (about 10 – 30% on a mass basis). Extremely wet soils decrease biodegradation because of limited oxygen availability (Verstraete et al., 1996). At low pH, survival of fungi is favoured, while at neutral to alkaline pH, bacteria and actinomycetes grow better. At neutral pH the rate of degradation increases by a factor of 1.5 to 2 compared to a pH of 4.2 and 9, respectively (Verstraete et al., 1995).

The availability of oxygen to soil microbes is often considered to be rate limiting in the mineralization of the organic substrate. Preventing flooding of the irrigated medium is important in maintaining aerobic conditions. Oxidation can continue in limited oxygen environments provided there are alternative electron acceptors available (e.g. nitrate).

Although organic matter oxidation may still proceed in lower redox states provided there are electron acceptors available (NO_3^-, Fe^{3+}, Mn^{4+}), the potential solubilzation of metals like Mn, Fe and Al may cause toxicity to plants and microbes, thereby limiting the rate of organic matter mineralization.

Micro-organisms influence the availability of inorganic nitrogen by three main processes: nitrification, the assimilation of nitrogen into their cells (immobilization) and the conversion of nitrogen compounds that may be lost to the air (denitrification). Nitrogen may also be lost through ammonia volatilisation in alkaline conditions.

For the N requirements of the decomposers to be satisfied, the C:N ratio of the substrate must be less than the C:N ratio of the microbial cells divided by the growth yield (F) of the microbial cells. The C:N ratio of microbial cells is highly variable, for example: 3.3 for the bacterium *Escherischia-Coli* and 13 for the fungus *Penicillium*. The growth yield, F, of the micro-organisms is defined as the C content of the micro-organisms divided by the total carbon assimilated (incorporated into cells and respired as CO_2). The critical C:N ratio of the effluent for aerobic degradation is therefore given by:

$$\frac{\text{C:N ratio of the microbial biomass}}{\text{Growth yield, F}}$$

The critical C:N substrate ratio for a biomass with C:N of approximately 5 and a growth yield ($C_{biomass}/(C_{biomass} + C_{respired})$) of 0.2 is 25 (White, 1997). This may be different for anaerobic degradation.

An imbalance in the C:N ratio of decomposing material may severely affect plant nutrition. High C:N ratios (e.g. 100:1 for cereal straws) may limit available nitrogen and force micro-organisms to draw on soil reserves to meet their own nutritional needs; soil nitrogen becomes immobilized. Low soil nitrogen may restrict microbial growth and reduce the rate of breakdown of organic matter (Harris, 1988).

In conclusion, biodegradation requires consideration of the following factors:

- Soil moisture content
- The substrate
- The presence of electron acceptors (dissolved and solid phase)

- Nutrients
- Fungi, bacteria and their enzymes
- Suitable pH/redox conditions
- The presence of potentially toxic metals

2.3.2 Disposal of Salts

Continual irrigation with wastewater has been found to result in a substantial increase in the contents of the inorganic nutrients within acclimatised soils compared to non-acclimatised soils (Chapman, 1995). The capacity of the soil to function as a repository for inorganic constituents in solution depends on the total permanent charge on silicate minerals and the pH as it affects the charge on variable-charge surfaces such as those of the Fe and Al(oxy)hydroxides. Chloride and sulphate ions are retained only by soils having large amounts of positively charged sesquioxide films on silicates. At low pH, the amount of retained anions increases although observations suggest that nitrate and chloride are adsorbed rather weakly compared to sulphate (Thomas and Hargrove, 1990).

In contrast to anion adsorption, the cation retention of soils is decreased in acidic conditions primarily because organic matter exchange sites become increasingly saturated with Al. Adding lime has been shown to increase the cation exchange capacity of most soils (Thomas and Hargrove, 1990). Simple organic acids and alcohols (both common constituents of distillery effluent), being both polar and soluble molecules, can be sorbed on the exchange complex. However, interactions of organic molecules with clay surfaces in aqueous systems depends on the extent of available surface and the ability of the adsorbing molecules to displace other molecules from the surface. Hence, organic molecules must displace cations by an exchange process or displace H_2O molecules from the outer coordination sphere of strongly held cations, or interact with the cation by neutralizing charge or donating electrons to empty d-orbitals in transition metals (Oades, 1989).

The base saturation status of the exchange complex will also determine the ability to sorb inorganic constituents although the soil solution concentration of the individual ions will determine the equilibrium between ions in solution and those sorbed. Carboxylic functional groups in humus have the ability of complexing metals, particularly Al and the transition metals, thereby reducing their flux through the soil.

Storage of salts may be possible provided there is sufficient porosity between the soil root zone and water table. This is likely to be no more than about 6 t/ha for each metre of the soil profile (Bond, 1998). Thus a 3m profile will begin to leach salts after 2 years of irrigation where the application rate of 1000mm/a and the effluent has a total dissolved solids concentration of 1000 mg/l (as approximately 10 t of salt are added to the soil per hectare per year).

2.3.3 Soil Improvements

Rudd (1987) found that continued irrigation of a red brown earth with wastewater generated by a winery led to an increase in the organic carbon content, and contents of P, N and K within the top 10cm layer of the soil. Repeated application of winery wastewater over 17 years has resulted in a 30 – 75% increase in the total organic carbon content within the 0 – 15 cm layer of a brown earth soil when compared to a non-irrigated soil (Chapman, 1995). A similar increase was noted in an acclimatised solod after only 2 years with irrigation from a winery-distillery.

As mentioned in section 2.3 the irrigation of soil with organic rich effluents increases the microbial biomass. Some researchers (Siegrist and Boyle, 1987 in Chapman, 1995) have found that the increase in suspended solids associated with an increase in biomass were responsible for soil pores becoming partially blocked. In contrast, the humification of soluble organic matter increases cation exchange capacity (CEC) of the soil as a result of the increased availability of functional groups available for complexing cations. Humic materials include highly diverse aggregates with numerous functional groups (predominantly COOH and OH) which are responsible for their high cation exchange capacities. Humic substances have a large influence on the CEC of the soil, often contributing more than half. These can range from 3000 – 5500 mmol$_c$/kg of organic matter in well drained, neutral soils, to between 500 –1200 mmol$_c$/kg in poorly drained acid soils (Wild, 1988). An estimation of the contribution of soil organic matter to the CEC has been made from the empirical relationship (McBride, 1995):

$$\text{CEC (mmol}_c\text{/kg)} = -600 + 500\ \text{pH}.$$

By increasing the CEC of a soil, its capacity to store acid cations (Al, Fe and Mn) on exchange surfaces is increased, thereby buffering changes in soil pH.

In some cases, sorption of organic molecules at mineral surfaces catalyzes changes in the organic molecule, sometimes degradation, and sometimes synthesis into the cells of the microbial biomass or the abiotic formation of humic substances. There is a large body of evidence indicating that humic substances are formed by heterogeneous catalytic effects of inorganic components in soil (Wang et al., 1986). In mineral soils, most humus is associated with inorganic materials, particularly clays, although bridging polyvalent cations must be present to neutralize the overall negative charge.

The increase in soil organic matter improves soil physical properties, which facilitates oxygen diffusion through the soil and infiltration of wastewater. The CEC afforded by humic substances can buffer the soil against the effects of acidification and retain inorganic solutes thereby preventing them from the contaminating groundwater.

2.4 Adverse Effects

2.4.1 Salinity

Salts accumulate in irrigated soil because most of the applied water is removed by evaporation. As with irrigated agriculture in many cases, careful management is required when such high concentrations of salt are applied. Problems arise when, through removal of water by evapotranspiration, salt accumulates to a concentration that is harmful to plants. Build up of salinity will impose osmotic stress on plants that results in wilting and scorching of leaves. There is also a specific toxicity effect associated with elevated concentrations of Na and Cl. It is therefore essential that effluent irrigation be designed to allow adequate leaching to remove salt from the root zone. In order to ensure sufficient leaching, the soil must be sufficiently permeable and this is an essential selection criterion for a successful irrigation site for most effluents (Bond, 1998).

The leaching requirement (LR) is defined as the fraction of irrigation water that must be leached through the root zone to keep the salinity of the soil below a specified value (Ayers and Westcot, 1985). It can be estimated by the ratio of the eletrical conductivity (EC) of irrigation water to that draining the soil. Low rates of leaching result in progressive salt accumulation, which can reach harmful levels; this is particularly the case in arid environments where salts are not flushed by adequate rainfall.

The leaching requirement to maintain soil salinity below a specified value depends on the specific salt tolerance of the plant under cultivation and the salinity of the irrigation water. Tolerance of most plants to salinity can be adequately described by reference to the electrical conductivity of the saturation extract of the soil (Reeve and Fireman, 1967 in Ginster, 1993). Some grasses may tolerate highly saline conditions. For example dry matter yield in *Pennisetum clandestinum* is not significantly reduced until EC is greater than approximately 1000 mS/m (Russell, 1976). Saline soils with EC > 400 mS/m, (Mc Bride, 1994) are usually well flocculated because of their high electrolyte concentration although when the exchangeable sodium percentage (ESP) exceeds 15%, swelling of clays (particularly the smectites) with subsequent dispersion is possible.

The rate of salinity accumulation in a soil is dependent on irrigation management, climate, soil type, aquifer salinity and depth (Ayers and Westcot, 1985). Irrigation management may1 influence the acceptable salinity level of the irrigated water. For example, more frequent or drip/trickle irrigation reduces the effect of salinity because the soil matrix potential is kept high and periodic drying cycles are prevented. However, for successful management of nitrates, periodic wetting and drying cycles are necessary (Ginster, 1993).

Shallow water tables where saline groundwater is less than 2 meters from surface may compound soil salinisation as capillary rise may bring saline water into the root zone. Suppression of the water table by sub-surface drains is often used to mitigate this hazard.

Maintaining salinity suitable to the vegetative cover on an irrigation site is the overriding short-term consideration. It is therefore inevitable that under effluent irrigation, there will be saline water moving from the root zone to groundwater. Increase recharge to groundwater is usually regarded as an inevitable consequence of irrigation. The quality of groundwater prior to irrigation will determine whether or not salt reaching the groundwater will have a detrimental impact.

2.4.2 Sodicity

Excessive sodium in irrigation water promotes soil dispersion and structural breakdown where Na:Ca >3 (Ayers and Westcott, 1985). Excess Na often leads to water infiltration problems due to dispersed clay particles plugging and sealing soil pores. Other related problems include soil crusting, poor seedling emergence, and lack of aeration, plant and root diseases and weed and mosquito control problems.

The adjusted Sodium Adsorption Ratio, adj R_{Na} (Ayers and Westcot, 1985, p. 63), accounts for changes in Ca in soil water due to precipitation or dissolution after irrigation. The modified Ca value accounts for the salinity of the applied water, the HCO_3/Ca ratio and the estimated partial pressure of CO_2 in the surface few millimetres of soil. However, the adj R_{Na} does not significantly change the SAR, values of which are calculated by the equation:

$$SAR = Na/(\sqrt{(Ca + Mg)/2})$$

Dilution of irrigation water on the site by heavy rainfall may bring about a moderate but temporary reduction in the infiltration rate. Rainfall constitutes low salinity water and irrigated areas frequently experience exceptionally low rates of infiltration resulting from excessive rainfall (Ayers and Westcott, 1985). Poor soil structure may theoretically be improved by increasing the salinity of irrigation water.

The sodicity of a soil is defined as the proportion of Na occupying the exchange sites (termed the exchangeable sodium percentage or ESP). A sodic soil typically has a pH > 9 and an ESP $> 15\%$. The combination of relatively high salinity and SAR in irrigation water is expected to cause the ESP in the soil to increase.

Soils with high ESP are predisposed toward swelling, surface crusting, sealing, erosion and other undesirable consequences of colloidal dispersion. The threshold concentration of the soil solution that results in dispersion of soil colloids is influenced by the Na status of the soil, soil solution composition (as well as that of the irrigation water) and soil type. Soils with expanding lattice type clay minerals are likely to disperse more with increased SAR than are highly weathered, sesquioxidic or kaolinitic soils. The Na and K hazard from irrigated effluents is reduced by the presence of NH_4 (as it keeps Na and K off the exchange surface) and by the higher apparent solubility of $CaCO_3$ precipitated from wastewaters containing soluble organic residues (Levy, Fine and Feigin, 1984 in Ginster, 1993).

For a given combination of high ESP and soil solution concentration, the likelihood of soil structural breakdown increases with increasing soil pH, increasing clay content, increasing proportion of smectitic and illitic clays, increasing mechanical disturbance, decreasing organic matter and decreasing proportion of sesquioxides (Sumner, 1993 in Bond, 1998).

The interaction between soil sodicity (ESP) and soil solution concentration means that while effluent irrigation continues, there is unlikely to be a deterioration in soil structure because the expected high salinity of the effluent will counterbalance the high SAR and associated ESP. Changed land-use after effluent irrigation (e.g. by returning the land to cultivation) may lead to structural deterioration. Similarly, a decrease in salinity or ionic strength, after returning to rain-fed agriculture, may result in breakdown in soil structure.

While unlikely to have an effect during effluent irrigation, increased soil sodicity may lead to considerable problems following the cessation of effluent irrigation and changed land-use. In terms of the definition that sustainable land-use should not render the land unsuitable for other uses in the future, effluent irrigation poses a high risk of not being sustainable. Gypsum is the most common soil ameliorant for alleviating soil sodicity problems but the amount required may be several times the normal agricultural application, depending on SAR and salinity of the effluent. Furthermore, while this may prevent problems in the root-zone, the sodium will be pushed deeper into the soil and may affect subsoil permeability (Bond, 1998).

The use of NaOH in the cleaning process in grape-processing factories has major implications for the sodicity of these effluents.

2.4.3 Deficit of Electron Acceptors (Low redox)

Meeting the oxygen requirements of the biomass to prevent odours resulting from anaerobiosis is one of the greatest challenges facing land treatment of organic rich effluents. Although not harmful in themselves, odours are an indication of a reduction in the rate of organic matter mineralization and poor performance of the treatment scheme.

The level of oxygen in wastewater generated by grape-processing industries is insufficient to meet their biological oxygen demands (BOD) and their irrigation can lower the redox conditions in the soil. Microbial metabolism of effluent will create an oxygen deficit in most soils, particularly where excessive irrigation leads to waterlogged ground (as the diffusion coefficient for oxygen in water is about 10^4 times less than in air). For example, a soil with a total pore volume of 50%, of which 10% remains air-filled after irrigation, will contain approximately 15 g of oxygen per m^3. An effluent with a BOD of 3g/l irrigated into this soil will have a BOD equivalent of 1200 g of oxygen per m^3. In practice, good management requires sufficient time between successive irrigations to allow re-aeration of the soil. Following irrigation only macropores (>30 microns) are expected to remain air-filled and therefore the presence of interconnecting macropores is essential for maintaining sufficient rates of oxygen diffusion to meet the needs of the biomass (Oades, 1984 in Chapman, 1995).

In situations of reduced O_2 availability, the extent of decrease in redox potential depends on the quantity of alternative reactive electron acceptors in the soil compared with the quantity of electrons generated by organic matter oxidation. These electron acceptors and their redox potential (in mV) are presented in table 2.2.

Table 2.2: Redox potential of different electron acceptors (Verstraete et al., 1989).

Electron acceptor	Eh (mV)*	Type of microorganism
$O_2\ e \Rightarrow 2\ H_2O$	+ 810	aerobic
$NO_3 \Rightarrow N_2 + H_2O$	+ 430	aerobic
$MnO_2 \Rightarrow Mn^{2+}$	+ 396	aerobic
$Fe^{3+} \Rightarrow Fe^{2+}$	+ 200	facultative
$R_2\text{-}C{=}O \Rightarrow R_2CHOH$	+ 200	facultative
$SO_4^{2-} \Rightarrow H_2S + H_2O$	– 200	anaerobic
$CO_2 \Rightarrow CH_4 + H_2O$	– 200	anaerobic
$2H^+ + 2e^- \Rightarrow H_2$	– 420	anaerobic

* pH = 7 and 25°C.

A decrease in redox potential is typically accompanied by a rise in pH unless the pH of the soil is >7, in which case pH will decrease because of precipitation of metal hydroxides or carbonates (McBride, 1994):

$$2Ca^{2+} + 2HCO_3^- = 2CaCO_3 + 2H^+$$

One of the most important causes of soil nitrogen loss by volatilization is microbial denitrification. The reduction to gaseous di-nitrogen or nitrous oxide can be brought about by numerous groups of predominantly facultative bacteria, which use oxides of nitrogen as an electron acceptor in the absence of free oxygen. Denitrification is favoured in warm and wet conditions where easily decomposable organic matter is abundant and can generate alkalinity in soil:

$$NO_3^- + 6H^+ + 5e^- \Rightarrow N_2 + 3H_2O$$

Conversely, the nitrification of ammonium, or ammonium-forming organic materials, are potential acid formers in soil (Mc Bride, 1994):

$$NH_4^+ + 2O_2 \Rightarrow NO_3^- + 2H^+ + H_2O$$

Organic additions to soil can enhance denitrification provided nitrate concentrations are high (Curtin et al., 1997). Where nitrate concentrations are low, the nitrate may be immobilized and assimilated by micro-organisms before significant denitrification has taken place. Nitrification and denitrification are reduced in soil pH < 6. However, information on the pH dependence of N mineralization (organic-N to NH_4) is inconsistent.

A very low concentration of dissolved oxygen of 4×10^{-6} M in the soil solution surrounding bacteria is required before reduction begins (Harris, 1988). However, soils, which appear well aerated, may yet reduce nitrate to nitrous oxide and nitrogen, particularly if the organic matter status is high because of the existence of microsites where the oxygen demand by the microbial population has exceeded the supply from the soil atmosphere. Hence, the interior of soil aggregates or crumbs may become anaerobic sites for denitrification.

The energy the bacteria derive from anaerobic biodegradation of glycerol is 15% that of aerobic mineralization (McCarty, 1972) and the rate is significantly less. A decrease in the redox of the soil may reduce the nutrient availability of some elements (e.g. nitrogen) whilst others (Mn, HS^-) may become soluble and result in toxicity to soil organisms.

2.5 Conclusions

Grape-processing effluents have a high organic content, may vary from acid to alkaline and have variable SAR. Most of the organic content is made up of readily biodegradable carboxylic acid, sugar and alcohol. This soluble organic matter is amenable to land treatment although distillery effluent may require pre-treatment or dilution to lower COD. The C:N ratio of grape effluents may constitute a constraint to optimal biodegradation. For optimal biodegradation the C:N ratio should be similar to that of the soil biomass. Effluents have characteristically high K concentrations and the cation concentrations are similar to that found in grapes.

The benefits derived from land treatment of grape-processing effluents include a reduction of up to 95% in the soluble organic matter 24 hours after irrigation. Biodegradation is more rapid in sandy loam than clay soils and occurs in the top 15 cm of the soil profile. Most of the organic matter is respired and volatilized as CO_2 while a lesser fraction is immobilzed as humic substances and within the soil biomass. Increased humic substances provide stability to the soil, increases the soil's CEC, which provides a buffer against rapid changes in effluent pH. The disposal of salts depends on the permanent charge of silicate minerals and pH as it affects the charge on variable charge oxides.

Soils generally have limited capacity to store salts and leaching from the root-zone is essential to prevent osmotic stress and Na and Cl toxicity to plants. Maintenance of soil permeability is critical to the sustainability of land treatment schemes. Sodic soils (ESP > 15% and pH > 9) may result from high SAR effluent and cause clay dispersion and pore clogging, particularly in soils with expansive lattice clay minerals. The moderately high salinity of the effluent, however, usually counter balances the effluent's sodicity (and associated ESP) but a return to rain fed agriculture may result in a breakdown in soil structure. The high-suspended organic load in the effluent can similarly result in loss of soil permeability.

Meeting the oxygen demands of the biomass to reduce the odours resulting from anaerobic biodegradation is one of the greatest challenges facing land treatment of organic rich effluents. This requires an adequate 'drying-out' period between successive irrigation to allow for re-aeration of the soil. Biodegradation may continue in oxygen deficit environments, albeit it a slower rate, provided there are other electron acceptors available. Microbial dentrification may account for the loss of nitrous oxides in the absence of free oxygen in wet and warm conditions. The reduction of Mn oxides may also occur at similar redox conditions to that of denitrification. The reduction of Mn oxides can also occur at similar redox conditions as than of denitrification.

Central to the design and management of effluent irrigation is an evaluation of the water and nutrient balance for the specific site. An understanding of the site's water balance is more readily achieved than development of a nutrient balance model. The relationships between C, N, P and the essential nutrients is much less well understood. This appears to be the case particularly in the quantitative prediction of the fate of nitrogen, specifically, especially through denitrification. Key limitations to the sustainable use of land for organic-rich effluent irrigation include excessive leaching of nitrate (and phosphorus in sandy soils) to groundwater, the accumulation of salinity and changes in the soils physical properties.

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CHAPTER 3

SITE DESCRIPTION, SAMPLING AND ANALYTICAL METHODS

This chapter describes the history and current operating parameters at the irrigation site and provides a site description. The sampling procedure and analytical methods are also described. The analytical results are provided in Appendices A to F.

3.1 The Robertson Site

3.1.1 Introduction

The Robertson irrigation site is located approximately 6 kms south-west of Robertson (Figure 3.1). Wastewater generated at the distillery and grape juice concentrator in Robertson is conveyed to a settling lagoon mid-way between the distillery and the irrigation site. From here, the wastewater is pumped to a holding dam for irrigation.

The Robertson irrigation site was originally commissioned in September 1975 to receive distillery effluent. In April 1984, due to additional effluent produced from grape juice concentrates, the site was extended northward to comprise the current site area of 35 ha. The southern half of the site has been in use since 1975 and is referred to as the 'old site' while the northern half is referred to as the 'new site'. A 44-cannon irrigation system was commissioned in 1995 prior to which flood irrigation of the effluent was carried out.

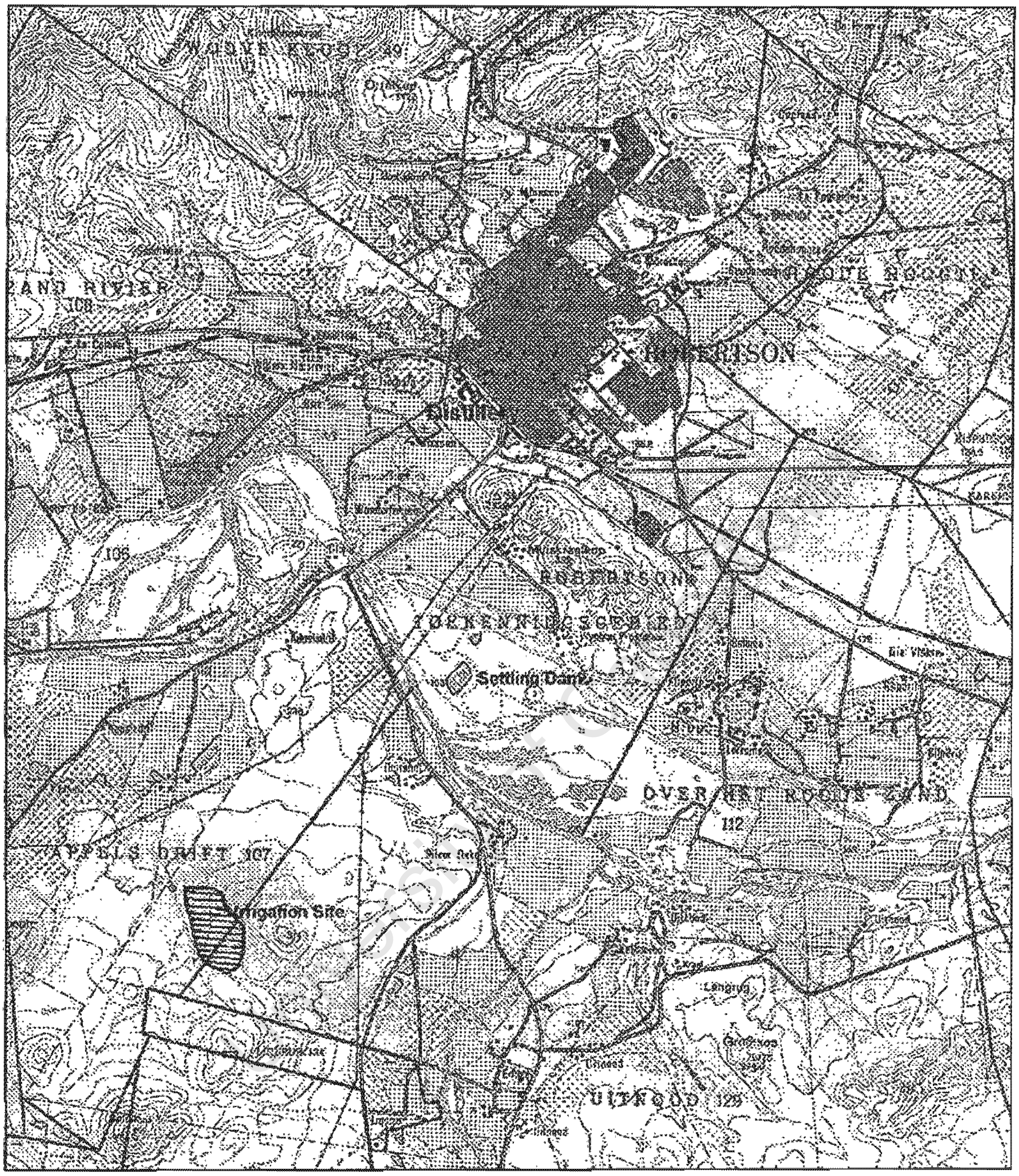

Figure 3.1: Locality plan indicating the irrigation site, settling lagoon and distillery and grape-juice concentrator in Robertson.

Normal operating procedure is for the simultaneous operation of two adjacent cannon sprinklers for an hour. Irrigation is reportedly continuous and controlled by level switches in the effluent holding dam at the irrigation site and in the settling lagoon. The soil is therefore irrigated every 22 hours. Each sprinkler is reportedly capable of irrigating up to 45 m^3/hr (plant manager, pers comm.) and has a theoretical application radius of 50m. The area covered by each canon is 0.785 ha. Given the maximum irrigation rate and assuming uniform coverage, each 1-hour irrigation period provides 6 mm m^{-2} day^{-1}. Effluent production for the first six months of 1999 was 132 megalitres; this is equivalent to 30 m^3/hr, a third of the designed application rate. The vintage season (when grapes are harvested, crushed and fermented) is from February to May each year. Effluent volumes and organic load reportedly reach a maximum in this period.

Seepage is collected in a drain situated on the western boundary of the site from where seepage gravitates to a sump and is pumped back to the site for re-irrigation. This seepage represents effluent that has received maximum treatment and a comparison with effluent provides an estimation of the overall efficiency of the land treatment scheme.

3.1.2 Physiography and Climate

The irrigation site has a westerly aspect and lies between 220 and 260 m above sea level. The slope is 1:6 on the steeper north-east side of the site, reducing to 1:18 near the western boundary fence. The site has been engineered to consist of a series of contoured ridges and furrows (see Figure 3.2).

Records from 2 weather stations near Robertson (NIVV and PP) were consulted to obtain information on historic climatic conditions. The record for station NIVV is from 1990 to 1997 whilst station PP is from 1995 until present. Averaged monthly precipitation, evaporation and net evaporation data for 1990 to 1997 are presented in Figure 3.3. The data indicate that the potential evaporative rate in summer is of the order of 6 – 9 mm/day. This reduces to 1 – 3 mm/day in the winter when most of the rain falls. Average maximum and minimum temperatures for January, the hottest time of the year, are 31° C and 16.7° C, respectively. In July the average maximum and minimum temperatures are 18.5° C and 5.7° C.

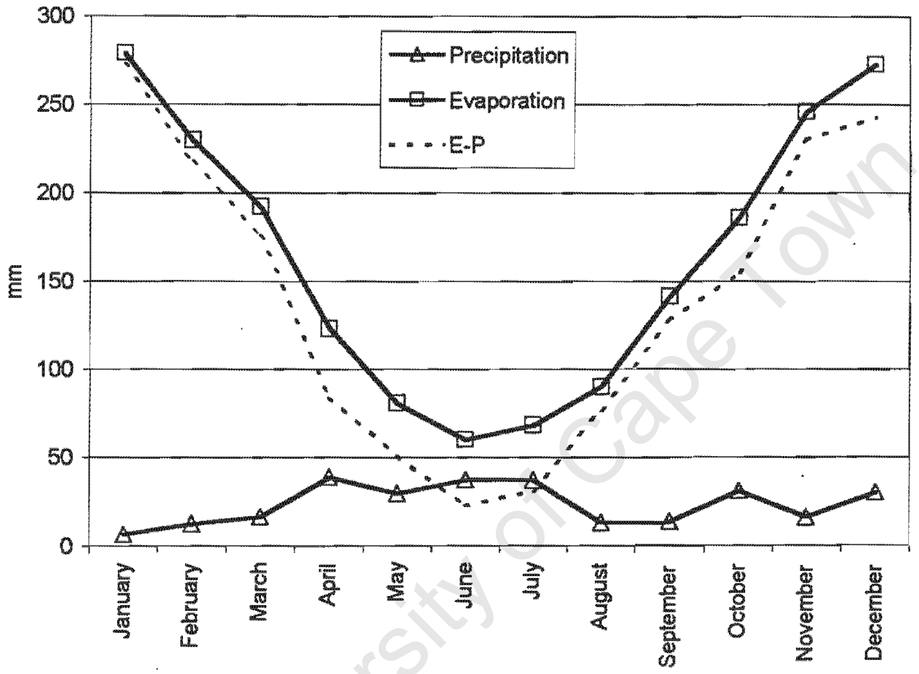

Figure 3.3: Averaged monthly precipitation and evaporation for 1990 – 1997, station NIVV, Robertson.

3.1.3 Geology and Hydrogeology

The irrigation site is underlain by shale of the Waboomberg Formation, which forms part of the Bokkeveld Group. The shale is folded and at the site appears to be dipping almost vertically (Figure 3.4). Shale outcrops are prevalent in the area because of poor soil cover. On the irrigation site, a westerly-thickening wedge of colluvium occurs; this cover is absent in the elevated (east) part of the site but reaches a

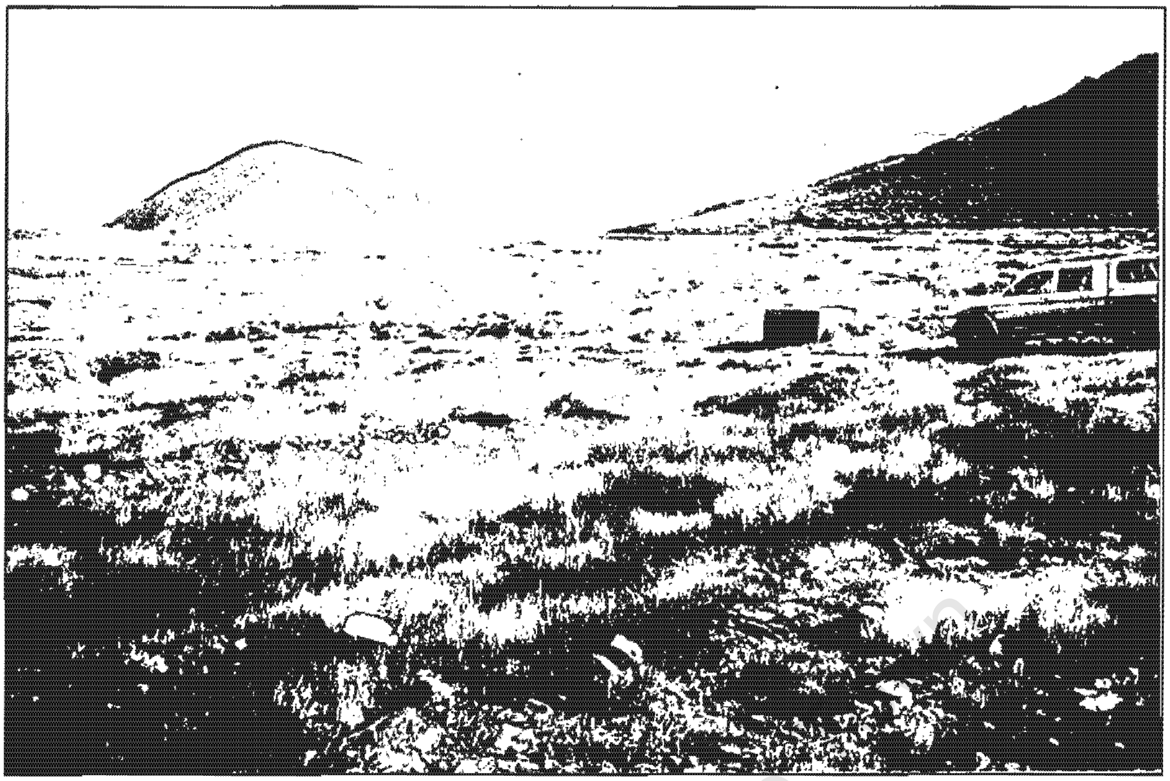

Figure 3.2: Irrigation site looking north-west with the Langeberg Mountains in the distance

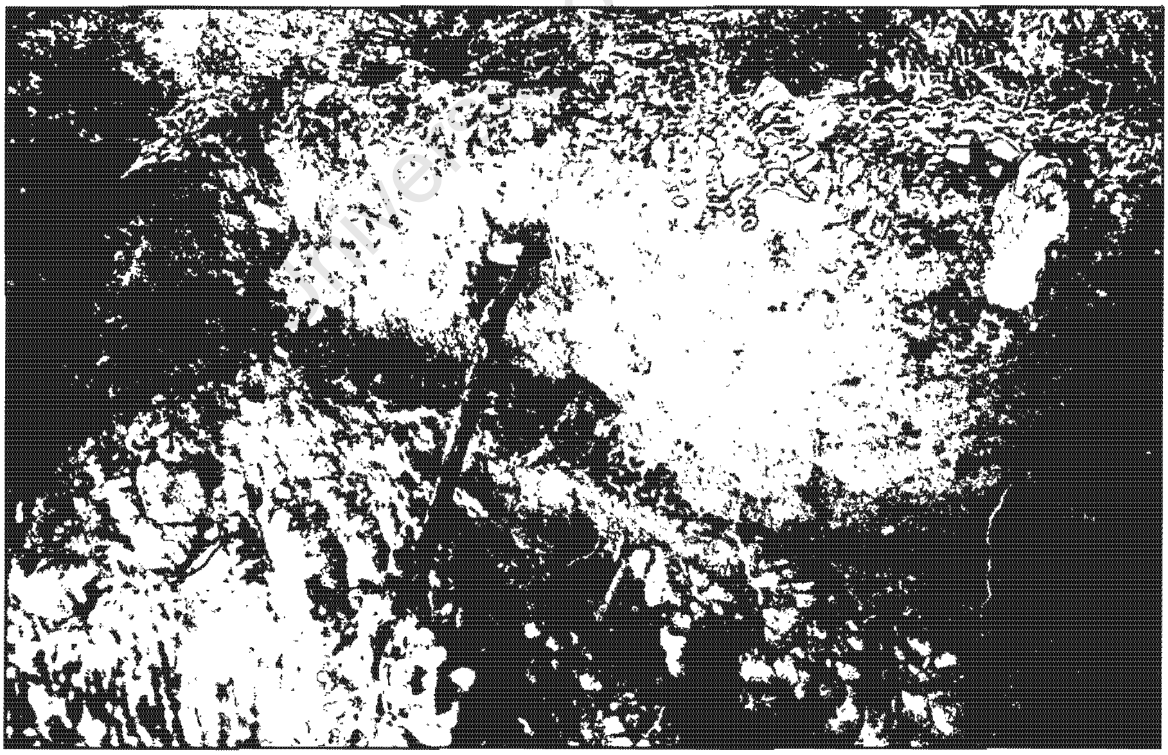

Figure 3.4: Colluvium overlying pebble bed and weathered shale

thickness of approximately 2m on the western boundary. The colluvium is believed to provide a preferential conduit by which effluent moves down-slope. The highly jointed shale may also provide a pathway through which effluent leaves the site, particularly when effluent ponds on the elevated parts of the site. The jointed shale is thought to have a significantly smaller permeability than the colluvium. To the north-west of the site an alluvial channel acts as a conduit for seepage leaving the site. Water levels in this material vary from 1 to 3 m below ground level. In this area groundwater in the Bokkeveld aquifer is usually found at considerable depths and is often brackish. The Bokkeveld is not normally considered an important aquifer in this area and no boreholes were located in proximity to the site. In the situation where recharge of a deep Bokkeveld aquifer were to occur immediately downstream of the site, effluent seeping from the site could be expected to adversely affect groundwater quality.

3.1.4 Soils and land-use

The semi-arid climate of the Robertson region has produced Aridisols of low organic matter content. The soils on the irrigation site have been highly disturbed and classification into soil form is therefore not considered appropriate. Tarras-Wahlberg (1993) described the soils in the area as belonging to the Mispah form (thin orthic A-horizon overlying an R-horizon, see figure 3.4) on the slopes and Glenrosa and Cartref forms where thicker soils are developed in the valleys. The Cartref form comprises an orthic A horizon underlain by an E horizon followed by a lithocutanic B horizon. The Glenrosa form is similar but does not contain the E horizon.

The farmer immediately north-west of the irrigation site conducts a sand-winning operation and grows vegetables and fruit with irrigation water from the Breede River.

3.1.5 Vegetation

A comprehensive survey of vegetation was not carried out. Earlier investigations (Tarras-Wahlberg, 1993) describe 10 species occurring on the effluent site not found on adjacent undisturbed areas. The current study identified a vegetation pattern resulting from the moisture status of the soils. Various grass species, in particular *kikuyu* grass (P. clandestinum) is prolific on the ridges around the irrigation cannons. In the furrows reeds occur where effluent has ponded. In drier areas, which did not appear to receive regular irrigation, there are salt-tolerant shrubs. In undisturbed areas, the vegetation is stunted and comprises shrubs and small bushes.

3.2 Sampling

Thirty-one water samples were collected between August and November, 1999 and their analyses are presented in Appendix A. A sampling locality plan is provided in Figure 3.5. The sampling dates were 25th and 26th August; 2nd September; 7th September; 7th October and 10th November. Slotted 4 inch PVC stand-pipes were installed with the aid of a back-acter in the alluvial channel north-west of the irrigation site to sample groundwater migrating from the site. The boreholes were sampled on 7th October and 10th November. Sixteen soil samples were collected from the site and surrounding land on the 25 August 1999.

3.2.1 Water Sampling

Water samples were taken of effluent from the site holding dam, effluent ponding on the site and groundwater collecting in a sump on the western boundary of the site. Groundwater samples were collected twice from the boreholes situated in the alluvium to the north-west of the site. The boreholes were less than 3.5 m deep and were purged prior to sampling. Seepage water from a wetland area situated approximately 400m north-west of the irrigation site was sampled at various places on

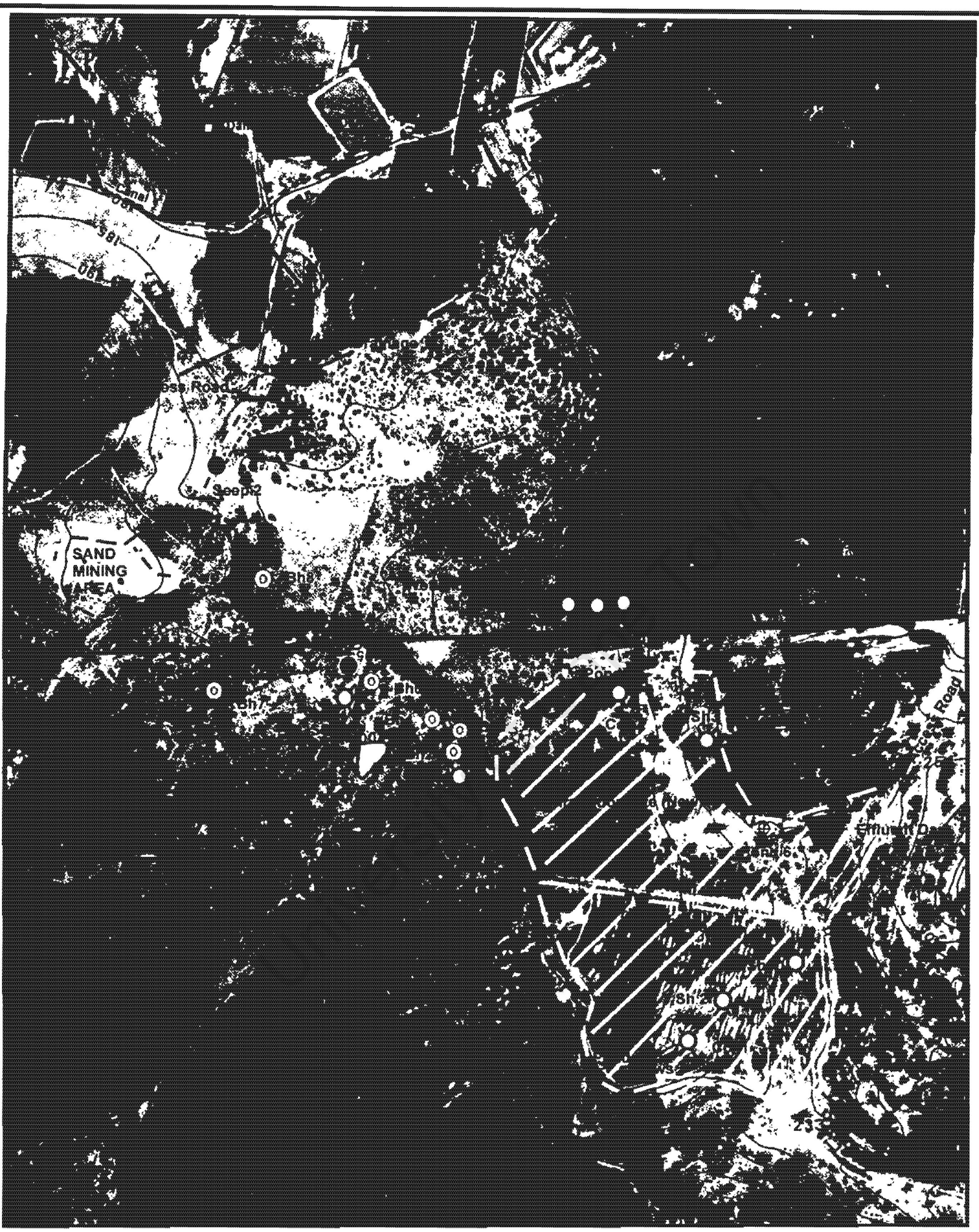

Figure 3.5: Sampling Locality Plan

3 occasions. Water flowing in a trench at the northern end of the wetland area was also sampled on 3 occasions as well as a dam into which this water flowed. A schematic representation of the sampling points is provided in Figure 3.6. The bold italic script in the schematic below indicates the sampling points, which are described in more detail below.

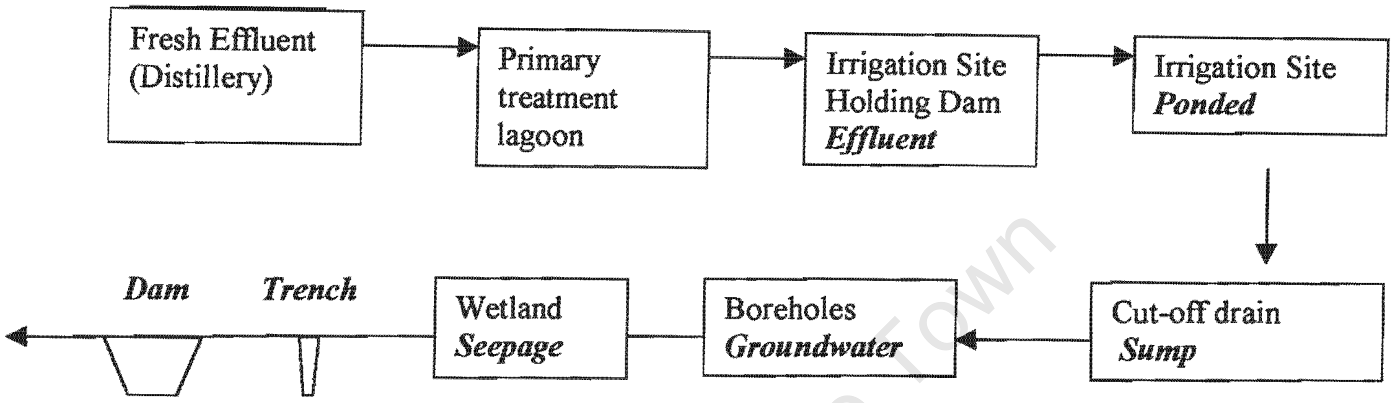

Figure 3.6: Schematic of Sampling Points

3.2.1.1 Effluent

The irrigation effluent was collected from the holding dam. The effluent is a thick, cloudy, soup-like liquid with a large suspended solids load and strong odour. Samples were collected on four occasions from the effluent holding dam over the period from the 25th August to the 10th of November. Two of these samples were taken within 24 hours of each other and analysed at different laboratories: the CSIR and the Geological Sciences Department at the University of Cape Town.

3.2.1.2 Ponded

Samples were collected where effluent had ponded in furrows. The moisture conditions were reportedly higher than normal because of rains that had occurred several days before the 25th August. The presence of extensive reed beds suggests that saturated conditions prevail in some furrows. An abundant and mobile micro-fauna was observed in effluent ponded in furrows. Rapid gas evolution from the sediment in the furrows was observed and caused meter drift whilst taking field pH measurements. Three samples were taken from differing elevations across the site: S1 from the lowest position on the site, S4 from an intermediate position and S6 near the top of the site. A sample from a dam (S3) that collects seepage from the site and run-off from a stormwater diversion trench is included in the ponded category.

3.2.1.3 Sump

A buried seepage cut-off drain is situated on the western boundary of the northern (new) site. This drain collects water moving through the colluvial material. Excavation into this drainage channel on the 25th August revealed a water table at a depth of 1.4 m below surface. Intercepted seepage flows into a concrete sump from where it is pumped back to irrigate a stand of *Eucalyptus* trees. Water samples were collected from the sump on 5 occasions between August and November 1999.

3.2.1.4 Groundwater

Concerns over the efficiency of the cut-off drain in intercepting seepage migrating from the site prompted the installation of shallow (±3m) monitoring boreholes on the farm immediately west of the irrigation site. The positions of the monitoring boreholes are shown in Figure 3.6. Groundwater was sampled on the 7 October, a day after piezometer installation. On the 7th October, samples could not be obtained from boreholes 2 and 3; these boreholes are the closest to the sump. Samples were filtered and acidified on-site for Fe and Mn analysis. Additional groundwater samples were collected on the 10th November.

3.2.1.5 Seepage

A seepage zone (wetland) is present approximately 400m north-west of the site boundary. Samples were collected from pools on the edge of which white mineral precipitates were noted. Samples were collected at the beginning of the seep on 3 occasions but on one of these occasions the wetland was sampled further downstream.

3.2.1.6 Trench

Samples were collected on 3 occasions from a trench situated approximately 1 km north of the site. The trench was excavated to divert water away from houses on the adjacent farm. This trench diverts flow to a small dam situated on the western boundary of the farm, which was also sampled.

3.2.1.7 Background water quality

A shallow dam, situated south and upstream of the wetland and isolated from any possible inflow from the irrigation site was sampled. The dam collects run-off from the hills south of the site and is considered to represent natural surface water quality in the catchment. An idea of the background groundwater quality could not be achieved, as boreholes were unavailable for sampling in the immediate vicinity of the site.

3.2.2 Soil Sampling

Soil samples were collected from the irrigation site and surrounding area. Sampling was initially based on different vegetation type (or soil moisture status) as a zoning of vegetation types could be seen around the irrigation cannons. The vegetation pattern suggests that the distribution of water is not uniform across the site.

Table 3.1: Radial zonation of vegetation around irrigation cannons

Distance from Irrigation Cannon	Dominant Vegetation
Up to 35m (to 45m on ridges)	Grasses
From 35-45m (in furrows)	Reeds
>45m	Karoo veld

The zoning of vegetation became less clear at lower elevation where colluvium occurs; here topsoil and subsoil samples were taken. Soil sampling points were selected around five irrigation cannons, they are Sh1, Sh2, Sh3, Col1 and Col2 with Sh representing shale-derived soil and Col, colluvium. The sample points provide variability in terms of elevation, soil type and period of irrigation; the 'old site' has received effluent since 1975 and the 'new site' since 1984. A classification of the soil samples is provided in the Table 3.2:

Table 3.2: Classification of soil samples based on sampling criteria

IRRIGATION SITE								
Soil	**Shale**			**Colluvium/Alluvium**				
Moisture	**Dry**	**Moist**	**Wet**	**Dry**	**Moist**		**Wet**	
Horizon	**All topsoils**			**topsoils**		**Sub-soil**	**topsoil**	**Sub-soil**
Old site	*Sh1/dry* *Sh2/dry*	*Sh1/moist*	*Sh1/wet* *Sh2/wet*	*Col2/dry*	*Col2/top*	*Col2/sub*		
New site	*Sh3/dry*	*Sh3/moist*					*Col1/top*	*Col1/sub*
				RIVER SECTION & SEEPAGE SOIL				
				RSI/top	*SSI*	*RSI/sub*		
				CONTROL				
				CP1-3				

Each sample represented a composite of 5 samples: a central sample and 4 surrounding samples collected 2 m east, south, west and north of the centre sample. The top 15 cm of material was sampled except for the colluvium samples where an aerobic 'topsoil' (0-15 cm) and anoxic 'subsoil' (15 – 30 cm) were collected.

Topsoil near the drainage channel on the western boundary of the site, which is immediately west of the drain that intercepts seepage leaving the site was sampled (RSI/top). Excavation beside the drainage channel encountered groundwater at a depth of 1.4 m below ground level. An abrupt sediment colour change from pale orange to a pale grey at the water table indicated an oxic/anoxic boundary. The anoxic sediment was also sampled (RSI/sub).

Topsoil was sampled from the wetland west of the irrigation site (SSI). A 'browning-off' of the vegetation was evident on the 25th August and attributed (distillery manager) to overland flow from the irrigation site several days prior to sampling because of heavy rain. Halophytes are dominant in the wetland and white mineral precipitates were seen on the edges of the seepage zones.

Control samples were collected from 3 pits excavated in non-irrigated soil north of the site (CP1, CP2 and CP3). This sandy colluvium varied in thickness from 0.3 – 0.75m; with thinner soil encountered higher up on the slope to the east. The colluvium is underlain by a pebble horizon, which rests on weathered shale. At each sampling site 5 samples of topsoil were collected, thoroughly mixed and re-sampled. In the laboratory, samples CP1 to CP3 were mixed and re-sampled as a single composite sample: CP1-3. A detailed description and classification of the irrigated soil is not appropriate, as the soils have been highly disturbed.

3.3 Sample Preparation and Analysis

Water samples were initially filtered through filter paper to remove organic debris. The samples were filtered through a 0.45 μm filter into plastic bottles that had been thoroughly rinsed with distilled water. The filtered samples were then stored in a refrigerator. The water samples collected on the 25th of August as well as saturated paste extracts from the soil samples were analysed were at the Department of Geological Sciences at the University of Cape Town. All remaining water analyses were conducted at the CSIR (Environmentek) laboratory in Stellenbosch.

The soil samples were air-dried. The sandier samples dried in a matter of hours whereas the clay-rich samples required a full day. Once dry, aggregated lumps of soil were crushed with a quartzite cobble and then sieved through a 2mm steel screen. The samples were stored in screw-top plastic bottles.

Major cations and anions were analysed using Ion Chromatography (IC) and minor to trace elemental concentrations by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at the Department of Geological Sciences, University of Cape Town. At Environmentek, atomic adsorption spectrometry (AA) was used for cation analysis and anions were analysed by colorimetric methods (Standard Methods, 1995). Environmentek also carried out COD, DOC and Kjeldahl N determinations. Exchangeable and soluble cations, soil organic carbon and particle size analysis were performed by the Agricultural Research Council (Infruitek) laboratories in Stellenbosch. The mineralogical determination of the soil clay content and major elemental composition was carried out in the Geological Sciences Department, University of Cape Town.

3.3.1 Electrical Conductivity, pH and Alkalinity

The electrical conductivity (EC) and pH were measured in unfiltered samples in the laboratory the day after sample collection. The pH was also measured in the field. Measurements of electrical conductivity were made using a *Crison microCM 2201* meter, conductivity probe and automatic temperature compensator. The pH of the samples was measured using using a Metrohm 691 pH meter with combined glass-calomel electrode. The pH meter was calibrated before use with buffer solutions 7.00 and 10.00.

Alkalinity was determined by potentiometric titration to a pH 4.5 end-point with an automated *TTT85 Titrator* and *ABU 80 Burette*. For both methods standard 0.01 M HCl and a Radiometer TTT85 auto titrator were used. The procedure involved determining the volume of HCl required to titrate 10 ml of each sample to the end point pH. Alkalinity was measured on unfiltered samples.

3.3.2 Major cations and anions

Water samples were analysed for major cation (Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) and anion (F^-, Cl^-, SO_4^{2-}, NO_2^-, NO_3^- and PO_4^{3-}) concentrations by ion chromatography (IC) using a Dionex DX300 series suppressed IC system coupled to AI-450 chromatography software.

Samples were first filtered through a 0.45 μm micropore membrane filter and diluted with ultrapure water to attain an EC around 100 $\mu S\ cm^{-1}$. The high conductivity of some samples required dilution of up to 250 times; this decreased the effective detection limit for minor constituents. Before injection, each sample was passed through a Dionex Onguard-P polyvinylprollidone cartridge to remove the phenolic fraction of humic acids, tannic acids, lignins, anthocyanins and azo dyes. These substances are known foulants of anion exchange resins.

Cation concentrations were determined with an IC-CG12A guard column and an IC-CS12A separator column, using H_2SO_4 (11 mM) eluent at a flow rate of 1 $mL.min^{-1}$ and a sample loop volume of 25 μL. Detection was by a Dionex CD20 electrical conductivity detector, using a CSRS-I cation self-regenerating suppressor to suppress eluent conductivity. The run time per sample was 15 minutes. Anion concentrations were obtained using a sample loop volume of 50 μL, an IC-AGAA guard column and an IC-AS4A separator column with a combined Na_2CO_3 (1.80 mM)/$NaHCO_3$ (1.70mM) eluent at a flow rate of 2 $mL.min^{-1}$. The choice of eluent precluded the determination of carbonate species. To suppress eluent conductivity an Anion MicroMembrane suppressor (AMMS) was used. Running time was 8 minutes per sample. The instrument is calibrated against a set of standards on a daily basis. On that basis accuracy can be estimated to be better than ± 2% for most ions except for K^+, for which it is ± 4%. The lower limits of detection are in the order of 0.001mg/l.

At Environmentek cation analyses were conducted using AA spectrometry. In this analytical method, the total elemental concentration of the solution is determined.

The assumption is made that most cations are in their ionic form. Anions were determined according to Standard Methods (1995).

3.3.3 Minor and trace element composition

Semi-quantitative Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was carried out at the Department of Geological Sciences, University of Cape Town. The instrument used is a Perkin-Elmer, Sciex ELAN 6000 ICP-MS. Analyses were performed on filtered samples to determine approximate concentrations of a broad range of elements. Results are presented in Chapter 5 for the following elements: B, Al, Si, Fe, Mn, Cu, Zn and Br. The accuracy of the semi-quantitative scan is within 10% for most elements (see table 3.4); however, Fe and Zn are the exceptions with 44% and 21% error, respectively. The lowest level of detection for this instrument is 0.01 ppb.

3.3.4 Chemical Oxygen Demand (COD) and Dissolved Organic Carbon (DOC)

The COD represents the oxygen required to oxidize both dissolved and solid organic matter whilst the DOC is the soluble (less than 0.45 μm) organic carbon content. The total organic carbon (TOC) content can be estimated from the chemical oxygen demand (COD) by considering the atomic mass of carbon relative to oxygen. Assuming that all the COD is utilized in the oxidation of organic matter to carbon dioxide, then according to the relationship:

$$C\ (12) + O_2\ (32) \rightarrow CO_2\ (44)$$

Multiplication of the COD by 0.375 (12/32) will provide an estimate of TOC. An estimate of the carbon to nitrogen ratio (C:N) can then be made using the TOC and total nitrogen.

3.3.4.1 Chemical Oxygen Demand (COD)

The COD of an effluent is a measure of the oxygen requirement to oxidize all reduced constituents. This includes both organic (e.g. acetate) and inorganic species (e.g. NO_2^-, Fe^{2+} and Mn^{2+}). The COD of organic rich effluents should preferably be measured on unfiltered samples since in grape processing effluents, the soluble organic fraction usually represents around 90% of the COD. The samples of the 25 August were filtered through a 0.45 μm filter thus underestimating COD and representing the COD of the dissolved organic matter.

The chemical oxygen demand (COD) was determined by potassium dichromate consumption (Standard Methods, 1995; 5220-B). In the open reflux method the sample is boiled in sulphuric and chromic acids with excess potassium dichromate ($K_2Cr_2O_7$). Oxidation of most organic compounds is 95 to 100% (Standard Method, pp. 5-12). After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulphate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidixable organic matter is calculated in terms of oxygen equivalent. High Cl and NO_2 may produce over-estimation of COD. This test should not be used for samples with a Cl concentration > 2 g/l.

3.3.4.2 Dissolved Organic Carbon (DOC)

Analysis of dissolved organic carbon (DOC) was performed according to the persulphate-ultraviolet oxidation method (Standard Methods, 1995, 5310 C) in which organic carbon is oxidized to CO_2 by persulphate in the presence of ultraviolet light. An infrared analyzer then measures the CO_2 evolved. Interference can result from high sample turbidity, which reduces the intensity of light reaching the sample matrix. Large organic particles such as tannins and humic acids may oxidize slowly, as persulphate oxidation is rate limited. Samples were filtered prior to analysis and had been stored at 4°C since collection to limit biological degradation of organic matter. The minimum detectable concentration is approximately 0.5 mg/l.

3.3.5 Kjeldahl Nitrogen

Kjeldahl N measures the organic nitrogen and ammonium ion concentration but does not determine the nitrite or nitrate ions present in a solution. The Macro-Kjeldahl Method (Standard Methods: 4500B-N_{org}) entails the conversion of amino-nitrogen in organic matter and free ammonia to ammonium in the presence of H_2SO_4 and K_2SO_4 using $CuSO_4$ as a catalyst. After addition of base, the ammonia is distilled from the alkaline medium and absorbed in boric or H_2SO_4. Ammonia is then determined colorimetrically.

3.3.6 The Saturated Paste

To measure the soluble salts within the soil samples, a saturated paste extract was prepared. Distilled water was added incrementally until the soils reached saturation. The moisture content varied from 0.2 – 0.6 ml/g with higher values for the clay-rich samples.

The soil solutions were extracted under vacuum using a Buchner funnel. The pH and EC were measured prior to filtration through a 0.45 μm nucleopore filter. The extracts were diluted to an EC of approximately 100 μS cm^{-1} prior to cation and anion analysis by IC and total elemental composition by ICP-MS.

3.3.7 Effective Cation Exchange Capacity (CECe)

Extractable/exchangeable cations were determined by the ammonium acetate method at the laboratories of the Agricultural Research Commission (Infruitec) in Stellenbosch. The method contacts approximately 5g of soil with 50 cm^3 of 1M NH_4OAc solution, which is shaken horizontally in a reciprocating shaker for 30 minutes. This is then filtered through a Buchner funnel and analysed by AA spectroscopy.

The method determines the sum of readily soluble (free) cations and those held on exchange sites. The exchangeable cations were calculated by subtracting the cation concentrations of the saturated paste extract (converted to cmol_c/kg) from the values determined by the ammonium acetate method.

3.3.8 Soil Organic Carbon Content

The Walkley-Black organic carbon method as described in Methods of Soil Analysis (Nelson and Sommers, 1982) was followed to determine the organic carbon content of the soil samples. The method utilises a potassium dichromate ($K_2Cr_2O_7$) and sulphuric acid mixture to oxidise the organic matter:

$$2Cr_2O_7^{2-} + 3C + 16H^+ = 4Cr_3^+ + 3CO_2 + 8H_2O$$

The excess dichromate remaining from the reaction is titrated with iron(II) ammonium sulphate hexahydrate and compared to the titration on a blank. The reduced dichromate is assumed to be equivalent to the organic carbon present in the sample.

3.3.9 Mineralogical Composition of the Clay Fraction

The clay minerals were identified by X-ray diffractometry (XRD), after the clay size (<2 μm) fraction had been separated from the coarser particle sizes. Separation was achieved by dispersing the sample with Na_2CO_3 followed by flocculation brought about from pH adjustment and addition of NaCl. The clay slurry was dialysed against distilled water, centrifuged to concentrate the clay and pipetted onto a glass slide. The clay was analysed using a Phillips PW 1390 X-ray diffractometer fitted with a Cu X-ray tube operating at 40 kV and 25 mA. A selection of seven samples were scanned through a range of 6° to 70° 2θ with a step-size of 0.1° 2-theta and a counting time of 1 second/step. The diffractograms were interpreted with Phillips X'pert Software (version 1.1b).

3.3.10 Bulk Element Concentration

Bulk element concentrations of major and minor elements (as % oxides) in the soils were determined by X-ray fluorescence spectrometry (XRFS) using a Philips PW1480 wavelength dispersive X-ray fluorescence spectrometer with a dual target Mo/Sc X-ray tube. All measurements are made with the tube at 50kV, 50mA. Calibration was by means of international standard rock reference materials.

Fusion discs were prepared for 7 selected samples from oven-roasted samples (1050°C) which had been ground in a carbon–steel vessel for 2 minutes using a Siebtechnik swing mill to produce a fine powder ($\leq$ 70 μm particle size). The moisture content was determined by drying the soil samples in an oven at 110°C overnight. The loss on ignition (LOI) was determined by placing the samples overnight in a furnace at 1050°C. Fusion discs were made by combining 0.7g of roasted sample with 6 g of Sigma 12:22 flux and 4 drops of wetting agent (2.9*M* LiBr.). Discs were produced in automatic mode by a Claisse Fluxy instrument, operating under program 8.

Determinations were made for SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, NiO and Cr_2O_3. The results are presented in Appendix F.

3.3.11 Particle Size Analysis

Particle size analyses were conducted at the Institute for Fruit Technology (Infruitek) in Stellenbosch according to hydrometer method (Standard Methods of Soil Analysis, 1986). Prior to analysis sediments were treated with hydrogen peroxide to remove organic matter. Amyl alcohol was added to make the sample foam-free. Calgon was used as a dispersant.

3.3.12 Geochemical modelling

Geochemical modelling was done using PHREEQC. The models are mathematical representations of solution samples at chemical equilibrium. PHREEQC is based on an ion pairing aqueous model and is derived from the Fortran program PHREEQE, but has been completely rewritten in C; the U.S. Geological Survey wrote the program and it can be downloaded from the USGS website: http://water.usgs.gov/software/phreeqc.html. PHREEQC essentially combines the capabilities of four earlier codes: PHREEQE, WATEQ4F, PHREEQ-M, and NETPATH, with some added capabilities and improvements.

3.4 Data Reproducibility

Duplicate analyses were carried out for 2 water samples and 1 saturated paste extract collected on 25th August to evaluate analytical reproducibility. The samples were submitted for major ions (IC) and minor and trace concentrations (ICP-MS).

Table 3.3: Duplicate analyses of a soil solution (RSI/sub) and effluent and trench water samples for major ions by IC (in mg/l).

Sample	K^+	NH_4^+	Na^+	Ca^{2+}	Mg^{2+}	F	SO_4^{2-}	Cl^-	NO_2^-	PO_4^{3-}	Br^-
RSI/sub(1)	166	B.d.	692	62	19	3	109	523	B.d.	B.d.	5
RSI/sub(2)	165	B.d.	696	109	18	3	112	526	B.d.	B.d.	5
Effluent(1)	79	5	241	43	32	49	89	119	56	9	B.d.
Effluent(2)	74	5	247	62	37	51	87	120	53	B.d.	B.d.
Trench(1)	128	B.d.	4580	605	1163	52	1960	9675	B.d.	B.d.	58
Trench(2)	95	B.d.	4508	745	1148	0	1890	9626	B.d.	B.d.	60

B.d. = below detection

Concentrations of most of the major ions are generally within several percent of each other. Calcium is the exception with up to 45% difference between concentration in duplicate sample RSI/sub. There are also discrepancies with F in the Trench sample and PO4 in the Effluent sample. This may be due to the large dilution factors required in preparing the samples for IC, which effectively lowered the detection limits.

Table 3.4: Duplicate analyses indicating data reproducibility for minor and trace element concentrations by ICP-MS (in mg/l).

	B	**Al**	**Si**	**Mn**	**Fe**	**Cu**	**Zn**	**Br**
NIST-1640	299.2	56.3	4595	124.5	49.4	95.1	64.6	14.3
CERT.	301.1	52	4730	121.5	34.3	85.2	53.2	N.a.
ERROR	1.9	4.3	135	3	15.1	9.9	11.4	N.a.
%ERROR	0.6	8.3	2.9	2.4	44.1	11.6	21.4	N.a.
RSI/sub	2.30	17.9	26.9	0.35	24.8	0.13	0.09	4.9
RSI/sub	2.19	17.0	25.2	0.33	23.1	0.15	0.07	5.0
Trench	1.29	1.2	5.7	0.69	2.7	0.29	2.42	45.8
Trench	4.96	1.2	13.9	0.46	2.1	0.23	1.98	47.1

N.a.: not available

The NIST-1640 is a standard against which the accuracy of the analytical method is tested. Precision for the saturated paste extract, RSI/sub is acceptable. However, the Trench water sample shows major discrepancy between the duplicate analyses for most elements (except Br). RSI/sub and the Trench sample were analysed on different days.

A comparison was made between IC and AA analysis of cations in a borehole 5 sampled on the 7th of October. This indicated that Na, K and Mg results were within 20% for the different analytical methods but the Ca concentration was 60% greater in the IC analysis (see Table 3.5).

Table 3.5: Cation analyses in a sample from Bh 5 by different analytical methods.

Cation	IC analysis	AA analysis
Na	1906 mg/l	2000 mg/l
K	272 mg/l	270 mg/l
Mg	312 mg/l	381 mg/l
Ca	530 mg/l	323 mg/l

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CHAPTER 4

COMPOSITIONAL CHANGES TO GRAPE PROCESSING EFFLUENT AND POTENTIAL ENVIRONMENTAL IMPACT

The collation and evaluation of all the data pertaining to the land treatment of the effluents is important as it allows for assessment of site performance as well as the potential environmental impact. Comparison is made between the concentration of constituents in land treated grape-processing effluents and water quality guidelines for irrigation and livestock watering. Assessment of environmental impact should forewarn affected parties of potential hazards arising from seepage leaving the site and assist the regulatory authority in determining license conditions for continued operation. The interpretation of compositional changes from a geochemical perspective will be carried out in Chapter 5. The aim of this chapter is to trace the pathway and compositional changes of the effluent with a view to assessing impact on the environment.

4.1 Reduction of Organic Matter

All water samples were analysed for their COD but determinations were not carried out on the saturated paste extracts. Groundwater samples were analysed for both COD and DOC. The excess of cations over anions (from 20 – 55%) in the effluent and ponded effluent may be attributed to organic anions the charge on which could not be determined (Appendix B). The high cation excess in the ponded effluent samples cannot be attributed solely to organic anions as these samples have lower COD than the effluent but, on average, larger cation excesses than the effluent.

4.1.1 Chemical Oxygen Demand (COD)

The samples taken on 25th August were filtered prior to COD determination and therefore are not a true measure of total COD (which should be determined on unfiltered sample) but represent the COD of the soluble organic matter in the effluent (COD_{sol}). Determinations of COD for filtered and unfiltered effluent from May 1999 (provided by KWV) indicate, however, that 90% of the COD is in a soluble form.

The variability in COD for the various water types is presented in Figure 4.1. Effluent samples from August to November had COD ranging from 2.5 – 3.3 g/l. Although the range of COD is fairly constant for the sampling period this may not be the case throughout the year as analysis of fresh distillery effluent indicated a COD of 66 g/l. The grape-processing effluent at Robertson is a mixture of grape juice and distillery effluents and the former probably dilutes the distillery COD. There is probably some COD reduction in the settling lagoon prior to irrigation.

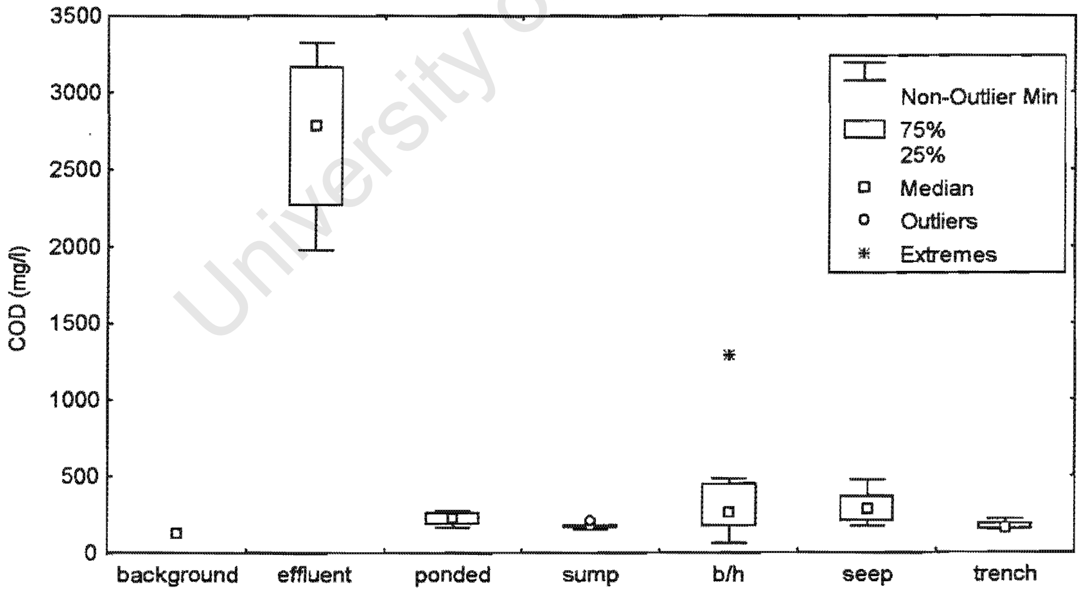

Figure 4.1: COD variation in relation to sampling location.

Effluent ponded in the furrows on the site had significantly lower COD_{sol} than the irrigation effluent: from 164 - 272 mg/l compared to 1980 mg/l for effluent sampled on 25th August. This represents a 90% reduction in the soluble organic content of the effluent through treatment in the topsoil. Chapman (1995) estimated up to 95% reduction of the soluble concentration of organic carbon in distillery effluent provided that the COD was reduced, prior to land treatment, to levels similar to that in winery wastewater.

The average COD_{sol} for ponded effluent samples from 25th August was 220 mg/l whereas the COD_{sol} of sump water on the same day was 178 mg/l. This suggests that further COD reduction occurs in the subsoil between the furrows and the sump. However, Tare and Bokil (1982) state that the treatment zone for organic substrates lies within the 0-15 cm layer of the soil. Removal of COD is less in the subsoil and may be attributed to the smaller COD value at depth in the soil, limited aerobic conditions and the remaining COD being more difficult to degrade (Chapman, 1995). Wastewater application volumes should not exceed 30% of the water holding capacity of this layer to prevent an unacceptable proportion of the soluble organic carbon moving beyond the 0-15 cm layer of the soil. Surface ponding should be avoided to limit rapid saturated flow through macropores. Comparison of COD of sump and effluent samples provides an indication of the biodegradation achieved at the site.

Table 4.1: Reduction in COD.

Date	**10/11**	**07/09**	**26/08**	**25/08 ***
Sample				
Effluent (mg/l)	3015	3325	2559	1980
Sump (mg/l)	154	165	177	209
COD Reduction	95%	95%	93%	89%

* COD = COD of soluble organic fraction.

The COD of groundwater collected from boreholes 4 (482 mg/l) and 5 (416 mg/l) was up to 3 times greater than that of sump water (165 mg/l) sampled on the 7th October. Similarly, on the 10th November, the COD of the groundwater from boreholes 4 (1292 mg/l) and 5 (256 mg/l) was significantly higher than in the sump (154 mg/l). This would not be expected if seepage were to have left the site via the colluvium and suggests that the effluent bypasses the sump, which is situated at the base of the colluvium.

A reduction in the COD of groundwater with distance from the site occurs: COD of 1292 mg/l in borehole 4 (60m from the site) is contrasted with a COD of 108 mg/l (800m from the site) in borehole 8. The COD of the seepage was 369 mg/l on 10th November whereas that in the trench was 154 mg/l. These samples had high salinity (EC up to 4900 mS/m) and a significant amount of their COD may be due to error associated with their high Cl content (see 3.3.4.1). For this reason, the dissolved organic carbon (DOC) was determined for the groundwater samples as well as effluent, sump and seepage samples from 10th November. Determination of DOC confirmed the effect a high Cl concentration has on COD (Table 4.2), e.g.: the difference in COD:DOC ratio between effluent and Bh7.

Table 4.2: Effect of Cl (mg/l) on COD:DOC ratio:

Sample	**COD/DOC**	**Cl**
Effluent	3.4	127
Bh5	4.7	4300
Bh7	26.2	20000

The COD of the background water sample was 128 mg/l (107 mg/l Cl). The South African General Effluent Standard (S.A. Government Gazette No. 9225, 1984) for COD is 75 mg/l (after applying a correction for Cl).

4.1.2 Dissolved Organic Carbon (DOC)

Effluent and sump samples from 10th November indicate a reduction in DOC from 890 mg/l to 12 mg/l, respectively. This represents a 98% reduction in the soluble organic content of the effluent. Chapman (1995) predicted that, for winery wastewater with COD around 3.7 g/l (TOC content of 1.4 g/l), the soil solution would contain approximately 100 – 150 mg/l of organic carbon as it drains from the topsoil to the subsoil. Although these results are not directly comparable because the sump sample represents groundwater whereas Chapman's data are from soil solutions, they do highlight the importance of the subsoil and aquifer in DOC reduction.

The DOC in groundwater sampled on 10th November ranged from 51 - 105 mg/l in boreholes closer to the irrigation site (Bhs 2, 4 and 5). Comparison of these values to that of the sump sample on this date (12 mg/l) suggests that, as mentioned above, groundwater reaching the boreholes occurs via a different pathway than that arriving at the sump. The DOC in samples from boreholes 7 and 8, approximately 800m from the site, is less than 10 mg/l. The South African Water Quality Guidelines for potable use (DWAF, 1993) specify a target range for DOC of 0-5 mg/l. Where the DOC exceeds 20 mg/l aesthetic affects may limit potability and the formation of trihalomethane during treatment may occur. Water from these boreholes is highly unlikely to be used as a potable source because of high salinity.

4.1.3 Nutrients related to Organic Matter Status

The growth of plants and the soil microbial population both rely on the provision of sufficient inorganic nutrients (e.g.: N, P, S, K and Ca). Limitation in the supply of one or more of these essential nutrients may limit microbial activity and organic matter degradation. However, it is unusual in agricultural soils for nutrient elements other than N to limit decomposition (Jenkinson, 1988).

Averaged concentrations of organic N, soluble N species and PO_4 for the water sample types is provided in Figure 4.2. Organic N was calculated by subtracting the NH_4 concentration from the Kjeldahl N. Nitrogen in the effluent occurred predominantly in the organic form particularly in the seep and trench samples. This may be due to biodegradation-resistant organic matter in these samples. The average organic N concentration is reduced by 87% from 19 mg/l in the effluent to 2.5 mg/l in the sump. This is probably due to ammonification of dead bacterial cells, plant matter and other protein-rich organic matter by microbes in the soil. Groundwater has higher average organic N content (11 mg/l) than sump water (2.5 mg/l), once again pointing to effluent by-passing the cut-off drain.

Figure 4.2 indicates that NO_2^- plus NO_3^- are the major N ions in the effluent. However, in 3 of the 4 effluent samples NH_4 concentrations were greater than NO_2^- + NO_3^- (see Appendix A). The elevated NO_2^- + NO_3^- in Figure 4.2 is due to a nitrite concentration of 56 mg/l detected in the sample of 25th August; in the other 3 samples NO_2^- + NO_3^- was less than 0.3 mg/l. Ammonium concentration decreases from the effluent to sump samples and is barely detectable in the seep and trench samples. The decrease in NH_4 in the samples is ascribed to uptake by plants and microbes and adsorption. Phosphate was above lower limits of detection in the effluent but barely detectable in all other samples.

The N concentration in groundwater leaving the site is well within the guideline levels for potable use and excessive nitrate leaching does not constitute a limitation on the sustainable use of this land for grape processing effluent irrigation.

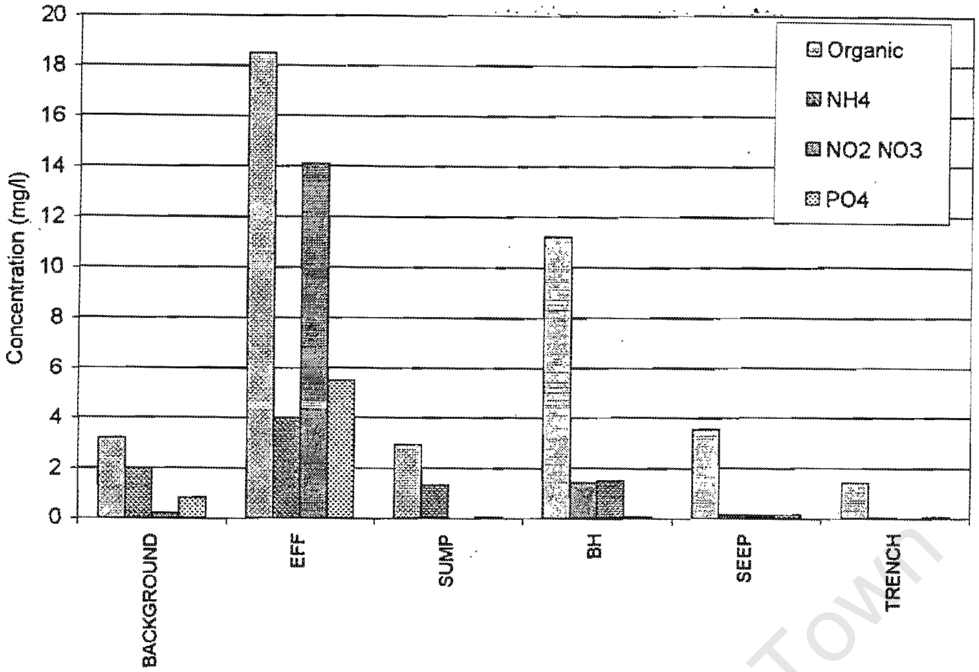

Figure 4.2: Nitrogen and phosphate abundance in water samples.

For samples from a specific source, chemical oxygen demand (COD) can be related empirically to organic carbon (Standard Methods). The total organic carbon (TOC) content of a wastewater was estimated from the COD by consideration of the atomic mass of carbon relative to oxygen. By assuming that all the COD results from the oxidation of organic matter to carbon dioxide, then according to the ratio of the atomic weight of C/O_2; multiplication of the COD by 0.375 (12/32) will provide an estimate of TOC. The estimated TOC of the water samples is given in Appendix A. The ratio of TOC to Kjeldahl N in the samples provides C:N ratios which are often used in assessing the biodegradability of organic matter. The C:N ratios for the effluent samples (Figure 4.3) ranged from 80:1 – 40:1, which according to White's (1997) optimal ratio of 25:1 for bacteria, with a C:N ratio of 5, suggests that the effluent is nitrogen deficient. The higher C:N ratios for the Robertson effluent are similar to those of winery effluent from 50 wineries in the Rhône basin of France (Doré, 1998) where the C:N ratio varied from 90 - 97. However, data for stillwash from distilleries in South Australia (Chapman, 1995) provide a C:N ratio of 13:1.

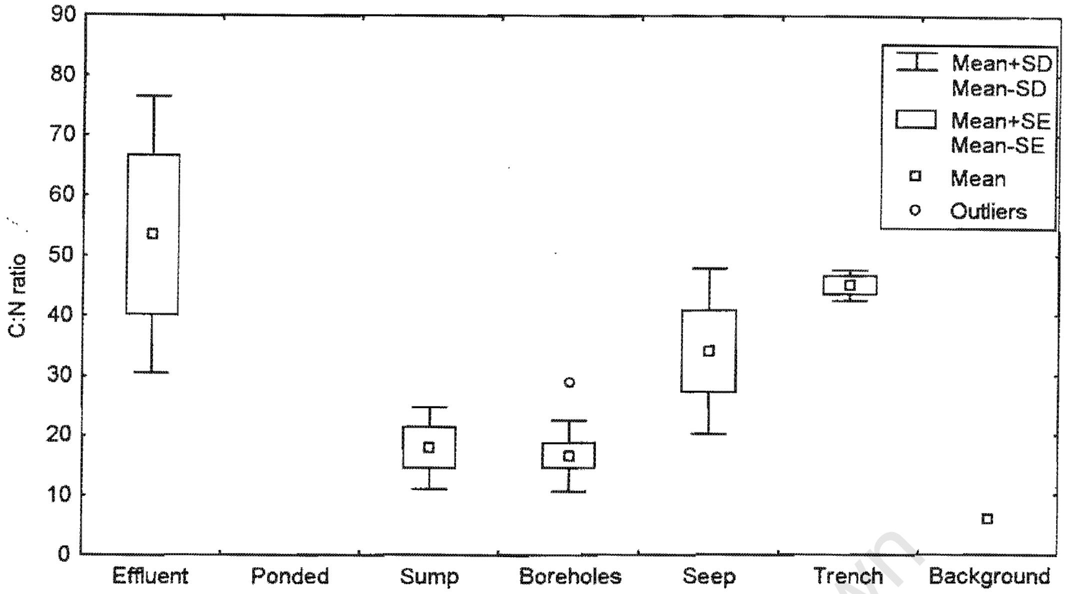

Figure 4.3: C:N ratio of water samples

In sump and groundwater samples the mean C:N ratio is less than 20 probably indicating removal of readily biodegradable organic matter volatilized as CO_2. The C:N ratio is 35 in seepage and 45 in trench samples possibly indicating organic input from the wetland around the seepage area. The C:N ratio of the grape-processing effluents at Robertson do not appear to restrict biodegradation as there was a 93 - 95% reduction in effluent COD during the sampling period.

4.2 Salinity

The electrical conductivity (EC) of the water samples and saturated paste extracts provides an indication of their salinity. The median and quartile ranges for EC values for the water sample types are illustrated in the box and whisker plot in Figure 4.4.

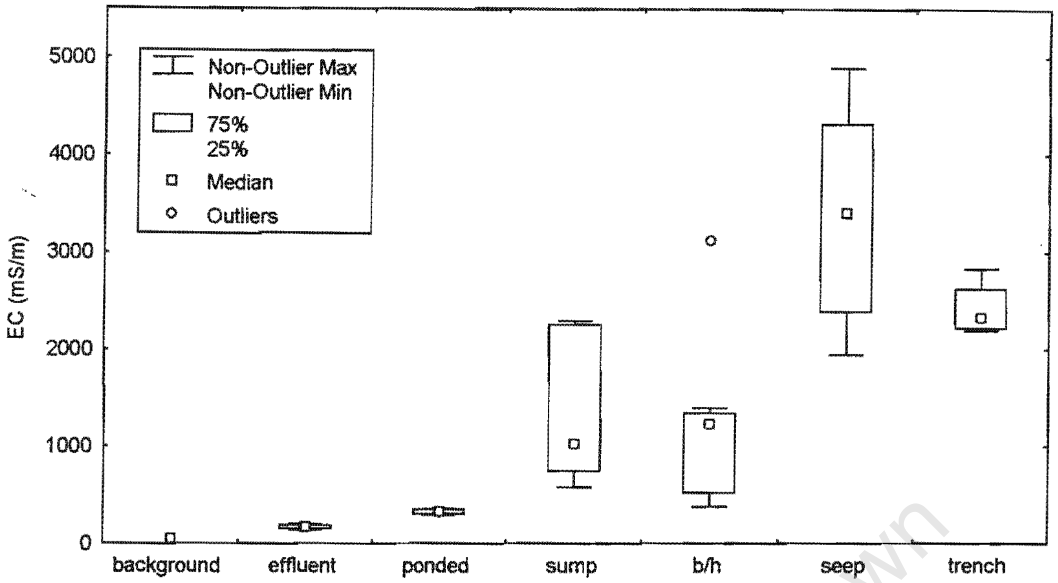

Figure 4.4: Box and whisker plot showing EC median and range for water sample categories.

The salinity of the effluent places it in Class III (90-270 mS/m) of the S.A. Water Quality Guidelines for Irrigation (DWAF, 1993). Irrigation with Class III water can maintain an 85% yield of moderately salt-tolerant crops provided a high frequency irrigation system is used although a leaching fraction of up to 0.2 may be required. Figure 4.4 illustrates the increase in salinity that takes place following effluent irrigation. A doubling in EC took place on 25th August between the effluent and effluent ponded on the site and 4-fold increase between the effluent and sump samples. This is attributed to the evaporative concentration of soluble salts, in particular Na and Cl. There is a slight increase in EC between the sump and the boreholes probably because of limited evapotranspiration in groundwater compared to surface water. Water from the seep is undergoing intense evaporation and therefore has high salinity. The salinity of the water leaving the site (sump sample) more than doubles by the time it reaches the trench, which is approximately 800m from the site.

The change in EC during the sampling period is illustrated in Figure 4.5. The EC of the effluent varied from 136 – 200 mS/m over the sampling period. This relatively constant level contrasts with that of sump water, which increased from 580 mS/m on 25th August to 2300 mS/m on the 10th November. The elevated EC of the sump water in November is probably a result of increased evaporation associated with the onset of summer conditions (Figure 3.1.2). The groundwater and trench samples exhibit less variation in EC compared to sump or seep water.

Sump water EC exceeded 540 mS/m, this being the maximum salinity in Class 4 of the South African Water Quality Guidelines for Irrigation (DWAF, 1993), on all sampling occasions, which could lead to unacceptable yield reductions if used for crop irrigation. Re-application of this water to the site may be acceptable in the short term although increased sodicity will promote soil clogging and may lead to Na and Cl toxicity in plants.

Most livestock can tolerate salinity up to 2200 mS/m (DWAF, 1993), although production and health are likely to be affected in the long run, particularly in pregnant and lactating animals. A general guideline for livestock is that Na plus Cl is less than 3000 mg/l, a condition only met in the sump water in August.

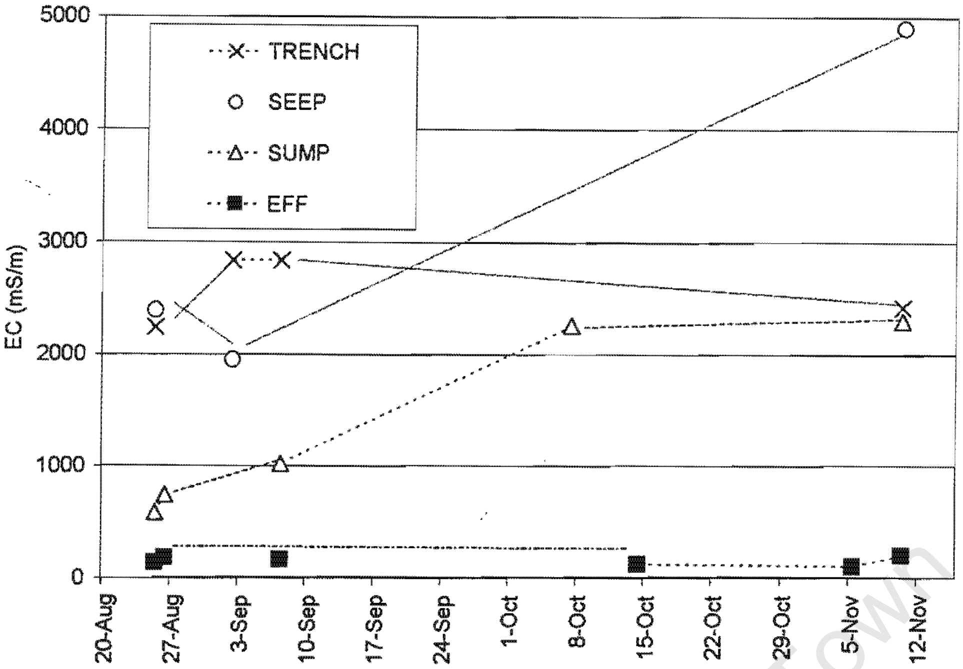

Figure 4.5: Salinity variability over sampling period.

The EC of the saturated paste extracts are compared to the ponded, sump and seep samples collected on the 25th August in Figure 4.6. The soils have been grouped according to their moisture status (dry, moist and wet). The background sample represents the EC of the saturated paste extract from the soil sample CP1-3. Figure 4.6 indicates a similar EC (300–400 mS/m) for the moist and wet soils and for effluent ponding on the site. The dry soils have more than twice the salinity of the moist and wet soils (median of 1000 mS/m). The dry shale soils in particular have extremely high salinity (up to 2790 mS/m) which is significantly more saline than dry colluvium samples; appendix C).

The moist and wet soils have EC approaching 400 mS/m, this being the value at which soils are usually classified as saline (Mc Bride, 1994, p301). The dry soils and soil from the wetland are highly saline and do not support the *kikuyu* grass that proliferates on the moist and wet soils of the irrigation site. This is probably because of dryness and not salinity although the EC of the dry soils (~1000 mS/m) is the salinity at which Russell (1976) noted significant decrease in dry matter yield for *kikuyu* grass (*Pennisetum clandestinum*).

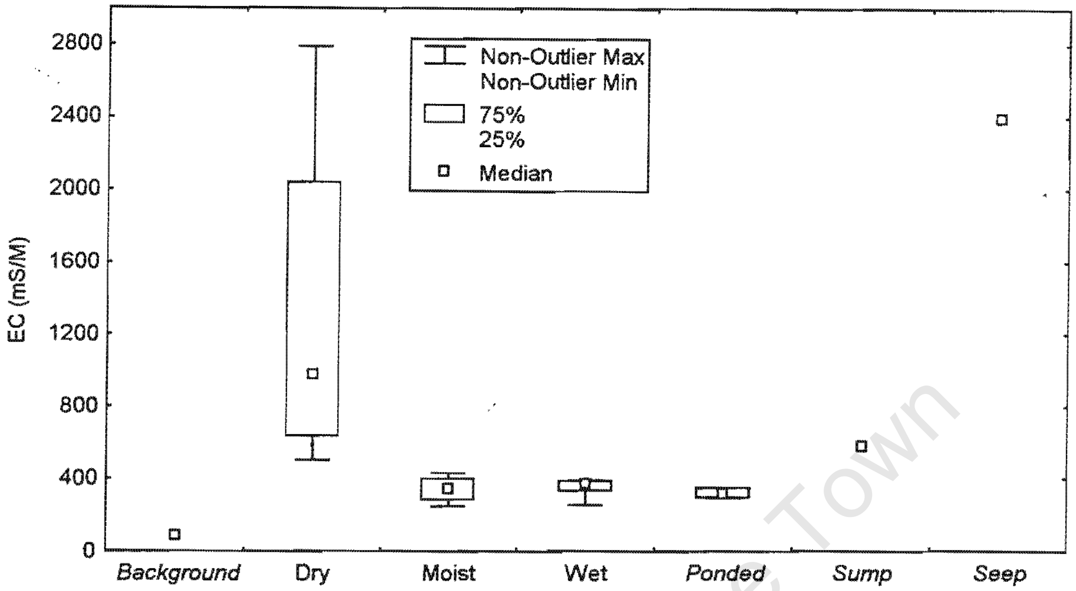

Figure 4.6: EC of soil saturated paste extracts and water samples from 25th August.

Elevated salinity in the dry soil samples probably results from irregular or insufficient irrigation. This reduces flushing of sparingly soluble salts (K, Na, SO_4, Cl) out of the soil. In addition, sparingly soluble salts may migrate by capillary action from saturated areas to adjacent areas not receiving adequate irrigation and increase in concentration from evapotranspiration. Soils from the longer irrigated section of the site do not have higher EC than the more recently irrigated soils. The subsoil solutions were up to 35% more saline than topsoil solutions in the colluvium. The average salinity of the soils of the irrigation site (391 mS/m) is significantly greater than that of the control sample CP1-3 (89 mS/m).

High salinity irrigation water increases the osmotic pressure generated by salts in solution and reduces the ability of plants to extract water from the soil (McBride, 1994). Sump water from 10th November with salinity of 23 mS/cm would result in an osmotic pressure of approximately 8 atmospheres. Most plants reach their permanent wilting point at about 15 atmospheres of water tension.

4.2 pH

The pH of effluent varied from pH 4.5 to 5.5 over the sampling period. The pH of fresh distillery effluent can be as low as 3.6 (data from KWV for May 1999) but can change from acid to alkaline on a daily basis (F Botha, pers. comm.). The settling lagoon, mid-way between the plant and the irrigation site, probably buffers these extreme swings in pH and results in a relatively uniform pH for effluent arriving at the irrigation site. The pH of the effluent changes from acidic to alkaline (pH > 8.5) after irrigation. The pH is highest in the ponded samples (up to pH 9) and is also high in seepage water but appears reduced by approximately 0.5 pH units in groundwater (see Figure 4.7). The background surface water sample was slightly alkaline with pH 8.1.

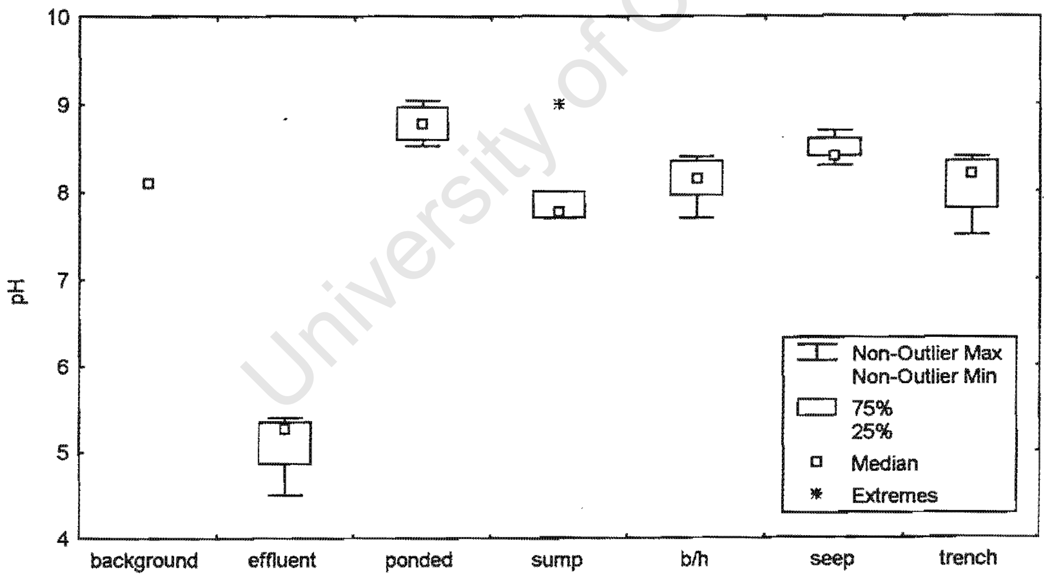

Figure 4.7: Variability in pH for water sample categories.

The difference between field and laboratory pH determinations was less than 0.5 pH except in the ponded sample (S1) where the field pH was 4.56 and the lab pH 8.52.

This sample is believed to represent effluent that was recently irrigated on the site at the time of sampling. The pH of the soil solutions varied from 7.7 to 9.4 and the average pH (8.52) is similar to that of the non-irrigated sample (pH 8.1) and average of ponded effluent samples (8.78). The dry soils and colluvial topsoil generally have higher pH than the moist, wet and subsoil samples. However, the role of Ca and Mg concentration in counteracting the increase in soil pH is evident from the analyses of soil samples Sh2/dry and Sh3/dry.

Table 4.3: Ca and Mg control of soil solution pH

Sample	pH	EC	Ca	Mg	Na
Sh2/dry	9.4	2790	270	120	8294
Sh3/dry	7.7	2040	828	1726	3546

4.3 Major Ion Chemistry

Cation and anion concentrations were determined by ion chromatography for the saturated paste extracts and water samples of the 25th August. All remaining water samples were analysed by AA spectrophotometry for cations and colorimetry for anions. The effluent and ponded effluent samples had cation excesses of up to 50% which is presumed to be due to dissociated soluble organic matter (e.g. acetic acid). The charge balance was less than 5% for all other sample types (Appendix B).

4.3.1 Cations

The relative abundance of cations in the various water samples is presented in Figure 4.8 and indicates an increase in all cation concentrations except ammonium (NH_4) from the effluent to the trench samples. The cation concentrations presented in Figure 4.8 are averaged over the sampling period except for pond and background samples, which were collected once.

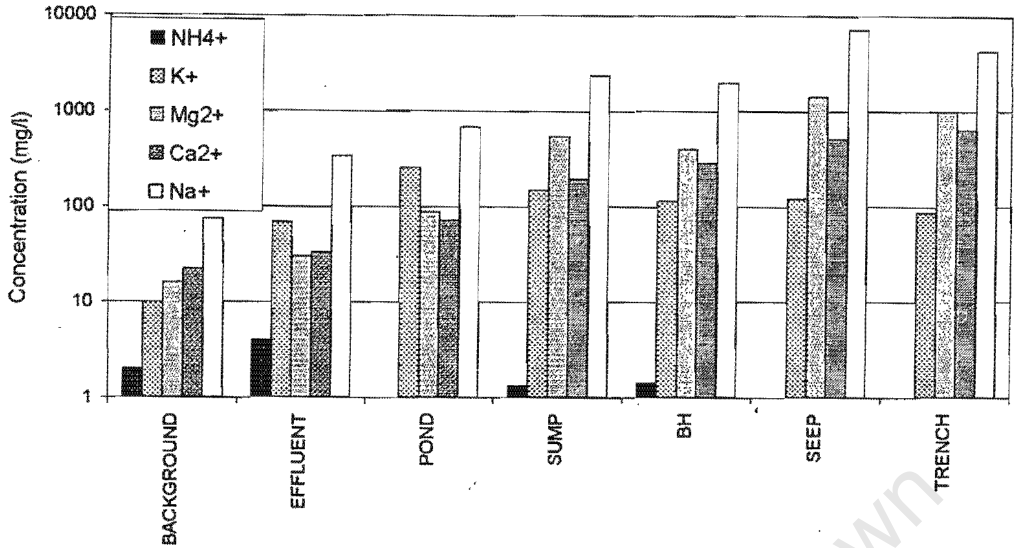

Figure 4.8: Cation abundance in water samples

The order of cation abundance in the background sample is Na > Ca > Mg > K > NH_4. The concentration of K is elevated to the second most dominant cation in grape-processing effluents and Na > K > Ca > Mg > NH_4. In the ponded samples the same cation order is seen, however, Mg is more abundant than Ca. A significant change is evident in sump, seepage and trench samples where the order of cation abundance is Na > Mg > Ca > K > NH_4. Groundwater in boreholes more distant from the site (bhs 5, 7 and 8) have the same order of cation abundance as that of sump and seepage water whereas in groundwater closer to the irrigation site (bhs 2 and 4) Na > Ca > K = Mg > NH_4, which is characteristic of effluent. The relative cation abundance indicates removal of Ca relative to Mg in the ponded effluent and removal of K in the soil as the effluent migrates to the sump.

Ammonium is the predominant N species in the effluent (range 2 - 6 mg/l), although a nitrite concentration of 56 mg/l detected on 25th August has skewed the data. Ammonium was not detected in the ponded samples although this may be due to the high dilution required to reduce sample EC prior to IC analysis. NH_4 was detected in all the sump samples in concentrations ranging from 0.9 to 2.5 mg/l. The NH_4 concentration in groundwater ranged from 0.1 to 6.2 mg/l but was less than 0.2 mg/l in seep and trench samples. In the background water sample NH_4 (2 mg/l) was also the predominant N species. A reduction in the NH_4 concentration between the effluent and sump water indicates that all or some of the following processes may take place: 1) uptake by the soil biomass, 2) adsorption to clay and organic matter and 3) volatilization of NH_3 (ammonia), particularly at high pH. The ammonium ion has low toxicity while ammonia has high toxicity, especially to aquatic life. The concentration of NH_4 in grape-processing effluents is less than the standard of 10 mg/l N for free and saline ammonia in effluents (General Effluent Standard, 1984).

Potassium, Mg and Ca are plant nutrients and high concentrations in irrigation water do not usually pose any constraints. However, high Ca and Mg concentrations can result in scaling water and clogging of irrigation equipment. High Mg imparts a bitter taste to water and when associated with high SO_4 (> 1000 mg/l) may cause diarrhoea in livestock. The salinity and sodicity limit the beneficial use of sump and groundwater down slope of the site.

The effluent became more sodic from August through to November whereas NH_4 and K concentrations decreased over this period. The $NaHCO_3$ signature of the effluent sample of the 10th November relative to the other effluent samples may originate from a higher proportion of cleaning wastewater to stillwash. Water ponded on the site represents effluent at various stages of treatment and evaporation. Pond sample S1 (Appendix A) is believed to represent recently irrigated effluent as it has a higher Ca concentration than the other pond samples. The bicarbonate alkalinity, pH and SAR are also less in S1 compared to the other pond samples. In time, however, they are expected to increase to levels similar to that of the other ponded samples.

The order of cation abundance in the saturated paste extracts is similar to that of the effluent (i.e. $Na > K > Ca > Mg > NH_4$) as the soil solution is expected to take on the characteristics of the irrigation water. Minor amounts (< 5 mg/l) of ammonium were detected in only 2 of the saturated paste extracts. Cation concentrations are higher in the saturated paste extracts than in ponded water samples (see figure 4.9). This is particularly so for the dry soil samples where average Na, K and Mg concentrations were approximately 5 times more concentrated compared to the ponded effluent and the moist and wet soils. The background soil sample has similar Ca and, to a lesser extent, Mg concentration to those of the wet and moist soils but significantly less Na and K. Data for the saturated paste extracts are presented in Appendix C.

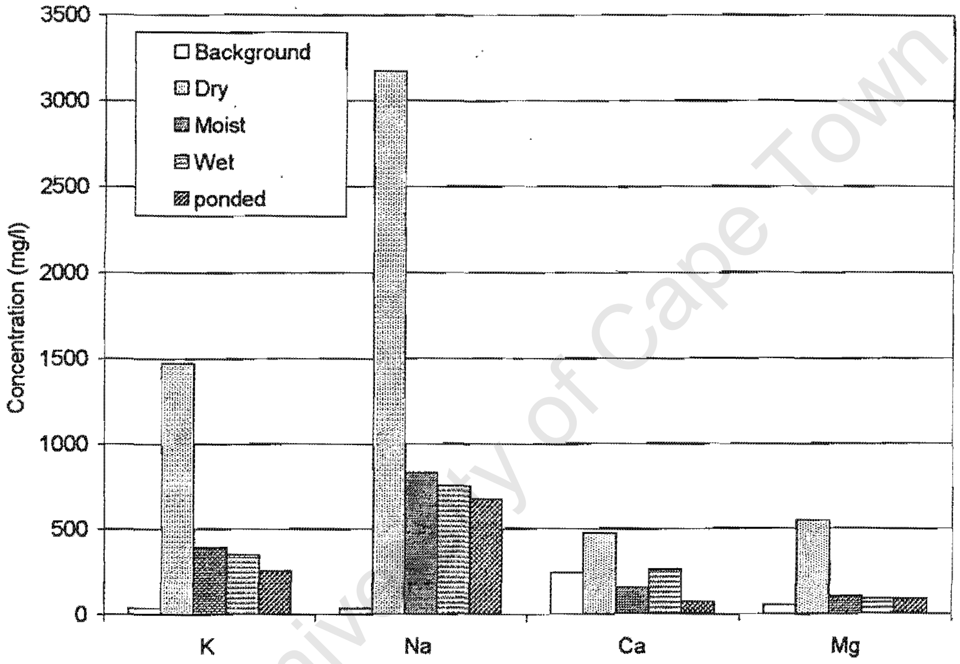

Figure 4.9: Average cation abundance in saturated paste extracts and ponded water samples.

4.3.2 Sodium Adsorption Ratio (SAR)

The sodium adsorption ratio (SAR) is a critical factor in land treatment and irrigation in general as it controls soil physical properties. The SAR for the water samples and saturated paste extracts is shown in Figure 4.10.

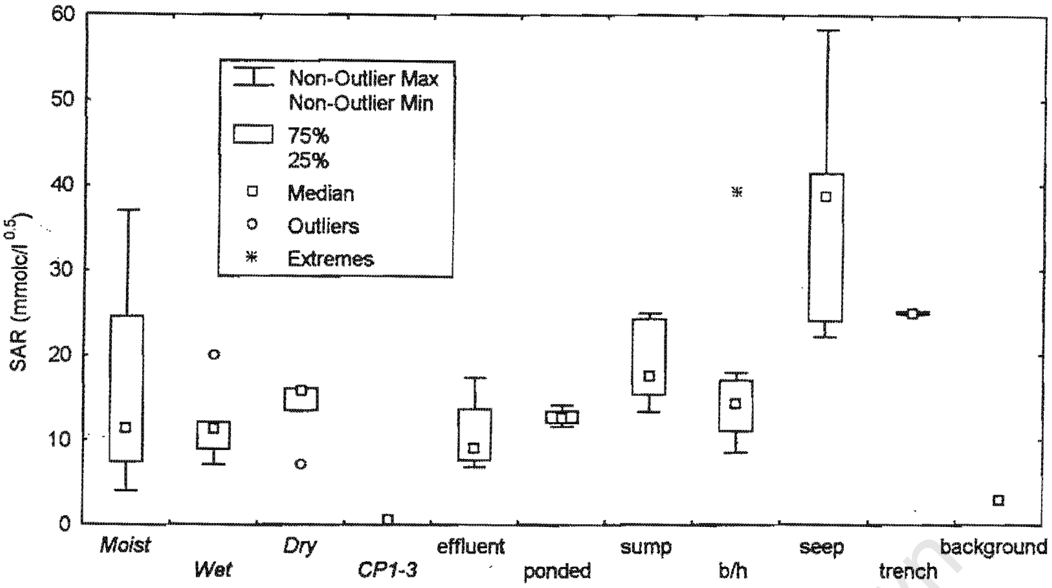

Figure 4.10: SAR for water samples and saturated paste extracts

The SAR of the moist and wet soils is similar to that of the effluent (~ 10 $\text{mmol}_c/\text{l}^{0.5}$). The exchangeable sodium percentage (ESP) can be calculated empirically from the SAR (McBride, 1994, p.281) and this theoretical approximation gives an average ESP values of <15% for wet and moist soils and 17% for dry soils (Ayers & Westcot, 1985, Fig. 1). The ESP at which a soil may develop sodicity problems is 15% although increased salinity reduces the potential for clay dispersion. A SAR > 10 may lead to increasing difficulty in maintaining the infiltration rate through soil amelioration (DWAF, 1993). The increase in salinity of sump and groundwater samples reduces their sodicity hazard in spite of increased SAR relative to the effluent (Figure 4.11).

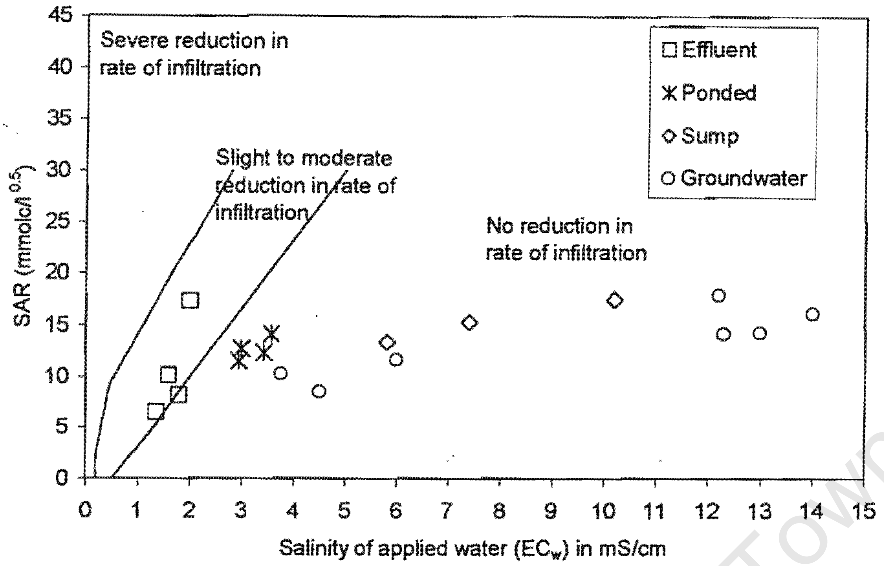

Figure 4.11: Sodicity Hazard Graph (Adapted from Ayers and Westcot, 1985).

The reduction in the sodicity hazard from increased salinity can be seen in Figure 4.11 in which the effluent has a slight to moderate sodicity risk associated with its use whereas ponded, sump and groundwater samples pose no risk to reduction of infiltration rate. Additional factors mitigating against effluent sodicity include the high base saturation of soils and NH_4 content in the effluent as it has been shown (Thompson, 1983 in Thompson, 1985) that ammonium salts exert an appreciably greater effect than expected in reducing adsorption of sodium by soils. In the case of red, highly weathered, sesquioxidic soils, it has been established (Thompson, 1985) that the soil remains permeable with ESP values approaching 40 where the conductivity of the soil solution is reasonably high (> 300 mS/m).

Re-irrigation of sump and groundwater down slope of the site is more likely to create sodium (and chloride) toxicity problems and nutritional imbalances (e.g., excessive Na uptake relative to Ca) in vegetation than infiltration problems. Sodium toxicity is not easily distinguished from Cl toxicity. Symptoms include leaf burn and dead tissue along the outside edges of leaves in contrast to Cl toxicity which manifests at the extreme leaf tip (Ayers & Westcot, 1985). The Na content of sump water varied from 1000-2000 mg/l and were it to be re-used, it should be applied to the soil surface rather than irrigated to limit wetting of foliage since a Na concentration of > 460 mg/l may cause foliar injury to plants (DWAF, 1993).

The Wilcox diagram in Figure 4.12 indicates that the sump and borehole waters fall into the medium sodicity hazard class (S2) and do not present an appreciable sodium hazard as soils on the Robertson site are coarse-textured and have high permeability. The salinity of these samples exceeds the very high salinity category (C4). Very high salinity water can be used where the soil is permeable, a large leaching fraction is maintained and salt tolerant crops are grown (Lloyd and Heathcote, 1985).

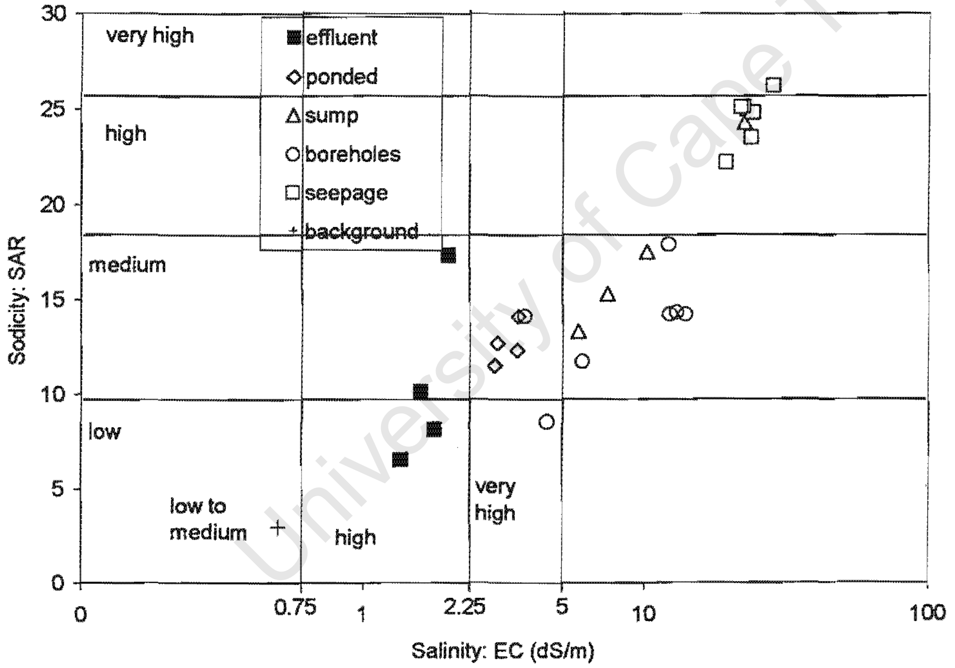

Figure 4.12: Wilcox diagram for water sample types.

4.3.2 Anions

The major anions in water and soil solutions are Cl, SO_4 and HCO_3 and generally occurred in concentrations greater than 100 mg/l. Significant concentrations of NO_2 and PO_4 (5-10 mg/l) were detected only in the effluent samples. Figure 4.13 illustrates the relative anion concentrations of the water sample types averaged over the sampling period. Figure 4.14 shows the relative anion abundance between the dry, moist, wet and background soils as well as ponded effluent. The water sample data are provided in Appendix A and the saturated paste extract data in Appendix C.

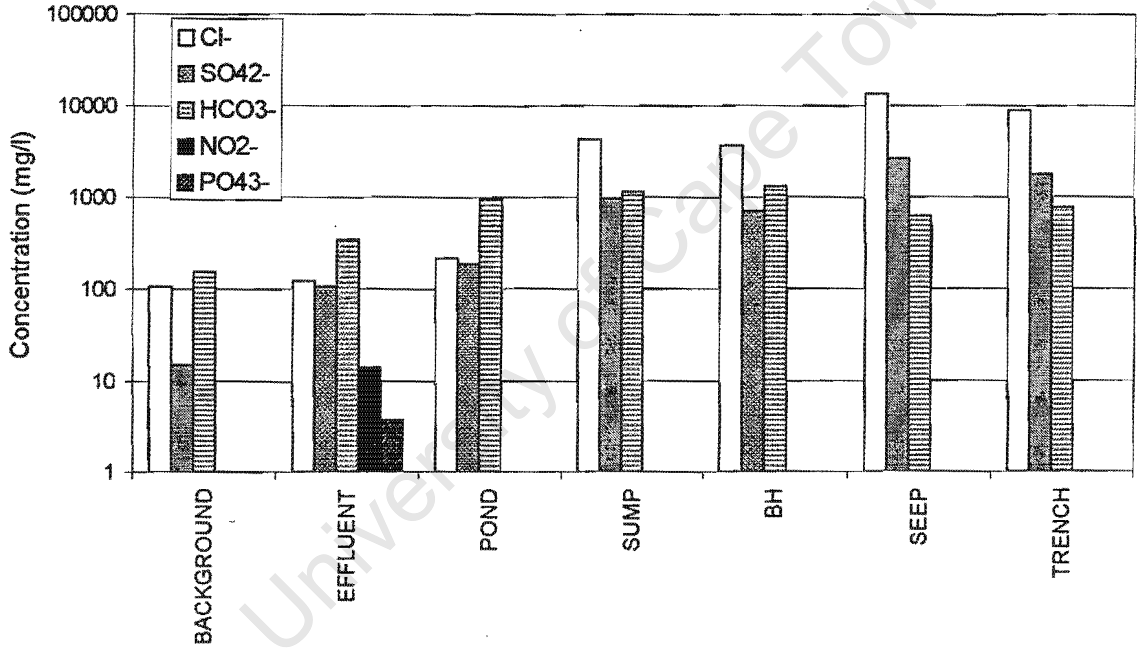

Figure 4.13: Anion concentration in water samples from different locations.

The order of anion abundance in the effluent and ponded effluent is generally HCO_3 > Cl > SO_4> NO2 > PO_4 although in ponded samples NO_2 and PO_4 were not detected. In the soil solution SO_4 concentration is greater than Cl for the shale soils possibly indicating SO_4 retention relative to Cl, as Cl concentration is generally greater in the effluent. In colluvial topsoil, however, Cl is predominant. The Cl and SO_4 concentration in the ponded effluent was, on average, greater than in the moist and wet soil samples but significantly less than in the dry soils.

In sump water, Cl predominates and $HCO_3 > SO_4$ in August and September but in October and November $SO_4 > HCO_3$. Groundwater within 60m of the site (bhs 2 and 4) have similar anion abundance as effluent (i.e. $HCO_3 > Cl > SO_4$), whereas with increasing distance from the site (bhs 5, 7 and 8) anion abundance is similar to that of sump samples: $Cl > HCO_3 > SO_4$. In seep and trench water $Cl > SO_4 > HCO_3$ with minor amounts (< 1 mg/l) of NO_2 and PO_4 occasionally detected. In the background water sample, $HCO_3 > Cl > SO_4$.

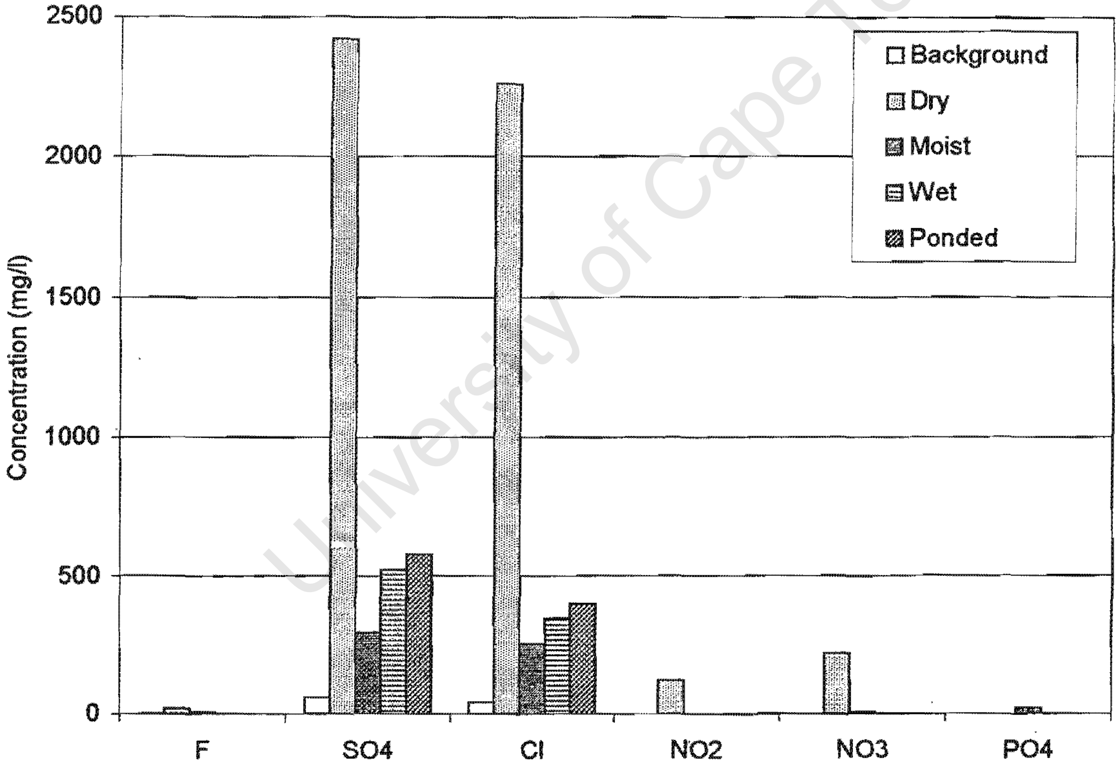

Figure 4.14: Anion concentration in saturated paste extracts and ponded water samples.

Bicarbonate and alkalinity are used synonymously below, as HCO_3 constitutes at least 99% of alkalinity even at pH 9. Bicarbonate is the dominant anion in the effluent and varied greatly over the sampling period from 0.4 to 10.7 mmol$_c$/l (Figure 4.15). Bicarbonate concentration increased from approximately 6 mmol$_c$/l in the effluent to between 11 and 23 mmol$_c$/l in the ponded samples from the 25th August and resulted in an increase of approximately 4 pH units (see Figure 4.7). A further increase in HCO_3 occurred in sump and groundwater (up to 41 mmol$_c$/l). However, a decrease in HCO_3 concentration in groundwater with distance from the site was noted. In samples taken on 10th November this decrease occurred from 27 mmol$_c$/l in Bh5 to 12 mmol$_c$/l in Bh 8 and to 5 mmol$_c$/l in Bh7. Seep and trench samples have average HCO_3 concentrations of approximately 10 and 13 mmol$_c$/l, respectively. Bicarbonate alkalinity showed a general increase over the sampling period but decreased in the sump. Alkalinity was not determined for the saturated paste extracts.

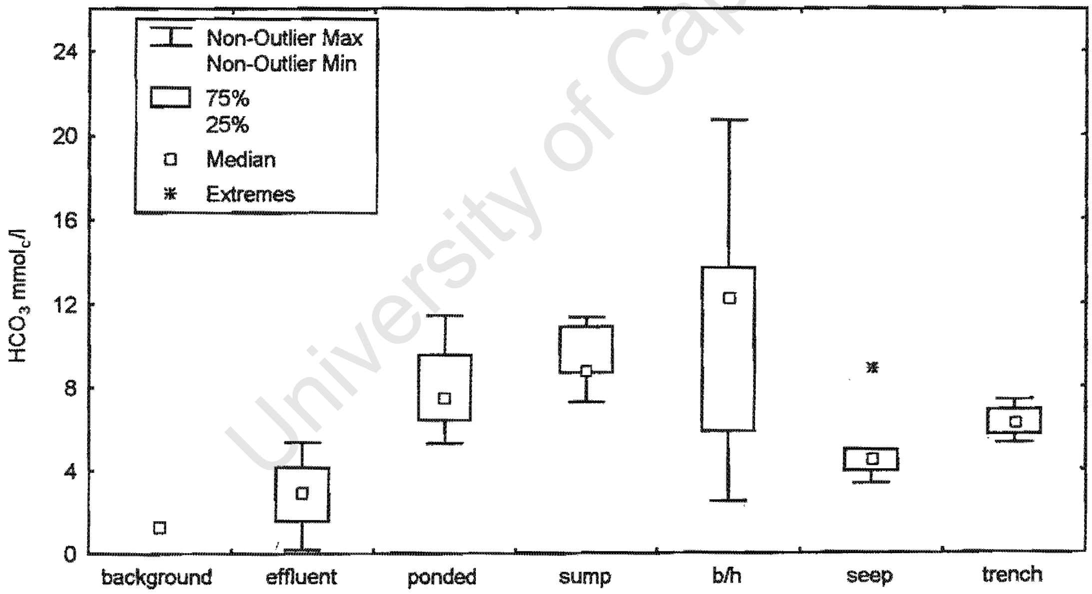

Figure 4.15: Bicarbonate alkalinity in water samples from different localities.

Evaporation of effluent brings about the precipitation of Ca and Mg as insoluble and relatively innocuous carbonates. Excess carbonate or bicarbonate not precipitated by Ca and Mg may pose an alkalinity hazard (Mc Bride, 1994). The alkalinity hazard can be measured as the residual sodium carbonate value (RSC), where RSC = $[HCO_3^- + CO_3^{2-}] - [Ca^{2+} + Mg^{2+}]$. An RSC greater than 2.5 indicates a high alkalinity hazard and there is potential to degrade soil properties, primarily through causing soil organic matter to disperse (Rowell, 1994). The RSC of the effluent was less than 2.5 on 3 of the 4 sampling days, however, on the 10th November the RSC was 7.9. The RSC of the ponded effluent is greater than 2.5 (except in S1). The high Mg concentration in groundwater reduces the alkalinity hazard.

Chloride is a conservative element implying that it does not readily react with other ions to form sparingly soluble salts; it therefore persists in solution relative to other anions. The high pH of the soils would preclude the potential for Cl sorption. The Cl content of the effluent was fairly constant at 3.5 mmol_c/l (~ 125 mg/l) over the sampling period whereas all other major anions showed considerable fluctuation. The Cl concentration of the sump, borehole and seep samples increased over the sampling period. The concentration factor between effluent and sump was 60 in November compared to 13 in August indicating the important role of temperature. The Cl concentration decreased in the trench samples over the sampling period possibly from precipitation of Cl salts between the site and trench.

The Cl in the effluent and ponded samples (of 25th August) did not exceed 350 mg/l, the concentration at which toxic effects in crops become especially severe (DWAF, 1993). Very salt tolerant crops (sorghum, barley and wheat grass) can tolerate levels of up to 2800 mg/l Cl in saturated soil extracts which is of the same order as the Cl concentrations observed in the dry soils. However, spray irrigation with sump water and groundwater from the boreholes is likely to cause foliar damage. For livestock watering, the Cl content should not exceed 1500 mg/l for non-ruminants and 3000 mg/l for ruminants as salt poisoning may occur. This excludes the use of sump water (except for August) and groundwater (except from Bh2 and 4) for stockwatering.

Sulphate is the predominant anion in the soil solution on the irrigation site, with a maximum concentration of 5.9 g/l (average 2.4 g/l), although in the drier colluvium samples Cl is dominant (maximum of 3.7 g/l and average of 2.3 g/l). This contrasted with effluent and ponded samples where Cl usually predominates and suggests that SO_4 is retained in the soil relative to Cl. Sulphate concentration decreased in the effluent, borehole and trench samples over the sampling period but increased in the sump samples.

Ion chromatography allowed for the differentiation between NO_2 and NO_3 whereas the colorimetric method did not. Nitrite is the major nitrogen species in the effluent but NO_3 was dominant in the soil solutions. Ion chromatography indicated that NO_2 and NO_3 were below detection levels in all other water samples. Much lower concentrations of NO_2 and NO_3 (0.2 – 0.3 mg/l) were detected in the effluent by colorimetric analysis but were also below detection levels in all other water samples. Nitrite was not detected in the ponded samples, which is to be expected given the chemical oxygen demand of ponded effluent (up to 272 mg/l). In O_2 poor conditions, NO_2 is likely to be readily utilized as an oxidant (electron acceptor) in biodegradation as it releases more energy than oxygen usage (McCarty, 1972).

Nitrate and NO_2 were detected primarily in dry soils (Figure 4.14). Nitrite was not detected in the moist and wet soils except in Sh3/moist (28 mg/l NO_3). Nitrification of protein-rich organic matter results in the occurrence of NO_2 and NO_3 in the dry soils. Nitrification is unlikely to take place in the wetter soils as NH_4 produced by ammonification of organic matter is probably immobilized by adsorption, uptake by soil microbial biomass and plants or volatilized as NH_3. The high NO_2 (up to 731 mg/l) and NO_3 (up to 555 mg/l) concentration in the dry soils is attributed to evaporative concentration in these low productivity, saline soils. Nitrite and NO_3 were generally not detected in sump or groundwater samples. Their absence suggests that denitrification may occur in the oxygen deficient subsoil. Leaching of nitrate is not considered a hazard at the Robertson site. The nitrate concentration is the background water sample was 0.2 mg/l.

Phosphate (PO_4) was detected in all effluent samples in minor concentrations (~ 5 mg/l) but was below detection levels in the ponded samples. Phosphate was generally not detected in the soil solution although up to 49 mg/l PO_4 was detected in the colluvial topsoil. Controls on PO_4 solubility include immobilization in the soil biomass, adsorption on sesquioxides and precipitation as $CaPO_4$ or $FePO_4$. Phosphate occurs in minor concentrations (< 0.5 mg/l) and is usually below detection levels in the sump, groundwater, seepage and trench samples. The background water sample had a PO4 concentration of 0.8 mg/l.

Fluoride was only analysed for in the samples taken on 25th August. A concentration of 50 mg/l was detected in the effluent but F was not detected in the ponded, sump or seepage samples but was detected in the trench sample (52 mg/l). The trench sample is, however, concentrated by a factor of 80 compared to the effluent. This indicates F retention in the soils and/or aquifer material. Fluoride was detected in 9 of the 16 soil solutions at a median concentration of 7 mg/l (up to 64 mg/l in Coll/dry) suggesting weak sorption particularly on colluvium. Fluorine has a low to moderate phytotoxicity and shows toxicity symptoms at concentrations from 50 – 500 μg/g (leaf dry weight) in plants that are neither highly sensitive nor tolerant (Kabata-Pendias, 1984 in McBride, 1994). Fluoride is not considered hazardous to vegetation although the 52 mg/l in the trench may constitute a risk to animals drinking this water as 2 mg/l F is the maximum guideline value for livestock watering (DWAF, 1993).

4.4 Minor and Trace Element Concentrations

Minor and trace element concentrations in water samples and saturated paste extracts from 25th August are presented in figures 4.16 and 4.17. The values for the dry, moist and wet soil solutions and the ponded effluent are averages of up to 5 samples whereas the other sample categories represent single analyses. The ICP-MS analyses were semi-quantitative and therefore serve as an indication of the relative abundance of minor and trace elements in the grape-processing effluent. The reproducibility of these results for some of the samples was presented in chapter 3. The solubility of non-conservative elements will be controlled by, for example, pH, Eh and ionic strength. The high salinity and organic content of the wastewaters, before consideration of any hazardous levels of minor and trace elements, implies that they are not potable and constitute a risk to aquatic life if discharged directly into streams and rivers.

In Figures 4.16 and 4.17 it can be seen that there is generally no significant difference in most trace constituents between the dry, moist and wet soils although Fe (7 mg/l) was significantly greater in wet soils and Br (21 mg/l) in dry soils. All samples, including the saturated paste extracts, have higher concentrations than the effluent for all analysed minor elements. Silicon appears to be the exception with a fairly constant concentration (~5 mg/l) for most water samples although only 1 mg/l was detected in the seep and 12 mg/l in wet soils. Silicon may be removed from solution by precipitation of silicates or as an amorphous silica gel.

Aluminium concentration increases from 0.5 mg/l in the effluent to between 1 and 2 mg/l for all other water samples. In the soil solutions, concentrations were generally less than 0.5 ppm and often below detection limits; however, in sample RSI/sub (subsoil near sump), 17.9 ppm Al was detected. At $pH > 6$ total Al solubility approaches 10^{-3} M but increases at $pH > 8$ as a result of $Al(OH)_4^-$ formation (McBride, 1994). The relatively high total Al concentration in sample RSI/sub may be due to colloidal clay minerals that were not completely removed during sample preparation. This sample also had the highest Si concentration (26.9 mg/l). Bromine is a conservative element and its concentration in all the samples is correlated with salinity.

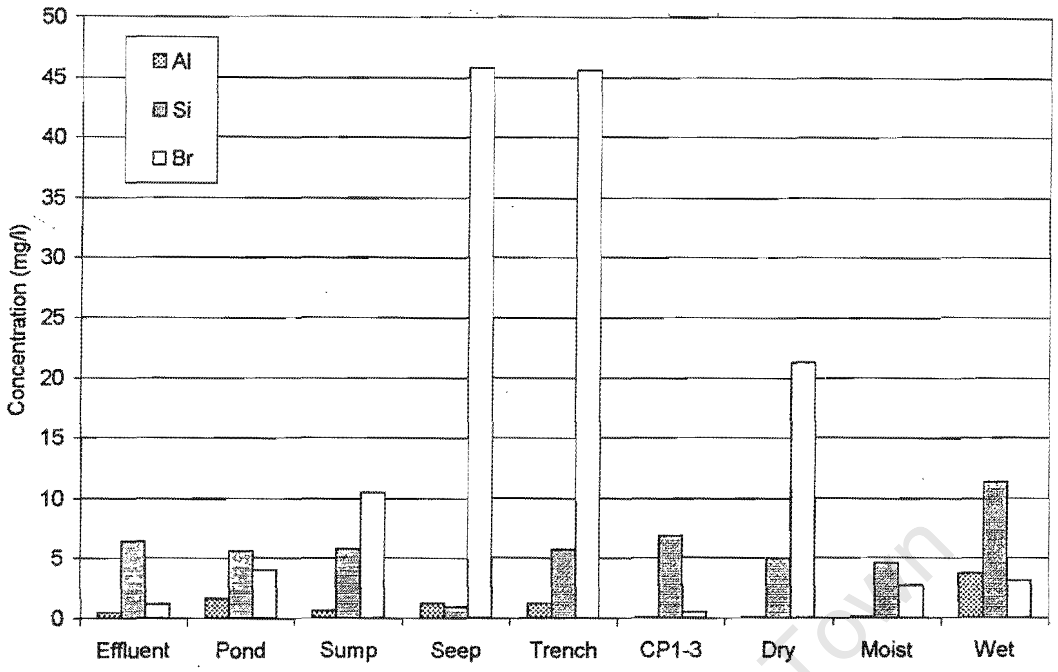

Figure 4.16: Concentration of Al, Si and Br in saturated paste extracts and water samples

Boron is rated as a relatively mobile element which concentrates in surface soil in arid and semi-arid climates (McBride, 1994). Boron mobility is indicated by increased concentration in all samples relative to the effluent. However, B concentration in the effluent is less than 1 mg/l and increases to between only 1 and 2 mg/l in all other water and soil solution samples (Figure 4.17). This indicates some retention on soils since salinity increases by a factor of up to 60 between effluent and sump samples. Boron is barely detectable in background soil solutions. Boron has a marked effect on plants from the standpoint of plant nutrition if B is deficient in soil, and of toxicity if present in excessive amounts (Mengel and Kirkby, 1978 in Ginster, 1993). The effluent does not have enough B to injure plants directly but the increase in B concentration due to evaporation (up to 8.2 ppm in Sh2/dry) may lead to eventual toxicity problems. Leaching in the wet and moist soils maintains the B level at less than 3 ppm. Higher B concentrations occur in the colluvium than in the shale soils (except for the dry shale soil) probably because of the lower clay content of the colluvium.

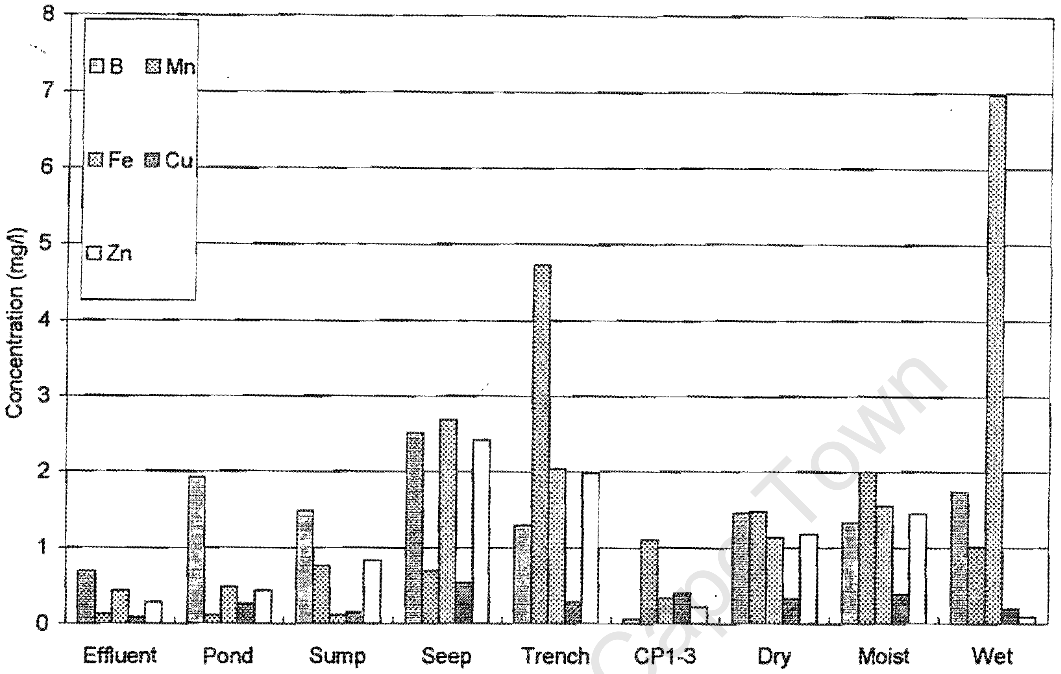

Figure 4.17: Concentration of B, Fe, Mn, Cu and Zn in saturated paste extracts and water samples.

The concentrations of Mn, Fe, Cu and Zn are all less than 0.5 mg/l in the effluent but are elevated in all other samples (Figure 4.17). This is contrary to expectation as reduced solubility is expected with increased pH as occurs after effluent irrigation. The elevated salinity of samples, other than the effluent, may explain the increased concentration of these metals. The organic content in grape-processing effluent may also increase metal solubility by complexation with organic ligands (e.g. carboxylate). The relatively high (> 1 mg/l) Fe and Mn concentrations of the seep, trench and soil solutions may be due to colloidal Fe & Mn oxides. However, Fe^{2+} and Mn^{2+} were detected in sump (and boreholes) samples at concentrations of approximately 2 mg/l. The high concentration of Fe in the wet soils (7 mg/l) relative to the moist and dry soils may point to the reduction of Fe-oxides during oxidation of organic matter. The Mn concentration exceeds the general effluent standard (0.4 mg/l) in all samples except the effluent and ponded samples but is unlikely to constitute a hazard to livestock or plants at the measured concentrations. The background soil solution (CP1-3) has higher Mn and Cu content compared to the effluent

The Cu concentration in the effluent was 0.1 mg/l and increased to 0.5 mg/l in the seep. The Cu concentration in the soil solutions is less than 1 mg/l and the general effluent standard for Cu is 1.0 ppm. The detected Cu is likely to occur as complexed with organic matter and sorbed onto colloidal oxides and clay (McBride, 1994). Zinc was detected at a concentration of 0.3 ppm in the effluent and increased up to 2.5 ppm in seepage. Like Cu, the activity of free Zn^{2+} is extremely low in alkaline conditions and the Zn in the samples may occur as Zn-organic complexes (McBride, 1994). In the soil solutions the Zn concentration is less than 0.3 ppm and often below detection limits in the saturated paste extracts, indicating strong sorption on soils. The Zn concentration does not exceed the general effluent standard (5 ppm) and at the detected concentrations is unlikely to pose any hazard.

4.5 Conclusions

Land treatment of grape-processing effluents near Robertson results in the transformation of a low salinity, organic rich effluent to a high salinity water of much lower organic matter content. The aridity of the area exerts strong control on the salinity levels in wastewater which leaves the site and in groundwater downslope of the site. The hydrogeology of the area results in surfacing of groundwater and evaporation, which produces salt efflorescences in a seepage zone some 400m downstream of the site. Groundwater analyses indicate leakage of effluent through the weathered shale saprolite beneath the site.

The salinity levels in the water leaving the site pose the major constraint on its beneficial re-use. The increased salinity and sodicity of the water leaving the site is likely to detrimentally affect agricultural activities below the site unless this shallow seepage water is significantly diluted with low-salinity irrigation water. The plume associated with movement of this saline water body is expected to have already reached the Breede River, some 2.5 km away. Re-solution of the salt efflorescence at the onset of winter rains will result in a pulse of highly saline water moving downstream with potentially harmful consequences for downstream irrigation schemes and add to the already serious problem of salt build up in the Breede river.

The total salt load originating from the irrigation scheme and reaching the Breede River is difficult to estimate without an adequate record of effluent volumes and salinity levels and will be difficult to differentiate from salts added by return flow from downstream irrigation schemes. The prevailing climatic and hydrological conditions will also determine the load reaching the river. A salt load, which was estimated from assuming that all Na and Cl and half the Mg and SO_4 in the effluent leave the site (but does not necessarily reach the Breede river) suggests that 400 kg/day is leaving the site.

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CHAPTER 5

GEOCHEMICAL ASSESSMENT OF THE PROCESSES AFFECTING SURFACE AND GROUNDWATER

5.1 Introduction

Chapter 5 described how grape-processing effluents are transformed from organic rich, low pH and low salinity wastewater to a Na, Mg, Cl, SO_4 brine. These changes result from a combination of bioochemical and geochemical processes that are operative primarily within the soil but also determine groundwater hydrochemistry down-stream of the site. The processes believed to occur include: biogenic mineralization of organic matter, evaporative concentration of soluble salts, precipitation of sparingly soluble salts, ion exchange and adsorption and the reduction of nitrogen species, Fe and Mn oxides and SO_4. This chapter discusses the evolution of the grape-processing effluent in terms of these processes.

5.2 Mineralization of Organic Matter

In chapter 4 it was shown that the Robertson site reduces effluent COD by up to 95%. Factors promoting the mineralization of organic matter include the nature of the organic matter; size of the bacterial population; availability of oxygen and other electron acceptors; temperatures between 20 - 30° C; soil moisture content; nutrients and suitable pH conditions (Verstraete et al., 1995).

Although analyses of the organic constituents of the effluent were not undertaken, analysis of fresh distillery effluent from May 1999, indicated that approximately 90% of the organic load is soluble. Soluble organic matter in grape-processing effluents contain readily biodegradable carboxylic acid, alcohol and sugars (Chapman, 1995). The strength of the effluent was relatively constant and is similar to winery effluent. Daily irrigation implies the soil contains an acclimatized (the right size for the organic load) microbial population capable of 95% COD removal rate (Chapman, 1995; Pearce et al., 1995). Meeting the oxygen demands of the decomposers possibly constitutes the main constraint for land treatment of organic rich effluents. Irrigating the effluent via cannons undoubtedly oxygenates the effluent and the coarse textured soils (sandy loam) of the Robertson site promote oxygen diffusion thereby increasing the rate of mineralization (Van Veen et al., 1985; Ladd et al., 1991). However, ponding of effluent (from over-irrigation or soil clogging) will decrease organic matter mineralization because of limited oxygen availability (Verstrate et al., 1995). The presence of NO_3 in the drier soils but complete absence in ponded water, sump water and groundwater suggests its utilization as an electron acceptor during mineralization of organic matter. This aspect will be discussed in more detail in section 5.6. The mean monthly temperatures at the Robertson site are between 20 and 30° C and optimal for organic matter degradation. High C:N ratios in the effluent indicate a possible N deficiency which does not appear to reduce the amount of COD reduction achieved. Organic matter decomposes more slowly in strongly acidic soils ($pH < 5$) (Jenkinson, 1988) but this is probably not impeded significantly over the range of pH observed in the irrigated soils.

5.3 Evaporative Concentration and Precipitation of Sparingly Soluble Salts

Evaporative concentration and the precipitation of carbonates play a dominant role in the evolution of the chemistry of grape-processing effluents at Robertson. Garrels and Mackenzie (1967) calculated that progressive evaporation of spring water from the Sierra Nevada would ultimately result in alkaline sodium carbonate brine. This occurs primarily because of the removal of Ca and Mg and persistence of Na in solution; the results of their calculations are shown in Figure 5.1. The figure shows the concentrations of individual solutes on a logarithmic scale plotted against the concentration factor (also log scale). The concentration factor is the ratio of the initial volume of water to the volume remaining after evaporation.

Chloride concentration usually increases linearly with increasing salinity. This behaviour is termed conservative as the total amount of solute remains in solution at all stages of evaporative concentration. Sodium also behaves conservatively although ion exchange at high ionic strengths may occur.

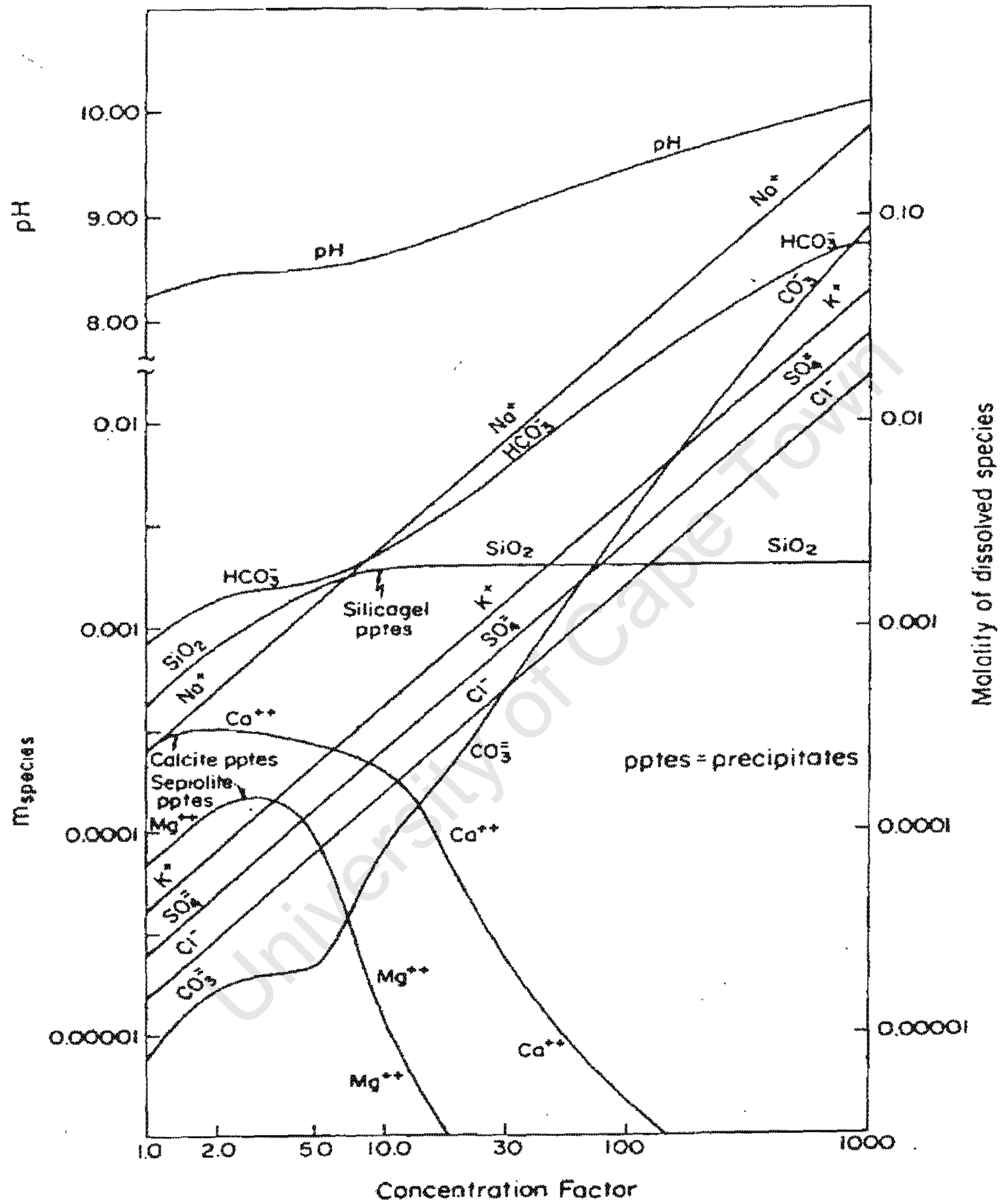

Figure 5.1: Calculated result of evaporating Sierra Nevada spring water (after Garrels and Mackenzie, 1967).

Solute concentrations can be plotted against Cl concentration to indicate behaviour during brine evolution. The plot of Na against Cl for the grape-processing effluents at Robertson indicate Na enrichment (relative to Cl) in the effluent and ponded samples, probably as a result of alkaline cleaning wastewater in the effluent stream.

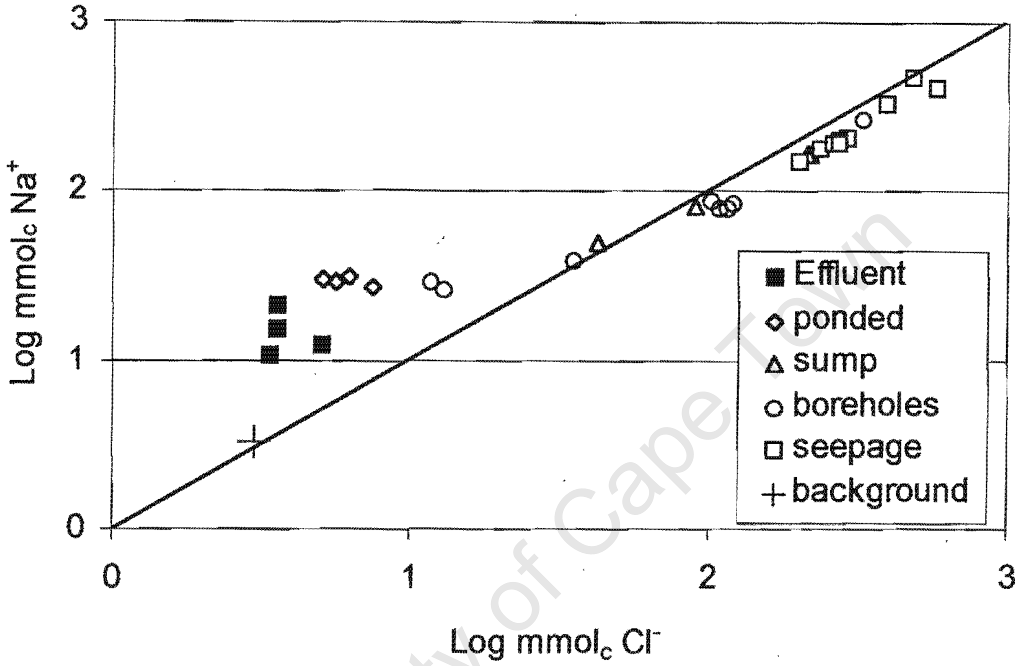

Figure 5.2: Na versus Cl concentration for water types.

Most of the groundwater and all remaining water samples display near perfect conservative behaviour for Na with solute concentration (Figure 5.2). Cyclic wetting and drying, which brings about the differential dissolution of efflorescent crusts may also modifies brine evolution. The complete evaporation of water and deposition of salts during a dry period is followed by partial re-solution of the salts during a wet period (Eugster, 1980). All solutes are deposited following evaporation but during re-solution the rate at which less soluble compounds dissolve may prevent their dissolution. The evaporation-solution cycle, therefore, enriches the resultant brine in highly soluble salts but depletes it in salts that have a slow rate of dissolution.

In their discussion of the evolution of non-marine brines, Hardie and Eugster (1970) introduced the concept of chemical divides. The operative principle in this concept is that whenever two ions are involved in precipitation of a salt during evaporation, one will build up in the solution while the concentration of the other will become very small. The Hardie-Eugster model interprets the chemistry of water undergoing evaporation in terms of a succession of chemical divides. Some of the possible paths for the evaporation of natural waters are shown in Figure 5.3.

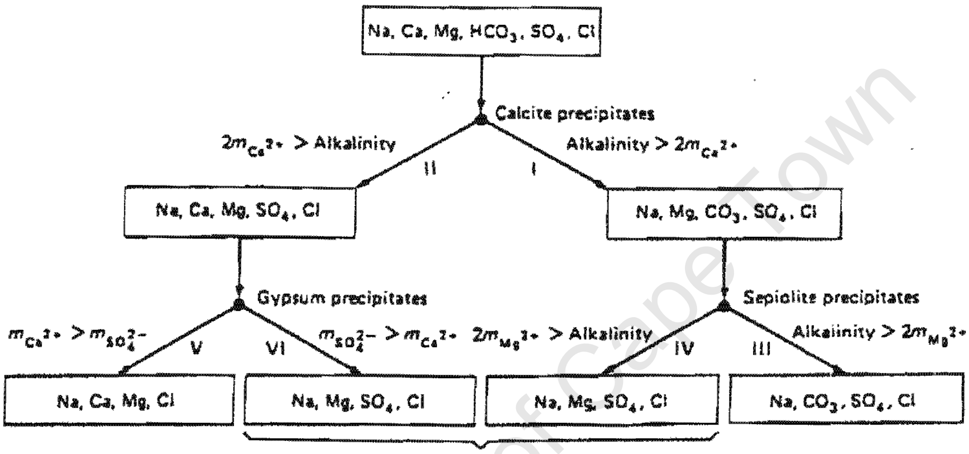

Figure 5.3: Some possible paths for the model evaporation of natural waters modified from Hardie and Eugster (1970) after Drever (1987; p. 331).

The non-conservative behaviour of calcite is indicated in Figure 5.1 and it is commonly the first mineral to precipitate during evaporative concentration. Calcite precipitation is inferred from the plot of Ca against Cl in Figure 5.4 because of the diminished rate of concentration of this cation relative to Cl. Contrary to the calculations of Garrels and Mackenzie (1967), which indicates complete removal of Ca at a concentration factor of around 100 (Figure 5.1), Ca concentration increases albeit at a diminishing rate with increasing chloride concentration. Calcium may be derived from resolution of sparingly soluble salts and Na exchange for Ca in the soil and aquifer.

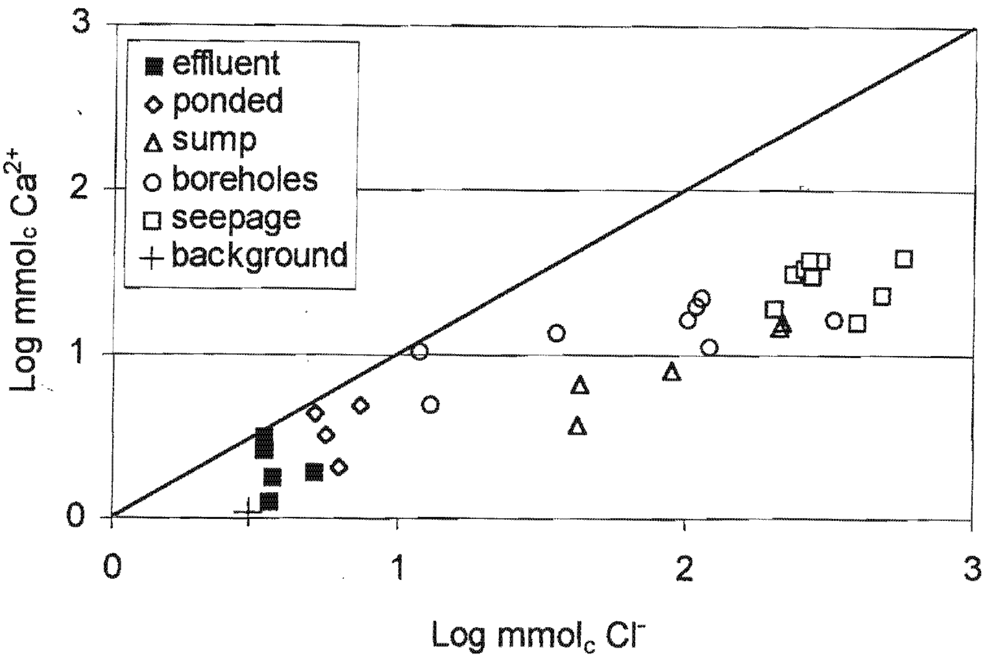

Figure 5.4: Ca versus Cl concentration for water types

Figure 5.4 indicates increasing Ca concentration with evaporative concentration. Removal of Ca is thermodynamically possible on the site since ponded samples have average calcite saturation indices of 1.7 (S.I.). The positive saturation index for calcite (Table 5.1) in all the water samples except the effluent indicates that the effluent remains supersaturated with respect to calcite and precipitation is likely over the entire concentration range in Figure 5.4. The S.I. < 0.5 for calcite in the sump water suggests that Ca solubility is controlled by this mineral.

Table 5.1: Saturation indices for a selection of minerals using PHREEQC.

Sample I.D.		**Effluent**	**Ponded**	**Sump**	**Bhs**	**Seep**	**Trench**	**Backgr.**
Sample Date		25-Aug	25-Aug	25-Aug	7-Oct	25-Aug	25-Aug	02-Sep
Phase								
Calcite	$CaCO_3$	-2.15	1.71	0.44	1.75	1.62	1.07	-0.12
Dolomite	$CaMg(CO_3)_2$	-4.12	3.91	1.50	3.93	3.89	2.79	-0.02
Gypsum	$CaSO_4.2H_2O$	-2.00	-1.86	-1.20	-1.01	-0.43	0.48	-2.85
Sepiolite	$Mg_4Si_6O_{15}(OH)_2.6H_2O$	-12.00	1.90	-2.90	-	0.47	-0.78	-
Quartz	SiO2	-	0.06	0.30	-	-0.46	0.26	-

Increased carbonate activity and evaporative concentration causes calcite to precipitate. Whilst Ca is available to precipitate as $CaCO_3$, a build-up in alkalinity is prevented and the system is buffered at a pH of around 8.4. With depletion of Ca and continued build-up of Na and alkalinity, pH increases. The availability of Ca to remove alkalinity ensures that the pH of the groundwater, seep and trench water remains below 8.6. The control that Ca exerts on solution pH is illustrated in the following equation (Drever, 1997):

$$2\text{pH} = 9.6 - \log(\text{Ca}^{2+}) - \log P_{\text{CO}_2}$$

where P_{CO_2} is the atmospheric partial pressure of CO_2 and (Ca^{2+}) is the activity of Ca in solution. The plot of bicarbonate alkalinity against Cl (Figure 5.5) indicates elevated HCO_3 in ponded samples and in Bh 2 (relative to conservative evaporative concentration). The increased alkalinity in the ponded samples is attributed to the degassing of CO_2 caused primarily from the degradation of the organic matter in the effluent, which produces bicarbonate alkalinity:

$$CH_3COO^- + 2O_2 \Rightarrow CO_2\uparrow + HCO_3^- + H_2O.$$

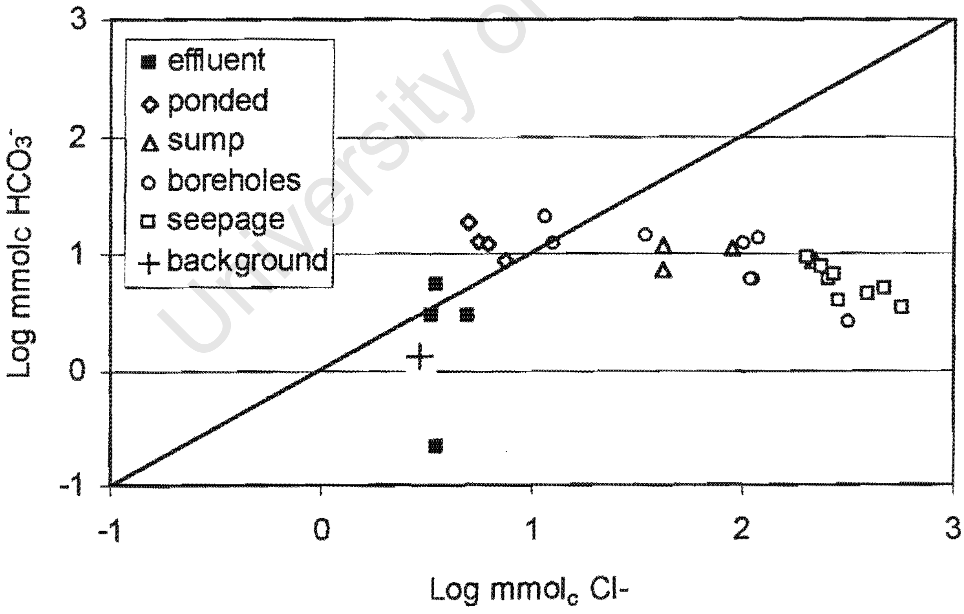

Figure 5.5: Bicarbonate alkalinity versus Cl concentration for water types

Depletion of bicarbonate in groundwater, seepage and trench water is attributed to the precipitation of Ca and possibly Mg-carbonates.

The slope of an imaginary trend line through the data points in Figure 5.6 indicates that Mg is also removed from solution with evaporative concentration but to a lesser degree than Ca. In Figure 5.6 removal of Mg appears to commence in groundwater and sump samples that have undergone a concentration factor of at least 4. Garrels and Mackenzie (1967) suggested that Mg may be removed as sepiolite ($Mg_4Si_6O_{15}(OH)_2.6H_2O$). Eugster & Hardie (1978) and Eugster (1980) use Mg-calcites and dolomite in their brine evolution models (Figure 5.3). Drever (1997) states that the most common Mg-containing phases in nature appear to be Mg-rich smectite, dolomite or high Mg-calcite. Sepiolite has a positive S.I. in the ponded samples indicating that it is thermodynamically possible for it to precipitate. However, sepiolite has an S.I. of –2.9 in the sump sample and remains undersaturated in the trench and close to equilibrium in the seep sample (Table 5.5). Dolomite has a positive S.I. in all samples except for effluent samples.

The solubility of minor and trace elements is likely to be limited by high pH as these are subject to co-precipitation with calcite. High soil pH increases the mobility of F as does Na concentration because of the formation of soluble NaF (McBride, 1994). Phosphate is generally the most strongly adsorbed anion and precipitation (as $CaPO_4$) may also occur although in alkaline soils, PO_4 solubility can be higher than in Ca-rich soils because Na suppresses precipitation and alkaline anions (HCO_3, CO_3, OH) displace phosphate from chemisorption sites on variable charge minerals (McBride, 1994). The low clay content and pH > 8.7 in the colluvium topsoils may account for the presence of PO_4 in these soil solutions.

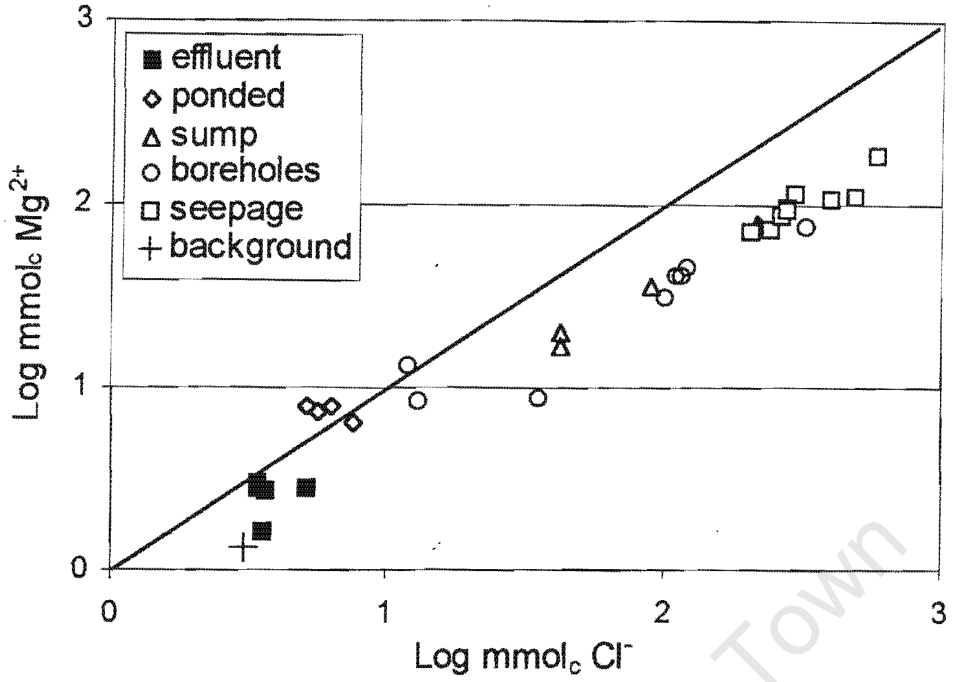

Figure 5.6: Mg versus Cl concentration for water types

The grape-processing effluent typically has greater concentrations of HCO3 than Ca and according to the modified brine evolution model of Hardie and Eugster (1978 in Drever, 1997) initial precipitation of calcite will result in a solution enriched in Na, Mg, CO_3, SO_4, and Cl (Path I in Figure 5.3). Further evaporation of this solution may result in the precipitation of sepiolite (or high Mg-calcite) and the positive S.I. for sepiolite mineral, at least in ponded samples, suggests that this is thermodynamically possible. Where $2m^{Mg2+}$ > alkalinity (meq), as is the case in the ponded water, and increasingly in all samples down gradient of the site, the solution will evolve along Path IV in Figure 5.3 and the final brine solution from continued solute concentration will be a carbonate-free Na, Mg, SO_4, Cl brine. In the effluent sample of 7th September (pH 4.5) $2m_{Ca}{}^{2+}$ > alkalinity and here evaporation may result in gypsum precipitation. The positive SI for gypsum in the trench sample suggests that it is possible for this mineral to eventually precipitate from the effluent provided the Ca concentration is sufficiently high. Thus the chemical divide principle of the Hardy-Eugster is not directly applicable because of compositional variability of grape-processing effluents. The original Hardie-Eugster model is an oversimplification of the real world as various processes other than evaporative concentration can affect the evolution of brines.

5.5 Ion Exchange and Adsorption

Ion exchange and adsorption reactions are likely to take place between dissolved components in the effluent and ions adsorbed on soils and sediments. Differential uptake of cations on exchange surfaces such as those provided by clays may account for some of the non-conservative behaviour of ions. Clay type and content, organic matter content and cation exchange capacity (CEC) of the soil determine the extent to which sorption may occur and the degree to which cation composition may change. The particle size distribution, organic matter content and exchangeable cations (1M NH_4OAc) of the soil samples are presented in Table 5.2.

Table 5.2: Particle Size Distribution (%), Organic Carbon Content (%) and Exchangeable Cations* (cmol/kg).

	Clay	Silt	Sand	Org C	K	Na	Ca	Mg
Sh1/moist	6	10.6	83.40	1.10	1.78	1.86	5.84	3.48
Sh1/wet	8.2	10.3	81.50	1.30	2.01	1.95	10.16	3.75
Sh1/dry	11.1	16.3	72.60	0.80	2.76	1.57	14.54	2.91
Sh2/wet	11.9	12	76.10	0.90	2.19	1.89	9.88	2.8
Sh2/dry	13.8	15.3	70.90	0.80	6.72	6.91	10.18	4.15
Sh3/moist	15	13	72.00	0.80	1.58	1.34	5.67	2.5
Sh3/dry	13.9	12.9	73.2	0.8	0.98	4.09	2.65	5.47
Col1/top	7.6	6.2	86.2	0.6	1.09	1.38	2.33	1.59
Col1/sub	8.8	6.5	84.7	1.5	0.55	0.73	1.29	0.84
Col1/dry	10	5.9	84.1	0.6	0.86	1.42	2.52	2.1
Col2/top	6.8	5.5	87.7	0.5	1.23	1.05	4.97	1.44
Col2/sub	2.8	4.3	92.9	1.6	1.7	1.17	3.36	1.51
RSI/top	5.6	4	90.4	0.3	0.29	0.26	2.43	0.71
RSI/sub	5.9	3.4	90.7	0.4	0.68	0.97	1.48	0.92
SSI	3.8	3.9	92.3	1.3	0.47	2.31	6.72	3.04
CP1-3	3.4	4.1	92.5	0.4	0.1	0.1	4.42	0.66

*Exchangeable Cations: determined by 1M ammonium acetate extraction and includes exchangeable and soluble cations.

The clay fraction of the soils consisted predominantly of mica and kaolinite (Appendix E). Kaolinite has low CEC compared to other layer silicates although 'edge-sites' may contribute up to 15 cmol/kg (Mc Bride, 1994). Mica, in particular illite, with its 10 Å c-spacing tends to trap K between silicate layers resulting in comparatively low CEC. Sesquioxides, although not detected by XRD probably because of their poor crystallinity and low concentrations, are believed to be present in the soil clay fraction (Fe_2O_3 content of soils in Appendix E). Fine-grained iron oxides and soil humus are anticipated to provide most of the CEC of the soils and sediments.

The soil CEC presented in Figure 5.2 also includes soluble cations and estimation of the effective CEC would require subtraction of soluble cations. The data indicate, however, that in spite of Na dominance in the effluent, the exchange sites are predominantly Ca saturated. The concentration-charge effect predicts that at higher electrolyte concentrations there is a shift in favour of lower charge cations on exchange surfaces (Mc Bride, 1994). This does not appear to be the case even for the saline soil samples such as SSI and Shl/dry, although exchangeable and soluble K plus Na exceeds Ca in sample Sh2/dry. It can be concluded that at the Robertson site, frequent leaching with low salinity effluent results in Ca and Mg dominance of exchange sites.

The ion most affected by ion exchange is K and it is usually depleted in saline waters relative to Na as a result of preferential adsorption, particularly in the interlayers of silicate clay minerals. Table 5.2 indicates that exchangeable (and soluble) K is frequently greater than Na and contrasts with Na > K in the soil solution. The attenuation of K at the Robertson site is illustrated in Figure 5.7. Potassium reaches maximum concentration in the ponded effluent but is subsequently removed as the effluent migrates through the soil and aquifer material.

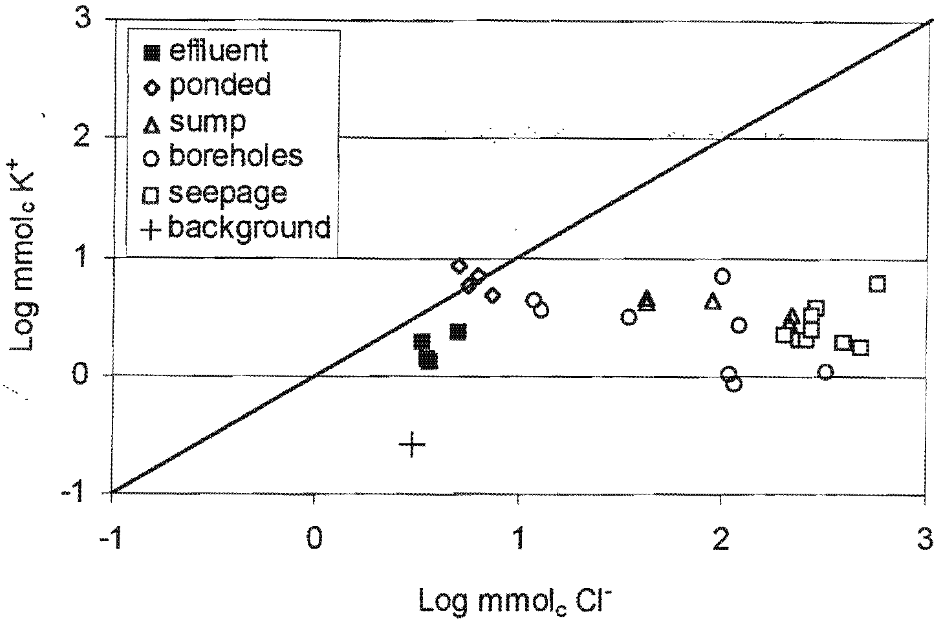

Figure 5.7: K versus Cl concentration for water types

The pH of the soils is likely to result in sorption of trace elements such as B, Cu and Zn onto Al and Fe oxides, organic matter and silicate minerals. Increasing pH may mobilize these elements although the soils are probably not alkaline enough to produce metal hydroxy/carbonate compounds (McBride, 1994).

5.6 Redox and Electron Acceptors

Where replenishment of dissolved oxygen is restricted, decomposition of organic matter causes the redox potential to decrease (Hickman, 1989). Oxidation reactions involved in metabolizing organic compounds are coupled with microbially mediated reduction reactions that proceed in a characteristic sequence as redox potential declines (Table 2.2). This sequence is paralleled by a succession of metabolic strategies used by the micro-organisms responsible for active decomposition in the order aerobic respiration, denitrification, fermentation, sulphate reduction and methanogenesis. The absence of nitrite/nitrate in seepage leaving the site is believed to result from denitrification in the subsoils although uptake by plants and the soil biomass may also account for N losses from the effluent. The detection of Fe^{2+} and Mn^{2+} (1 – 2 mg/l) in sump and groundwater samples (Table 5.3) collected on the 7th September may indicate that Mn and Fe oxides are used as electron acceptors during oxidation of organic matter in the reducing conditions expected in saturated soils and the aquifer:

Table 5.3: Fe^{2+} and Mn^{2+} concentrations in sump and groundwater

	Sump	Bh4	Bh5	Bh8
Fe^{2+}	1.9	1.7	0.94	0.05
Mn^{2+}	1.8	2.3	2.5	0.17

When redox potential becomes sufficiently low, reduction of sulphate to sulphide species can reduce sulphate in natural waters. Methanogenesis may also occur although sulphate reducing bacteria usually inhibit the production of methane (Hickman, 1989). Sulphate reduction results in an equivalent amount of alkalinity, which may precipitate as a Ca or Mg carbonate or build up in the solution (Drever, 1997). Figure 5.8 illustrates the behaviour of SO_4 with evaporative concentration and indicates that sulphate is depleted in the middle part of its concentration range (i.e. between log Cl: 1 – 2) corresponding to sump and groundwater samples. In the seepage and trench samples, sulphate appears to behave nearly conservatively, as indicated by the alignment of the composition points parallel to the solid line indicating conservative behaviour.

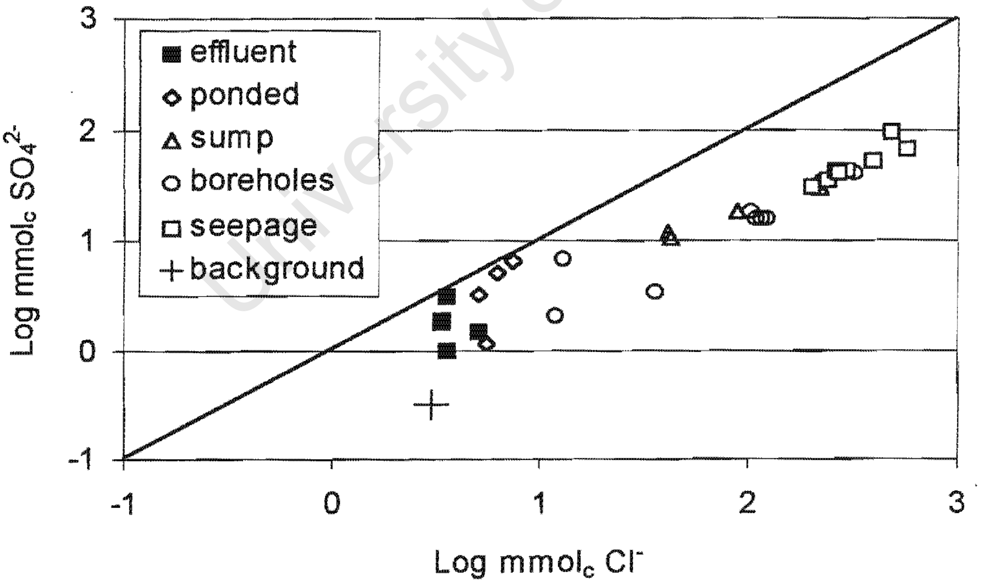

Figure 5.8: SO_4 vs. Cl concentration for the various water types

Whilst surface adsorption and ion exchange may account for some SO_4 removal, it is believed that biogenic reduction of sulphate occurs in soils and groundwater at the Robertson site. The sulphate reduction reaction is termed a fermentation reaction and bacteria use SO_4 as a terminal electron acceptor in the oxidation of organic matter to CO_2:

$$SO_4^{2-} + 2C_{organic} + 2H_2O \Rightarrow H_2S\uparrow + 2HCO_3^-$$

Although sulphide species are the final reduction product, thiosulphates (HS-) are more likely where pH > 7. Thiosulphate is responsible for some of the strong odours associated with anaerobic biodegradation of grape-processing effluents.

Reducing conditions may mobilize Zn and this may explain the slightly elevated concentrations in the sump, seep and trench samples. However, reducing conditions in the soils are probably not prolonged enough to allow for significant metal mobility. Soil re-aeration after irrigation coupled with high pH is expected to limit trace element mobility.

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The main findings of this investigation are summarised in section 6.1 from which it can be concluded that the key objectives of the study have been met. Management recommendations for improved operation and discussion of areas that merit further research are presented in 6.2. Application of geochemical principles permits an understanding of the behaviour of the various constituents in grape-processing effluents as they are affected by land treatment and modified in groundwater down the hydraulic gradient. The Hardy-Eugster model of non-marine brine evolution in closed basins provides a useful framework to assess the fate of various constituents in grape-processing effluents and the compositional pathway of these wastewaters in semi-arid environments. This model does not, however, account for all the observed changes in composition. Geochemical processes such as ion-exchange, adsorption and reduction need also to be applied in explaining more fully the compositional evolution of the effluents.

6.1 Conclusions and Implications for Sustainable Use of the Site

Land treatment of grape-processing effluent at Robertson results in a reduction of from 89 - 95% in COD of the effluent. A maximum effluent COD of 3325 mg/l can be compared to a maximum COD of 209 mg/l in the sump, on the perimeter of the site. The reduction in the DOC of the effluent is almost 99% and the difference between COD and DOC reduction is attributed to particulate organic matter in sump water as well as the effect of high Cl on COD measurement. The estimated C:N ratio of the effluent does not appear to limit the efficiency at which COD is reduced by land treatment. The data indicate that biodegradation continues but to a limited degree in saturated subsoil and aquifer material compared to topsoil. In sump samples undetectable levels of NO_2 and NO_3 may indicate utilization as electron acceptors (oxidants) in continued biodegradation in oxygen-poor conditions. With depletion of NO_2 and NO_3 and biodegradable organic matter still present, the redox potential falls and alternate electron acceptors such as Fe oxide and SO_4 are ultilized as oxidants. Evidence of low redox potential includes dark grey colour of some subsoil samples (characteristic of reduced Fe) and the odour emanating from the site (from volatilization of reduced sulphur species). The generation of odours is one of the more important environmental impacts arising from land treatment of grape-processing effluents.

Further reduction of COD and DOC occurs in groundwater with increasing distance from the site. The detection of Fe^{2+} and Mn^{2+} in groundwater may indicate the participation of aquifer solids in further biodegradation. The behaviour of SO_4 as demonstrated by the plot of SO_4 against Cl concentration points to significant deviation from conservative behaviour during evaporative concentration, particularly in sump samples and groundwater. The COD of the effluent is reduced to background levels (~ 90 mg/l) within 800m of the site.

The pH of the effluent changes from acidic (pH 4.5 – 5.5) to alkaline (pH ~8.5) after irrigation and is attributed, at least initially, to removal of soluble organic matter entailing volatilization of CO_2 during biodegradation. Subsequently, precipitation of carbonate occurs because of evaporative concentration, which buffers the pH around 8.5 by removing carbonate from the system. Further accumulation of alkalinity is controlled by Mg concentration, which increases after irrigation relative to bicarbonate.

The log of major ion concentrations was compared to that of Cl to establish behaviour with evaporative concentration. Relative to Cl, the concentrations of Ca, K and HCO_3 are significantly reduced in the effluent leaving the site. This is attributed to calcite precipitation and K adsorption on clay. Reduction of Mg and SO_4 concentration also occurs but to a lesser degree than that of Ca, K and HCO_3. Non-conservative behaviour of Mg is attributed primarily to Mg-carbonate/silicate precipitation whereas SO_4 reduction is evident from groundwater composition data. The solution migrating from the site and ultimately reaching the Breede river is a Na, Mg, Cl, SO_4 brine, as predicted by the Hardy-Eugster model of non-marine brine evolution.

The semi-arid climate of the Robertson area plays a significant role in reduction of COD and the increase in salinity observed in the grape processing effluents. The concentration factor between effluent and water in the sump increased by a factor of 3 between August and November. Salinity levels exceeding 2000 mS/m and average SAR of 25 $mmol_c/l^{0.5}$ in October and November preclude the beneficial re-use of sump water for irrigation or livestock watering. Groundwater from boreholes close to the irrigation site (4 & 5) could be returned to the site provided this water is not spray irrigated, as Na and Cl may cause foliar damage. Groundwater seeps to the surface approximately 400m north-west of the site boundary where it undergoes further evaporative concentration. Copious salt efflorescence was noted in this seepage zone, particularly in November.

A significant increase in soil salinity occurs from irrigation with grape processing effluents. Soils receiving regular irrigation are sub-saline (EC < 4mS/cm) but dry soils are saline with particularly high concentrations of Na, K, SO4 and Cl compared to wet and moist irrigated soil samples and background soil samples. Average salinity of dry soil samples was approximately 1000 mS/m, this being close to the limit of survival for the Kikuyu (*Pennisetum Clandestinum*), a grass that flourishes in well irrigated areas.

In spite of the enrichment in Na in the effluent and an average SAR or around 10 in the effluent and 20 in soil solutions, Ca dominates the soil exchange complex. Factors that may promote loss of permeability include carbonate precipitation and a high content of suspended and relatively non-biodegradable organic matter in the effluent. Precipitation of carbonate on organic particles may further limit biodegradation and reduce soil infiltration capacity. The ponding of effluent observed in furrows on the site may simply result from over-irrigation; the evaporation rate from April to June is less than half the effluent irrigation rate.

Changes in soil properties as a result of effluent irrigation included an approximate doubling in soil organic content compared to background soils. Subsoils had elevated organic content compared to topsoils and moist and wet samples had higher organic content compared to dry soils probably resulting from reduced rates of biodegradation in saturated conditions. An increase in CEC of irrigated soils compared to that of non-irrigated soils could not be established unequivocally as the clay content of the soils appears more important in determining soil exchangeable cations than whether or not the soil receives effluent.

The semi-arid climate of the Robertson area necessitates continuous irrigation to prevent a build-up of salinity in the soil which may threaten survival of the vegetation cover. It appears that, provided that salinity of the soil solution is kept below an EC of approximately 1000 mS/m, the persistence of grass species appears ensured. A good vegetation cover also increases the rate of evapotranspiration and promotes soil permeability and cohesion. Salts need to be flushed from the soil to maintain conditions conducive to bacterial and plant growth. This implies that there will be a salt load leaving the site just as would occur under normal crop irrigation. An estimate of the salt load leaving the site was made based on the data from August to November. Assumptions are that site operation is continuous at a rate of 30 m^3/hr and all Na and Cl and half of the Mg and SO_4 in the effluent is leached from the site. An average effluent TDS of 1100 mg/l (EC x 6.6) in which leachable salts make up approximately 50% of the salt load is estimated to produce a salt load of 400 kg/day (or 1.1 kg/ha/day).

Minor and trace elements in the soil solution and seepage leaving the site do not occur at concentrations toxic to plants or livestock. The pH (7 – 9) of the soil solutions and the postulated precipitation of calcite ensure a sink for most metals. De-commissioning of the site may, however, result in calcite dissolution and desorption of metals and other potentially hazardous elements. Whether these constituents would persist in solution or occur at elevated concentrations to pose a hazard will require further investigation.

There has undoubtedly been a significant environmental impact on the irrigated soils and hydrology downstream of the Robertson site from irrigation of grape-processing effluents. Although the site has favourable soil and climatic conditions for land treatment, the hydrogeological conditions pose operational problems for this site. The current *modus operandi* does not appear to have had a deleterious impact on soils in as much as they support a bacterial community with the capacity to effectively biodegrade the organic matter in the effluent and sustain a thriving (albeit an alien) plant community. Sterilisation of land downstream of the irrigation site and the salt load to the Breede River will, however, put constraints on the operation of the site.

6.2 Recommendations

Management of the site is faced with the dilemma of downstream water pollution and salinisation of soils where groundwater levels come close to surface versus a build-up in soil salinity on the site. Recycling water from the sump and boreholes will ultimately lead to an increased salinity levels in the soil that may compromise the sustainability of the scheme in its entirety.

The cut-off drain on the site's north-west perimeter appears effective in intercepting seepage leaving the site via the colluvium. This was inferred from the relatively dry sediment in boreholes 1 and 2 immediately down stream of the sump. Significant amounts of inflow were noted during the installation of boreholes 4 and 5, which are further from the site than boreholes 1 and 2. Groundwater from boreholes 4 and 5 exhibit a geochemical signature characteristic of effluent and indicate that effluent by-passes the cut-off drain. It is postulated that effluent ponding on shale-derived soil infiltrates the underlying jointed and fractured shale as per the schematic below.

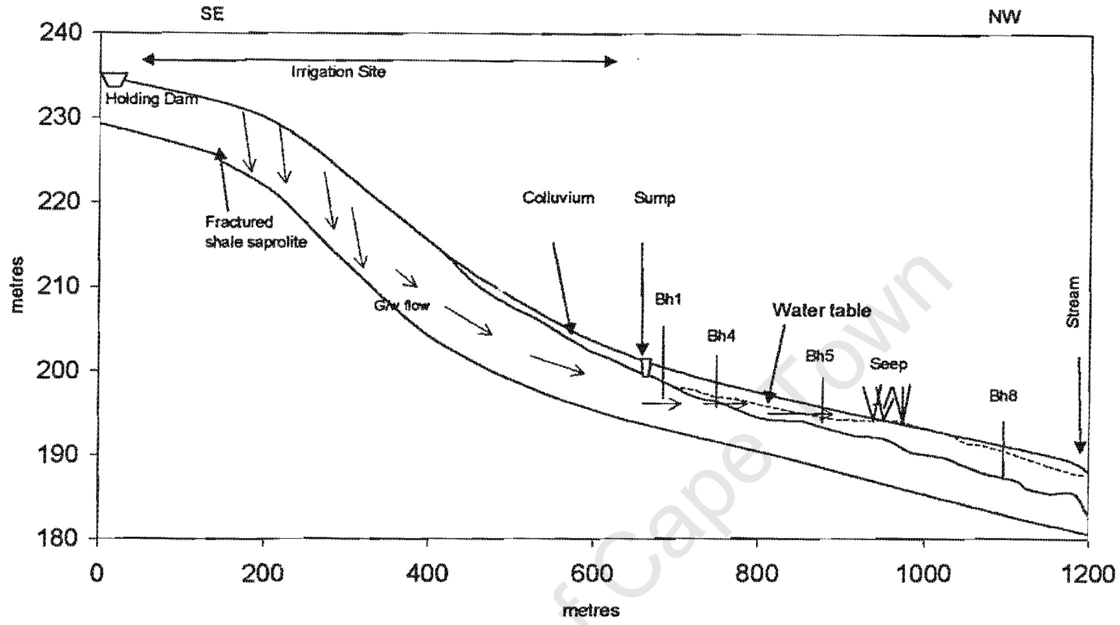

Figure 6.1: Conceptual hydrogeological model of the site

Although the organic content of the grape processing effluent is reduced to background levels within the alluvium downstream of the site, the additional flow in the shallow aquifer is believed to result in surfacing of groundwater. In an attempt to manage this situation it is recommended that ponding of effluent on the site is limited particularly on the shale-derived soils. This will require regular monitoring of the site's moisture status and the option of temporarily stopping irrigation from some of the cannons. A constant water level in the sump should be maintained as far as possible to allow groundwater to leave the site at a flow that maintains the groundwater level near the base of the alluvium. This may reduce the amount of evaporative concentration of groundwater and the extent of salt precipitation on adjacent land.

The occurrence of highly saline dry soils on the periphery of the reach of the irrigation cannons suggests that there is unequal distribution of effluent over the 35 ha site. For example, reduced pressure in the reticulation system may have reduced the reach of the irrigation cannons. This would mean that the full extent of the site is unutilized which may have implications for overall treatment efficiency. The actual area receiving effluent should be assessed against the design specifications to ensure that all areas receive equal amount of effluent.

Permitting livestock to graze on the site may enhance nutrient cycling as well as promote re-growth and vigour of vegetation. However, the nutrient content of the vegetation as well as that of potentially harmful elements like F and Cu should be assessed.

The beneficial utilisation of this effluent as an irrigation supplement should be tested on a variety of crop types. Success has been demonstrated in Australia in the irrigation of woodlots as well as blended into water for vineyard irrigation (Chapman, 1998). This may detract from the purely disposal nature of this irrigation site and possibly result in imposition of less stringent discharge standards.

Ongoing monitoring and the compilation of an historical record are essential to evaluate treatment efficiency, sustainability and potential environmental impacts. Monthly determination of pH, EC, COD, Na, Ca and Mg for the effluent and sump samples is recommended. Comprehensive water analyses, as provided in Appendix A, are recommended quarterly for the effluent, sump and some boreholes. The volume of irrigated effluent should also be measured to assist in the determination of a salt balance.

6.3 Future Lines of Scientific Enquiry

Although there appears to be effective attenuation of potentially toxic trace elements on the site, their build up in the soil and potential bioavailability may place a limit on future use of the site. It would therefore be instructive to determine the levels of accumulation of elements like B, F, Cu and Zn in the soil and a number of different plant species on the site. The latter would also be of use in assessing vegetation suitability for livestock. Leaching tests of site soils with simulated rainwater should also be carried out to establish the extent to which B, F, Cu and Zn may become mobile after termination of effluent irrigation.

The irrigation scheme has been in operation for 25 years and it is anticipated that the plume down stream of the site has already reached the Breede River. Confirmation of this assumption could be achieved by installation of monitoring boreholes in the drainage channel leading northwards to the Breede River. The rate of plume migration could also be calculated and a better estimate of the salt load to the Breede River achieved.

The odours produced by anaerobic biodegradation may be reduced by the addition of nitrogenous fertilizer to the effluent. This would provide the bacterial biomass with an oxidant that produces innocuous gaseous waste products (N_2 and NO) unlike the odorous sulphides and mercaptans produced by SO_4 reduction. Nitrogenous supplements may also increase the rate of accumulation of humified organic matter as well as the rate at which the COD is reduced.

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8 APPENDICES

APPENDIX A	Water Sample Analyses
APPENDIX B	Charge Balance for Water Sample Analyses
APPENDIX C	Analyses of Major Elements in Soil Solutions and Water Samples from 25th August
APPENDIX D	Minor and Trace Element Analyses in Soil Solutions and Water Samples from 25th August
APPENDIX E	X-ray Diffractograms of Soil Clay Fraction
APPENDIX F	Bulk Elemental Concentration for Selected Soil Samples

Appendix A: Analyses of Effluent and Ponded Effluent Samples

Sample I.D.	**Effluent**	**Effluent**	**Effluent**	**Effluent**	**Ponded(S1)**	**Ponded(S4)**	**Ponded(S6)**	**Ponded(S3)**
Date sampled	***10/11/99***	***07/09/99***	***26/08/99***	***25/08/99*****	***25/08/99*****	***25/08/99*****	***25/08/99*****	***25/08/99*****
pH(lab)	5.4	4.5	5.3	5.23	8.52	8.89	8.66	9.04
EC (mS/m)	200	160	179	136	294	357	342	299
Alkalinity(as $CaCO_3$)	536	21	293	291	529	742	1146	761
COD (mg/l)	3015	3325	2559	1980*	200	164	272	245
TOC (mg/l)*	1131	1247	960	743	75	62	102	92
Kjeldahl N (mg/l)	28	16	24	N/a	N/a	N/a	N/a	N/a
DOC (mg/l)	890	N/a	N/a	N/a	N/a	N/a	N/a	N/a
C:N	40:1	80:1	40:1	N/a	N/a	N/a	N/a	N/a
Suspended Solids (mg/l	N/a	77	249	N/a	N/a	N/a	N/a	N/a
SAR	17.3	10.1	8.3	8.7	11.5	14.1	12.3	12.7
Major Cations (mg/l)								
K^+	54	51	92	79	185	272	331	227
NH_4^+	3	2	6	5	Bd	Bd	Bd	Bd
Na^+	479	348	284	241	627	720	694	667
Ca^{2+}	25	35	35	38	97	41	87	64
Mg^{2+}	20	32	33	34	77	95	94	88
Major Anions (mg/l)								
F^-	N/a	N/a	N/a	50	Bd	Bd	Bd	Bd
Cl^-	127	119	128	180	265	223	182	200
SO_4^{2-}	46	89	150	69	306	238	157	55
$NO_3^-(+NO_2^-)$	0.3	0.18	0.1	56	Bd	Bd	Bd	Bd
PO_4^{3-}	2.3	1.9	2.8	8.8	Bd	Bd	Bd	Bd

*TOC = 0.375 x COD. **COD determined on filtered sample. Bd = below detection. N/a = not analysed

Appendix A: Analyses of Sump and Background Water Samples

Sample I.D.	**Sump**	**Sump**	**Sump**	**Sump**	**Sump**	**Background**
Date sampled	***10/11/99***	***07/10/99***	***07/09/99***	***26/08/99***	***25/08/99*****	***02/09/99***
pH(lab)	9.0	7	7.7	8	7.2	8.1
EC (mS/m)	2300	2260	1020	740	581	50
Alkalinity(as $CaCO_3$)	880	868	1088	1136	730	128
COD (mg/l)	154	165	177	209	178	87
TOC (mg/l)*	58	62	66	78	67	33
Kjeldahl N (mg/l)	2.8	2.4	6.8	5.1	N/a	5.2
C:N	21:1	26:1	10:1	15:1	N/a	6:1
DOC (mg/l)	12	N/a	N/a	N/a	N/a	N/a
Suspended Solids,mg/l	N/a	N/a	88	43	N/a	N/a
Total Fe (mg/l)	N/a	1.9	17.4	8.5	N/a	62
SAR	25	24.3	17.5	15.3	13.3	2.9
Major Cations (mg/l)						
K^+	130	108	169	177	162	10
NH_4^+	1.3	0.91	2.5	1.9	Bd	2
Na^+	3862	3833	1869	1133	1119	74
Ca^{2+}	314	289	160	75	133	22
Mg^{2+}	910	965	430	207	243	16
Major Anions (mg/l)						107
Cl^-	7706	7589	3187	1500	1521	107
SO_4^{2-}	1446	1550	859	557	508	15
$NO_3^-(+NO_2^-)$	Bd	Bd	Bd	Bd	Bd	0.2
PO_4^{3-}	Bd	Bd	Bd	0.17	Bd	0.8

*TOC = COD X 0.375. **COD determined on filtered sample. N/a = not analysed. Bd = Below detection

Appendix A: Analyses of Groundwater Samples

Sample I.D.	**Bh2**	**Bh4**	**Bh4**	**Bh5**	**Bh5**	**Bh7**	**Bh8**	**Bh8**
Date sampled	***10/11/99***	***10/11/99***	***07/10/99***	***10/11/99***	***07/10/99***	***10/11/99***	***10/11/99***	***07/10/99***
pH(lab)	7.7	8.4	8.4	7.9	8.3	8.2	8.0	8.1
EC (mS/m)	600	450	375	1400	1220	3120	1300	1230
Alkalinity(as mg/l $CaCO_3$)	1389	2074	1215	1356	1231	251	586	584
COD (mg/l)	240	1292	482	256	416	262	108	63
TOC (mg/l)*	90	485	181	96	156	98	41	24
Kjeldahl N (mg/l)	5.5	56	15.5	5.9	10.4	5.2	1.4	1.4
C:N	16:1	9:1	12:1	16:1	15:1	19:1	29:1	17:1
DOC (mg/l)	51	105	67	46	88	10	5	4
SAR	13.3	8.5	10.2	14.2	17.9	39.3	14.3	14.2
Major Cations (mg/l)								
K^+	122	166	139	105	270	42	34	40
NH_4^+	0.43	6.2	2.2	2.1	0.35	0.11	Bd	Bd
Na^+	897	670	607	1977	2000	6148	1828	1793
Ca^{2+}	271	211	97	557	323	333	439	401
Mg^{2+}	106	160	103	557	381	925	490	491
Fe^{2+}	N/a	N/a	1.7	N/a	0.94	N/a	N/a	0.05
Mn^{2+}	N/a	N/a	2.3	N/a	2.5	N/a	N/a	0.17
Major Anions (mg/l)								
Cl^-	1262	420	458	4293	3600	19968	4049	3875
SO_4^{2-}	165	99	316	762	881	1964	746	759
$NO_3^-(+NO_2^-)$	Bd	Bd	Bd	Bd	Bd	12	Bd	Bd
PO_4^{3-}	Bd	Bd	0.1	Bd	0.46	0.18	Bd	Bd

*TOC = COD x 0.375. Bd = below detection. N/a = not analysed.

Appendix A: Analyses of Seepage and Trench water Samples

Sample I.D.	**Seep1**	**Seep1**	**Seep1**	**Seep2**	**Seep3**	**Trench**	**Trench**	**Trench**	**Dam**
Date sampled	***10/11/99***	***02/09/99***	***25/08/99*****	***02/09/99***	***02/09/99***	***10/11/99***	***02/09/99***	***25/08/99*****	***02/09/99***
pH(lab)	8.6	8.4	8.3	8.7	8.4	8.3	8.1	7.5	8.4
EC (mS/m)	4900	1950	2390	3400	4318	2420	2840	2240	2200
Alkalinity(as $CaCO_3$)	336	894	390	453	500	739	607	647	530
COD (mg/l)	369	175	209*	286	476	154	218	164*	159
TOC (mg/l)*	138	66	78	107	179	58	82	62	60
Kjeldahl N (mg/l)	4.9	3.2	N/a	3.1	3.4	1.3	1.7	N/a	1.4
C:N	28:1	21:1	N/a	35:1	53:1	44:1	48:1	N/a	43:1
DOC (mg/l)	37	N/a	N/a	N/a	N/a	15	N/a	N/a	N/a
SAR	38.8	22.2	23.5	31.5	50.3	24.8	25.2	25.1	24.5
Major Cations (mg/l)									
K^+	235	85	145	74	70	80	80	128	57
NH_4^+	0.11	0.21	Bd	0.1	0.1	Bd	Bd	Bd	0.1
Na^+	9383	3420	4725	7477	10900	4099	4480	4580	4119
Ca^{2+}	774	384	743	314	462	617	668	605	667
Mg^{2+}	2225	855	1413	1300	1330	878	1050	1163	896
Fe^{2+}	N/a	1.8	Bd	0.73	0.44	N/a	8.9	Bd	9.7
Mn^{2+}	N/a	N/a	Bd	N/a	N/a	N/a	N/a	bd	N/a
Major Anions (mg/l)									
F^-	N/a	N/a	N/a	N/a	N/a	N/a	N/a	52	N/a
Cl^-	20325	7152	10287	14000	17033	8400	9230	9675	8400
SO_4^{2-}	3080	1430	2020	2500	4432	1641	1974	1960	1630
$NO_3^-(+NO_2^-)$	Bd	0.5	Bd	Bd	Bd	Bd	Bd	Bd	Bd
PO_4^{3-}	0.16	0.31	Bd	0.1	0.15	Bd	0.1	Bd	Bd

*TOC = BOD x 0.375. * *COD determined on filtered sample. Bd = below detection. N/a = not analysed

Appendix B: Charge Balance for Water Sample Analyses

Sample Type			**Effluent**	**Effluent**	**Effluent**	**Effluent**	**Effluent**	**Ponded(S1)**	**Ponded(S3)**	**Ponded(S4)**	**Ponded(S6)**
Sample Date			10th Nov	7th Sept	26th Aug	25th Aug	25th Aug	25th Aug	25th Aug	25th Aug	25th Aug
	Mass	Charge	mmolc/L	mmolc/L	mmolc/L	mmolc/L	mmolc/L	mmolc/L	mmolc/L	mmolc/L	mmolc/L
Na^+	23	1	20.8	15.1	12.4	10.5	10.7	27	29	31	30
$NH4^+$	18	1	0.2	0.1	0.3	0.3	0.3	b.d.	b.d.	b.d.	b.d.
K^+	39	1	1.4	1.3	2.4	2.0	1.9	4.7	5.8	7.0	8.5
Mg^{2+}	24	2	1.6	2.6	2.7	2.8	3.0	6	7	8	8
Ca^{2+}	40	2	1.2	1.7	1.7	1.9	3.1	5	3	2	4
Total cations			**25.3**	**20.9**	**19.5**	**17.5**	**19.0**	**43.2**	**45.2**	**48.1**	**50.7**
F^-	19	1	n.d.	n.d.	n.d.	2.6	2.7	b.d.	b.d.	b.d.	0.5
Cl^-	35	1	3.6	3.4	3.6	3.4	3.4	7	6	6	5
NO_2^-	46	1	0.0	0.0	0.0	1.2	1.1	b.d.	b.d.	b.d.	b.d.
Br^-	80	1	n.d.	n.d.	n.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
PO_4^{3-}	95	3	0.1	0.1	0.1	0.3	b.d.	b.d.	b.d.	b.d.	b.d.
SO_4^{2-}	96	2	1.0	1.9	3.1	1.8	1.8	6	1	5	3
HCO_3^-	61	1	10.7	0.4	5.9	5.8	5.8	11	15	15	23
Total anions			**15.3**	**5.7**	**12.7**	**15.1**	**14.8**	**24.4**	**22.0**	**26.1**	**31.8**
cations - anions			9.9	15.2	6.8	2.4	3.5	18.8	23.2	22.1	18.9
Total ions			40.6	26.6	32.2	32.6	33.8	67.6	67.2	74.2	82.5
Cation excess (%)			**24.5**	**57.2**	**21.2**	**7.3**	**10.3**	**27.7**	**34.5**	**29.7**	**22.9**
pH			5.4	4.5	5.3	5.2	5.2	8.5	9.0	8.9	8.7
COD (mg/l)			3015.0	3325.0	2559.0	1980.0	1980.0	200.0	245.0	164.0	272.0
EC (mS/m)			200.0	160.0	179.0	136.0	136.0	294.0	299.0	357.0	342.0
SAR ($mmolc/l^{0.5}$)			17.3	10.2	8.3	6.8	8.7	11.5	12.7	14.1	12.3

Appendix B: Charge Balance for Water Sample Analyses

	Seep1 10th Nov mmolc/L	**Seep1** 2nd Sept mmolc/L	**Seep2** 2nd Sept mmolc/L	**Seep3** 2nd Sept mmolc/L	**Seep1** 25th Aug mmolc/L	**Trench** 10th Nov mmolc/L	**Trench** 2nd Sept mmolc/L	**Trench** 25th Aug mmolc/L	**Trench- dupl** 25th Aug mmolc/L	**Dam** 2nd Sept mmolc/L	**Background** 2nd Sept mmolc/L
Na$^+$	408	149	325	474	206	178	195	199	196	179	3.2
NH4$^+$	0.0	0.0	0.0	0.0	b.d.	b.d.	b.d.	b.d.	b.d.	0.0	0.1
K$^+$	6.0	2.2	1.9	1.8	3.7	2.0	2.0	3.3	2.4	1.5	0.3
Mg^{2+}	183	70	107	109	116	72	86	96	94	74	1.3
Ca^{2+}	39	19	16	23	30	31	33	30	37	33	1.1
Total cations	**635.8**	**240.4**	**449.7**	**608.4**	**355.6**	**283.4**	**316.6**	**328.3**	**330.1**	**287.6**	**6.0**
F$^-$	n.d.	n.d.	n.d.	n.d.	b.d.	n.d.	n.d.	b.d.	2.7	n.d.	n.d.
Cl$^-$	573	202	395	480	290	237	260	273	272	237	3.0
NO$_2^-$	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Br$^-$	n.d.	n.d.	n.d.	n.d.	0.8	n.d.	n.d.	0.7	0.8	n.d.	n.d.
PO$_4^{3-}$	0.0	0.0	0.0	0.0	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.0
SO$_4^{2-}$	64	30	52	92	42	34	41	41	39	34	0.3
HCO$_3^-$	7	18	9	10	8	15	12	13	13	11	2.6
Total anions	**644.1**	**249.4**	**456.0**	**582.8**	**340.8**	**285.9**	**313.6**	**327.4**	**327.3**	**281.5**	**5.9**
cations - anions	-8.3	-9.0	-6.3	25.6	-14.6	-2.5	3.0	-28.5	-30.9	6.1	0.1
Total ions	1279.9	489.9	905.8	1191.1	696.4	569.3	630.2	655.7	657.4	569.1	11.9
Cation excess (%)	**-0.6**	**-1.8**	**-0.7**	**2.2**	**-2.1**	**-0.4**	**0.5**	**-4.4**	**-4.7**	**1.1**	**0.8**
pH	8.6	8.4	8.7	8.4	8.3	8.3	8.1	7.5	5.2	8.4	8.1
COD (mg/l)	369.0	175.0	286.0	476.0	209.0	154.0	218.0	164.0	164.0	159.0	128.0
EC (mS/m)	4900.0	1950.0	3400.0	4318.0	2390.0	2420.0	2840.0	2240.0		2200.0	150.0
SAR (mmolc/l^0	38.8	22.2	41.5	58.3	24.0	24.8	25.2	25.1	24.2	24.5	2.9

Appendix B: Charge Balance for Water Sample Analyses

	Sump 10th Nov mmolc/L	**Sump** 7th Oct mmolc/L	**Sump** 7th Sept mmolc/L	**Sump** 26th Aug mmolc/L	**Sump** 25th Aug mmolc/L	**BH2** 10th Nov mmolc/L	**BH4** 10th Nov mmolc/L	**BH4** 7th Oct mmolc/L	**BH5** 10th Nov mmolc/L	**BH5** 7th Oct mmolc/L	**BH7** 10th Nov mmolc/L	**BH8** 10th Nov mmolc/L	**BH8** 7th Oct mmolc/L
Na^+	168	167	81	49	49	39	29	26	86	87	267	80	78
$NH4^+$	0.1	0.1	0.1	0.1	b.d.	0.0	0.3	0.1	0.1	0.0	0.0	b.d.	b.d.
K^+	3.3	2.8	4.3	4.5	4.1	3.1	4.2	3.6	2.7	6.9	1.1	0.9	1.0
Mg^{2+}	75	79	35	17	20	9	13	8	46	31	76	40	40
Ca^{2+}	16	14	8	4	7	14	11	5	11	16	17	22	20
Total cations	**261.9**	**263.3**	**129.1**	**74.7**	**79.4**	**64.4**	**57.4**	**43.4**	**145.9**	**141.4**	**361.2**	**142.6**	**139.4**
F^-	n.d.	n.d.	n.d.	n.d.	b.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cl^-	217	214	90	42	43	36	12	13	121	102	324	114	109
NO_2^-	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Br^-	n.d.	n.d.	n.d.	n.d.	b.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PO_4^{3-}	b.d.	b.d.	b.d.	0.0	b.d.	b.d.	b.d.	0.0	b.d.	0.0	b.d.	b.d.	b.d.
SO_4^{2-}	30	32	18	12	11	3	2	7	16	18	41	16	16
HCO_3^-	18	17	22	23	15	28	41	24	27	25	5	12	12
Total anions	**265.1**	**263.7**	**129.5**	**76.6**	**68.1**	**66.8**	**55.4**	**43.8**	**164.1**	**144.5**	**369.5**	**141.5**	**136.8**
cations - anions	-3.2	-0.4	-0.4	-1.9	4.7	-2.4	2.1	-0.4	-18.1	-3.1	-8.3	1.1	2.6
Total ions	527.0	527.1	258.7	151.3	147.5	131.2	112.8	87.2	310.0	285.9	730.7	284.1	276.2
Cation excess (%)	**-0.6**	**-0.1**	**-0.2**	**-1.3**	**3.2**	**-1.8**	**1.8**	**-0.5**	**-5.8**	**-1.1**	**-1.1**	**0.4**	**1.0**
pH	9.0	7.0	7.7	8.0	7.2	7.7	8.4	8.4	7.9	8.3	8.2	8.0	8.1
COD (mg/l)	154.0	165.0	177.0	209.0	178.0	240.0	1292.0	482.0	256.0	416.0	262.0	108.0	63.0
EC (mS/m)	2300.0	2260.0	1020.0	740.0	581.0	600.0	450.0	375.0	1400.0	1220.0	3120.0	1300.0	1230.0
SAR (mmolc/l$^{0.5}$	25.0	24.3	17.5	15.3	13.3	11.7	8.5	10.2	16.1	17.9	39.3	14.3	14.2

Appendix C: Analyses (IC) of major elements in soil solutions and water samples from the 25/08/99

	pH	**EC** mS/m	**K^+** mg/l	**Na^+** mg/l	**Ca^{2+}** mg/l	**Mg^{2+}** mg/l	**NH_4^+** mg/l	**F^-** mg/l	**SO_4^{2-}** mg/l	**Cl^-** mg/l	**NO_2^-** Mg/l	**NO_3^-** mg/l	**Br^-** mg/l	**PO_4^{3-}** mg/l	**SAR**
Soil Solutions															
Sh1moist	8.3	433	348	1006	333	214	Bd	6	117	78	Bd	Bd	Bd	Bd	10.6
Sh1wet	8.0	389	297	683	366	200	Bd	Bd	404	240	Bd	Bd	Bd	Bd	7.1
Sh1dry	8.9	503	876	1068	275	125	Bd	Bd	750	371	55	210	Bd	Bd	13.4
Sh2wet	8.7	393	429	954	379	57	Bd	Bd	404	240	Bd	Bd	Bd	Bd	12.1
Sh2dry	9.4	2790	5397	8294	270	120	Bd	24	5951	2642	555	731	Bd	Bd	106
Sh3/moist	8.4	366	186	265	163	103	4	7	525	299	Bd	28	Bd	Bd	4
Sh3/dry	7.7	2040	424	3546	828	1726	Bd	Bd	3683	3728	Bd	107	Bd	Bd	16
Col1/top	9.0	321	840	1474	74	28	Bd	10	277	325	Bd	Bd	Bd	39	37
Col1/sub	8.3	374	407	612	163	124	Bd	Bd	1151	539	Bd	Bd	Bd	Bd	8.8
Col1/dry	8.6	635	308	655	287	216	Bd	64	561	2455	Bd	43	Bd	Bd	7
Col2/top	8.8	248	203	563	56	65	Bd	6	260	317	Bd	Bd	Bd	49	12
Col2/sub	8.7	336	464	827	338	43	Bd	6	536	194	Bd	Bd	Bd	Bd	11.3
RSI/top	8.2	176	99	223	181	86	Bd	Bd	201	259	Bd	Bd	Bd	Bd	3.4
RSI/sub	8.5	257	166	692	62	19	Bd	3	109	523	Bd	Bd	5	Bd	20
SSI	8.1	980	354	2286	703	551	Bd	12	1159	2112	Bd	Bd	Bd	Bd	15.7
CP1-3	7.7	89	37	35	241	50	1	1	61	42	Bd	Bd	Bd	Bd	0.5
Water Samples															
effluent	5.2	136	79	241	43	32	5	49	89	119	56	Bd	Bd	9	8.7
ponded	8.5	294	185	627	97	77	Bd	Bd	306	265	Bd	Bd	Bd	Bd	11.5
ponded	9.0	299	227	667	64	88	Bd	Bd	55	200	Bd	Bd	Bd	Bd	12.7
ponded	8.9	357	272	720	41	95	Bd	Bd	238	223	Bd	Bd	Bd	Bd	14.1
ponded	8.7	342	331	694	87	94	Bd	9	157	182	Bd	Bd	Bd	Bd	12.3
sump	7.8	581	162	1119	133	243	Bd	Bd	508	1521	Bd	Bd	Bd	Bd	13.3
seep	8.3	2390	145	4725	743	1413	Bd	Bd	2020	10287	Bd	Bd	60	Bd	23.5
trench	7.5	2240	128	4580	605	1163	Bd	52	1960	9675	Bd	Bd	58	Bd	25.1

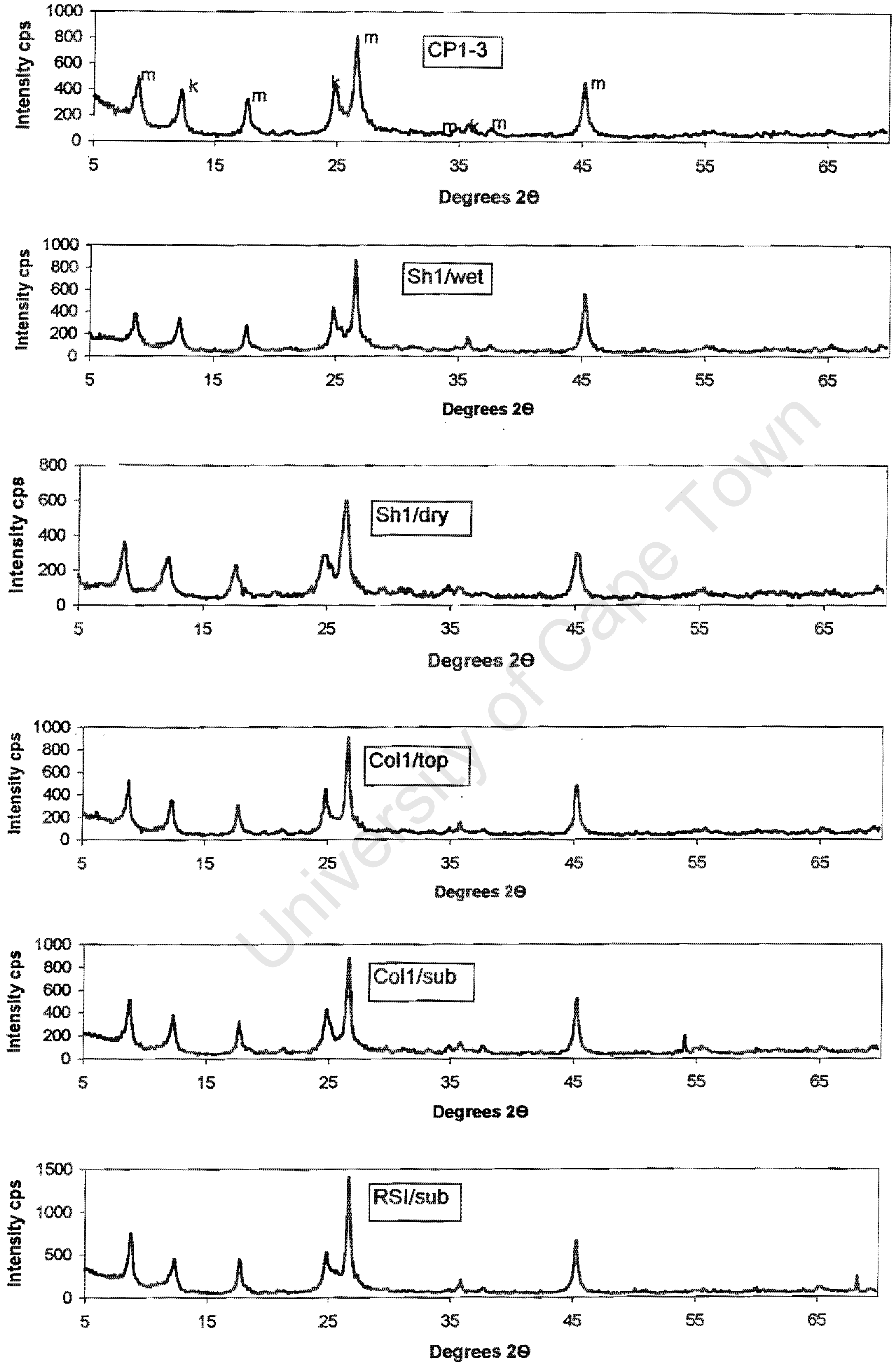
Bd: Below detection

Appendix D: Minor and Trace Element Analyses (by ICP-MS) for Soil Solutions and Water Samples from 25th August.

	B ppm	**Al** ppm	**Si** ppm	**Mn** ppm	**Fe** ppm	**Cu** ppm	**Zn** ppm	**Br** ppm
Soil Solutions								
Sh1/moist	0.29	0.2	21.7	1.3	6.0	0.2	Bd	2.6
Sh1/wet	0.48	0.2	14.1	2.3	6.4	0.3	Bd	2.4
Sh1/dry	3.26	Bd	3.5	Bd	0.6	0.2	Bd	8.6
Sh2/wet	0.92	0.1	5.0	0.5	Bd	0.2	Bd	2.2
Sh2/dry	8.17	0.1	1.6	0.8	1.1	0.7	0.2	21.0
Sh3/moist	0.56	Bd	10.7	2.3	10.9	0.3	0.1	2.4
Sh3/dry	0.51	Bd	0.7	5.2	11.1	0.2	0.3	20.5
Col1/top	1.76	Bd	5.7	0.2	1.0	0.2	0.1	2.1
Col1/sub	2.72	0.1	5.7	0.4	0.8	0.3	0.1	3.2
Col2/top	1.62	Bd	4.3	0.5	3.5	0.8	Bd	3.7
Col2/sub	2.25	0.2	4.7	1.4	2.9	0.1	0.2	2.9
Col2/dry	1.14	0.5	3.6	1.8	2.4	0.3	0.1	9.1
RSI/top	0.43	0.4	14.5	1.9	2.6	0.2	0.3	1.5
RSI/sub	2.30	17.9	26.9	0.3	24.8	0.1	0.1	4.9
SSI	1.60	Bd	8.0	2.7	Bd	0.7	0.3	8.8
CP1-3	0.06	Bd	6.8	1.1	0.3	0.4	0.2	0.5
Water Samples								
Effluent	0.7	0.5	6.4	0.1	0.4	0.1	0.3	1.2
Pond	1.4	1.6	4.4	0.1	0.2	0.2	0.6	3.0
Pond	1.6	1.8	5.7	0.1	Bd	0.1	0.3	3.6
Pond	2.0	1.4	1.9	0.1	0.2	0.5	0.3	3.7
Pond	2.0	1.3	3.9	Bd	1.1	0.2	0.3	4.7
Sump	1.5	0.6	5.8	0.8	0.1	0.1	0.8	10.4
Seep	2.5	1.2	0.9	0.7	2.7	0.5	2.4	45.8
Trench	1.3	1.2	5.7	4.7	2.1	0.3	2.0	45.6

Bd Below detection

Appendix E: X-Ray Diffractorgrams of soil clay fraction indicating prevalence of mica (m) and kaolinite (k).



Appendix F: Bulk Elemental Concentration for Selected Soil Samples (% Oxides)

	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	*H2O	**LOI	Total
Sh1/moist	67.31	0.66	10.12	4.96	0.02	0.93	0.31	0.45	1.92	0.30	3.30	9.30	99.63
Sh1/dry	75.15	0.65	8.57	4.11	0.10	1.23	1.82	0.32	1.58	0.12	1.30	4.40	99.40
Sh3/moist	74.92	0.64	9.82	3.39	0.02	0.76	0.24	0.21	1.82	0.20	1.60	5.10	98.76
Sh3/dry	78.35	0.66	8.74	3.56	0.02	0.69	0.10	0.37	1.68	0.09	1.50	3.60	99.39
Col2/top	87.32	0.44	4.54	2.14	0.01	0.33	0.18	0.20	0.93	0.12	1.30	1.80	99.40
Col1/top	90.48	0.30	3.86	1.91	0.01	0.22	0.09	0.00	0.81	0.10	1.40	2.10	101.28
CP1-3	94.41	0.25	2.34	1.09	0.01	0.17	0.13	-0.08	0.46	0.02	0.60	1.10	100.58

*Oven dried (110°C for 24 hrs).

**Loss on Ignition (950°C for 24 hrs).