Effects of solutions with high monovalent cation concentrations and high pH on soil properties

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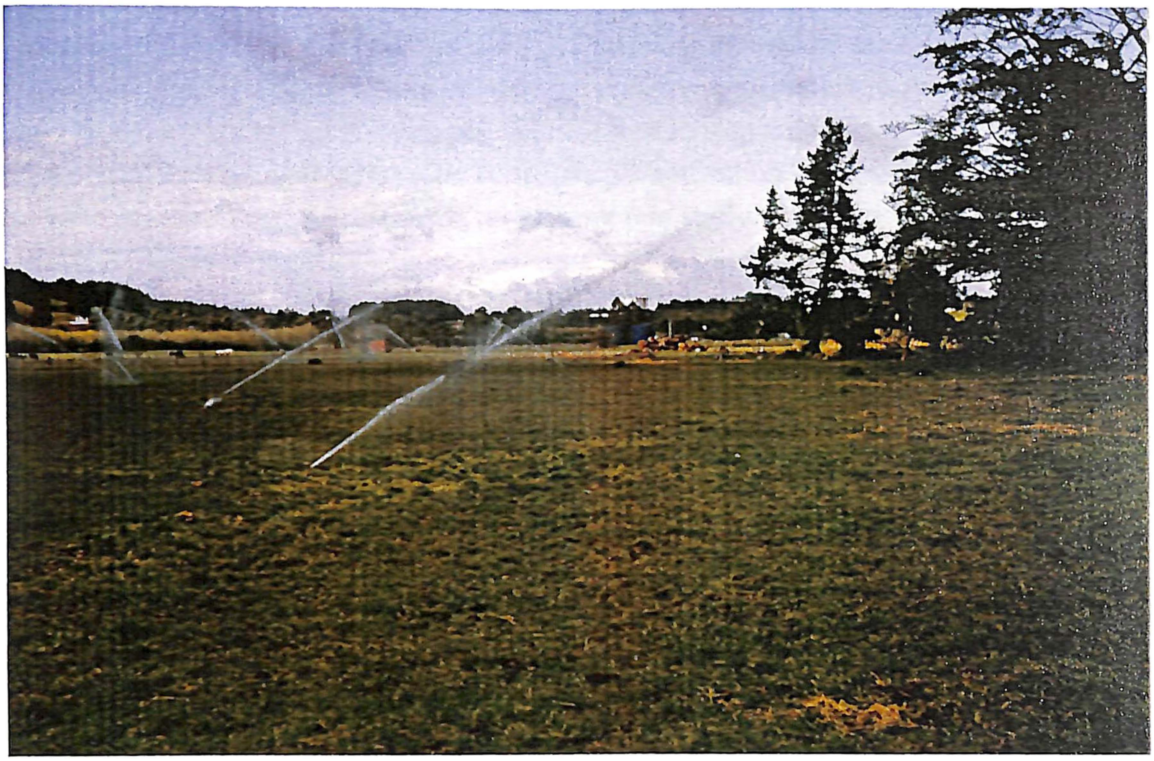

Frontispiece - Land treatment of high pH dairy factory liquid wastes using spray irrigation at Kauri, Whangarei.

Abstract

The effects of solutions with high monovalent cation concentrations and high pH on selected soil physical and chemical properties were investigated using a range of New Zealand soil types.

Some industries produce liquid wastes which are characterized by high pH and high monovalent cation concentrations. However, land treatment of these liquid wastes have been observed to cause adverse effects on soil properties, especially structural deterioration of the 0-10 cm depth of soil. To establish the mechanisms which cause the observed adverse effects, laboratory experiments were conducted to investigate the processes which occur when high pH solutions which contain monovalent cations (NaOH and KOH) are applied to soil. To isolate pH and cation effects, NaCl and KCl solutions were also used as treatments throughout this study. In addition to laboratory experiments, a field trial was conducted to examine the short term (12 months) effects of a surface applied amendment (gypsum, applied at 5 t ha^{-1}) on selected properties of a soil which had been irrigated with high pH dairy factory liquid wastes.

Single-step extraction experiments showed that hydroxide solutions dissolved organic carbon (OC) through the range of concentrations typically found in high pH liquid wastes (i.e. pH 10.5 - 13.5) and OC dissolution increased with increasing hydroxide concentration (i.e. increasing solution pH). Although NaOH dissolved more OC than KOH in the short term (after a single extraction), repeated treatment of soil with fresh hydroxide solution (using multi-step extractions) caused OC dissolution to increase though no cationic differences were measured in the longer term. In contrast to hydroxide solutions, chloride solutions dissolved minimal amounts of OC.

The saturated hydraulic conductivity (K_s) of the soils used in this study decreased over time when hydroxide solutions were used as influent solutions. Aggregate stability was also shown to decrease when soils were treated with hydroxide solutions. A two-stage process was proposed to explain the decrease in K_s when high pH solutions were applied to soil. First, OC is dissolved at the surface of the soil (i.e. 0-1 cm depth of soil) where the high pH solution is in contact with soil aggregates. The time required for dissolution to weaken aggregates being concentration dependent. Second, once a critical amount of OC had been removed, increased repulsion of soil particles (associated with increased negative charge on variable charge components in the soil due to increased pH) was thought to cause dispersion and deflocculation of clays and movement of the dislodged particles into pore spaces resulted in decreased K_s. In contrast to hydroxide solutions, aggregate stability was unaffected when soil was treated with chloride solutions and K_s was maintained or increased when chloride solutions were used as influent solutions. Decreasing the electrolyte concentration of the soil solution (by replacing the influent chloride solutions with distilled water) caused K_s to decrease, consistent with widely accepted diffuse double layer theory.

Cation exchange capacity (CEC) increased with increasing hydroxide concentration whereas chloride solutions had no effect on CEC. The increase in CEC in hydroxide-treated soil was attributed to negative sites being generated on components possessing variable charge characteristics. In general, higher exchangeable sodium percentage (ESP) and exchangeable potassium percentage (EPP) were found in hydroxide-treated soil compared to chloride-treated soil and were attributed to the new negative sites being counter-balanced by the monovalent cation present in the hydroxide solution (either Na^+ or K^+). Equations commonly used to predict ESP and EPP values from the composition of the soil solution (Richards, 1954) accurately prediced ESP and EPP in chloride-treated soil but did not accurately predict ESP or EPP in hydroxide-treated soil. These prediction equations do not take into account the increased total negative charge of the soil system and can therefore not be used to accurately predict ESP and EPP when high pH solutions are applied to soil.

The field trial showed that gypsum application increased infiltration rates in the irrigated soil by decreasing both the ESP and EPP of the soil and increasing the exchangeable Ca^{2+} concentration. Generally, gypsum did not affect any of the other measured properties (pH, OC, CEC, and bulk density) over the duration of the trial. In non-irrigated soil, the lack of effect of gypsum on any of measured soil properties was attributed to the high initial exchangeable Ca^{2+} concentration and low exchangeable Na^+ and K^+ concentrations compared to the irrigated soil.

It was concluded that for successful land treatment of liquid wastes with high monovalent cation concentrations and high pH, pH neutralisation of the liquid is essential to decrease the likelihood of OC dissolution and a build-up of negative charge on soil particles occurring. In addition, divalent cations should either be added to the liquid waste prior to disposal or should be applied to the soil in a relatively soluble form, in order to decrease the magnitude of problems associated with accumulation of monovalent cations on exchange sites. A conceptual model was proposed to describe the reactions that occur in soils when liquid wastes with high monovalent cation concentrations and high pH are applied using land treatment systems.

Dedication

This work is dedicated to my mother,

Maria (Ria) Johanna Lieffering

25-10-38 ~ 7-4-81

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List of symbols and abbreviations

θ_w	volumetric moisture content
ρ_b	bulk density
K_s	saturated hydraulic conductivity
K_{si}	initial saturated hydraulic conductivity
AgTU	silver thiourea
CEC	cation exchange capacity
DDL	diffuse double layer
DTA	differential thermal analysis
EC	electrolyte concentration
EPP	exchangeable potassium percent
erf	error function
ESP	exchangeable sodium percent
KCl	potassium chloride
KOH	potassium hydroxide
MWD	mean weight diameter
NaCl	sodium chloride
NaOH	sodium hydroxide
OC	organic carbon
PAR	potassium adsorption ratio
PSA	particle size analysis
S.E.	standard error of mean
SAR	sodium adsorption ratio
WSA	water stable aggregates
XRD	X-ray diffraction
h	hours
t ha^{-1}	metric tons per hectare
min	minutes
t	time
+G	gypsum treated
-G	non-gypsum treated

Chapter 1
Introduction

Chapter 1
Introduction

1.1 Introduction

This chapter discusses the background information of the study and outlines the layout and structure of the thesis.

1.2 Background

1.2.1 Project initiation

This project was initiated by Chemical Cleaning Ltd. (CCL) of Mount Maunganui who are manufacturers and suppliers of industrial cleaning agents to many industries throughout New Zealand. One of CCL's major clients is the dairy manufacturing industry - an industry which contributes nearly 17% of total national exports (New Zealand Official Yearbook, 1994). The liquid wastes from many dairy manufacturing plants are spray irrigated onto soil as a method of disposal (Barnett and Upchurch, 1992). However, at some sites the irrigation of liquid wastes has resulted in deterioration of soil structure and formation of a surface crust in the top 10 cm of the soil profile. It was initially considered that the deterioration of soil structure was due to high sodium (Na^+) loading rates onto the soil arising from the use of NaOH-based solutions during the cleaning cycle in the manufacturing plant (alkali cleaning solutions are used to remove milk deposits off stainless steel) which eventually enter the liquid waste. Therefore, CCL decided to develop and trial a new hydroxide formulation to examine its cleaning effectiveness on stainless steel and to investigate its effects on soil properties (after irrigation onto the soil). The research presented in this thesis represents a project aimed to understand the effects of hydroxide based solutions on selected soil properties.

Although the problems associated with disposal of hydroxide based liquid wastes occur in the field, the main focus of this thesis was to investigate the effects these solutions have on soils and to identify the processes involved. Therefore, the majority of work done in this thesis was laboratory based to ensure that the study was conducted under controlled conditions so that effects could be identified and isolated.

1.2.2 Cleaning chemicals

The primary use of CCL's chemicals in the dairy manufacturing industry are to clean milk deposits off stainless steel tubing within the manufacturing plant. Milk deposits are primarily made up of protein, minerals, and fat. Protein and fat are alkali soluble whilst mineral deposits are acid-soluble. As a result, a two stage cleaning cycle is usually employed involving an alkali clean followed by an acid rinse. The type of alkali most commonly used in the dairy manufacturing industry is NaOH due to its cleaning efficiency and relatively low cost. The common acids used include nitric, sulphuric, and phosphoric acid. However, the volumes of alkali used are generally much greater than the volumes of acid used and the liquid wastes from many dairy factories are typically alkaline with high Na^+ concentrations (Barnett *et al.*, 1994). The nature of the liquid wastes varies considerably (Marshall, 1975) and is largely dependent on the type of dairy product being produced at any one manufacturing plant (see Chapter 2).

1.2.3 Disposal of liquid wastes from dairy factories

Traditional methods of disposal of high pH liquid wastes from dairy factories have included direct discharge into local waterways and disposal into urban sewage systems. However, since the introduction of the Resource Management Act (1991), the use of direct discharge has declined as it often contravenes Section 70 of the Act which states:

"any discharge of a contaminant or water into water; or a discharge of a contaminant onto or into land under circumstances which may result in that contaminant entering water must not: i) produce conspicuous oil or grease films, scums or foams, or floatable or suspended materials; ii) produce any conspicuous change in colour or visual clarity; iii) produce any emission of objectionable odour; iv) render fresh water unsuitable for consumption by farm animals; or v) produce significant adverse effects on aquatic life"

The most common alternative method of disposal used in the dairy industry is the use of land treatment systems, with spray irrigation being the most common land treatment option presently in use (Barnett and Upchurch, 1992).

1.2.4 Observed problems associated with land treatment of liquid wastes from dairy factories

Spray irrigation of high pH liquid wastes occurs at many dairy factory sites throughout New Zealand (Parkin *et al.*, 1984; Barnett and Parkin, 1985; New Zealand Dairy Research Institute, 1993; New Zealand Dairy Research Institute, 1994). Structural deterioration of the topsoil has been observed (e.g. Fig. 1.1) at several sites in New Zealand including the Kauri site near Whangarei (Northland Dairy Company Ltd.), Hautapu site near Cambridge (Anchor Products Ltd.), and the Tui site near Pahiatua (Tui Dairy Products Ltd.). Where surface crusting occurs (Fig. 1.1), continued application of liquid wastes can result in surface ponding (Fig 1.2) and in some cases overland flow of the wastes into local waterways may occur.

1.2.5 New cleaning formulations

As mentioned previously, NaOH is currently the most commonly used caustic chemical for cleaning purposes in the dairy manufacturing industry. CCL were interested in developing a new caustic formulation consisting of a blend of KOH and NaOH which might alleviate problems associated with land treatment of the liquid wastes observed at many sites throughout New Zealand. A previous study showed that KOH removed milk deposits from stainless steel at a greater rate than NaOH and the nature of the liquid waste using the NaOH/KOH blend allowed for more reuse to occur (Murphy, 1994), thereby potentially reducing the total volume of wastewater produced.

Fig. 1.1 Structural deterioration of the surface horizon of soil which has been spray irrigated with dairy factory liquid waste with high monovalent cation concentrations and high pH at Kauri, Whangarei.

Fig. 1.2 Surface ponding due to surface crust development in a soil which has been spray irrigated with dairy factory liquid waste with high monovalent cation concentrations and high pH at Kauri, Whangarei.

1.3 Objectives of this study

The initial aims of the study were to investigate whether KOH solutions affected soils differently to NaOH solutions. However, a review of the pertinent literature (see Chapter 2) revealed that research on the effects of high pH solutions on soil properties had not received much attention. The aims of the study were therefore to investigate the effects of solutions with high pH and monovalent cation concentrations (i.e. NaOH and KOH) on selected soil physical and chemical properties. In order to differentiate between cation and anion effects within treatments, comparisons were made throughout this study between NaOH, KOH, NaCl, and KCl solutions. Concentration effects were also investigated by selecting concentrations representing a range typically found in high pH liquid wastes.

Therefore, the objectives of this study were to:

1) quantify the amount of organic carbon dissolved by a range of concentrations (those typically found in high pH liquid wastes) of NaOH and KOH solutions using a range of New Zealand soils.

2) investigate the effect of a range of concentrations of NaOH and KOH solutions on aggregate stability and saturated hydraulic conductivity in a range of soil types.

5) examine the effects of NaOH and KOH solutions on cation exchange properties in soils with differing mineralogies.

6) study the short term effects that a surface-applied soil amendment (gypsum) has on selected physical and chemical properties in a soil which has been irrigated with liquid wastes with high monovalent cation concentrations and high pH.

1.4 Layout of thesis

The thesis is structured so that four chapters (Chapters 4, 5, 6, and 7), which contain the main research results presented in this thesis, are manuscripts which have either been published, accepted, are under review, or have been submitted for publication in internationally recognized, peer-reviewed journals.

Chapter 2 reviews the available literature pertinent to this study and identifies the major areas of research where information is lacking in the knowledge of how high pH solutions affect soil physical and chemical properties. Chapter 3 introduces and characterises the soil types used in the study and details the methodologies used. Details of the chapters submitted for publication and presented as manuscripts are as follows:

Chapter 4 - The effect of hydroxide solutions on dissolution of organic carbon in some New Zealand soils. This paper was published in *Australian Journal of Soil Research* 1995, v. 33 (5): 873-881.

Chapter 5 - The effect of strong hydroxide solutions on the stability of aggregates and hydraulic conductivity of soils. This paper has been accepted for publication in *European Journal of Soil Science*. Details of the volume and page numbers have not yet been advised.

Chapter 6 - The effect of high monovalent cation concentration and high pH solutions on cation exchange properties. This paper is currently under review in *Australian Journal of Soil Research.*

Chapter 7 - The short term effects of surface-applied gypsum on selected soil properties of a soil irrigated with high pH dairy factory liquid wastes. This paper will be submitted for publication in *Soil Technology.*

All the manuscripts are authored by R. E. Lieffering and C. D. A. McLay. The manuscripts were initially written by, and all diagrams, tables, and graphs drafted by R. E. Lieffering. Dr. C. D. A. McLay was the chief supervisor for the study. Each chapter has an introductory section which makes reference to appropriate Appendices (presented following Chapter 8) which contain additional data, photographs and supplementary information not contained in the manuscripts. It should also be noted that because the thesis is structured to contain a series of "stand alone" manuscripts, some repetition exists between the manuscripts (such as parts of the introduction and details of the soils used).

Chapter 8 summarises and discusses the results of the study and provides a synthesis of the information of the effects of high pH solutions on soil properties. Following Chapter 8 are four appendices (A, B, C, and D) which include additional information, data, and photographs relevant to each of the four main chapters of this thesis.

It should also be noted that each chapter contains a separate list of references at the end the chapter and there is, therefore, no master reference list included at the end of the thesis.

1.5 References

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Chapter 2
Literature Review

Chapter 2
Literature Review

2.1 Introduction

The purpose of this chapter is to review the available literature pertinent to the study of land treatment of high monovalent cation concentration, high pH liquid wastes with particular emphasis of the effects these solutions have on soil physical and chemical properties. The chapter is divided into five major sections: i) Section 2.2 describes the types of high pH liquid wastes which are disposed of using land treatment systems, their characteristics, and the design of disposal systems; ii) Section 2.3 covers aspects of chemical reactions which take place in the soil environment, with particular emphasis on monovalent-divalent cation reactions and pH effects; iii) Section 2.4 discusses the importance and function of soil organic matter in soils, particularly its importance in the formation and stability of soil aggregates; iv) Section 2.5 reviews the theory of water movement in soils and the effects of exchangeable cations and solution composition on hydraulic conductivity; and v) Section 2.6 presents a brief overview of the available information and indicates areas of research which are lacking with respect to effects of high pH, high monovalent cation content solutions on soil properties.

2.2 Land treatment of liquid wastes in New Zealand

2.2.1 Introduction

The land treatment of liquid wastes is seen as an attractive alternative to traditional methods of disposal with the number of land treatment sites and the area of land being used for land treatment increasing worldwide (Parkin *et al.*, 1984). Of special interest is the disposal of high pH liquid wastes, which are produced by a number of different industries, using the land treatment option because the effects on soil properties and ground water quality are relatively unknown and often unpredictable. The following section discusses the types of high pH liquid wastes commonly disposed of using land treatment systems, their typical characteristics, the design and methods of disposal commonly used, and some reported effects on soil properties and groundwater quality.

2.2.2 Types of high pH liquid wastes

2.2.2.1 Introduction

High pH liquid wastes can originate from many industrial sources and their specific composition is dependent on the source of the wastes. In nearly all cases, however, it is the use of hydroxide solutions either in the processing, or for cleaning purposes, which accounts for the high pH in the liquid wastes. Industries which may produce high pH liquid wastes include dairy factories (Marshall, 1975; Marshall and Harper, 1984; Barnett and Upchurch, 1992; Barnett *et al.*, 1994), meat processing plants (Keeley and Quin, 1979), and tannery plants (Mason, 1981).

2.2.2.2 Dairy factory liquid wastes

High pH liquid wastes from the dairy manufacturing industry are characterised by high pH and high sodium (Na^+) concentrations. However, not all liquid wastes from the dairy manufacturing industry have high pH as the composition depends primarily on the specific production output of each factory (see Table 2.1). In general, factories which produce only milkpowder and butter have high pH liquid waste whereas liquid wastes from cheese/casein factories tend to have slightly acidic liquid wastes (Barnett and Upchurch, 1992). Liquid wastes from both types of factories typically have high Na^+ contents, however, there are higher concentrations of divalent cations (calcium (Ca^{2+}) and magnesium (Mg^{2+})) in the cheese/casein liquid wastes compared to milkpowder/butter factories. Marshall (1975) reports that the pH of liquid wastes from a single factory producing dried buttermilk ranged from pH 2.1-12.3, illustrating the variability possible from a single plant. Dairy factory liquid wastes consist of residues of milk and milk products, detergents, sanitising agents, oil and grease, and are highly variable in composition (Marshall and Harper, 1984), not only from process to process, but also throughout the season and even over a 24 hour period (Marshall, 1975).

Deposits from milk fluids are usually composed of protein, minerals, and fat. Protein and fat are alkali soluble whereas the mineral component is acid soluble (Murphy, 1994). As a result, a two stage cleaning cycle is usually employed involving an alkali clean followed by an acid rinse, the acid also being a passivating agent and corrosion inhibitor of stainless steel (Murphy, 1994). Nitric acid (HNO_3) is the most commonly used acid in the dairy industry, however, phosphoric (H_3PO_4) and sulphuric (H_2SO_4) acid are also used. In most milkpowder/butter manufacturing plants, the volume of alkali used is much larger than the volume of acid used, therefore, the resultant liquid wastes tend to alkaline.

Table 2.1 Typical liquid waste characteristics from dairy factories.

Chemical parameter[a]	Cheese/Casein[1]	Milkpowder/ Butter[1]	Milkpowder/ Butter[2]	Milkpowder/ Butter[3]
pH	4.5-6.0	10-12	2.1-12.3	3-13.2
BOD_5	8000	1500	40-1420	90-12 400
Na	380	560	-	-
K	160	13	-	-
Mg	14	1	-	-
Ca	95	8	-	-
Fat (% w/w)	0.04	0.04	0.02-0.13	0-0.21
Nitrogen	200	70	40-80	1-70
Phosphorous	100	35	12-56	4-150

[a] all units are g m^{-3} except pH and Fat.

Sources: [1] Barnett and Upchurch (1992); [2] Marshall (1975); [3] Marshall and Harper (1984).

2.2.2.3 Other sources of high pH liquid wastes

Other major sources of high pH liquid wastes include meat processing/fellmongery and tannery plants. Table 2.2 lists the typical characteristics of liquid wastes produced from these industries.

In meat processing plants which include a fellmongery (sheep skin processing) process, the pH of the liquid wastes can be as high as 11.4 (Keeley and Quin, 1979). The high pH results from the use of hydroxides (either $Ca(OH)_2$ or NaOH) for de-hairing or de-wooling the pelts (Carter, 1994). The liquid wastes from meat processing plants without fellmongery processing capabilities generally have neutral pH (Tarquin, 1974; Tarquin and Bautista, 1976). Meat processing plants with fellmongery capabilities nearly always combine the liquid waste streams from the two sources. Depending on the type of hydroxide used and the ratio of volumes of the two liquid waste streams, the Na^+ content of meat processing/fellmongery liquid wastes can be very high (see Table 2.2) but can also be highly variable from site to site. Where fellmongery plants operate on their own, the liquid wastes tend have the highest pH values (up to pH 12.0) as no dilution occurs (Mason, 1981).

Table 2.2 Characteristics of other high pH liquid wastes.

Chemical parameter	Fellmongery[1]	Meat processing - Fellmongery[1]	Meat processing - Fellmongery[2]	Hide processing[3]	Pickled pelt production[3]
pH	11.4	10.2	6.5-11.7	9-10	9.5-12.0
Na ($g\ m^{-3}$)	2000	230	310	-	-
K ($g\ m^{-3}$)	50	90	-	-	-
Mg ($g\ m^{-3}$)	10	7	17	-	-
Ca ($g\ m^{-3}$)	300	140	5.8	-	-
TSS[a] ($g\ m^{-3}$)	1800	1900	981	2150	1000-2000
COD[b] ($g\ m^{-3}$)	4000	4100	930-7750	3100-3400	3000

[a] Total suspended solids
[b] Chemical oxygen demand
Sources: [1] Keeley and Quin (1979); [2] Carter (1994); [3] Mason (1981)

Tannery processing encompasses a variety of processes and the liquid wastes from these industries are therefore highly variable (Mason, 1981). In general, liquid wastes from hide processing and pickled pelt production tend to have high pH (see Table 2.2). The high pH arises from the use of $Ca(OH)_2$ for de-hairing and de-wooling processes (Mason, 1981). In some of the processing procedures, Na-based salts are used and the resultant liquid wastes may also have high Na^+ concentrations.

2.2.3 Methods of disposal and design

Traditional methods of disposal of liquid wastes were through direct discharge into local waterways or into local urban sewage systems. In New Zealand, the introduction of the Resource Management Act (RMA) in 1991 has meant that direct contamination of local waterways is prohibited as it is seen to be unsustainable and damaging to the environment. Alternative methods of disposal, such as land treatment, are therefore being used for the disposal of liquid wastes both from industrial and agricultural sources.

In the New Zealand dairy manufacturing industry, the number of processing plants has decreased over the past 25 years through amalgamation of many smaller processing sites (Barnett *et al.*, 1994). However, the quantity of whole milk processed each year has increased over the same period (Marshall and Harper, 1984), resulting in dramatic increases in volumes of liquid waste produced per plant per year. Spray irrigation of dairy factory liquid wastes onto land has also increased markedly over the past 25 years and is now the most common method of disposal (Barnett and Upchurch, 1992). Other methods of disposal include border-dyke (overland flow) irrigation (Keeley and Quin, 1979; Ross *et al.*, 1982) and rapid infiltration (Stevenson, 1984). Liquid wastes from meat processing and tanneries are also commonly spray irrigated onto pastures (Wells and Whitton, 1970; Balks, 1990; Donninson and Ross, 1992; Hart and Speir, 1992).

Land treatment systems, using spray irrigation, are designed so that the hydraulic loading (i.e. irrigation rate) is less than the infiltration capacity of the soil types being sprayed so that water-logging and surface ponding is avoided. However, the composition of the liquid waste must be taken into consideration because some components (e.g. suspended solids, cations, and anions) may decrease the infiltration capacity of the soil over time (Parkin and Marshall, 1976). Three main types of spray irrigation methods which are commonly employed are travelling irrigators, fixed guns, and hand shift systems. Of these, the fixed gun system is the most expensive to set up but has more benefits (less leaks, less wind drift, lower application rates, more versatile, and more controllable) than the other two and is therefore recommended by the New Zealand Dairy Research Institute (NZDRI) (NZDRI, 1993). In the New Zealand dairy manufacturing industry, it is normal practice to spray irrigate liquid wastes at a rate of 6 mm h^{-1}, with a total cumulative daily dose of 25 mm (250 m^3 ha^{-1} day^{-1}). In addition, a minimum resting period of 16-20 days is recommended before spraying is resumed (Barnett and Upchurch, 1992). In some cases where free draining soils are being irrigated, the total cumulative daily application may be up to 75 mm (750 m^3 ha^{-1}) over 3 days (Barnett and Upchurch, 1992).

Prior to spray irrigation, liquid wastes from the dairy manufacturing industry typically go through a series of pretreatment processes to assist in successful land treatment of the wastes. Firstly, wastewater from the manufacturing plant enters a fat/solids trap where milkfat and floatable solids are collected at the surface (NZDRI, 1993). These solids are removed regularly (through skimming procedures) to allow efficient operation of the fat traps, the collected solids often being fed to pigs. At some sites, acid dosing (using sulphuric or hydrochloric acid) is undertaken to lower the pH of the liquid wastes prior to irrigation (NZDRI, 1993), however, problems may arise in attaining the desired pH due to: i) incoming wastewater is often not being well mixed and "slugs" of extreme pH can occur; ii) variations in flow rates which may affect neutralisation efficiency by altering detention time and mixing characteristics; iii) pH sensors which may become coated and lose sensitivity; iv) the buffering capacity of the liquid wastes varying over time; and v) good in-line mixing of neutralising reagent with large volumes of wastewater being difficult to achieve (NZDRI, 1993). To decrease the potentially harmful effects of high monovalent content of the liquid wastes, calcium salts may be introduced into the waste stream prior to irrigation, thereby lowering the sodium adsorption ratio (SAR see Section 2.3.2.4) of the liquid (Barnett and Upchruch, 1992).

Pretreatment of liquid wastes from the meat processing industry includes sedimentation or dissolved air floatation (DAF) (Cooper *et al.*, 1979). In most tanneries, a series of chemical pretreatments, such as pH correction or oxidisation of sulphides, and physical pretreatments, such as settling and screening, are used prior to disposal (Mason, 1981).

2.2.4 On-site impacts from land treatment of high pH liquid wastes

2.2.4.1 Introduction

Changes in soil properties and groundwater quality are the main on-site impacts of land treatment of liquid wastes with high monovalent cation concentrations and high pH. Some problems may arise from odour complaints but in most cases the irrigation site is situated in rural settings or an appropriate buffer zone is set aside between the irrigation site and adjacent lodgings which decreases the likelihood of odour being a problem.

2.2.4.2 Soil properties

Liquid wastes with high monovalent cation concentrations and high pH can cause significant changes to the physical and chemical status of the soil. Barnett and Parkin (1985) reported that in the Waikato region, soil pH levels had increased from 5.8 in the topsoil of non-irrigated Horotiu silt loam and Te Kowhai silt loam soils to pH 7.2 in soils which had been irrigated with high pH dairy factory liquid wastes. Increases in exchangeable sodium concentrations, especially in the Te Kowhai soil which is dominated by halloysite, were measured down to a depth of 60 cm as a result of irrigation (Barnett and Parkin, 1985). Barnett and Upchurch (1992) showed that irrigation of high pH liquid wastes from the dairy manufacturing industry caused no changes in clay mineralogy.

Liquid wastes with high monovalent cation concentrations and high pH which are applied to soil may cause degradation of soil structure to occur if: i) saturation of the soil for extended periods occurs due to the hydraulic loading exceeding the infiltration capacity of the soil; ii) divalent cations are displaced by monovalent cations on soil exchange sites resulting in dispersion of soil aggregates; iii) poor stock management (i.e. placing heavy stock in the irrigation paddocks too soon before or too soon after irrigation, or the use of intensive grazing practices such as "strip grazing") which can cause physical disintegration of aggregates into smaller particles, stock hooves smearing openings to soil pores, and compaction to occur; and iv) use of travelling irrigators, which may compact the topsoil as the wheels ride over irrigated soil, rather than fixed in-ground systems (NZDRI, 1993). In addition, soil pores may get blocked by fat and fine particles if primary treatment (pretreatment) of the liquid waste is inadequate (NZDRI, 1993) and slime forming bacteria may also block soil pores if organic loading is too high (NZDRI, 1993). Other studies on the effects of dairy factory liquid wastes on soil and plant compositions have been conducted in New Zealand (e.g. Wells and Whitton, 1966; Christie, 1970; McAuliffe *et al.*, 1979) but these studies examined the effect of liquid wastes from cheese/casein factories which had slightly acidic pH values.

The effects that land treatment of high pH meat processing/fellmongery and woolscouring liquid wastes have on soil properties have also been investigated by a number of researchers. Keeley and Quin (1979) investigated the effect that high pH meat processing/fellmongery liquid wastes had on soil properties of a Lismore stony silt loam in Canterbury (New Zealand) and found that soil pH had increased from 6.1 in control sites to 6.4 in irrigated sites. Hart and Speir (1992) measured increases in soil pH from 6.0 in control sites to 6.9 in irrigated sites used by the same meat processing plant. In addition, exchangeable Ca^{2+}, Na^{+}, and potassium (K^{+}) concentrations had all increased in irrigated sites with exchangeable sodium percentages (ESP, see Section 2.3.2.4) increasing from 4.4% to 6.3% in the topsoil (0-15 cm), and from 3.8% to 6.0% at the 15-30 cm depth (Keeley and Quin, 1979). Balks (1990) reported increases in exchangeable Na^{+}, pH, ESP, and cation exchange capacity (CEC) since the introduction of a fellmongery effluent stream into liquid wastes from a meat processing plant that had been spray irrigated onto a Lismore soil. Campbell *et al.* (1980) measured significant increases in soil pH in a Waimakariri soil irrigated with slightly alkaline woolscour effluent which had high K^{+} concentrations and showed that while exchangeable K^{+} increased, no increase in total CEC had occurred.

2.2.4.3 Groundwater chemistry

The chemistry of shallow groundwaters may or may not be affected due to the application of high cation concentration liquid wastes on soil. Parkin *et al.* (1984) measured various chemical parameters in the shallow groundwaters surrounding a dairy farm near Te Awamutu in the Waikato region which had been receiving dairy factory liquid wastes through spray irrigation (with application doses of up to 65 mm $dose^{-1}$) and found that there was no measurable contamination of groundwaters. It was concluded that there was sufficient soil (>1.7 m) to prevent serious leaching of nutrients to the groundwater (Parkin *et al.*, 1984). In contrast, Barnett and Parkin (1985) reported that nitrate (NO_3^-), Na^+, and K^+ concentrations in shallow groundwaters around the central area of the farm used by Waikato Dairy Company at Hautapu, near Cambridge, were elevated in areas which were irrigated with dairy factory liquid wastes.

Investigations of shallow groundwater quality have also been conducted under areas receiving high pH meat processing/fellmongery liquid wastes. Keeley and Quin (1979) reported that the nutrient status of a Lismore soil had increased to a point where most of the applied nutrients are lost in drainage and eventually reach the saturated (shallow groundwater) zone.

2.2.5 Remediation and soil amendments

2.2.5.1 Introduction

Unfavourable soil conditions which can develop due to application of liquid wastes with high monovalent cation concentrations and high pH can, in theory, be ameliorated by various chemical and physical means. This section reviews some of the common amelioration methods employed to minimise or reverse the effects of liquid wastes with high cation concentrations and high pH.

2.2.5.2 Chemical amendments

Applications of lime ($CaCO_3$) or gypsum ($CaSO_4.2H_2O$) have been used to increase divalent cation (i.e. Ca^{2+}) concentrations in soil solutions which lowers the sodium adsorption ratio (SAR, see section 2.3.2.4) of the soil water and can prevent aggregate dispersion and deterioration of other soil physical properties. The mechanisms by which Ca^{2+} exchanges for Na^+ are discussed in Section 2.3.2.6 .

Some studies have shown soil amendments to be successful in reversing the effects of liquid wastes with high cation concentrations and high pH, whereas other have not. Carter (1994) examined the effects of applying $Ca(OH)_2$ ("quick lime") and $CaCO_3$ to a Lismore soil in Canterbury which received meat processing/fellmongery liquid wastes with high Na^+ concentrations and high pH, and found that neither amendment resulted in improvements in chemical or physical properties of the soil. The lack of improvement was attributed to dissolution of organic matter by the hydroxide component in the liquid waste which inhibited any effects that Ca^{2+} addition may have had (Carter, 1994). Barnett and Upchurch (1992) applied $CaCO_3$ (0-6 t ha^{-1}) to Horotiu and Te Kowhai soils which had received dairy factory liquid waste with high Na^+ concentrations and high pH, and found that the applied lime had no effects on the bulk density of the Horotiu soil (clay mineralogy dominated by allophane) but decreased the bulk density of the Te Kowhai soil (clay mineralogy dominated by halloysite). Soil pH, and exchangeable Na^+ and Ca^{2+} concentrations had all significantly increased due to the additions of lime in both soil types (Barnett and Upchurch, 1992). Chemical remediation is usually not a rapid process and the positive effects on soil structure may take months to occur, however, other factors such as stock management, irrigation scheduling, and soil type will all affect the speed of recovery.

2.2.5.3 Physical remedial methods

Physical mechanisms of amelioration are often used to improve soil physical properties if rapid amelioration is required. Some recommended physical amelioration procedures have recently been reported (NZDRI, 1993) which relate to the improving the physical condition of soil spray irrigated with dairy factory liquid waste with high monovalent concentrations and high pH.

Surface ripping (the dragging of metal vanes through the surface of the soil) has been recommended for improving soil drainage and increasing soil aeration where surface crusts have developed (NZDRI, 1993). Subsoil ripping can be used to improve physical properties of the lower horizons (up to 70-90 cm depth) thereby increasing drainage rates in subsoil (NZDRI, 1993). Installation of intensive drainage networks may be necessary where naturally poorly drained soils are to be used for high pH liquid waste irrigation purposes. It has also been suggested that the drainage pipes being placed at a depth >90 cm below the surface of the soil so that full "treatment" of the liquid waste is able to take place (NZDRI, 1993). In some situations "mole ploughing" may be necessary to assist drainage, however, this is generally not recommended as an open slit is formed in the ground which may allow untreated liquid wastes to "short circuit" the treatment phase and directly enter drainage pipes or shallow groundwaters without treatment occurring (NZDRI, 1993). Subsoiling may also be necessary in soils where dense layers (pans) are present which decrease the movement of soil solutions into the shallow groundwater or drainage systems. Subsoiling will not only loosen the dense pan material but also increase the aeration of the surface horizons and decrease the bulk densities.

2.3 Effect of liquid waste application on soil chemical properties

2.3.1 Introduction

The application of liquid wastes to soil causes changes to the chemical status of the soil if the composition of the liquid waste differs to that of the soil solution. Changes to soil chemical properties may affect other soil properties and plant growth, and it is therefore important to consider soil chemical reactions to understand the effects that liquid waste application will have on soil properties. The following sections introduce cation exchange theory (with particular emphasis on monovalent-divalent cation reactions), discusses the chemical processes involved in flocculation of soil components, the effects of pH and anions on cation exchange, and the reactions of common chemical amelioration methods.

2.3.2 Principles and theory of cation exchange

2.3.2.1 Sources of charge in soil systems

Soils are a multi-component system where the soil solution is in contact with a wide variety of surfaces which can exhibit either permanent or variable charges of both polarities (either positive or negative). Layer silicate clay minerals commonly possess a permanent negative charge which arises through isomorphous substitution or through vacancies within the crystal lattice of the clay minerals. Commonly, Al^{3+} substitutes for Si^{4+} in tetrahedral positions, and Mg^{2+} for Fe^{3+} and Al^{3+} in octahedral positions (McBride, 1989). This substitution results in the overall charge of the crystal structure to be "net negative" and is termed permanent charge because the charge is not affected by the soil solution pH or electrolyte concentration (EC) (Fig 2.1a). It has previously been suggested that the permanent negative charge sites of most phyllosilicate clay minerals are located on the basal planes of the minerals (van Olphen, 1977).

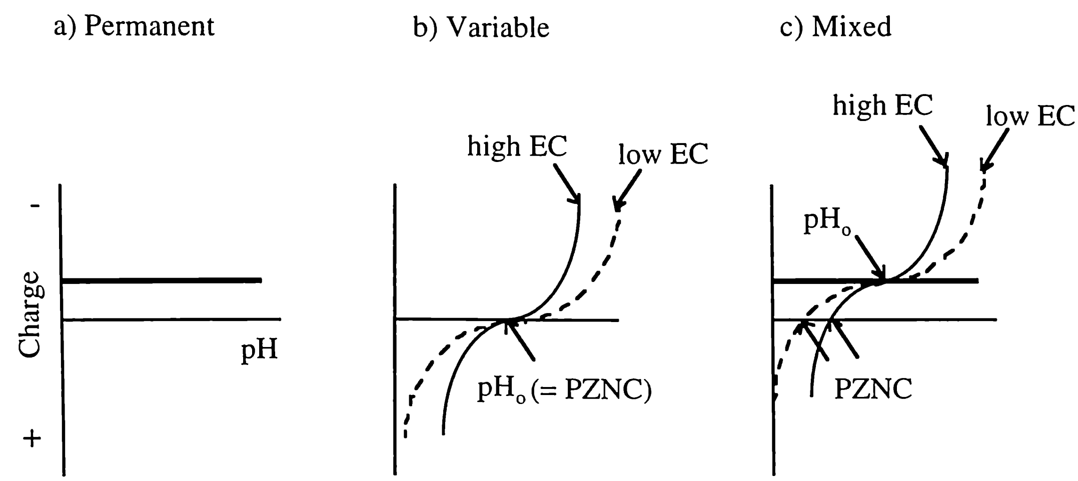

Fig. 2.1 Variation in charge with pH and electrolyte concentration (EC) of the soil solution for permanent (a), variable (b), and mixed (c) charged systems (pH_0 = pH where there are equal number of positive and negative sites on variable charge surfaces and PZNC = point of zero net charge, see text) (after Sumner, 1993).

The surfaces of some soil components (such as organic matter, the edge sites of many phyllosilicate minerals, and surfaces of sesquioxides) can carry both positive and negative charge, depending on the conditions in equilibrium solution. The phenomenon of a surface to have the ability to posses either positive or negative charge is termed "variable charge" (Parfitt, 1980). The number of negative charges on the variable charge surfaces increases as the pH and EC increases above pH_0 (Fig 2.1b), where pH_0 is the pH at which an equal number of positive and negative sites exist on the surface of the particle. Most soils contain components which have both permanent and variable charge characteristics. Hence, the theoretical curves which describe the magnitude to either positive or negative charge in the soil system according to the pH of the soil solution are moved upwards and to the left (Fig 2.1c), and at pH_0 the overall charge is now negative. The point at which all negative charges are equal to positive charges is termed the Point of Zero Net Charge (PZNC Fig 2.1c) which, for most soil systems, is always less than pH_o.

2.3.2.2 Diffuse double layer

All constituents of the clay fraction behave similarly with regards to the diffuse electrical double layer surrounding any charged surface. The diffuse double layer consists of the charge on the surface and the swarm of ions, which are predominantly of opposite charge to the surface, which neutralise the surface charge.

The distribution of the counter ions away from the surface is exponential in nature and the distance from the surface within which the counter ions occur is inversely proportional to the soil solution concentration and to the valence of the counter ion (Sumner, 1993). The equation which describes the effective "thickness" of the diffuse double layer is (Sumner, 1993):

$$\frac{1}{\kappa} = \frac{\varepsilon \mathrm{kT}}{\sqrt{8\pi \mathrm{e}^2 \mathrm{z}^2 \mathrm{n}}} \qquad (2.1)$$

Where:

$\frac{1}{\kappa}$ = effective "thickness" of the double layer

ε = dielectric constant for the medium

k = Boltzman constant

T = absolute temperature

e = electron charge

z = valence of counter ion

n = electrolyte concentration in the bulk solution

Equation 2.1 shows that divalent cations (particularly Ca^{2+} and Mg^{2+} in soil systems) present as counter ions around negatively charged surfaces, result in a thinner or more compressed double layer than when monovalent cations such as Na^+ or K^+ are present. The main reason for this is that divalent cations are attracted and held much more tightly than monovalent cations at charged surfaces. Divalent cations also have a greater charge density than monovalent cations and therefore attract waters of hydration more strongly (Bohn *et al.*, 1979), resulting in smaller hydrated radii than hydrated monovalent cations. Ions of smaller hydrated radius can approach charged surfaces more closely and thus their coulombic attraction by the surfaces is correspondingly increased (Bohn *et al.*, 1979). The EC of the soil solution also has significant effects on the thickness of the double layer. According to Equation 2.1, the greater the EC of the bulk soil solution, the more compressed the double layer for any given system (Shainberg and Lety, 1984).

2.3.2.3 Flocculation and dispersion

The thickness of the diffuse double layer has great importance with respect to the behaviour of clay systems and the stability of soil structure. As the thickness of the diffuse double layer increases so too do the repulsive forces between soil colloidal particles and the easier the system can become dispersed. Sumner (1993) suggests that at distances twofold greater than $\frac{1}{\kappa}$, repulsive forces predominate. Sodium is very weakly held by negatively charged surfaces and therefore has a relatively thick double layer which is very efficient at promoting dispersion of soil colloidal particles. When the repulsive forces are less than the attractive forces (through van der Waals forces), the system will remain flocculated. Therefore, the balance between the attractive and repulsive forces determines whether a system will be dispersed or flocculated (Sumner, 1993). The concentration of the electrolyte solution necessary to maintain a net attractive balance (i.e. the system remains flocculated) is referred to as the Critical Flocculation Concentration (CFC), Critical Coagulation Concentration (CCC) (Sposito, 1989; Goldberg *et al.*, 1991), or Critical Salt Concentration (CSC) (Arora and Coleman, 1979). The CFC is greatly influenced by the valence of the counter ion present - as the valence increases, the CFC decreases.

Flocculation occurs due to the attractive forces which exist between soil colloids. Two of the primary interactions responsible for flocculation of soil colloids are coulombic (electrostatic) and van der Waals forces. Coulombic forces exist between any charged particles and can either be attractive, where the charges are of opposite polarity, or repulsive, where like charges are involved. Most clay minerals in the soil environment can be considered as platelets which possess a net negative charge on their faces due to isomorphous substitution (as discussed in section 2.3.2.1). However, at the edges of clay platelets, the silica tetrahedral sheets and the octahedral alumina sheets are disrupted and primary bonds are broken (van Olphen, 1977). The charges of these edge sites are pH dependent and can thus be positively charged at pH values below pH_0 (see Fig. 2.1). In pure clay systems, particles may associate through three different arrangements of the clay platelets: face-to-face (FF); edge-to-face (EF); or edge-to-edge (EE) (van Olphen, 1977). At low pH values, below pH_0, electrostatic attraction of the positive edge sites and the negatively charged faces will result in a EF coordination (Fig. 2.2) and flocculation may occur (Russell, 1973).

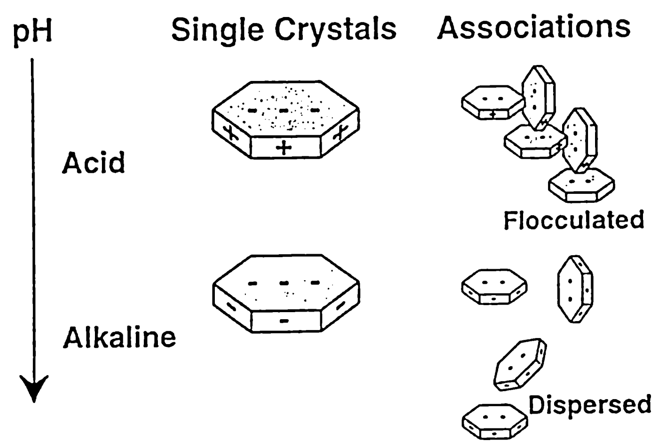

Fig. 2.2 Schematic representation of the effect of pH on kaolinites and their associations. Left: effect of pH on individual crystals (edges become positively charged at low pH, and negatively charged at high pH). Right: consequent effect of pH on associations of kaolinites (from Churchman *et al.*, 1993).

Platelets whose edge sites are negatively charged can, however, remain flocculated as long as the distance between the particles is small enough for van der Waals forces to operate. The van der Waals forces occur due to the deviations of charge over very short time periods on non-polar molecules. Over relatively large time periods ($>10^{-16}$ s), the distribution of electronic charge surrounding a nonpolar molecule is geometrically spherical. However, over time periods $<10^{-16}$ s the charge distribution exhibit significant deviations from spherical symmetry, taking on a flickering dipolar character (Sposito, 1989). These distortions persist long enough to induce distortions in neighbouring molecules and produces an attractive interaction between the two molecules, the force of which diminishes with separation distance, and at small distances van der Waals forces can be strong enough to cause particles to stick together and flocculate (Sposito, 1989).

Many workers have investigated the phenomena of dispersion and flocculation of pure clays (Schofield and Samson, 1954; Arora and Coleman, 1979; Oster *et al.*, 1980; Rengasamy, 1983; Goldberg and Forster, 1990; Tarchitzky *et al.*, 1993), particularly montmorillonite, illite, vermiculite, and kaolinite. Flocculation and dispersion studies have also been conducted using soil clays (Arora and Coleman, 1979; Oster *et al.*, 1980; Rengasamy, 1983; Goldberg and Forster, 1990; Miller *et al.*, 1990). In most cases, the CFC decreased with increasing EC and valence of saturating cation, but pH also had significant effects. At high pH values, the variable charge sites (the edge sites of pure clays) become negatively charged and thus decreases the interactions between oppositely charged surfaces (E-F interactions) and increased CFC values are observed (Richards, 1954; Goldberg and Forster, 1990; Miller *et al.*, 1990). Kaplan *et al.* (1993) showed that the CFC of two Ultisols increased between pH 5.0-7.0 and attributed this to increased negative charges on the variable charge components which promoted more dispersive behaviour. Goldberg and Glaubig (1987) report that comparison of CFC values for a wide range of minerals is difficult due to the large effects pH has on the charges of some soil components. Kaolinite has been reported to be highly sensitive to dispersion with increasing pH (Samson and Schofield, 1954; Arora and Coleman, 1979; Goldberg and Glaubig, 1987).

The type of cation present on exchange sites in soils have also been shown to be important in affecting CFC values. Most of the previous research on dispersion and flocculation phenomena have used Na/Ca systems, and has shown that the presence of small amounts of Na^+ in Ca-saturated systems can greatly increase CFC values (Oster *et al.*, 1980). Rengasamy (1983) investigated the effects of Mg^{2+} and K^+, in addition to Na^+ and Ca^{2+}, as saturating cations and observed that CFC values increased in the order $Ca^{2+}<Mg^{2+}<K^+<Na^+$ for both pure clay systems and soil clays.

Pure clay systems are useful for describing the processes involved in flocculation and dispersion but cannot be applied to field situations where a mixture of mineral types, organic constituents, and oxides are present (Sumner, 1993). Goldberg and Forster (1990) found that CFC values for soil clays tended to be between 2x and 10x greater than for pure clay systems. Pure clay systems do not take into account organic and inorganic cements which bind clays together and soils are seldom in a state of suspension under field conditions.

The differences between swelling and dispersion are important to understand as both determine the permanent damage which may occur. Swelling involves the separation of clay particles or groups of particles and is, in theory, a reversible process (Shainberg and Lety, 1984), whereas dispersion, which may be either spontaneous or require some energy input, occurs when the repulsive forces in the soil system exceed the attractive forces and the particles cannot approach each other close together enough for van der Waals forces to operate.

2.3.2.4 Exchange reactions

When liquid wastes are irrigated onto soils it is important to be able to predict what cation exchange reactions will occur and what exchangeable cations will be present on exchange sites after equilibration with a given solution. Cation exchange equations are often required for such deductions.

A number of equations have been developed and used to describe cation exchange reactions in soil systems, each having its own set of characteristics. However, certain limitations are inherent in most of the proposed cation exchange equations (Bohn *et al.*, 1979):

1. separate cation and anion exchange is frequently considered, but rarely is their simultaneous presence acknowledged.
2. the cation or anion exchanger is assumed to possess constant exchange capacity.
3. simple stoichiometric ion exchange is generally assumed.
4. complete reversibility of reactions is usually taken for granted.

In many soils, Ca^{2+} is the dominant cation occupying the exchange sites and one of the most studied reactions is the exchange of Ca^{2+} by Na^{+}. The mass action exchange relationship for this reaction is usually presented as (Bohn *et al.*, 1979; Shainberg and Lety, 1984):

$$CaX + 2Na^{+} \Leftrightarrow 2NaX + Ca^{2+} \tag{2.2}$$

where X denotes the exchange surface. The above reaction results in the following reaction exchange coefficient:

$$K_k = \frac{(NaX)^2(Ca^{2+})}{(CaX)(Na^{+})^2} \tag{2.3}$$

where the parentheses denote the activities of the soluble or exchangeable cations. The major problem with calculation of these equations has been the measurement of the activities of the adsorbed cations (Bohn *et al.*, 1979). The Gapon equation is a slight variation on Equation 2.3 and takes the concentrations, rather than the activities, of the cations into account and has the form:

$$\frac{[NaX]}{[Ca_{1/2}X]} = K_G \frac{[Na^{+}]}{[Ca^{2+}]^{1/2}} \tag{2.4}$$

where exchangeable cation concentrations are in $cmol_c\ kg^{-1}$ soil, and solution cation concentrations are in $mmol\ L^{-1}$. The exchange coefficient, K_G, is known as the Gapon selectivity coefficient. The Gapon equation is unsatisfactory if applied over all possible Na-Ca compositions but is suggested to work reasonably well over the range of compositions commonly found in irrigation waters (Bohn *et al.*, 1979). Other exchange coefficients which are commonly used for describing monovalent-divalent cation exchange reactions include the Gaines-Thomas selectivity coefficient, designated K_{GT}, which assumes the activities of the cations are equal to their equivalent fractions (the ratio of equivalents of one cation to the total equivalents of all cations on either the exchanger or in the soil solution), and the Vaneslow selectivity coefficient, designated K_V, where the activity of a cation is equal to its mole fraction (the ratio of moles of one substance to the total moles of all substances on either the exchanger or in the soil solution) (Shainberg and Lety, 1984).

Although ion activities are different from molar ion concentrations (i.e. $a = m\,\gamma$, where a is the cation activity, m is the molar ion concentration, and γ is the molar activity coefficient) over the concentration ranges common to sodium affected soils, the ratio of ion concentrations is very similar to the corresponding ratio of ion activities (Shainberg and Lety, 1984). This is because activity coefficients for divalent cations decrease more rapidly with increasing salt concentration than do activity coefficients of monovalent cations, however, the square root operation on the divalent cation in Equation 2.4 results in a fairly constant ratio of monovalent cation activity coefficient to the square root of divalent cation activity coefficient (Shainberg and Lety, 1984).

Because Ca^{2+} and Mg^{2+} are the most common divalent cations in soil environments, they are often considered together. Equation 2.4 can therefore be re-arranged as:

$$\frac{[\mathrm{NaX}]}{[\mathrm{CaX}+\mathrm{MgX}]} = K_G \frac{[\mathrm{Na}^+]}{[\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}]^{1/2}} \qquad (2.5)$$

The term on the left hand side of Equation 2.5 is termed the Exchangeable Sodium Ratio (ESR) and the term on the right hand side, excluding K_G, is termed the Sodium Adsorption Ratio (SAR) when the values in the parentheses (of the right hand side of the equation) are concentrations in mmol L^{-1}. Analyses of a large number of soil samples from the western United States of America led to the empirical Gapon equation (Richards, 1954):

$$\mathrm{ESR} = 0.01475\ (\mathrm{SAR}) - 0.0126 \qquad (2.6)$$

More widely used is the prediction of Exchangeable Sodium Percentage (ESP) which is a measure of the sodium saturation of the total cation exchange capacity of a soil, and can be estimated by measuring the SAR of irrigation waters and/or soil solutions (Richards, 1954; Sumner, 1993). The following equation was developed from Equation 2.6 to relate ESP and SAR of irrigation waters (Richards, 1954):

$$ESP = \frac{100\,NaX}{CEC} = \frac{100\,ESR}{1+ESR} = \frac{100\,(-0.0126+0.01475\,SAR)}{1+(-0.0126+0.01475\,SAR)} \tag{2.7}$$

Equation 2.7 can be used as an estimate of ESP from SAR values, but for more accurate predictions, a unique relationship should be derived experimentally for each individual soil (Suarez, 1981; Shainberg and Lety, 1984). From Equation 2.7, it is evident that SAR and ESP values are almost equal for most ESP ranges found in agricultural soils (Fig 2.3), and these two terms are therefore often used interchangeably (Shainberg and Lety, 1984).

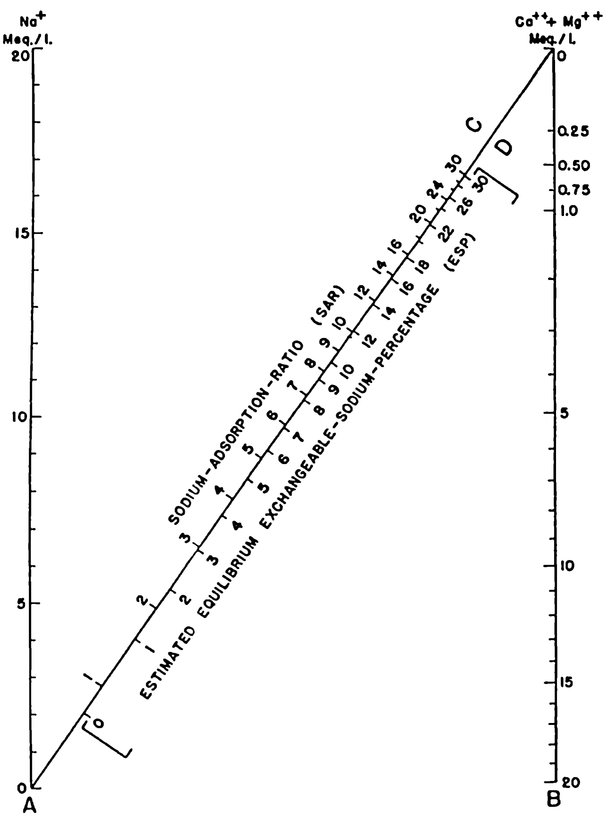

Fig. 2.3 Nomogram for determining the SAR values of irrigation waters and for estimating the corresponding ESP values of a soil equilibrated with this water (Richards, 1954).

The above discussion referred to monovalent-divalent cation exchange between Na^+ and Ca^{2+} (and/or Mg^{2+}) but did not consider K^+ exchange. However, similar equations as those developed for Na^+-Ca^{2+} exchange can be applied to K^+-Ca^{2+} exchange reactions where the Potassium Adsorption Ratio (PAR) is defined as (Richards, 1954):

$$\mathrm{PAR} = \frac{[K^+]}{[Ca^{2+} + Mg^{2+}]^{1/2}} \tag{2.8}$$

The Exchangeable Potassium Percentage (EPP), which is a measure of degree of K^+ saturation of the total cation exchange capacity of a soil, can be estimated by the following empirical relationship based on analyses of a large number of soil samples from the western United States of America (Richards, 1954):

$$\mathrm{EPP} = \frac{100\,(0.036 + 0.1051\ \mathrm{PAR})}{1 + (0.036 + 0.1051\ \mathrm{PAR})} \tag{2.9}$$

Some researchers have calculated selectivity coefficient values in a wide range of soils (e.g. Sheta *et al.*, 1981; Guth and Brown, 1985; Levy *et al.*, 1988; Parfitt, 1992). In general, the monovalent-divalent exchange reactions, usually Na^+-Ca^{2+}, have been fairly well predicted by either the Vaneslow, Gaines-Thomas, or Gapon selectivity coefficients. Levy *et al.* (1988) found that all three exchange coefficients were usually larger for K^+-Ca^{2+} exchange than for Na^+-Ca^{2+} exchange in kaolinitic soils and attributed this to high charge density in kaolinites, which enhances K^+ dehydration and therefore results in a high affinity of the clay mineral for K^+. Parfitt (1992), using Gaines-Thomas selectivity coefficients, showed that some New Zealand soils retained K^+ in preference to Ca^{2+} and Mg^{2+}. Oxidic, Allophanic, and Ultic soils had the least preference for K^+ and soils dominated by vermiculite and mica clays had the greatest preference, due to K^+ selective sites on the clay minerals.

2.3.2.5 Effects of anions and pH on cation exchange

Early workers generally considered that anions had little significant effect on cation adsorption on exchange sites (Sommerfeldt and Peterson, 1963). However, more recent research has shown that the pH of the soil environment and the anions present in soil solutions can affect the amount of Na^+ (or K^+) accumulation on the exchange sites. Babcock and Schulz (1963) found that more exchangeable Na^+ was present when sulphate anions were present than when chloride anions were present. Sommerfeldt (1962) investigated the effects of several anions (OH^-, Cl^-, CO_3^{2-}, and SO_4^{2-}), using different sodium salts, on the amount of Na^+ retained by a sandy loam soil and a non-calcareous bentonite (smectite) and found that the hydroxide and carbonate anions caused the CEC of both soils to increase markedly and therefore also increased the amount of Na^+ retained. Sommerfeldt and Peterson (1963) found that hydroxide anions present in the soil solution caused significantly more Na^+ to be adsorbed on a non-calcareous bentonite than when other anions (Br^-, I^-, Cl^-, SO_4^{2-}, HCO_3^-) were present. Studies by Kelley (1957) concluded that metallic cations are adsorbed from chemically alkaline solutions in greater quantities than from neutral solutions.

2.3.2.6 Chemical reactions of soil amendments

As mentioned previously (section 2.2.5.2), the application of divalent based salts (normally Ca^{2+} and Mg^{2+}) to soils is often practiced to alleviate the problems associated with the accumulation of monovalent cations, usually Na^+, on exchange sites in soils irrigated with high monovalent cation concentration waters. The most common sources of Ca^{2+} used are gypsum ($CaSO_4.2H_2O$), lime ($CaCO_3$), quick lime ($Ca(OH)_2$), and occasionally $CaCl_2$. In all the above cases, the Ca-based salt is dissolved by the infiltrating soil water which increases the Ca^{2+} concentration in the soil solution and therefore lowers the SAR (Equation 2.5) which, in theory, therefore also decreases the ESP of the soil (Equation 2.7). The calcium which is dissolved into solution as Ca^{2+} ions can exchange for the monovalent Na^+ (or K^+) on the exchange sites by the following reaction:

$$2NaX + Ca^{2+}_{(aq)} \Rightarrow CaX + 2Na^+_{(aq)} \qquad (2.10)$$

Where X denotes a negatively charged exchange surface (in this case representing one equivalent of the anionic exchanger). The displaced Na^+ may either be leached or combine with anions present in the soil solution, with precipitation of Na-based salts possible. Ideally, Na^+ would be leached from the soil profile to minimise the likelihood of reversing the reaction and a return to the high exchangeable Na^+ concentrations. The amount of Na^+ that will be displaced is ultimately dependent on the solubility of the applied Ca-based salt, the more soluble the salt the higher the Ca^{2+} concentration in the soil solution and the more Na^+ will be displaced. The solubility of the common amelioration salts is in the order $CaCO_3 < Ca(OH)_2 < CaSO_4.2H_2O << CaCl_2$. However, due to cost and availability of the various salts it is often uneconomic to apply the most soluble form ($CaCl_2$), and the most common Ca-based salt applied in New Zealand is lime. Overseas, where Na^+ accumulation problems arise due to natural causes (i.e. Australia and the Middle East), gypsum is the most common amendment used, usually because of its abundance and low cost in these areas. Although lime is the most insoluble of the salts used, the supply of Ca^{2+} from lime can be increased by using acidification techniques, commonly sulphuric acid (H_2SO_4), or elemental sulphur (S) (Miyamoto *et al.*, 1975; Bohn *et al.*, 1979). The elemental S needs to be oxidised to sulphuric acid by soil microorganisms before it can become effective, and the following reaction sequence can occur (Bohn *et al.*, 1979):

$$2S + 3O_2 + 2\,H_2O \Rightarrow 2H_2SO_4 \qquad (2.11a)$$

$$CaCO_3 + H_2SO_4 \Rightarrow CaSO_4 + H_2O\ \{+ CO_2 \uparrow\} \qquad (2.11b)$$

$$2NaX + CaSO_4 \Leftrightarrow CaX + Na_2SO_4 \qquad (2.11c)$$

The addition of Ca^{2+} to soils dominated by monovalent exchangeable cations can have positive effects on soil physical properties. Most of the work regarding the reclamation of soils dominated by monovalent cations (mainly Na^+) has investigated the effects of gypsum amelioration and to a lesser extent $CaCl_2$ and lime application. Shainberg *et al.* (1989) presents a detailed review on the use of gypsum in reclamation of sodic soils, as an amendment for dispersive soils, and as an amelioration agent for subsoil acidity. The amount of gypsum required depends on the amount of exchangeable Na^+ in the soil profile (Richards, 1954). Several "gypsum requirement" tests have been derived (Richards, 1954; Oster and Frenkel, 1980; Keren and O'Connor, 1982) based on the cation exchange contribution of the dissolution of gypsum and is dependent on the amount of exchangeable Na^+. Table 2.3 shows the amount of gypsum, lime, and calcium chloride required to lower the ESP of soils to <10% through application to the surface of the soil.

Table 2.3 Quantity of soil amendment (gypsum, lime, and calcium chloride) required to lower exchangeable sodium (Na^+) values (Overcash and Pal, 1979).

Exchangeable Na ($cmol_c$ kg^{-1} soil)	Gypsum ($CaSO_4.2H_2O$)	Lime ($CaCO_3$)	Calcium chloride ($CaCl_2$)
	------------------------	tonnes ha^{-1} m^{-1} depth	-----------------
2	24.2	14.2	15.6
4	48.4	28.4	31.2
6	72.6	42.6	46.8
8	96.8	54.8	62.4
10	121.0	70.0	78.0

The effects of the dissolution of gypsum on hydraulic conductivity are twofold (Shainberg *et al.*, 1989). Firstly, the dissolution results in an available supply of Ca^{2+} in the soil solution which lowers the SAR, and, if sufficient Ca^{2+} is present, displaces Na^+ from exchange sites (thereby decreasing the ESP of the soil). Secondly, the dissolution of gypsum increases the EC of the soil solution which, in theory, compresses the diffuse double layer surrounding clay particles. This enhances flocculation and therefore hydraulic conductivity should be maintained or increase. It has been suggested (Keren and O'Connor, 1982) that repeated applications of gypsum may be required to maintain EC levels which are adequate to maintain soil hydraulic conductivity where only high quality (i.e. low EC) water is available for irrigation. Loveday (1976) reported that gypsum rapidly improved infiltration rates in a saline soils due to the increased EC effect (although it was also quickly lost due to gypsum leaching) and also improved infiltration rates in the longer term through the progressive decrease in sodicity (i.e. displacement of exchangeable Na^+ by Ca^{2+} and subsequent Na leaching). Increases in total porosity and macroporosity were not observed by Blackwell *et al.* (1991) in sodic soils treated with gypsum, but increases in intrinsic permeability at -10 kPa were observed.

Many other studies (e.g. Keren and Shainberg, 1981; Shainberg *et al.*, 1982; Greene *et al.*, 1988; Frenkel *et al.*, 1989; Zahow and Amrhein, 1992; Ilyas *et al.*, 1993) have reported that gypsum application to Na^+ affected soils increases the hydraulic conductivity of soils. Figure 2.4 shows the effects of various gypsum application rates on the relative hydraulic conductivity of an Alfisol from Israel.

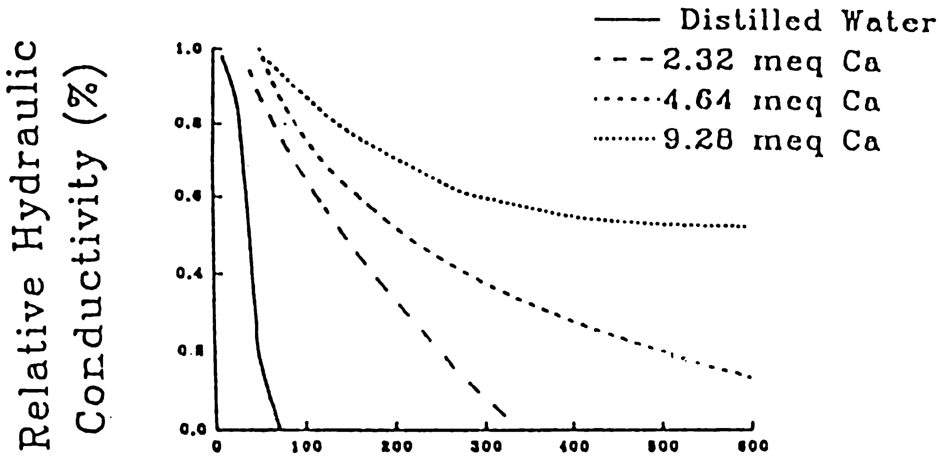

Fig. 2.4 Effect of various application rates of gypsum on the relative hydraulic conductivity of a Golan soil (Typic Rhodoxeralf) (Shainberg *et al.*, 1982).

The effect of placement of applied gypsum within the soil profile on sodic soil amelioration has also been studied. Gobran *et al.* (1982) concluded that applying gypsum, irrespective of particle size, to the surface of a soil resulted in lower ESP values than when the gypsum was mixed through the soil. In contrast, Frenkel *et al.* (1989) found that mixing the gypsum through the soil was more efficient in the reclamation of a sodic soil compared to surface application. The particle size of the gypsum can affect the time required for reclamation with increasing particle size requiring longer periods for reclamation (van den Elshout and Kamphorst, 1990). Shainberg *et al.* (1982) compared the effects of gypsum and calcium chloride, using equivalent amounts of Ca^{2+}, on the hydraulic conductivity of three Israeli soils and found that both amendments resulted in similar Na^+-Ca^{2+} exchange rates, but that the gypsum resulted in maintenance of hydraulic conductivities for longer periods of time due to the longer term EC effect.

The importance of lime ($CaCO_3$) in reclamation processes has mainly focused on soils containing free $CaCO_3$ within the soil profile (calcareous soils) where dissolution of the lime is very slow due to the relatively high pH of the soil environment (Richards, 1954). However, in non-calcareous soils, the application of lime has been shown to be beneficial in increasing soil hydraulic conductivity of saline soils. Shainberg and Gal (1982) reported that decreases in hydraulic conductivity (Fig. 2.5) and clay dispersion were less in two soils after mixing powdered lime into the soil during leaching with distilled water influent solution after a 0.01 N influent solution (SAR of 20) had been leached through the soils. The EC increase in the soil solution due to $CaCO_3$ dissolution was suggested as the mechanism responsible for the beneficial effect of lime (Shainberg and Gal, 1982). McKenzie *et al.* (1993) suggest that both gypsum and lime can improve aggregate stability and reduce clay dispersion.

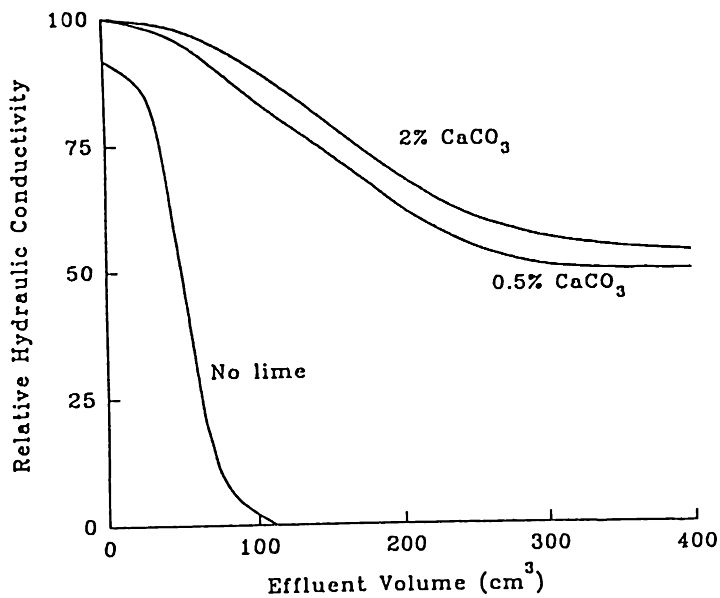

Fig. 2.5 Effect of additions of lime to a non-calcareous Hermon soil (Typic Rhodoxeralf) on the hydraulic conductivity decrease with distilled water following leaching with a 0.01 N solution (SAR=20) (Shainberg and Gal, 1982).

2.4 Organic carbon

2.4.1 Introduction

The following section reviews the importance of organic carbon (and organic matter) in soil systems. This section is included because high pH solutions are known to affect and react with organic carbon (see section 2.4.3). Because soil organic matter is an important constituent in soil systems, it is necessary to review its roles and functions with emphasis on its chemical importance and its significant effects on soil structure.

2.4.2 Importance of organic carbon in soils

2.4.2.1 Introduction

Soil organic matter performs a number of functions in soils such as: a source of nutrients for plants, formation and stabilisation of soil structure, water storage, and heat adsorption (McLaren and Cameron, 1990). Organic carbon in soil makes up between 50-58% of soil organic matter and an empirically derived conversion factor ranging between 1.7-2.0 (Nelson and Sommers, 1982) is often used to convert measured soil organic carbon concentrations to organic matter contents of soil. For the purposes of this discussion, soil organic matter and soil organic carbon can be considered as interchangeable terms.

Soil organic matter encompasses a whole range of organic materials in the soil including living organisms, dead and decaying plant and animal remains, and the amorphous dark coloured material known as humus (McLaren and Cameron, 1990). In its most restricted sense, "soil organic matter" may refer to the humus component alone and for the remainder of this review when organic matter is referred to it is the humus component which is concerned. The importance of soil humus on various soil physical, chemical, and biological parameters are listed in Table 2.4.

Table 2.4 Properties of soil humus and effects on soil properties (after Stevenson, 1982).

Property	Comments	Effect on soil
Colour	The typical dark colour of soils is caused by organic matter	May facilitate warming of soil environment
Water retention	Organic matter can hold up to 20 times its weight in water	Helps prevent drying and shrinking. May significantly improve the moisture-retaining properties of sandy soils
Combination with clay minerals	Cements soil particles into structural units (aggregates)	Permits exchange of gases. Stabalises structure. Increases permeability
Chelation	Forms stable complexes with Cu^{2+}, Mn^{2+}, Zn^{2+}, and other polyvalent cations	May enhance the availability of micronutrients to higher plants
Solubility in water	Insolubility of organic matter is because of its association with clay. Also, salts of divalent and trivalent cations with organic matter are insoluble. Isolated organic matter is partly soluble in water	Little organic matter is lost by leaching
Buffer action	Organic matter exhibits buffering in slightly acid, neutral, and alkaline ranges	Helps maintain a uniform reaction in the soil
Cation exchange	Total acidities of isolated fractions of humus range from 300-1400 $cmol_c$ kg^{-1} soil	May increase the CEC of the soil. From 20-70% of CEC of many soils is caused by organic matter
Mineralisation	Decomposition of organic matter yields CO_2, NH_4^+, NO_3^-, PO_4^{3-}, and SO_4^{2-}	A source of nutrient elements for plant growth
Combines with organic molecules	Affects bioactivity, persistence and biodegradability of pesticides	Modifies application rate of pesticides for effective control

2.4.2.2 Soil structure and stability

Soil organic matter is the major constituent in soil responsible for the formation and stability of soil structure. Soil structure may be defined as "the spatial heterogeneity of the different components or properties of soil" (Dexter, 1988) and refers to soil components of many different size scales in the soil. Soil structure can be considered as a hierarchy with the lowest hierarchical order referring to the combination of single mineral components, such as clay plates, into a basic type of compound particle, such as a floccule or domain of clay plates (Dexter, 1988). The next hierarchical order is larger compound particles such as clusters of domains, this hierarchical order occurs when a number of clusters are combined into microaggregates, and so on (Dexter, 1988). Aggregate hierarchy exists in soil where aggregate stability is primarily controlled by organic materials (Oades and Waters, 1991).

Tisdall and Oades (1982) proposed a model for describing the stages of aggregation in Red-brown Earth soils but may also be applied to other soils where soil organic matter is the main binding agent (i.e. many New Zealand soils). The four stage model of progression is (Tisdall and Oades, 1982):

$$<0.2\ \mu m \Rightarrow 0.02\text{-}2\ \mu m \Rightarrow 2\text{-}20\ \mu m \Rightarrow 20\text{-}250\ \mu m \Rightarrow >2000\ \mu m \qquad (2.12)$$

The formation of aggregates in the <2 μm diameter size range arises from the flocculation of clay plates by van der Waals forces, H-bonding, and coulombic attraction, the details of which have been discussed previously (see section 2.3.2.3). However, certain fractions of the organic matter in soils may adsorb to clay surfaces to form "clay-organic complexes" (Greenland and Hayes, 1981). The association between organic material and clay particles is predominantly through surface complexes such as those formed when carboxylic and phenolic functional groups of humic materials act as ligands for ions such as aluminium at the clay surfaces (Greenland and Hayes, 1981).

Aggregates in the range 2-20 μm (microaggregates) are thought to form through two main mechanisms (described in detail by Tisdall and Oades, 1982), both of which are characterised by the bonding of <2 μm particles by persistent organic bonds. The last type of microaggregates are those in the 20-250 μm range and consist largely of particles and/or smaller aggregates 2-20 μm bonded together by various cements including persistent organic materials, crystalline oxides, and highly disordered aluminosilicates (Tisdall and Oades, 1982).

Macroaggregates are defined as those >250 μm and are held together primarily by the root and hyphae network of the vegetation and by transient binding agents (Tisdall and Oades, 1982). Tisdall (1991) reviewed the effect of fungal hyphae on the stability of macroaggregates and reported that temporary binding agents, especially vesicular-arbuscular (VA) micorrhizal hyphae, bind stable microaggregates into stable macroaggregates. Tisdall and Oades (1979) found that the root system of ryegrass was more efficient than that of white clover in stabilising macroaggregates because the ryegrass supported a larger population of VA mycorrhizal hyphae. Figure 2.6 illustrates a model, proposed by Tisdall and Oades (1982), of aggregate organisation with the major binding agents involved for each size range.

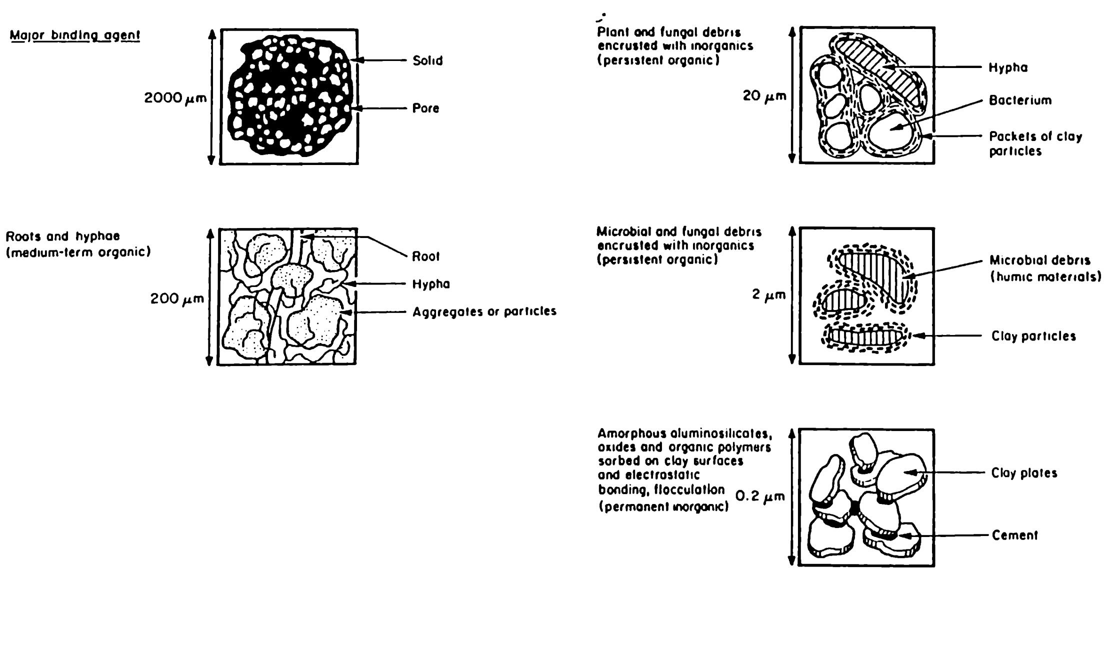

Fig. 2.6 Model of aggregate organisation with major binding agents indicated (Tisdall and Oades, 1982).

Many workers (e.g. Tisdall and Oades, 1982; Chaney and Swift, 1984; Churchman and Tate, 1987) have investigated the effect that organic matter has on aggregate stability and, in general, a good correlation exists between organic matter levels and aggregate stability (e.g. Fig. 2.7).

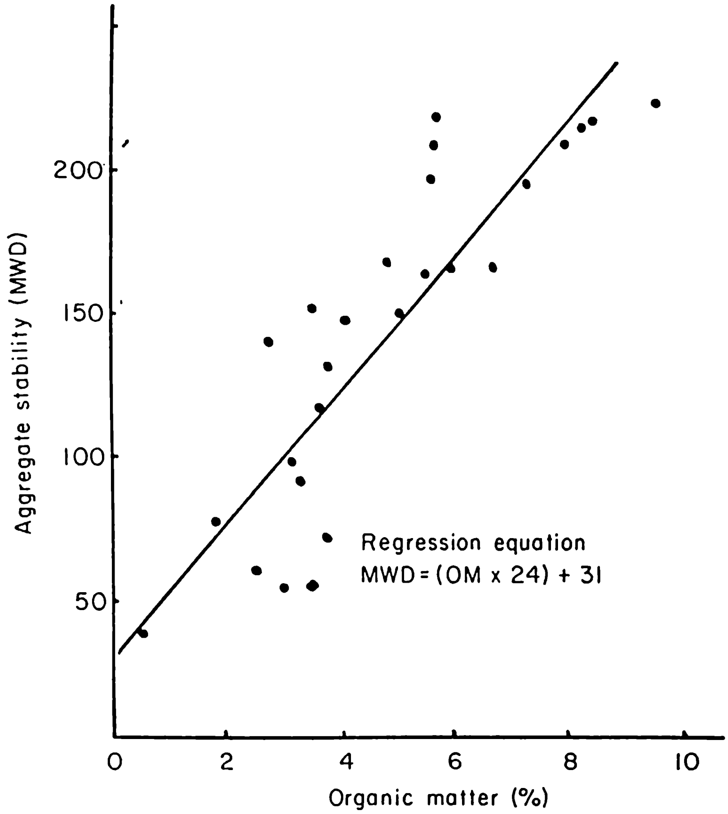

Fig. 2.7 Relationship between aggregate stability (expressed as mean weight diameter (MWD)) and organic matter content for 26 British soils (Chaney and Swift, 1984).

However, organic matter can also cause dispersion when present in small amounts, particularly when it comprises high concentrations of low molecular weight acids, and when the negative charge on the clay-metal oxide-organic matter conglomerate is expressed at relatively large distance from particles because there is Na^+ on exchange sites (Churchman *et al.*, 1993). Organic matter can also suppress swelling by lowering the surface area of soil minerals through coatings and linkages (Churchman *et al.*, 1993)

2.4.2.3 Soil fauna

Soil fauna, particularly earthworms, have significant effects on soil structure and other soil physical properties. Earthworms burrow in search of food and create a network of macropores which aid in the aeration of soil and assists in the formation of macroaggregates. Earthworm densities vary from soil to soil but are usually in the range of 100-300 m^{-2} but can be as high as 2000 m^{-2} (Lee and Foster, 1991). The type of burrow is dependent on the species present in any particular soil, some species may have burrows which open at the surface and can extend to depths >1 m. Earthworms only improve soil structure where a good supply of nutritive organic matter is available. Adequate supply of food increases intestinal bacteria, some of which produce gums which can glue the earthworm casts into stable aggregates (Swaby, 1949). Earthworm casts can make up a large percentage of the aggregates found in surface horizons of soils, however, their stability is time dependent. Fresh casts tend to be less stable than other soil aggregates but over time they become more stable than other soil aggregates (Lee and Foster, 1991).

The pH and calcium contents of soil can have important effects on earthworm health and activity. Springett and Syers (1984) investigated the effect of both pH and Ca^{2+} content of soil on cast production of one species earthworm, *Allolobophora caliginosa* (Savigny) species, through application of various Ca-based salts to soil cores and found soil pH was more important than Ca^{2+} concentration in influencing earthworm activity. Cast numbers increased with increasing pH up to pH 7.3 when $CaCO_3$ was added, and up to pH 6.7 when $Ca(OH)_2$ was used, however, earthworms soaked in pH 12.1 $Ca(OH)_2$ solution died within minutes whereas those soaked in $CaCO_3$ remained alive although their osmotic pressures were the same (Springett and Syers, 1984).

2.4.2.4 Importance for fertility

Soil organic matter is a major contributor to the fertility of most soil through its cation exchange capabilities and decomposition processes. The essential elements required for plant growth are usually divided into macro- and micro-nutrients, with nine elements being classified as macro-nutrients: O, H, C, N, P, K, S, Ca, and Mg (Allison, 1973; Campbell, 1978). Not all of these nutrients are obtained from soil organic matter but any one or all of the above may be a part of the organic matter at some time (Allison, 1973). Of these, the O, H, and C are readily obtained from soil air (CO_2) and soil water (Campbell, 1978). Under natural conditions, plants absorb most of their N from the soil solution in mineral form and small amounts as organic substances (Campbell, 1978). The main source of N for plant growth is soil organic matter, however, it is in a form which is unavailable to plants unless it is converted by microorganisms, through hydrolysis of amino acids, into ammonium and is further oxidised (nitrification) to form nitrate, both of which can be utilised by plants (Allison, 1973). Soil organic matter normally constitutes between 15-80% of the total P in soil (Allison, 1973), however, organic-P is extremely stable and relatively unavailable for plant unless mineralised to the plant available inorganic phosphate ions, $H_2PO_4^-$ and HPO_4^{2-} (McLaren and Cameron, 1990). The bulk (90% or more) of total S in soils is present as organic-S and unavailable to plants and must first be mineralised to sulphate (SO_4^{2-}) before it can be utilised. The other macro-nutrients (K, Ca, and Mg) can be released from organic matter through cation exchange processes (Allison, 1973; Stevenson, 1982; McLaren and Cameron, 1990). Organic acids, such as fulvic acid, can also attack the mineral phase of the soil resulting in the release of plant nutrients (McLaren and Cameron, 1990).

Organic matter is a major contributor to the cation exchange capacity (CEC) of soils, particularly in the topsoil where there is generally a greater proportion of organic matter. Humic substances are made up of a variety of complex structures but can be broadly divided into humic acids, fulvic acids, and humins (Kononova, 1966; Schnitzer, 1978; Oades, 1992). The major oxygen-containing functional groups in humic substances are carboxyls, hydroxyls, and carbonyls (Schnitzer, 1978) and these represent the sites at which cation exchange processes occur. It is thought that the carboxyl and phenolic hydroxyl functional groups contribute most of the CEC of humic material (Talibudeen, 1981). The charge of the functional groups is dependent on the pH of the soil solution and may release or take up H^+ depending on the pH of the soil solution (Singer and Munns, 1991; Oades, 1992). As the pH of the soil solution increases, H^+ dissociation (deprotonation) occurs, resulting in an increased negative charge and thus an increased CEC (Bohn *et al.*, 1979). Helling *et al.*(1964) investigated the effect of pH on CEC of the organic matter component of 60 Wisconsin soils and found that a linear relationship existed of increasing CEC with increasing pH, from 36 meq 100 g^{-1} at pH 2.5 to 213 meq 100 g^{-1} at pH 8.0. The amount of organic matter in a soil has been directly correlated with CEC, however, the contribution of organic matter to the total CEC of a soil is disproportionate compared to the common phyllosilicate minerals found in soil environments due to the higher charge density of organic matter (see Table 2.5). Helling *et al.* (1964) showed that at pH 2.5 only 19% of CEC was associated with organic matter whereas at pH 8.0 the percentage increased to 45%. The CEC of isolated organic matter will always be greater than *in situ* CEC values because some of the "potential" exchange sites will be occupied by complexes of polyvalent cations and some of the sites will be lost through associations with clay particles (Stevenson, 1982).

Table 2.5 Summary of selected properties of solid phase components (Bohn *et al.*, 1979; Dixon and Weed, 1989; Sumner, 1993).

Component	Mineral type	CEC ($cmol_c$ kg^{-1} soil)	pH dependency of charge	Specific surface area (m^2 g^{-1})
kaolinite	1:1	1-10	extensive	5-40
halloysite	1:1	2-10	(extensive)	21-43
montmorillonite	2:1	80-120	minor	600-800
vermiculite	2:1	120-150	minor	400-800
mica (illite)	2:1	20-40	medium	60-200
chlorite	2:1:1	20-40	extensive	70-150
allophane	SRO[a]	10-150	extensive	1000
organic matter	-	100-300	extensive	800-900

[a] Short Range Order mineral

2.4.3 Alkali solutions and organic carbon

2.4.3.1 Introduction

Alkali solutions have the ability to dissolve organic matter and have been used extensively for the extraction of organic matter from soils for characterisation purposes (e.g. Tinsley and Salam, 1961; Kononova, 1966; Schnitzer and Skinner, 1968; Ortez de Serra and Schnitzer, 1972; Schnitzer and Schuppli, 1989a,b). However, little information exists in the literature with respect to the relationship between quantity of organic matter dissolution and the nature and concentration of the extracting solution.

2.4.3.2 Organic matter dissolution

The mechanisms by which organic matter is dissolved by alkali solutions appears to be complex. At relatively low pH, organic molecules, such as humic and fulvic acids, remain insoluble in water because their negative sites, which arise from the dissociation of H^+ from the functional groups, are occupied by a variety of polyvalent cations (Stevenson, 1982). When NaOH (or KOH) is added, the monovalent cations displace the polyvalent cations (which precipitate out as their hydroxides) (Russell, 1973) and dissociation of Na-saturated functional groups occurs (Oades, 1989). The organic fraction then forms polyvalent anions which become hydrated (solvated) and water soluble (Hayes, 1986). The alkali also increases the solution pH and results in an increase in negative charge on the organic components after dissociation of the Na-saturated functional groups which results in increased electrostatic repulsive forces, and therefore increasing the dispersion effect (Oades, 1989). Alkaline monovalent salts have been reported to dissolve more organic matter than when neutral monovalent salts are used, such as $Na_4P_2O_7$ buffered at pH 7.0 (Stevenson, 1982). Neutral Na-salts are thought to extract organic matter by the exchange of organically bound polyvalent cations by Na^+ (the exchanged polyvalent cations forming insoluble precipitates or soluble complexes), the Na-organic matter complex being water soluble (Schnitzer and Schuppli, 1989a,b). At neutral pH, it is also unlikely that all of the divalent and polyvalent cations are exchanged and that phenolic structures would not be ionized under these conditions (Hayes, 1986).

The concentration of NaOH extracting solution used affects the amount humic material extracted. Levesque and Schnitzer (1966) reported that the amount of organic matter extracted from a podzol using NaOH increased with concentration up to 0.1 M, and thereafter the amount extracted decreased as hydroxide concentration increased. In contrast, Gascho and Stevenson (1968) found that a similar amount of organic matter was extracted over a range of 0.05-0.5 M NaOH. No work appears to have been published on the effect of KOH concentration on organic matter extraction.

2.4.4 Effect of exchangeable cations on aggregate stability and soil strength

The type and quantity of cation on soil exchange sites can affect the stability of soil aggregates and soil strength. In general, divalent cations on exchange sites lead to more stable soil aggregates. Ahmed *et al.* (1969) found that the stability of aggregates increased according to the type of cation on exchange sites in the order Ca^{2+}=Mg^{2+}>K^{+}≥Na^{+}, however, exception to this trend have been reported. For example, Cecconi *et al.* (1963) found that more stable aggregates were formed in K^{+} treated soil than Ca^{2+}, Mg^{2+}, or Na^{+} treated soil.

The strength of soil is also affected by the type of adsorbed cations. In general, Na^{+} on the exchange sites results in a higher tensile strength (Dexter and Chan, 1991; Barzegar *et al.*, 1994) and higher modulus of rupture (MOR) (Reeve *et al.*, 1954; Gerard, 1965; Greene *et al.*, 1988) compared to Ca^{2+} dominated soil. Ravina and Markus (1975) found that K^{+} on exchange sites behaved similarly to Ca^{2+} with respect to soil mechanical properties. Dowdy and Larson (1971) found that the tensile strength of montmorillonite decreased in the order K^{+}≥Na^{+}>Ca^{2+} and Reeve *et al.* (1955) reported that the MOR increased linearly with increasing ESP but there was no effect with increasing EPP. The MOR in soil tends to increase with increasing ESP (Aylmore and Sills, 1982) which, in many cases, can lead to "hardsetting" of the surface of the soil profile upon drying. Longenecker (1959) showed that the type of anion present with a monovalent cation also affected the MOR of soil, with nitrate and chloride resulting in the lowest MOR values and carbonate and bicarbonate producing the highest MOR values.

2.5 Soil water movement

2.5.1 Introduction

The movement of water and solutions through soil is important to study as it affects how much liquid waste can be applied to the soil and is influenced by the texture, structure, mineralogy, and biota of the soil. This section introduces the theory of water movement in soils and discusses the effects of exchangeable cations, composition of percolating solution, and the effect of pH on hydraulic conductivity.

2.5.2 Principles and theory

2.5.2.1 Saturated hydraulic conductivity

Saturated flow occurs when all the soil pores (voids) are filled with water and no air is present. In normal field conditions the direction of flow is downwards but horizontal flow also occurs to some extent.

The rate of flow of water through soil can be described by Darcy's Law which states that the flux of water (q) is proportional to the hydraulic gradient multiplied by the hydraulic conductivity of the soil (McLaren and Cameron, 1990):

$$q = \frac{Q}{A} = -K\frac{\Delta H}{L} \tag{2.13}$$

where:

q = water flux density (m s^{-1})

Q = discharge rate (m^3 s^{-1})

A = cross sectional area of soil (m^2)

K = hydraulic conductivity of soil (m s^{-1})

ΔH = total hydraulic head (m)

L = length of soil (m)

$\left(\frac{\Delta H}{L}\right)$ = hydraulic gradient

One of the assumptions of Equation 2.13 is that the system is at steady-state (i.e. Q remains constant over time). When considering saturated conditions, the hydraulic conductivity is termed the saturated hydraulic conductivity and is normally denoted by K_s. Therefore, K_s is a measure of the maximum drainage rate of a soil and is greatly influenced by: i) the size of pores involved in water transport; ii) the distribution of cracks (soil structure); and iii) the tortuosity of the pores (Hillel, 1980).

2.5.2.2 *Infiltration*

The infiltration rate is a measure of how fast water can enter the surface of a soil and is used to determine irrigation rates and the likelihood of surface flooding or overland flow. The equation which describes the infiltration of water into soil was developed by Philip (1957):

$$I = \frac{Q}{A} = St^{0.5} + K_i t \qquad (2.14)$$

where:
I = cumulative quantity of water infiltrating the soil (m s^{-1})
Q and A as in Equation 2.13
S = the sorptivity of the soil (mm $s^{-1/2}$)
t = time (s)
K_i = hydraulic conductivity (m s^{-1})

In the early stages of infiltration into an unsaturated soil, sorptivity is the dominant process responsible for water movement. Sorptivity is the ability of the soil matrix to absorb water and is dependent on the moisture content of the soil, the drier the soil the greater the matrix suction gradient and therefore the faster the soil can absorb water. As the soil wets up the moisture content increases and thus the sorptivity decreases. At later stages (when t gets large), the conductivity becomes the dominant term in Equation 2.14 and, in theory, as the soil wets up to saturation K_i should equal K_s (Hillel, 1980). The infiltration of a soil is dependent on many of the soil properties such as texture, structure, and pore characteristics. However, the structural stability of the soil and the presence of swelling clays will also have a large effect on infiltration.

2.5.3 Effects of exchangeable cations on hydraulic conductivity

The hydraulic conductivity of a soil can decrease through the processes of clay swelling and dispersion. Exchangeable cations have a significant effect on the hydraulic conductivity of a soil depending on the clay mineralogy, organic matter content, soil solution composition, EC of the soil solution, influent solution composition and concentration, soil pH, influent solution pH, and type of cation on the exchange complex.

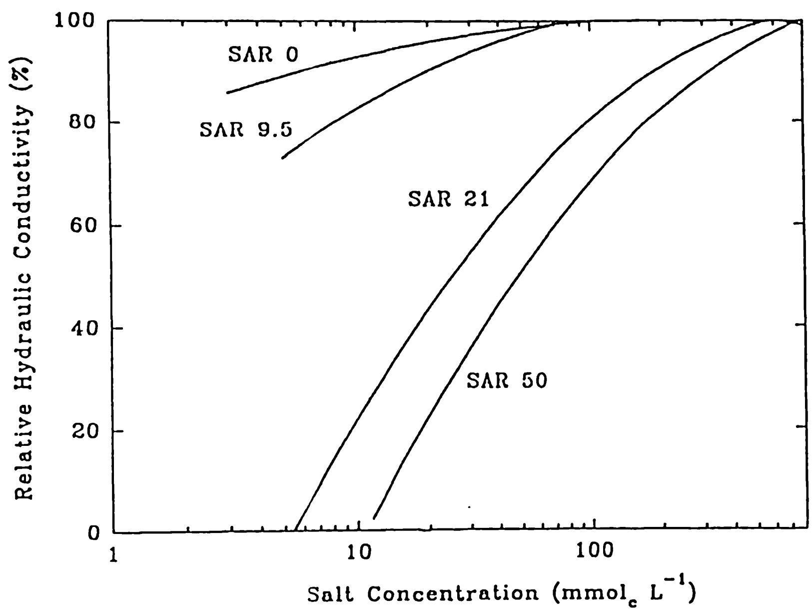

Fig. 2.8 Effects of varying SAR and EC on relative hydraulic conductivity for a Lindley soil (Acidic Paleustalf) (Cass and Sumner, 1982b).

Most studies investigating the effects of exchangeable monovalent cations on hydraulic conductivity have used Na^+. As discussed previously (section 2.3.2.2), the thickness of the diffuse double layer around soil colloids varies depending on the ESP and the EC of the soil solution, which in turn affects the amount of swelling and potential for dispersion in soil. Therefore, the hydraulic conductivity of a soil is also dependent on both the ESP and EC of the percolating solution. The higher the SAR (and therefore

ESP) and the lower the EC of the pecolating solution, the greater the decrease in hydraulic conductivity usually observed (Fig. 2.8).

Quirk and Schofield (1955) proposed the concept of "threshold concentration" to understand the effects of EC of the soil solution on hydraulic conductivity. The threshold concentration was defined as the concentration required to maintain soil permeability at an acceptable level relative to that measured with a strong salt solution for any particular ESP or SAR value. Many workers (e.g. McNeal and Coleman, 1966; Cass and Sumner, 1982a,b,c) have applied this approach to different soils and shown that different soils have a unique threshold concentration at a particular SAR which corresponds to a given decrease in hydraulic conductivity.

The two major mechanisms that have been proposed for decreases in hydraulic conductivity as the EC of the percolating solution decreases are clay swelling and dispersion (Quirk and Schofield, 1955; Rowell *et al.*, 1969; McNeal and Coleman, 1966; Frenkel *et al.*, 1978; Pupisky and Shainberg, 1979; Agassi *et al.*, 1981; Shainberg *et al.*, 1981; Cass and Sumner, 1982 b). At SAR values above 10, swelling of clays begins as the EC of the soil solution is lowered (Cass and Sumner, 1982b) and this process is, in theory, reversible if the EC of the soil solution is increased. In contrast to swelling, clay dispersion is essentially non-reversible and dependent on the soil texture (Sumner, 1993). In sandy textured soils, it is suggested that clay dispersion predominates when the EC falls below the CFC, whereas in heavy textured soils (i.e. higher clay contents) with high ESP values, decreases in EC cause a decrease in hydraulic conductivity due to swelling, at least initially (Sumner, 1993). Where dispersion occurs, decreases in hydraulic conductivity are more marked than when swelling predominates (Shainberg and Lety, 1984).

The decrease in hydraulic conductivity due to decreased EC in Na-dominated soils has been shown to occur in many soils by many authors (e.g. Quirk and Schofield, 1955; McNeal and Coleman, 1966; McNeal *et al.*, 1968; Chen and Banin, 1975; Pupisky and Shainberg, 1979; Shainberg *et al.*, 1980; Abu-Sharar *et al.*, 1987; Keren and Singer, 1988; Levy *et al.*, 1988; Curtin *et al.*, 1994). For example, the effect of lowering the EC of leaching solutions, in a soil pre-leached with high concentration (1.0 M) NaCl solution, on soil hydraulic conductivity is shown in Fig 2.9. Decreasing the EC has the effect of causing a greater decrease in hydraulic conductivity of the soil.

The effects of exchangeable K^+ on hydraulic conductivity has received considerably less attention than that of Na^+. The findings of previous reports on the effect of exchangeable K^+ on hydraulic conductivity is debatable because results often vary or conflict, possibly due to differences in clay mineralogy and sample preparation techniques (Levy & van der Watt, 1990). For example, some workers (e.g. Ahmed *et al.,* 1969) have shown that K^+ behaves similarly to Na^+ with respect to decreases in hydraulic conductivities whereas others (Reeve *et al.,* 1954; Quirk & Schofield, 1955; Brooks *et al.,* 1956; Gardner *et al.,* 1959; Chen *et al.,* 1983; Levy & van der Watt, 1990) suggest that relative to Ca^{2+} and Na^+, exchangeable K^+ had an intermediate effect on decreases in hydraulic conductivities. In addition, some reports (e.g. Ravina, 1973) indicate that K^+ saturated soils result in larger aggregates with greater stability than those saturated with divalent cations suggesting that K^+ on the exchange sites may increase the hydraulic conductivity of the soil. Ravina and Markus (1975) reported that K^+ saturated soil had positive effects with respect to infiltration rate compared to natural soil dominated by Ca^{2+}.

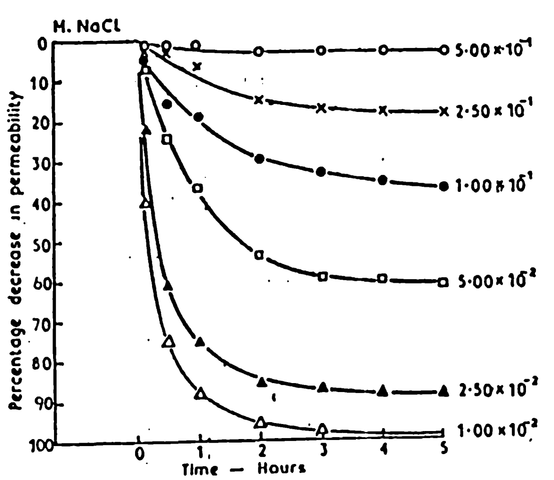

Fig. 2.9 Decrease in permeability for soil leached with decreasing concentrations of NaCl after being initially leached with 1.0 M NaCl solution (Quirk and Schofield, 1955).

2.5.4 The effect of pH on hydraulic conductivity

The pH of the soil environment can also affect hydraulic conductivity and clay dispersion of Na^+ saturated soils. Previous studies have generally shown that increasing the soil pH decreases the hydraulic conductivity of the soil (Suarez *et al.*, 1984; Chiang *et al.*, 1987). Suarez *et al.* (1984) found that montmorillonitic and kaolinitic soil were more sensitive to pH changes compared to a vermiculitic soil and that all decreases in hydraulic conductivity were non-reversible when high EC solutions were introduced. Clay dispersion was measured and found to increase with increasing pH and was therefore attributed as the major mechanism of hydraulic conductivity reduction with increasing soil pH (Suarez *et al.*, 1984). Other authors (Gupta *et al.*, 1984; Chorom *et al.*, 1994) have also measured increased clay dispersion with increasing soil pH. In contrast to the results of these studies, Frenkel *et al.* (1992) reported that the hydraulic conductivity of pure kaolinite-sand mixtures actually increased when leached with 0.001 M NaOH, despite measuring significant dispersed clay in the leachate. Varying the pH of the solutions (but keeping the Na^+ content the same) resulted in decreased dispersion of clay when pH was lowered from pH 11.0 to 10, and the solutions having lowest pH (8.2 and 7.2) had no measurable dispersed clay in the leachate.

The effect of anions on clay swelling, dispersion, and hydraulic conductivity has received little attention in the literature (Frenkel *et al.*, 1992). Shanmuganathan and Oades (1983) reported that, in a kaolinitic soil, clay dispersion increased in the presence of several organic and inorganic anions. The CFC of Na-montmorillonite clay increased five to six times with the addition of anions to suspensions and that of Na-kaolinite increased by an order of magnitude (Frenkel *et al.*, 1992).

Very little work appears to have been conducted on the effect of influent solution pH on hydraulic conductivity of soils. Nakagawa and Ishiguro (1994) investigated the effects of Na-based influent solutions with different pH on hydraulic conductivity in an allophanic soil (organic carbon content of 1.16%) and found that both low and high pH (3 and 11) influent solutions resulted in dramatic decreases in hydraulic conductivity. They attributed this decrease to clay dispersion and aggregate collapse in the upper 1 mm layer of the soil. The shape of the curves for the decrease in hydraulic conductivity appear to be logarithmic in nature (Fig. 2.10)

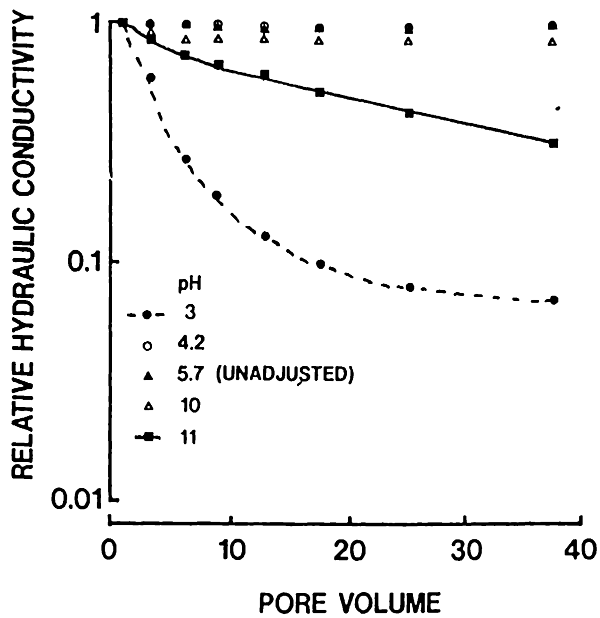

Fig. 2.10 The effect of influent solution pH on relative hydraulic conductivity in an Allophanic soil (Nakagawa and Ishiguro, 1993).

2.6 Conclusions

The effect that high pH solutions *per se* have on soil chemical and physical properties appears to have received little attention in the literature. A large amount of information exists on the effects that monovalent cations have on soil physical properties and their chemical reactions on exchange surfaces within the soil are relatively well-understood. However, the combination of high pH and high monovalent cation concentration solutions in the soil environment has not directly been researched, particularly using concentrations and pH values typically found in high pH liquid wastes from industrial sources. Several conclusions can be made from the available literature:

- attempts have been made to characterise high pH liquid wastes from a variety of industrial sources. Precise compositions are often difficult to establish due to a wide variety of reasons (e.g. daily and seasonal variations, the site-specific nature of the liquid wastes, and industry confidentiality).

- the effect of land treatment of high pH liquid wastes on soil properties and groundwater quality has been studied at some sites in New Zealand. However, very few researchers have investigated the chemical and physical processes involved which have led to the observed findings.

- many studies have investigated monovalent-divalent (particularly Na^+-Ca^{2+}) cation exchange reactions in soils and pure clay systems. A majority of these studies used soils from arid areas (which usually have low organic matter contents) where Na^+ is a problem due to the accumulation of soluble Na-salts or the use of high Na^+ concentration irrigation waters. However, the effect that anions have on cation exchange reactions has received limited attention.

- alkali solutions (particularly NaOH) have been used for many years to dissolve organic matter from soils for characterisation purposes. However, the nature of the extracting solution and the effect of hydroxide concentration on organic matter extraction appears to debatable as results often conflict (due to experimental differences). The effect of KOH on organic matter extraction does not appear to have been investigated. The importance of organic matter in the soil environment is well understood and its functions are many and varied.

- many workers have investigated the effects of swelling and dispersion on water movement in soils and the results can often be predicted and explained by diffuse double layer theory. However, the effects of K^+ on hydraulic conductivity are debatable as results often vary. The effect of anions, in particular hydroxide (and therefore solution pH), present in the infiltrating solution on water movement in soils has received very little attention.

The review of available literature has shown that studies on the effects of solutions with high monovalent cation concentrations and high pH, (using concentrations and pH values typically found in industrial liquid wastes) on physical and chemical properties of soils appear to be limited. Many studies which have been reviewed in this chapter have obvious relevance to the present study but the study of high monovalent cation concentrations in high pH environments in the soil system appears to be lacking. This study, therefore, attempts to address some of the aspects not covered by previous researchers.

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Chapter 3
Soils and Methods

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Soils and Methods

3.1 Introduction

This chapter describes the characteristics of the soils and methodologies used in the study. The soils had contrasting clay mineralogies and represented a range of other soil characteristics. Only the topsoil (A horizons, generally 0-10 cm depth) of each soil type was sampled and used in the experiments. The 0-10 cm sampling depth was chosen because structural deterioration had previously been observed in the surface horizons of soils spray irrigated with high pH liquid wastes and the effects of the high pH solutions would have the greatest effects in this depth range. Three of the soils (Horotiu silt loam, Manawatu silt loam, and Wairua silty clay) were chosen because they are currently used for spray irrigation of high pH dairy factory liquid wastes in North Island, New Zealand. The Hopai silty clay was chosen to include a soil with significant amounts of smectitic clay minerals, to investigate whether it behaved differently with high pH solutions than the other soils which contained different clay mineralogies.

3.2 Soil types

3.2.1 Horotiu silt loam

Horotiu silt loam is a free draining soil found in the Waikato Basin and is formed from rhyolitic volcanic alluvium deposited by the Waikato river. It was chosen because it is dominated by the short range order (SRO) clay mineral allophane (Singleton, 1991) and because it is currently used for land treatment of high pH dairy factory liquid wastes by the Hautapu Dairy Factory near Cambridge. The important features of Horotiu silt loam are a low bulk density, relatively low cation exchange capacity (CEC) at field pH, and dominance of allophane in the clay fraction (Table 3.1). The sampling site for the soil used in this study was from the HortResearch experimental station on Blands Estate approximately 5 km south of Hamilton.

3.2.2 Manawatu silt loam

Manawatu silt loam is a moderately free draining soil found on both the eastern and western sides of the Tararua Range (i.e. in Wairarapa and Manawatu). This soil forms from river alluvium derived from greywacke and calcareous mudstone deposited by the Mangatainoka and Manawatu Rivers. Manawatu silt loam is used for land treatment of high pH dairy factory liquid wastes by The Tui Dairy Factory, near Pahiatua in Wairarapa (G. Shepherd, pers comm.) and was sampled from their spray irrigation farm at a site which has never been spray irrigated with high pH liquid wastes. The important features of Manawatu silt loam is its relatively high bulk density compared to the other three soil types used in this study, and the presence of significant amounts of chlorite in the clay fraction (Table 3.1).

3.2.3 Wairua silty clay

Wairua silty clay is a very poorly drained soil found in low lying areas surrounding Hikurangi township just north of Whangarei and is formed from alluvium/colluvium derived from surrounding basaltic scoria cones (Sutherland *et al.*, 1981). The soil is used for land treatment of high pH dairy factory liquid wastes by The Northland Dairy Company, based at Kauri. Wairua silty clay was also chosen because surface sealing problems had been observed in this soil prior to the instigation of this project and a large area of land had recently been purchased by The Northland Dairy Company for further spray irrigation purposes which had Wairua silty clay as one of the dominant soil types. The sampling site was a site which had never been spray irrigated with any high pH liquid wastes and was adjacent to those currently spray irrigated by The Northland Dairy Company. The important features of Wairua silty clay soil are the drainage status and the high proportion of kaolinite and vermiculite in the clay fraction (Table 3.1). The soil is very prone to swelling and shrinking depending on the moisture status of the soil, therefore in summer months large surface cracks exist whereas in winter months these disappear. The swelling nature of Wairua silty clay also affects the nature of the surface crust (shown previously in Fig. 1.1) which develops in Wairua silty clay at the Kauri site. In winter months the crust is very soft whereas in summer months the crust becomes extremely hard and dense.

3.2.4 Hopai silty clay

Hopai silty clay is a poorly drained soil found on the lower terraces adjacent to the Piako River and Awaiti Canal on the Hauraki Plains and is formed from clayey estuarine-alluvial sediments (McLeod, 1992). As mentioned above, this is the only soil chosen for this study which is not currently being irrigated with high pH liquid wastes, but was chosen as it was known or suspected to contain significant amounts of smectitic (mainly montmorillonite) clay minerals in the topsoil. The sampling site was the same location sampled by DSIR Land Resources during their study of the soils of the Hauraki Plains (see McLeod, 1992). The important features of Hopai silty clay are the presence of smectite clay minerals, relatively high organic carbon, and high CEC values both at field pH and pH 7.0 (Table 3.1).

3.3 Methods of soil analysis

3.3.1 Particle size analysis

Particle size analysis (PSA) is a measure of the size distribution of the individual particles in a soil sample. PSA was only determined on the Wairua silty clay as data was available for the other three soils from various sources (i.e. DSIR Land Resources Lab No. SB 09640; G. Shepherd pers comm.; Kendall, 1991 - DSIR Land Resources Lab No. SB 9944).

The pipette method (Gee and Bauder, 1986; Lewis, 1984) was used for PSA of Wairua silty clay using 50 g air-dry soil which had been treated with 100 ml 20% hydrogen peroxide (H_2O_2) to oxidise organic matter and dispersed with 30 mL 5% sodium hexametaphosphate (Calgon). The sand fraction was analysed using a nest of sieves comprising of 600, 250, and 63 µm aperture sieves, the mass retained on each sieve calculated.

3.3.2 Clay mineralogy

The clay mineralogies of all soil types (except Horotiu silt loam) were determined using X-ray diffraction (XRD) and differential thermal analysis (DTA) techniques on the <2 µm size fraction. The clay mineralogy data for Horotiu silt loam has been published elsewhere (Whitton and Percival, 1991). The three other soils were analysed either at The University of Waikato or Landcare Research-Manaaki Whenua (Palmerston North). The XRD machine used at The University of Waikato was a Philips PW 1840 x-ray diffractometer with the following settings:

voltage = 35 kV
current = 30 mA
chart speed = 10 mm min^{-1}
range = 5 x 10^3
slit width = 0.2 mm
time constant = 1 s

XRD samples were prepared according to the methods outlined in Whitton and Churchman (1987) and Hume and Nelson (1982) using both drop-on-glass-slide and smear-on-glass-slide techniques for oriented mounts. Whole soil analyses as well as analyses of the clay fraction were completed. The clay sample slides were subjected to different treatments (K^+ saturation, Mg^{2+} saturation, glycolation, and heat) to enable more accurate determination of clay minerals present. Dried clay powder samples were used for DTA analysis. DTA analysis was used to obtain semi-quantitative amounts of 1:1 clay minerals (i.e. kandite = kaolinite + halloysite) and gibbsite present. Semi-quantitative analyses were conducted using the XRD traces to estimate the proportions of the other clay minerals present in each sample according to the methods presented by Whitton and Churchman (1987).

3.3.3 Exchangeable cations and cation exchange capacity

A variety of methods are available for measuring exchangeable cations and cation exchange capacity (CEC) depending on the end use for the data. The most commonly used method is the ammonium acetate (1 M) method buffered at pH 7. Methods which use buffered salts have the advantage that comparisons can be made between soils but they do not give an accurate representation of the chemical status of the soil at its true field pH. For this reason, several methods have been developed which measure the exchangeable cations and CEC of the soil at its natural pH using unbuffered salts, such as silver thiourea (AgTU) (Gillman, 1979; Pleysier and Juo, 1980), ammonium chloride (Shuman and Duncan, 1990), and barium chloride (Hendershot and Duquette, 1986).

The method used in this study was the unbuffered AgTU method (Blakemore *et al.*, 1987) because some of the treatment solutions (i.e. the high pH hydroxide solutions) used in Chapter 6 had effects on the CEC of the soils and an unbuffered measure of exchangeable cations and CEC was required to examine the true chemical status of the soil after the different treatments. The AgTU complex is a very efficient exchanger of cations on clay surfaces, and exchange takes place at low ionic strength ($I = 0.01$ M), similar to that of many soil solutions (Edmeades, 1983). The CEC of the soil is calculated by difference between the amount of Ag^+ in the equilibrated solution and the amount initially added. Pleysier and Juo (1980) recommend this method for routine use on tropical soils and Searle (1986) evaluated the method on a range of New Zealand soils and found it to be in agreement to the ammonium acetate method. The details of the AgTU method are presented in Chapter 6. CEC data using the buffered ammonium acetate method were also available for some of the soils and are included in Table 3.1 for comparison purposes.

3.3.4 Soil pH

Soil pH was measured according to Blakemore *et al.* (1987) using 10 g air-dry (<2 mm) and 25 mL distilled water. The soil and water were stirred vigorously and left to stand overnight and pH measurements were taken by placing the pH electrode into the clear supernatant solution.

3.3.5 Soil organic carbon

A slight variation of the Modified Mebius Method (Nelson and Sommers, 1982), using potassium dichromate digestion, was used for organic carbon analysis. Details of the method are presented in Chapter 4.

3.3.6 Aggregate stability

The stability of soil aggregates was measured using a slight variation of the method presented by Kemper and Rosenau (1986) and is discussed in detail in Chapter 5. The method is a wet sieving technique and the data obtained expresses aggregate stabilities as mean weight diameters (MWD) (Chaney and Swift, 1984). A higher value (maximum is 300) represents more stable aggregates than lower values.

3.3.7 Bulk density

Soil bulk density was measured by carefully inserting brass cores (4.5 cm internal diameter x 3.5 cm long) into the surface of the soil. The cores were then extracted from the soil, vegetation and excess soil trimmed off each core, and plastic plates were placed on the ends of the cores (to prevent soil loss during transportation) prior to the cores being wrapped in plastic.

3.3.8 Profile descriptions

Profile descriptions were recorded for two of the soils, Wairua silty clay and Manawatu silt loam. Profile descriptions of the other two soils have been reported by other workers (Hopai silty clay: McLeod, 1992; Horotiu silt loam: Singleton, 1991) and are included for comparison. Procedures and terms used are according to those presented by Milne *et al.* (1991). Soil classification is according to Hewitt (1992) for the New Zealand Classification System and according to Soil Survey Staff (1994) for US Taxonomy Classification.

3.4 Soil characteristics

3.4.1 Selected physical and chemical properties

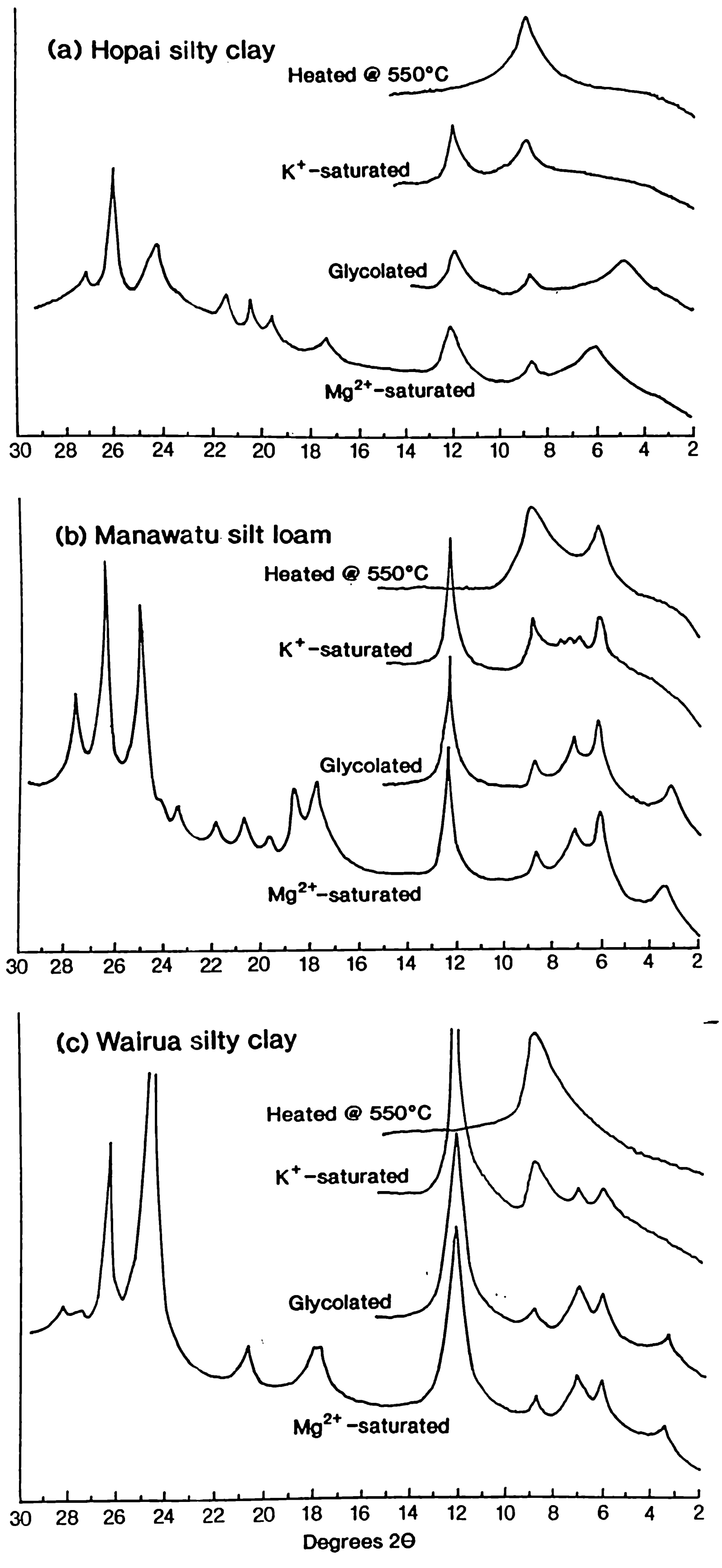
The results of selected physical and chemical properties of all four soil types are presented in Table 3.1. The XRD traces for Hopai silty clay, Manawatu silt loam, and Wairua silty clay after different treatments are presented in Fig. 3.1a-c. The ratings used (indicated in parentheses in Table 3.1) for chemical properties are according Blakemore *et al.* (1987). Ratings for bulk density are from Taylor and Pohlen (1979), and ratings for clay, silt, and sand abundance are from Singleton (1991). Note that the some of the data presented and profile descriptions are from other sources. Information on Hopai silty clay from McLeod (1992) and M. McLeod (pers comm.); Horotiu silt loam from Singleton (1991), P. L. Singleton (pers comm.), and T. Livingston (pers comm.); and Manawatu silt loam from G. Shepherd (pers comm.).

Table 3.1 Summary of selected physical and chemical properties of Hopai silty clay; Horotiu silt loam; Manawatu silt loam; and Wairua silty clay.

Parameter		Hopai silty clay	Horotiu silt loam	Manawatu silt loam	Wairua silty clay
pH[1] (H_2O)		5.6 (mod. acid)	5.1 (strongly acid)	5.6 (mod. acid)	5.2 (strongly acid)
Organic carbon (%)		9.2 (medium)	7.9 (medium)	4.9 (medium)	4.2 (medium)
CEC[2] ($cmol_c\ kg^{-1}$)		38.7 (high)	28.2 (high)	20.0 (medium)	32.2 (high)
Base saturation (%)		62 (high)	49 (medium)	-	80 (v. high)
CEC[3] ($cmol_c\ kg^{-1}$)		22.0	6.0	14.0	16.0
Bulk density ($Mg\ m^{-3}$)		0.85 (medium)	0.85 (medium)	1.12 (medium)	0.90 (medium)
Dominant minerals in the clay[4] fraction (<2 μm)		M - 48% I - 25% K - 8% C - 7% V - 5% Q - 5%	A - 80% K - 8%	I - 20% V - 20% C - 18% I-M - 10% I-V - 10% Q - 9% F - 6% K - 5%	K - 31% V - 20% I - 15% I-M - 12% I-V - 10% Q - 8%
PSA	% clay	55 (high)	20 (mod)	32 (mod)	38 (mod high)
	% silt	34 (mod)	50 (high)	50 (high)	51 (high)
	% sand	11 (mod low)	30 (mod)	18 (mod low)	11 (mod low)
WSA[5]		251	285	-	285

[1] soil:water = 1:2.5
[2] ammonium acetate (pH 7.0) buffered method
[3] unbuffered silver thiourea method
[4] XRD (see Fig 3.1 a-c) and DTA: minerals - M=montmorillonite; I=illite (mica); C=chlorite; K=kandite (kaolinite+halloysite); V=vermiculite; Q=quartz; A=allophane; F=feldspars
[5] water stable aggregates expressed as mean weight diameters (MWD) (minimum=0, maximum=300)

Fig. 3.1 X-ray diffraction traces for three soils: a) Hopai silty clay; b) Manawatu silt loam; and c) Wairua silty clay. The traces produced after different treatments (Mg^{2+}-saturated, glycolated, K^{+}-saturated, and heated @ 550°C for 1 h) are shown for each soil type.


(a) Hopai silty clay
Heated @ 550°C
K⁺-saturated
Glycolated
Mg²⁺-saturated
30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
(b) Manawatu silt loam
Heated @ 550°C
K⁺-saturated
Glycolated
Mg²⁺-saturated
30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
(c) Wairua silty clay
Heated @ 550°C
K⁺-saturated
Glycolated
Mg²⁺-saturated
30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
Degrees 2Θ

3.4.2 Profile descriptions

Soil type: **Hopai silty clay** (see Fig. 3.2)
Location: Near Wani Rd., Hauraki Plains
Grid reference: NZMS 260 T13 394233 (from NZMS 1 N53 084985)
Altitude: 5 m
Slope: 0-5°
Aspect: N/A
Topography: on alluvial flats, about 500 m from stop-bank
Drainage: poorly drained
Rainfall: 1200 mm
Temperature: annual average of 14°C
Vegetation: - past: kahikatea bush, manuka, and flax
- present: ryegrass/clover
Land use: grazing dairy cattle
Parent material: estuarine-alluvial sediment
Classification: NZ - Acidic Orthic Gley Soil
USDA - Aeric Fluvaquent

Ap 0-8 cm	Brownish black (10YR 3/1) silty clay, moderately weak, brittle, non-sticky, strong medium granular, many fine roots, distinct irregular boundary.
Bw 8-16 cm	Dull yellowish brown (10YR 6/3) silt loam with few distinct yellowish brown (10YR 5/6) mottles and few thin grayish yellow brown (10YR 4/2) coats on ped faces, some Ap movement down cracks, moderately weak, brittle, slightly sticky, very plastic, few fine pores, strong fine nut, many fine roots, distinct irregular boundary.
Bg1 16-36 cm	Olive yellow (5Y 6/3) clay with many distinct bright brown (7.5YR 5/6) to brown (7.5YR 4/6) mottles, some Ap down cracks, moderately firm, brittle, slightly sticky, very plastic, many fine and few medium pores, strong medium prismatic, few roots, indistinct wavy boundary.
Bg2 36-63 cm	Olive yellow (5Y 6/3) clay with many distinct elongated (vertical) yellowish brown (10YR 5/6) mottles, thin brown

	(10YR 4/4) coatings on ped faces, few manganese flakes, moderately weak, brittle to semi-deformable, moderately sticky, very plastic, many fine and medium pores, strong medium prismatic, few fine roots, indistinct wavy boundary.
Bg3 63-86 cm	Olive yellow (5Y 6/3) clay with many distinct yellowish brown (10YR 5/6) to bright brow (7.5YR 5/6) and few reddish brown (5YR 4/6) mottles, many thin dull yellowish brown (10YR 5/3) to grayish yellow brown (10YR 5/2) coats on ped faces, moderately weak, semi-deformable, slightly sticky, very plastic, many fine and medium pores, weak medium prismatic breaking to fine and medium blocks, few fine roots, indistinct irregular boundary.
Cg 86-109+ cm	Dull yellow (2.5Y 6/3) clay with abundant distinct medium reddish brown (5YR 4/6) to brown (7.5YR 4/6) mottles, moderately weak, semi-deformable, moderately sticky, very plastic, many coarse pores, weakly developed medium prismatic breaking to strong medium and fine block, few fine roots.

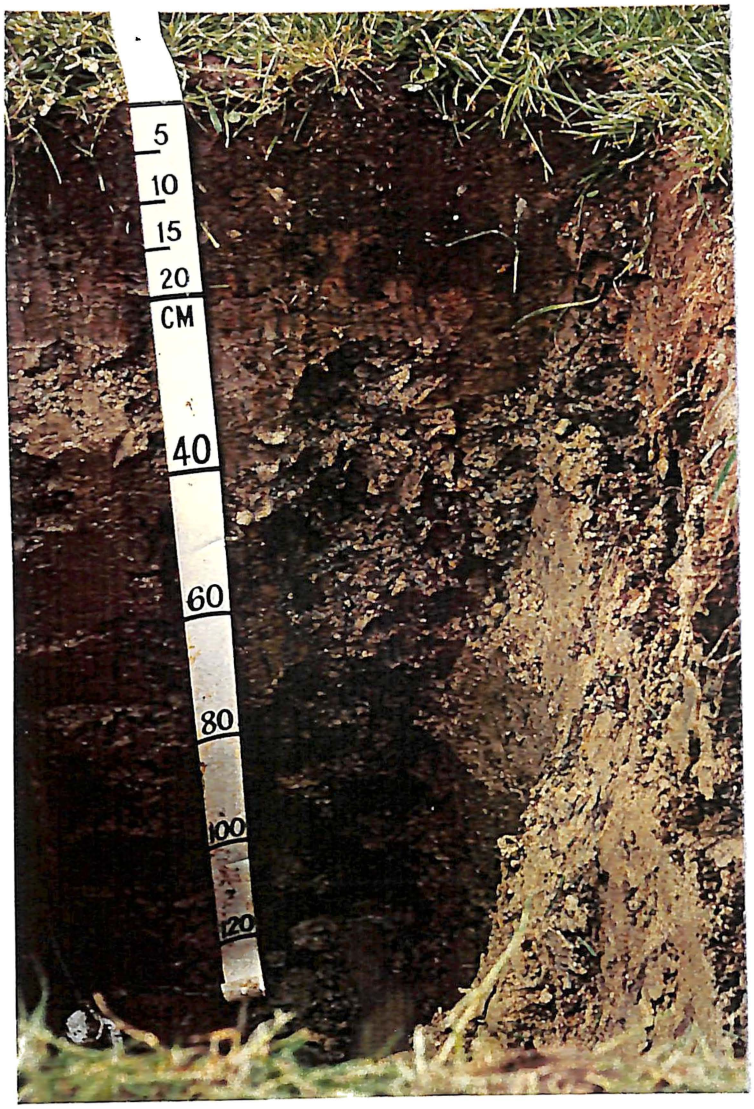


Fig. 3.2 Profile of Hopai silty clay soil.

Soil type: **Manawatu silt loam** (see Fig. 3.3)

Location: 500 m from State Highway 2, approximately 2 km south of Pahiatua township

Grid reference: NZMS 260 T24 490784

Altitude: 125 m

Slope: 0-5°

Aspect: N/A

Topography: flat, river terrace (approx. 250 m from Mangatainoka River)

Drainage: moderately well drained (water table >65 cm depth)

Rainfall: 1200 mm

Temperature: average annual of 11°C

Vegetation: - past: mixed broadleaf-podocarp
- present: ryegrass/clover

Land use: grazing for dairying

Parent material: river alluvium

Classification: NZ - Mottled Fluvial Recent Soil
USDA - Aquic Dystric Eutrochrept

Ap 0-10 cm	Dull yellowish brown (10YR 5/3) silt loam, firm, non-sticky, non plastic, well developed coarse blocky, many roots, boundary indistinct.
AB 10-25 cm	Dull yellowish brown (10YR 5/4) silt loam, firm, slightly sticky, slightly plastic, moderately developed medium to coarse block, some roots, indistinct boundary.
Bw(f) 25-65 cm	Dull yellowish brown (10YR 6/4) silty clay loam with some bright yellowish brown (10YR 6/8) mottles, firm, sticky, plastic, moderately developed medium to coarse blocky, few roots

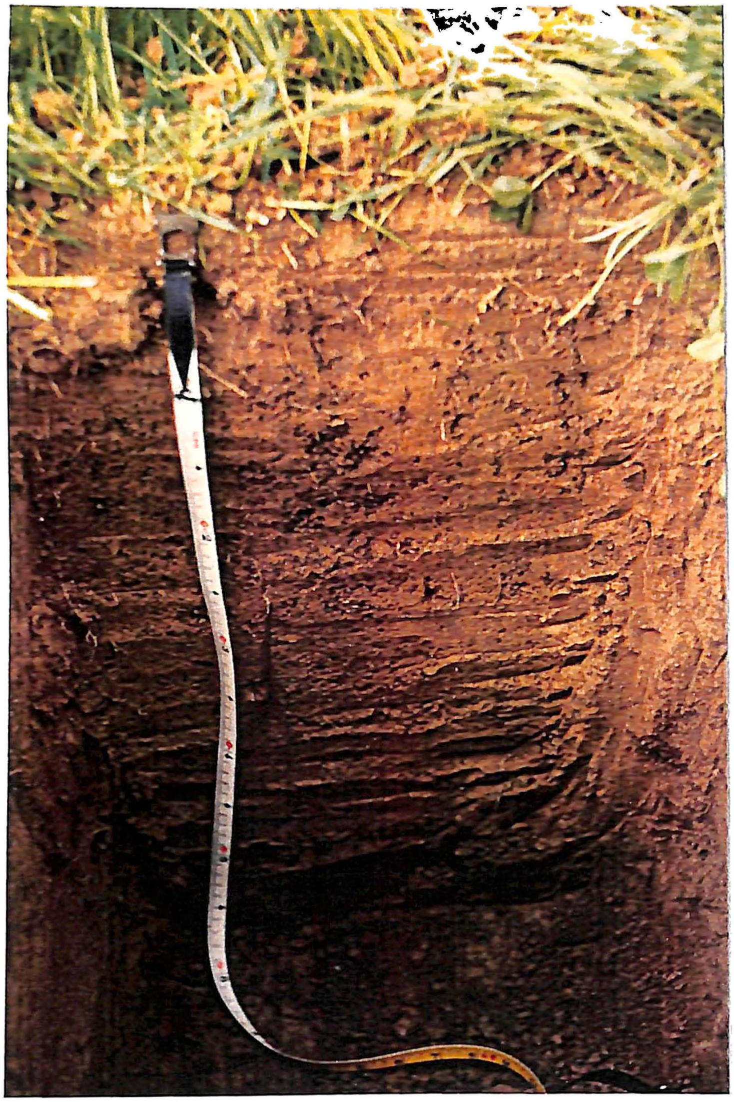


Fig. 3.3 Profile of Manawatu silt loam soil.

Soil type: **Wairua silty clay** (see Fig. 3.4)
Location: 800 m from Jordan Valley Rd.
Grid Reference: NZMS 260 Q06 253205
Altitude: 90 m
Slope: 0-5°
Aspect: N/A
Topography: flats between basalt flows
Drainage: poorly drained, extensive drainage system installed, water table at 90 cm.
Rainfall: 1650 mm per year.
Temperature: annual average of 19°C
Vegetation: - present: rye-grass/clover
- past: broadleaf podocarp
Land use: dairying.
Parent material: alluvium/colluvium
Classification: NZ - Typic Perch-gley Ultic Soil
USDA - Aeric Endoaquult

Ap 0-10 cm	Dull yellowish brown (10YR 4/3) silt loam, firm, slightly sticky, slightly plastic, moderately developed medium nut breaking to medium crumb, many worms and many roots, distinct smooth boundary.
ABg 10-20 cm	Dull yellowish brown (10YR 5/4) silt loam with many small distinct reddish brown (5YR 4/6) mottles, firm, plastic, slightly sticky, moderately developed medium blocky breaking to medium granular, many roots, distinct smooth boundary.
Bg1 10-80 cm	Dull yellow (2.5Y 6/3) clay loam with many distinct large orange (7.5YR 7/6) mottles. Moderately developed coarse blocky breaking to coarse granular structure. Very firm, very plastic, very sticky. Some roots with fungus. Boundary diffuse.
Bg2 80-90 cm	Light grey (2.5Y 8/2) clay with profuse distinct large orange (7.5YR 8/6) mottles. Weakly developed coarse blocky breaking to fine blocky structure. Very firm, very plastic, very sticky. Few roots. Water table at 90 cm depth.
90-200 cm	Auger samples: same as above (Bg2)

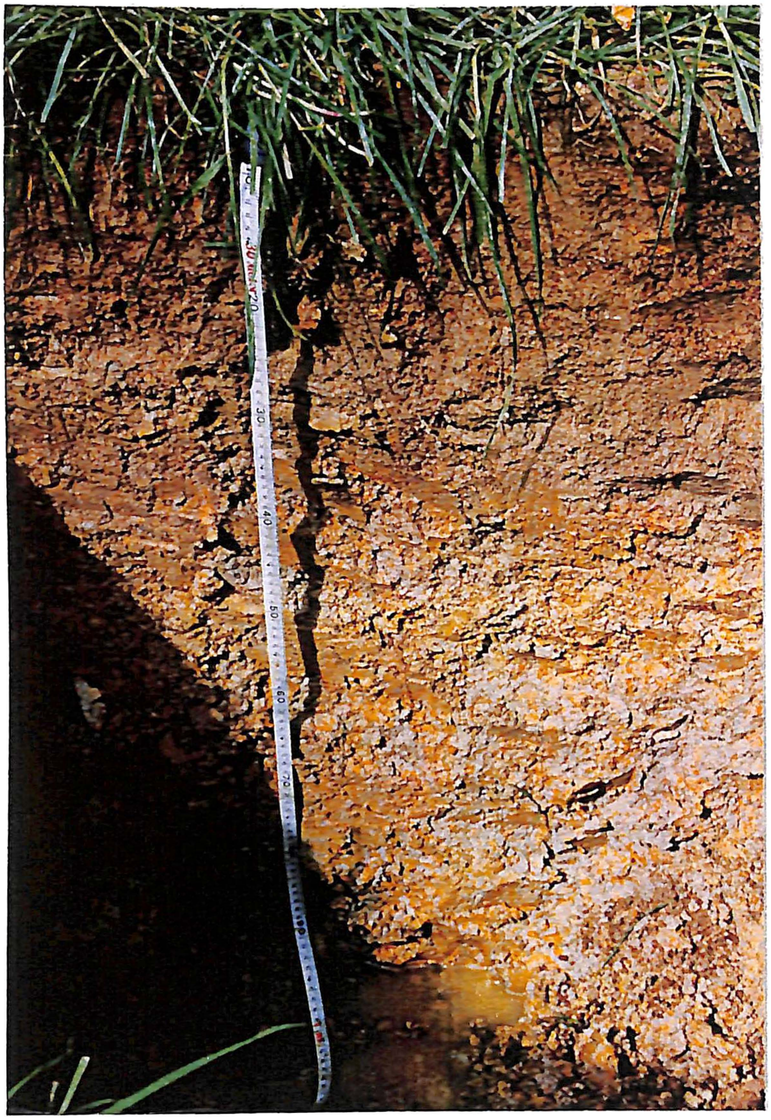


Fig. 3.4 Profile of Wairua silty clay soil.

Soil type: **Horotiu silt loam** (see Fig. 3.5)

Location: 30 m from State Highway 3 on Bland Estate (HortResearch experimental station)

Grid reference: NZMS 260 S15 145689

Altitude: 55 m

Slope: 0-5°

Aspect: N/A

Topography: on levee part of aggradational terrace formed by the Waikato River

Drainage: moderately to well drained

Rainfall: 1200 mm

Temperature: annual average of 13°C

Vegetation: - past: manuka scrub and bracken fern
- present: ryegrass/clover since 1976

Land use: grazing for dairying

Parent material: rhyolitic alluvium (Hinuera Formation)

Classification: NZ - Typic Orthic Allophanic Soil
USDA - Vitric Hapludand

Ap 0-17 cm	Brownish black (7.5YR 3/2) silt loam, slightly sticky, slightly plastic, very friable, weakly developed fine to medium granular, some quartz grains (<1 mm), allophanic, many roots, distinct wavy boundary.
Bw 17-51 cm	Bright brown (7.5YR 5/6 sandy loam, slightly sticky, slightly plastic, weakly developed v. fine to medium crumb, some quartz grains, black nodules in upper half of horizon, moderately to strongly allophanic, some roots, indistinct boundary.
BC 51-72 cm	Brown (10YR 4/6) loamy sand, very friable, slightly sticky, slightly plastic, apedal single grained, weak to moderate allophanic, distinct wavy boundary.
C 72 cm+	Dull yellow (2.5Y 6/4) sand, non-sticky, non-plastic, loose apeadal single grained, poorly sorted pumice and gravel and sand, weak to moderately allophanic.

Fig. 3.5 Profile of Horotiu silt loam soil.

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Chapter 4
Organic Carbon Dissolution

Chapter 4
Organic carbon dissolution

4.1 Introduction

A search of the available literature (Chapter 2) revealed that alkali solutions have been used for many years as extraction solutions for the purpose of characterisation of organic matter in soils. A series of laboratory experiments were conducted to quantify the effects that NaOH and KOH solutions have on organic carbon dissolution in a range of New Zealand soils.

The following pages are a copy of the manuscript entitled "The effect of hydroxide solutions on organic carbon dissolution in some New Zealand soils" which was published in *Australian Journal of Soil Research* 1995 **33** (5) 873-881. The manuscript has been slightly reformatted (reference style and figure and table positions) from the original manuscript to maintain consistency throughout this thesis. A reprint of the manuscript is enclosed in the pocket at the end of this thesis.

The reader is referred to Appendix A: Supplementary information and data for Chapter 4, for additional information and photographs pertaining to the experiments conducted for this manuscript.

The Effect of Hydroxide Solutions on Dissolution of Organic Carbon in Some New Zealand Soils

Abstract

The disposal of high pH, hydroxide based, liquid wastes using land treatment systems is becoming increasingly common in New Zealand. For effective disposal of high pH liquid wastes to land, it is necessary to understand the effects of different hydroxide based solutions on organic carbon dissolution to ensure soil physical properties are not adversely affected. Single-step and multi-step extraction experiments were designed to investigate the effect of high pH solutions on organic carbon dissolution in four New Zealand soils. In the single-step extraction experiments soil was shaken with varying concentrations of NaOH and KOH (0.003, 0.01, 0.03, 0.1, and 0.3 M) at a 1:5 soil to solution ratio for 18 h. Organic carbon dissolution occurred at very low concentrations and increased linearly with hydroxide concentration, with up to 45% of the total initial organic carbon dissolved when 0.3 M NaOH was used. KOH dissolved slightly less organic carbon than NaOH, indicating that a cation difference occurred. When the anion was changed to chloride, the amount of organic carbon dissolved was very small (<2% of total initial organic carbon) for all concentrations, indicating that the hydroxide anion was most important in causing organic carbon dissolution. Multi-step experiments involved repeatedly shaking soil with fresh hydroxide extracting solutions, and showed that the difference between NaOH and KOH in dissolving organic carbon decreased as the number of extractions increased. The cumulative amount of organic carbon dissolved increased from c. 45% after a single-step extraction to c. 75% after 5 extractions. Organic carbon dissolution with different solutions tended to be higher in an allophanic soil, but similar in soils dominated by phyllosilicate clay minerals. The results indicate that factors such as the chemical composition of the liquid waste and soil type need to be considered prior to land disposal to prevent adverse effects on soil physical properties.

Introduction

Hydroxide solutions, especially sodium hydroxide, are widely used as cleaning agents in many industries. Land treatment of the high pH liquid wastes, usually by spray irrigation, is becoming an increasingly common method of disposal in New Zealand. The chemical nature of these wastes is usually highly variable (Marshall, 1975) and site specific, but are often characterised by high pH (>pH 10) and high sodium concentrations (Keeley and Quin, 1979; Barnett *et al.*, 1994). It is often difficult to obtain information on the nature of high pH wastes and their effects on soil properties due to industry confidentiality. Keeley and Quin (1979) reported that soil pH and exchangeable sodium increased following spray irrigation of high pH fellmongery wastes from meat processing factories and Barnett and Parkin (1985) reported similar trends for soils having received high pH dairy factory wastewaters. However, few other reports on the effect high pH liquid wastes have on soil properties exist in the literature.

Although alkali solutions have been commonly used to remove, quantify, and characterise soil organic matter in the past (Tinsley and Salam, 1961; Kononova, 1966; Schnitzer and Skinner, 1968; Ortez de Serra and Schnitzer, 1972; Schnitzer and Schuppli, 1989 (a, b)), little information exists in the literature with regards to the relationship between organic carbon (OC) dissolution and the nature of the extracting solution. Levesque and Schnitzer (1966) reported that the amount of OC extracted, using NaOH, from a podzol increased with concentration up to 0.1 M, and thereafter the amount extracted decreased as hydroxide concentration increased. In contrast, Gascho and Stevenson (1968) found that a similar amount of OC was extracted over a range of 0.05-0.5 M NaOH. The effects of cations on the OC dissolution process by hydroxide solutions also appears to have received little attention. The lack of available information makes it difficult to predict the possible effects of high pH liquid wastes on soil OC.

The importance of organic matter for the formation and stability of soil structure is well documented (Tisdall *et al.*, 1978; Tisdall and Oades, 1982; Chaney and Swift, 1984; Oades, 1984; Chaney and Swift, 1986; Wierzchos *et al.*, 1992). If land treatment methods are to be considered a viable option for the disposal of high pH liquid wastes, it is essential that the effects of hydroxide solutions on soil OC are properly understood.

The overall aim of this study, therefore, was to investigate the properties of high pH solutions which affect OC dissolution in soils. The objectives were to: 1) investigate the effect of time of shaking on OC dissolution; 2) determine the relationship between OC dissolution and hydroxide concentration for soils with different mineralogies; and 3) establish whether cation or anion differences affected the amount of OC dissolution.

Materials and Methods

Laboratory experiments were used to minimise technical difficulties which would be involved in conducting field experimentation. The composition of industrial high pH liquid wastes is very site specific and would differ depending on the source of the waste and the level of pretreatment prior to disposal. Therefore, for this study, pure hydroxide solutions were chosen to represent high pH liquid wastes and corresponding chlorides were used for comparison purposes.

Soils

Four New Zealand soils were used: Hopai silty clay, Horotiu silt loam, Wairua silty clay, and Manawatu silt loam. The surface horizons (0-10 cm) were sampled, air-dried, and passed through a 2 mm sieve. Selected properties of the soils used are shown in Table 1. Classification of soils used according to New Zealand Soil Classification (Hewitt, 1992) and USDA Soil Taxonomy (Soil Survey Staff, 1994) were:

Hopai silty clay: Acidic Orthic Gley Soils; Aeric Fluvaquents
Horotiu silt loam: Typic Orthic Allophanic Soils; Vitric Hapludands
Wairua silty clay: Typic Perch-gley Ultic Soils; Aeric Endoaquults
Manawatu silt loam: Mottled Fluvial Recent Soils; Aquic Dystric Eutrochrepts

Table 1. Selected properties of soils used

Parameter	Hopai	Horotiu	Wairua	Manawatu
pH[1] (H_2O)	5.6	5.1	5.2	5.6
Organic carbon (%)	9.2	7.9	4.2	4.9
CEC[2] ($cmol_c$ kg^{-1})	34.5	28.2	32.2	20.0
Bulk density (Mg m^{-3})	0.85	0.85	0.90	1.12
% clay	58	20	38	32
Clay mineralogy[3]	M, K, I	A	K, V, I	I, C, V

[1] soil: water = 1:2.5

[2] Ammonium acetate (pH 7.0)

[3] XRD and DTA; Clay minerals: M, montmorillonite; K, kaolinite; A, allophane; V, vermiculite; C, chlorite; I, illite

Organic Carbon Analyses

Analyses of OC were conducted using a slight variation of the Modified Mebius method (Nelson and Sommers, 1982), which is based on the Walkley-Black (Walkley and Black, 1934) procedure for determining OC. Air-dry (<2 mm) soil (0.5 g) was weighed into 250 mL boiling flasks, 20 mL of 50 g L^{-1} $K_2Cr_2O_7$ was pipetted into each flask and 20 mL concentrated H_2SO_4 was rapidly added, the flasks were then boiled for 30 min with condensers attached to prevent any loss of solution vapour. After boiling, the flasks were allowed to cool for 30 min and about 1 mL indicator solution (0.1 g N-phenylanthranilic acid and 0.107 g Na_2CO_3 dissolved in 100 mL water) was added. The solution plus indicator was then titrated against 0.5 M $Fe(NH_4)_2(SO_4)_2.6H_2O$. Blanks containing no OC were also run to calculate the exact concentration of the ferrous ammonium sulphate solution. Six replicates were conducted on each soil type.

The method used for the dissolved OC in the aliquots of filtered supernatant solution after centrifuging (see below) was similar except that only 10 mL of potassium dichromate solution and 10 mL of sulphuric acid were used.

Effect of Shaking Period on OC Dissolution

To ensure that the maximum amount of OC was dissolved for a single-shake, with any one solution type, an initial experiment using the Horotiu silt loam was conducted where high and low concentrations (0.3 M and 0.003 M) of NaOH were shaken with soil for varying periods of time up to 48 h. A 1:5 soil to solution ratio (5 g soil and 25 mL solution) was shaken for periods of 10, 30, 60, 180, 1080, and 2880 min using an end-over-end shaker. All treatments was replicated in triplicate. After shaking for each time period, the tubes were centrifuged @ 4000 r.p.m. for 10 min. The supernatant was then pressure filtered through 0.45 μm Whatman membrane filters. The filtrate collected was defined as the "dissolved" component of the total solution. Either a 5 mL or 3 mL aliquot, depending on the approximate OC content, was pipetted from the dissolved fraction and OC determined.

Single-step Extraction Experiments

All the soil types were used for single-step extraction experiments. The solutions used were NaOH, KOH, NaCl, KCl, and distilled water. Five concentrations of hydroxide solutions (0.003, 0.01, 0.03, 0.1, and 0.3 M), and two concentrations of chloride solutions (0.003 M and 0.3 M) were shaken with air-dry soil (<2 mm) at a 1:5 soil to solution ratio for 18 h on an end-over-end shaker. The hydroxide concentrations used were selected to span a range of concentrations that caused OC dissolution in the soils used. All treatments were replicated in triplicate. The tubes were then centrifuged, filtered, and an aliquot of the filtered solution was analysed for OC. For the NaCl and KCl solutions, $AgSO_4$ was added to the sulphuric acid (25 g $AgSO_4$ L^{-1} acid) prior to addition into the potassium dichromate solution to prevent Cl^- interference (Walkley, 1947).

Multi-step Extraction Experiments

To determine whether repeated additions of hydroxide solutions affected OC dissolution, a multi-step extraction experiment was conducted on the Horotiu silt loam using high concentrations (0.3 M) of NaOH and KOH. Both treatments were replicated in triplicate. The procedure was similar to the single-step extraction procedure described above where an aliquot of the supernatant, after centrifuging, was used to measure OC. The tube and centrifuged soil was then weighed to calculate the amount of entrained hydroxide solution. Approximately 20 mL of fresh extracting solution was added to re-establish a 1:5 soil to solution ratio. The soil was then mechanically dispersed and shaken for a further 18 h. This procedure was repeated until a total of 5 extractions for each treatment had been made with OC analyses conducted immediately following each 18 hour shaking period.

Results

Initial Organic Carbon Content In Soils

All four soils had medium (i.e. 4-10%) OC contents according to the classification of Blakemore *et al.* (1987) for New Zealand soils (Table 1). The highest OC levels were recorded in the Hopai silty clay and the lowest in the Wairua silty clay.

Effect of Shaking Period

The amount of OC dissolved by NaOH increased logarithmically as the shaking period increased for both the high and low concentrations (Fig. 1). After 18 h (1080 min), the amount of OC dissolved was not significantly different ($P<0.05$) to the amount dissolved after 48 h. However the amount dissolved after 18 h was more ($P<0.05$) than the amount dissolved after shorter time periods. A shaking period of 18 h was therefore used for the experiments reported in this paper.

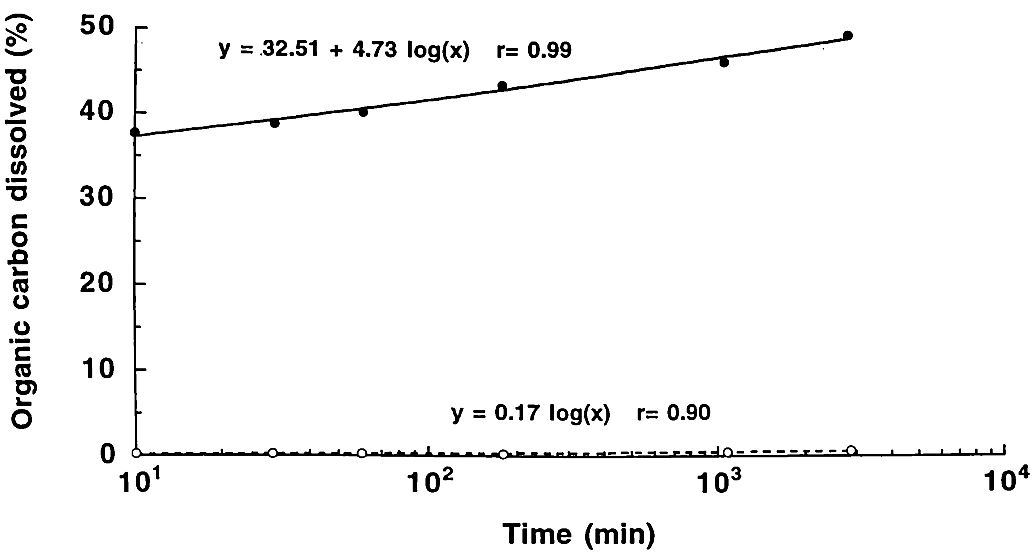

Fig. 1. Effect of shaking period on organic carbon dissolution by 0.3 M (●) and 0.003 M (O) NaOH extracting solutions in a Horotiu silt loam. (N.B. All standard errors of means when plotted appear smaller than symbol)

Single-step Extraction Experiment

Figure 2 shows the amount of OC remaining in each of the four soil types after a shaking period of 18 h versus concentration of hydroxide solution used. In all soils, the amount of OC dissolved by NaOH at any given concentration was generally greater ($P<0.05$) than that dissolved by the same concentration of KOH. The relationship between the amount of OC dissolved and concentration of shaking solution was linear for both NaOH and KOH for all soil types.

A similar amount of OC was dissolved (c. 35% of total initial OC) for the Hopai, Wairua, and Manawatu soils when the highest concentration (0.3 M) of hydroxide was used as the extracting solution. The Horotiu soil had a slightly higher amount (c. 45%) of OC dissolved, at the 0.3 M concentration, compared to the other three soils.

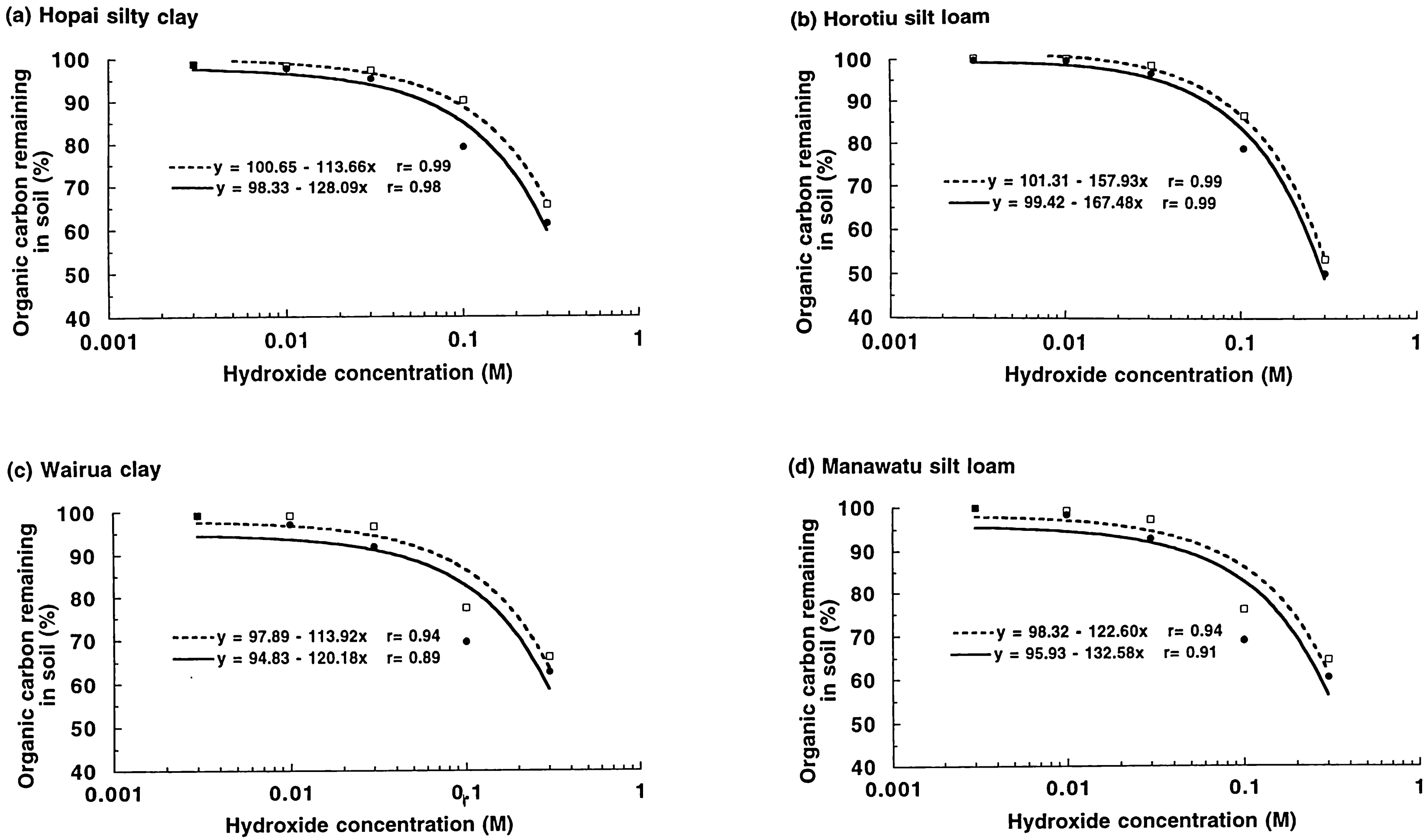

Fig. 2. Effect of hydroxide concentration on organic carbon dissolution using NaOH (●) and KOH (□) on Hopai silty clay (a); Horotiu silt loam (b); Wairua clay (c); and Manawatu silt loam (d). (N.B. All standard errors of means when plotted appear smaller than symbol)

When all the soils were shaken with either NaCl, KCl, or distilled water, only a small a small amount of dissolution, <2% of total initial OC, was recorded (Table 2).

Table 2. Organic carbon dissolved (% total initial organic carbon) by chloride solutions and distilled water.

Soil Type	NaCl		KCl		H_2O
	0.003 M	0.3 M	0.003 M	0.3 M	
Hopai	0.5	0.1	0.3	0.8	0.5
Horotiu	0.6	0.6	0.4	0.4	0.0
Wairua	0.7	1.4	0.5	0.9	0.2
Manawatu	0.6	0.6	0.6	1.6	0.0

Multi-step Extraction

The single-step extraction experiment showed that NaOH dissolved more OC than KOH after 18 h shaking. Multi-step extraction experiments were designed to investigate whether the cation differences were maintained if further extracting solution was added.

The total amount of OC dissolution increased with increasing number of extractions (Table 3). However, the amount of OC dissolved in each extraction decreased as the number of extractions increased for both NaOH and KOH (Table 3). While NaOH caused more (P<0.05) OC dissolution than KOH in the first extraction, OC dissolution was greater (P<0.05) using KOH in the second and third extractions. A similar amount of OC dissolution was recorded using both solutions for the fourth and fifth extractions.

The cumulative effect of these results (Table 3) showed that a similar amount of OC was dissolved using both extracting solutions after the initial difference. Only after the single-step extraction (1 shaking) was there a difference (P<0.05) between NaOH and KOH. However, for extractions 2-5 both hydroxide solutions cumulatively dissolved the same amount of OC. The total cumulative amount of OC dissolved from the Horotiu silt loam after 5 extractions was substantially higher (c. 75% of total initial OC) than the amount dissolved after a single-step extraction (c. 45% of total initial OC).

Table 3. Organic carbon dissolution during multiple extractions using 0.3 M NaOH and KOH on a Horotiu silt loam.

Values represent means of triplicate analyses (± standard error of mean).

Extraction number	Organic carbon dissolved per extraction (mg OC g^{-1} soil)		Cumulative organic carbon dissolved (% of total initial OC)	
	NaOH	KOH	NaOH	KOH
1	36.4 (0.3)	33.4 (0.7)	46.3 (0.4)	42.4 (0.9)
2	13.4 (0.2)	15.9 (0.2)	63.3 (0.3)	62.7 (1.0)
3	5.0 (0.1)	5.6 (0.1)	69.7 (0.3)	69.7 (1.1)
4	2.6 (0.1)	2.6 (0.1)	73.0 (0.3)	73.0 (1.1)
5	1.3 (0.0)	1.3 (0.0)	74.6 (0.3)	74.6 (1.1)

Discussion

The dissolution of OC from soil was mainly affected by the concentration of hydroxide solution used, and to a lesser extent, the shaking period, type of monovalent cation employed, and soil type.

The increase in the amount of OC extracted from the soil that was recorded as the concentration of the hydroxide solutions increased, and the lack of a similar effect when chloride solutions were used, indicates that it is the hydroxide concentration (i.e. solution pH) which was mainly responsible for the dissolution of OC. The mechanism by which hydroxide caused dissolution of organic substances is probably by the conversion of acidic components to water soluble ions (Stevenson, 1982). The linear increase in OC dissolution with concentration observed in this study differs to previously reported studies (Levesque and Schnitzer, 1966; Gascho and Stevenson, 1968), which showed that increasing the concentration of hydroxide did not increase the amount of OC extracted, and indicates that either diluting or neutralising high pH liquid wastes would be advantageous prior to disposal using land treatment methods.

The true chemical nature of high pH liquid wastes is difficult to establish due to the variety of sources, daily and seasonal variation (Marshall, 1975), and industry confidentiality. It is known, however, that many liquid wastes from the meat processing (Keeley and Quin, 1979) and dairy industry (Marshall, 1975; Barnett *et al.*, 1994) have pH values >11 (i.e. hydroxide concentration > 0.001 M) and our observations have indicated that this can be as high as pH 12.5 (i.e. 0.03 M hydroxide). It is likely, therefore, that liquid wastes with hydroxide concentrations in the low to medium range of those used in this study (i.e. 0.003-0.03 M), are commonly spray irrigated onto soils. Although the amount of OC dissolved at these concentrations was fairly low, generally less than 10% of initial OC, it is possible that continual regular application of these wastes would have deleterious effects on soil physical properties, especially at the surface of the soil. Indeed, recent measurements at field-irrigated sites (unpublished data) showed that OC concentrations at the 0-1 cm depth are up to 30% lower than control sites receiving no high pH liquid wastes, causing surface crusting to develop and subsequent water-logging during the winter months.

The slightly higher amount of OC which was dissolved in the Horotiu silt loam (c. 45%) than in the other three soils (c. 35%) when 0.3 M hydroxide solutions were used indicates that allophanic soils may be more susceptible to OC dissolution by high pH solutions than soils dominated by phyllosilicate clay minerals. This may be related to differences in the physico-chemical interactions between organic and mineral phases.

Changing the cation from Na^+ to K^+ in the hydroxide solution did not appear to have any advantage for minimizing OC dissolution in the longer term. However, in the short term (as shown by the single-step extraction experiment), K^+ caused less dissolution than Na^+. Potassium may also be a preferable cation for plant growth.

Dissolution of OC was shown to be time dependent, although some OC dissolution occurred very rapidly (within 10 min), especially at higher hydroxide concentrations. In field situations, spray irrigation usually occurs over a period of many hours which would enable sufficient contact time to effect dissolution. In laboratory experiments it is recommended that a shaking period of at least 18 h be used to measure the effects of hydroxide solutions on OC dissolution.

Direct application of the results presented in this paper to field conditions is limited by the experimental conditions used. However, the increase in OC dissolution which was observed with increased hydroxide concentration and time, and the greater amount of dissolution in an allophanic soil than in soils dominated by phyllosilicate clay minerals, are important factors that should be considered when designing land treatment systems for disposal of high pH liquid wastes.

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Chapter 5
Aggregate Stability and Hydraulic Conductivity

Chapter 5
Aggregate stability and hydraulic conductivity

5.1 Introduction

The results of Chapter 4 showed that hydroxide based solutions dissolve significant amounts of organic matter from soils. It is well known that organic matter is an important constituent in the formation and the stability of soil aggregates. Any dissolution of organic matter would, in theory, have detrimental effects on aggregate stability and also hydraulic conductivity. A series of experiments were therefore conducted to investigate the effect of hydroxide solutions on both aggregate stability and saturated hydraulic conductivity in a range of New Zealand soils.

The following chapter is a copy of a manuscript entitled "The effect of strong hydroxide solutions on the stability of aggregates and hydraulic conductivity of soils" which has been accepted for publication in *European Journal of Soil Science.* The manuscript has been slightly reformatted from the original manuscript to maintain consistency throughout this thesis. Reference made to Lieffering and McLay (1995) in this manuscript corresponds to Chapter 4 (Organic carbon dissolution). Likewise, reference made to Lieffering and McLay (unpublished data) discussing changes in cation exchange properties corresponds to Chapter 6 (Chemical exchange properties).

The subject matter of this Chapter is also being presented at the *First International Conference on Contaminants in the Soil Environment in the Australasian-Pacific Region* to be held in Adelaide in 1996 and a copy of the extended abstract is enclosed in the pocket at the end of this thesis.

The reader is referred to Appendix B: Supplementary information and data for Chapter 5, for additional information and photographs pertaining to the experiments conducted for this manuscript.

The effect of strong hydroxide solutions on the stability of aggregates and hydraulic conductivity of soils

Summary

The effect of two hydroxides (NaOH and KOH) and two chlorides (NaCl and KCl) on aggregate stability and saturated hydraulic conductivity (K_s) was studied in three New Zealand soils using concentrations (0.003, 0.03, and 0.3 M) typical of the range of pH found in strongly alkaline industrial liquid wastes. The soils were treated with the solutions before measurement of aggregate stability and used as influent solutions during K_s measurements.

The concentration of hydroxide appeared to be the most important factor affecting aggregate stability and K_s in all soils. Aggregate stability and K_s decreased with increasing hydroxide concentration, but were generally unaffected by chloride solutions. Relative K_s decreased to <2.5% of initial K_s with all hydroxide concentrations, but the time until a decrease occurred depended on concentration. In contrast, relative K_s remained ≥100% with chloride solutions, but decreased substantially when distilled water replaced the chloride solutions. Differences in aggregate stability and K_s due to the cation present (either Na^+ or K^+) appeared to be very small. A surface crust formed in the upper 1 cm of the soils leached with hydroxide solutions. This surface crust had substantially less organic carbon than the upper 1 cm of soil from cores leached with chloride.

A two-stage process explains the decrease in K_s when strongly alkaline solutions are applied to soil. First, organic matter dissolution decreases aggregate stability, with the rate of organic matter dissolution depending on hydroxide concentration; and second, increased repulsion of soil particles (due to increased pH) causes movement of dislodged particles into pore spaces, resulting in decreased K_s.

Introduction

The use of soil as a medium for the treatment and disposal of industrial liquid wastes is becoming increasingly common. The nature of the liquid waste depends on the origin or source of the waste, and can be highly variable (Marshall, 1975). Liquid wastes from some industries are characterized by high pH (sometimes exceeding pH 13) and large monovalent cation concentrations, especially where sodium hydroxide (NaOH) or potassium hydroxide (KOH) are used in processing or for cleaning purposes. Typically, strongly alkaline industrial liquid wastes tend to be in the range pH 10-12 in the meat processing-fellmongery (Keeley and Quin, 1979) and dairy (Marshall, 1975; Barnett *et al.,* 1994) industries and can be as high as pH 13.2 (Marshall and Harper, 1984).

There are few reports describing the effect of applying strongly alkaline solutions to soil. Recently, Nakagawa and Ishiguro (1994) examined the effect of a range of influent solution pHs on relative saturated hydraulic conductivity (K_s) in an allophanic soil. They concluded that both acid and alkaline (pH 3 and 11) solutions caused a dramatic decrease in K_s, and they suggested that it resulted from the dispersion of clay which caused aggregates to collapse and clog the soil pores in the upper 1 mm of the soil. Others (e.g. Suarez *et al.,* 1984; Chiang *et al.,* 1987) have investigated the effects of initial soil pH on K_s using influent solutions of varying sodium adsorption ratio (SAR), and found that K_s generally decreased with increasing pH at any given SAR. They have all concluded that the decrease in K_s was due to clay dispersion as a result of increased repulsion of clay particles. In contrast, Frenkel *et al.* (1992) reported that the K_s of pure mixtures of kaolinite and sand actually increased when leached with 0.001 M NaOH despite measuring significant dispersed clay in the leachate. Other authors have shown that the extent of clay dispersion at a given soil pH is related to the clay mineralogy (Gupta *et al.,* 1984; Goldberg and Forster, 1990; Chorom *et al.,* 1994).

The type of cation on the exchange sites of clay particles and the electrolyte concentration of the percolating solution both affect the K_s of a soil (Shainberg and Lety, 1984). Sommerfeldt (1962) and Sommerfeldt and Peterson (1963) showed that more Na^+ was adsorbed on soils treated with NaOH than those treated with other Na-based salts. Also the K_s decreases with increasing exchangeable sodium percentage

(ESP) and decreasing soil solution electrolyte concentration due to swelling or dispersion (or both) of the clay (e.g. Quirk and Schofield, 1955; McNeal and Coleman, 1966; Rowell *et al.*, 1969; Frenkel *et al.*, 1978; Agassi *et al.*, 1981; Cass and Sumner, 1982). Sumner (1993) has recently reviewed the effect that exchangeable Na^+ has on K_s of soils and discussed the mechanisms of dispersion, swelling, and deflocculation.

The stability of soil aggregates against dispersion, therefore, is a major factor determining the effect that liquid wastes applied to soil will have on the resulting K_s. Aggregate stability has been shown to be affected by factors such as clay mineralogy, organic carbon content (e.g. Tisdall *et al.*, 1978; Tisdall and Oades, 1982; Chaney and Swift, 1984; Cheshire *et al.*, 1984; Oades, 1984; Chaney and Swift, 1986; Haynes and Swift, 1990), and type of exchangeable cations (Martin and Richards, 1959; Ahmed *et al.*, 1969). Aggregate stability generally increases with increasing organic carbon in soil. The type of adsorbed cations also affects aggregate stability, with increasing aggregate stability for adsorbed cations in the order $Ca^{2+} = Mg^{2+} > K^+ > Na^+$ (Martin and Richards, 1959; Ahmed *et al.*, 1969). However, the effect that solutions with high pH *per se* have on aggregate stability appears to have received little attention.

The use of hydroxides for removing and characterizing organic matter is well established (e.g. Levesque and Schnitzer, 1966; Kononova, 1966). Recently we showed that the amount of organic carbon dissolved from soil increased with increasing hydroxide concentration (Lieffering and McLay, 1995). Furthermore, we showed that NaOH dissolved more organic carbon than KOH initially, but in the longer term both hydroxides dissolved similar amounts of organic carbon. Because organic matter helps to bind soil aggregates, any dissolution of organic matter may lead to decreased stability and ultimately complete collapse of the aggregates, and so to a decrease in soil K_s and permeability.

The aim of the present study, therefore, was to investigate the effect strongly alkaline solutions have on aggregate stability and K_s. To differentiate pH effects from other anion or cation effects a comparison of Na^+, K^+, Cl^- and OH^- solutions was made.

Materials and Methods

Soils

The surface horizons (0-10 cm) of three New Zealand soils were used: Hopai silty clay (Aeric Fluvaquent, Soil Survey Staff, 1994), Horotiu silt loam (Vitric Hapludand), and Wairua silty clay (Aeric Endoaquult). Relevant properties of the soils are listed in Table 1.

Table 1. Relevant properties of soils used.

		Soil type	
Parameter	Hopai	Wairua	Horotiu
pH[a] (H_2O)	5.6	5.2	5.1
Organic carbon (%)	9.2	4.2	7.9
Bulk density (Mg m^{-3})	0.85	0.90	0.85
% clay	58	38	20
Clay mineralogy[b]	M, K, I	K, V, I	A

[a] soil: water = 1:2.5

[b] XRD and DTA; Clay minerals: M, montmorillonite; K, kaolinite; A, allophane; V, vermiculite; I, illite

Solutions

For experiments on both aggregate stability and K_s, five solutions were used as treatments: NaOH, KOH, NaCl, KCl, and distilled water. Three concentrations (0.003, 0.03, and 0.3 M) of both hydroxide solutions (having pH values of 11.5, 12.5, and 13.5 respectively) and two concentrations (0.003 and 0.3 M) of both chloride solutions (having pH values between 5.2-6.3) were replicated in triplicate.

Pure hydroxide solutions were used in the study to simulate strongly alkaline liquid wastes. It is not possible to accurately simulate strongly alkaline industrial liquid wastes due to high natural variability (Marshall, 1975) and the site specific nature of the liquid wastes, as discussed above. However, in all strongly alkaline liquid wastes, it is the hydroxide component which is responsible for high pH. The concentrations of hydroxide chosen for this study, therefore, span the pH range typically found in such wastes (i.e. 0.003 M hydroxide = pH 11.5, and 0.3 M hydroxide = pH 13.5).

i) Aggregate stability

Approximately 30 g air-dry aggregates (2-4 mm) were placed on sieves having 2 mm diameter holes in shallow basins. The appropriate treatment solution was slowly added to the basin so that the surface of the solution was just in contact with the soil aggregates on the sieve. The aggregates were moistened by capillary action for a 1 hour prior to determination of aggregate stability.

Water stable aggregates were measured using a slight variation of the wet-sieving method of Kemper and Rosenau (1986). After pretreatment, each sieve was placed on top of 2 sieves, the upper one having holes 1 mm diameter and the lower one 0.5 mm. Any aggregates which had collapsed or fallen through the 2 mm sieve into the shallow basin during the soaking phase were washed through the top sieve. The nest of sieves was then placed in a water bath and were set in motion at a rate of 30 oscillations per minute for 30 minutes, ensuring that the aggregates remained totally submerged throughout each vertical stroke of 100 mm. After this the mass of aggregates remaining on each sieve was weighed. The water in the oscillation bath was changed regularly to ensure that the electrical conductivity of the water remained less than 200 $\mu S\ cm^{-1}$.

The data for aggregate stability are presented as the mean weight diameter (MWD), which is the sum of the percentage of soil on each sieve multiplied by the mean diameter of adjacent sieves (in this case, 3.0, 1.5, 0.75, and 0.25 mm), i.e. MWD = Σ (% of sample on sieve x mean intersieve size) (Chaney and Swift, 1984).

ii) Saturated hydraulic conductivity

Field-moist, sieved (<2 mm) soil was repacked into polyvinyl chloride (PVC) cores (10 cm internal diameter x 10 cm length). Brass gauze was taped to the bottom of each core, and filter paper (Whatman #114, 11.0 cm) was placed on the gauze to prevent loss of soil. The soil was packed to a depth of 4 cm at the same bulk density as in the field (see Table 1), taking into account the moisture status of the soil which had been predetermined. Cores were saturated slowly, using distilled water, by capillary action and left to soak for 24 hours before measuring K_s.

Filter paper (Whatman #114, 11.0 cm) was placed on top of the soil in each core to protect the soil surface from physical disruption by the influent solutions. A constant head of 20 mm (± 5 mm) was maintained above each core. All cores were leached with distilled water for 1 hour before solutions were introduced to establish the initial K_s (K_{si}). Preliminary experiments had shown that the soils used in this study remained stable (i.e. no decrease in K_s was measured) when distilled water was leached through the soils. The K_s was calculated, using Darcy's Law, by measuring the flux of water from the base of each core over 5 minute intervals. For comparison, the relative K_s values were calculated for a given interval as a percentage of K_{si} $\left(\text{i.e. relative } K_s = \frac{K_s}{K_{si}} \times \frac{100}{1}\ (\%)\right)$.

iii) Organic carbon

The upper 1 cm of soil was collected from the soil cores that were leached with the largest concentration (0.3 M) of NaOH and NaCl for determination of organic carbon content. The method used was a slight variation of the Modified Mebius Method (Nelson and Sommers, 1982) using 0.5 g air-dry soil, 20 ml 50 g $K_2Cr_2O_7$ l^{-1}, and 20 ml 98% H_2SO_4. For the soil leached with chlorides, $AgSO_4$ was added to the sulphuric acid (25 g $AgSO_4$ l^{-1} acid) to prevent chloride interference (Walkley, 1947).

Results

Aggregate stability

In general, aggregate stability decreased with increasing concentration of pretreatment hydroxide solution used, with the greatest decrease occurring between 0.03 and 0.3 M for both NaOH and KOH. Aggregate stabilities were significantly less ($P<0.05$) in all soils when the most concentrated (0.3 M) hydroxide solutions were used as pretreatments, but they were similar to the distilled water treatment when weaker hydroxide solutions were used (Table 2). Aggregates of the Wairua silty clay and Horotiu silt loam were somewhat less stable ($P<0.05$) when pretreated with 0.3 M NaOH than when treated with 0.3 M KOH, but no cation differences were recorded at the weaker concentrations. In contrast to the above, the difference in cation made no difference to stability of the Hopai silty clay at any of the hydroxide concentrations. No differences were measured between any of the concentrations of either NaCl or KCl and distilled water (data not presented). The aggregates of the Hopai silty clay were somewhat less stable to wet-sieving than those of the other two soil types under all treatments.

Table 2. Aggregate stability (expressed as mean weight diameter (MWD)) of three soil types as influenced by NaOH and KOH treatments.

Values presented represent means of triplicate analyses, S.E.= standard error of mean

		NaOH			KOH		
Soil type	Conc. (M)	MWD	S.E.	% of water[a]	MWD	S.E.	% of water[a]
Hopai	0	251	3	100	251	3	100
	0.003	246	2	98	251	8	100
	0.03	237	4	94	237	2	94
	0.3	124	6	49	138	1	55
Horotiu	0	285	5	100	285	5	100
	0.003	289	1	101	281	1	98
	0.03	278	1	98	278	1	98
	0.3	184	3	65	202	4	71
Wairua	0	285	2	100	285	2	100
	0.003	284	2	100	268	1	94
	0.03	280	1	98	261	2	92
	0.3	163	7	57	195	12	68

[a] $\% \text{ of water} = 100 \times \dfrac{\text{MWD (treatment)}}{\text{MWD (distilled water)}}$

Hydraulic conductivity

The relative K_s versus time for the cores which received only distilled water as influent solution is shown in Fig. 1. For all three soil types the relative K_s of the soil was maintained at, or very close to, 100% for the entire duration of leaching with distilled water.

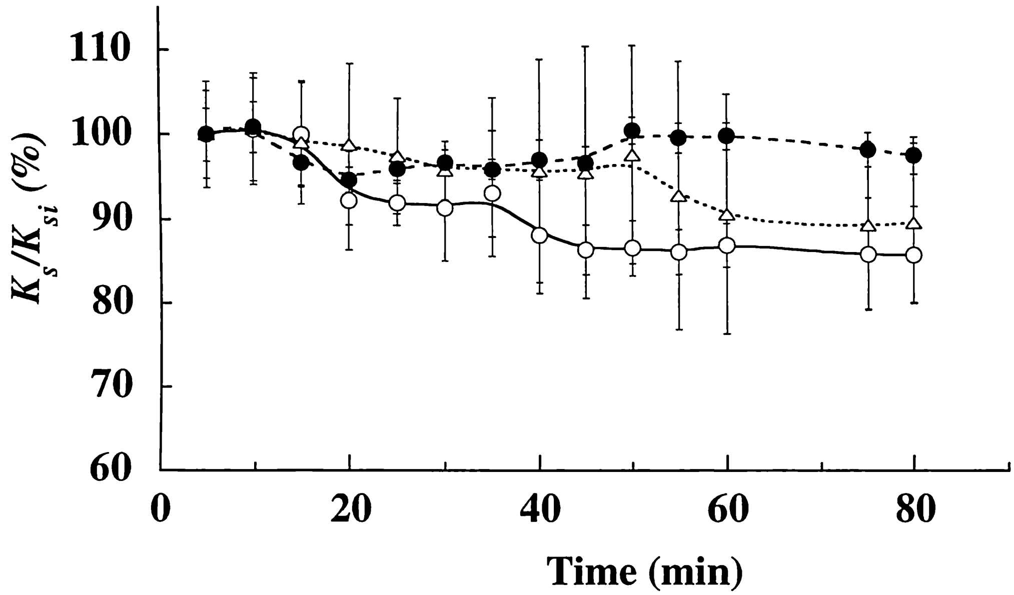


Fig. 1. Relative hydraulic conductivity $\left(\frac{K_s}{K_{si}}\right)$ using distilled water as influent solution on Hopai silty clay (Δ), Wairua silty clay (O), and Horotiu silt loam (●). Error bars represent standard error of the mean of triplicate measurements.

In contrast, when NaOH or KOH were used as influent solutions relative K_s decreased substantially in all soils for all concentrations (Fig. 2a-c). The larger the concentration, the more rapid was the decrease in relative K_s. The shape of all the curves conform to that of a reverse sigmoid, which can be described by Equation (1):

$$K_s(t) = \frac{K_{si}}{2}\left[1 - erf\left(\frac{ln(t) - \alpha}{\beta\sqrt{2}}\right)\right] \qquad (1)$$

where $K_s(t)$ = expected relative saturated hydraulic conductivity at time (t)

K_{si} = initial relative hydraulic conductivity (100%)

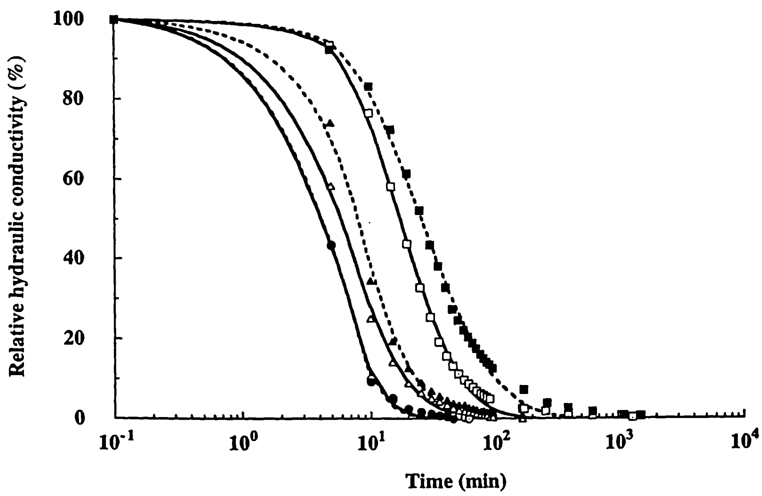
α = curve fit parameter 1

β = curve fit parameter 2

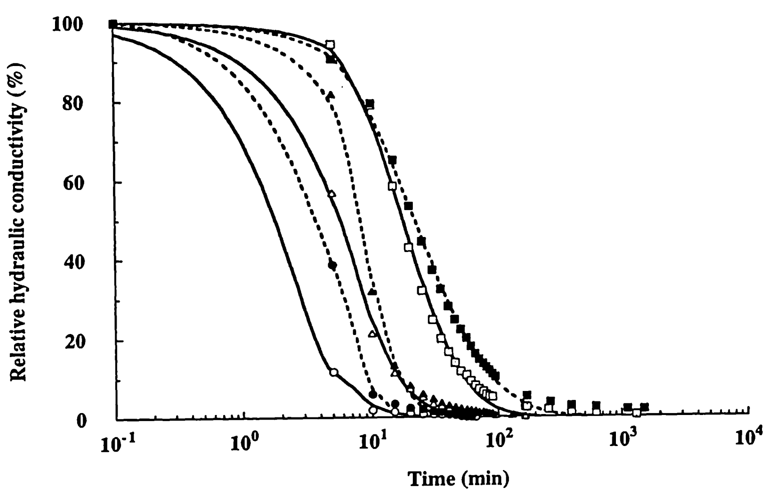
The two parameters, α and β, correspond to the initial time delay before a decrease occurred (or horizontal shift in the curve), and the rate of decrease in relative K_s (the slope of the linear portion of the curve), respectively. Values of α and β were computed for each replicate soil core, and the treatment means were compared using analysis of variance to determine whether differences existed in α or β between the different influent solutions (Table 3). The curve fitting parameter that describes the initial time delay, α, decreased substantially ($P<0.05$) as the hydroxide concentration in the influent solution increased for all soil types (Table 3), whereas no consistent relationship between β and hydroxide concentration was apparent.

Differences in the decrease of relative K_s existed between soil types as a result of the cation present in the hydroxide solutions. In the Hopai silty clay and Wairua silty clay, which are dominated by phyllosilicate clay minerals, NaOH generally caused an earlier decrease in relative K_s than KOH at most concentrations (i.e. the decrease occurred after a shorter time). However, in the Horotiu silt loam, which is dominated by allophane, KOH generally caused an earlier decrease in relative K_s than NaOH at most concentrations. In all three soil types, the final resultant relative K_s at all concentrations of hydroxides used as influent solution was <2.5% of K_{si}.

a) Hopai silty clay



b) Wairua silty clay



c) Horotiu silt loam

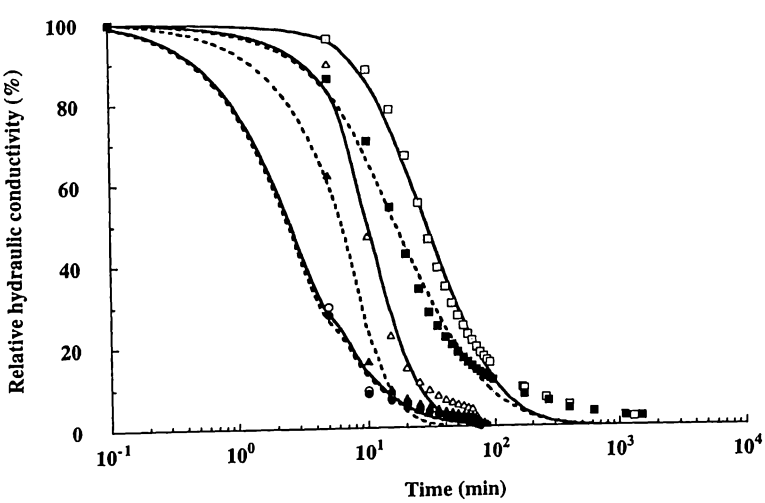


Fig. 2. Relative hydraulic conductivity $\left(\frac{K_s}{K_{si}}\right)$ of Hopai silty clay (a), Wairua silty clay (b), and Horotiu silt loam (c) using different hydroxide influent solutions: 0.003 M NaOH (□), 0.003 M KOH (■), 0.03 M NaOH (Δ), 0.03 M KOH (▲), 0.3 M NaOH (O), and 0.3 M KOH (●). Lines are fitted curves (see text) according to Equation (1), dashed lines correspond to KOH and solid lines correspond to NaOH.

Table 3. Curve fitting parameters[a] (α and β) and coefficients of determination (r^2) for hydraulic conductivity curves using hydroxide solutions as influent solutions on three soil types (Hopai, Wairua, and Horotiu).

Values represent means of triplicate measurements

Solution	Concentration	Hopai			Wairua			Horotiu		
		α	β	r^2	α	β	r^2	α	β	r^2
	0.003M	2.87	0.79	0.99	2.92	0.84	0.99	3.33	1.02	0.99
NaOH	0.03M	1.80	0.74	0.99	1.73	0.71	0.99	2.29	0.63	0.98
	0.3M	1.48	0.67	0.99	0.35	1.04	0.99	0.86	1.29	0.99
	0.003M	3.26	1.01	0.99	3.10	1.08	0.99	2.82	1.26	0.99
KOH	0.03M	2.07	0.77	0.99	2.08	0.56	0.99	1.78	0.68	0.98
	0.3M	1.50	0.64	0.99	1.44	0.60	0.99	0.78	1.31	0.99
L.S.D.[b] $_{(0.05)}$		0.61	0.13		0.42	0.12		0.39	0.22	

[a] See text for details

[b] Least significant difference

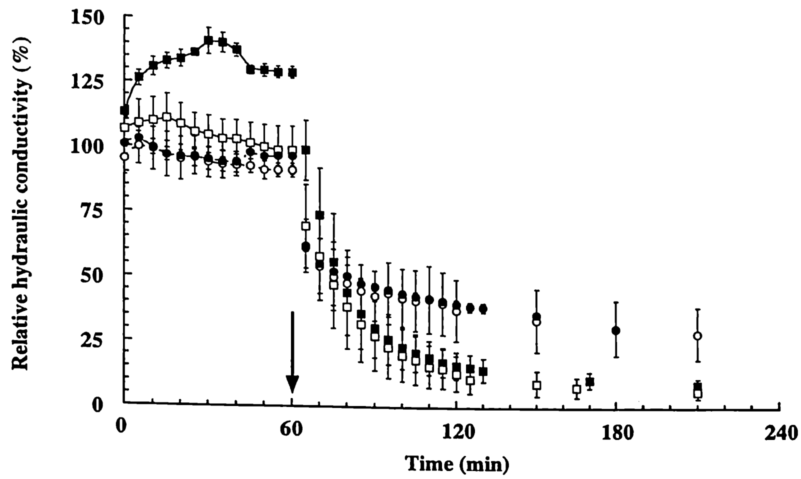
Differences were also observed between anions. When the anion present in the influent solution was chloride, relative K_s remained ≥100% (Fig. 3a-c, 0-60 minutes). In the Hopai silty clay and Wairua silty clay, relative K_s increased with increasing chloride concentration, with a larger increase in relative K_s using NaCl than with KCl. However, in the Horotiu silt loam this trend was not observed. The introduction of distilled water following leaching with the chloride solutions (Fig. 3a-c, 60-210 minutes) caused the relative K_s to decrease logarithmically over time in all soil types. Cores that had been leached with larger initial chloride concentration caused a more rapid decrease in relative K_s using distilled water than cores leached with weaker solutions. However, no cationic differences were observed between relative K_s when distilled water was used as influent solution following leaching with either NaCl or KCl. In the Hopai silty clay and Wairua silty clay the resultant relative K_s was greater (about 20-30% of K_{si}) in cores which had originally been leached with weak (0.003 M) chloride solutions than in cores which had originally been leached with strong ones (0.3 M) (about 3-10% of K_{si}, Table 4). In contrast, Horotiu silt loam was less sensitive to changes in relative K_s, no concentration or cation effects could be differentiated, and the magnitude of the decrease in relative K_s was less than in the other two soils.

Organic carbon of surface crusts

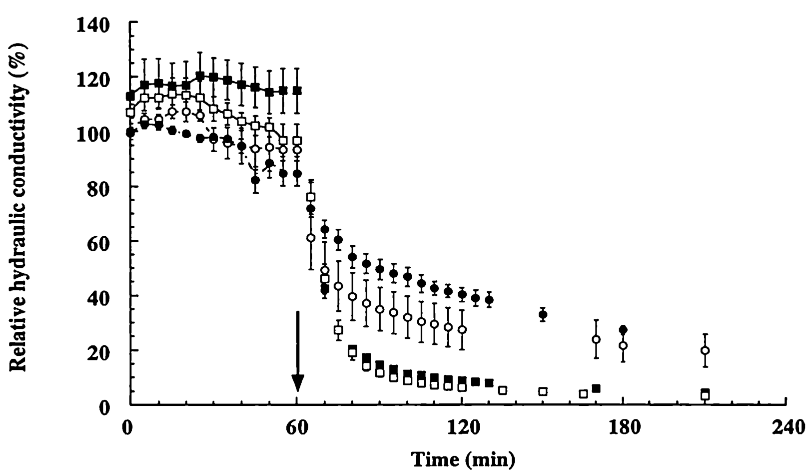
Cores that had been leached with hydroxide solutions developed a distinct surface crust in the upper 1 cm of the soil where the aggregates had completely collapsed. A surface crust was not observed in the cores leached with chloride solutions. In all soil types organic carbon contents were substantially less (P<0.05) in the surface crust of soil leached with hydroxide than in the upper 1 cm of that leached with chloride (Table 5).

Fig. 3. Relative hydraulic conductivity $\left(\frac{K_s}{K_{si}}\right)$ of Hopai silty clay (a), Wairua silty clay (b), and Horotiu silt loam (c) using different chloride influent solutions (t = 0-60 minutes): 0.003 M NaCl (O), 0.003 M KCl (●), 0.3 M NaCl (■), and 0.3 M KCl (□). From t > 60 minutes (as indicated by arrow), distilled water was introduced as the influent solution. Error bars represent standard error of the mean of triplicate measurements.

a) Hopai silty clay



b) Wairua silty clay



c) Horotiu silt loam

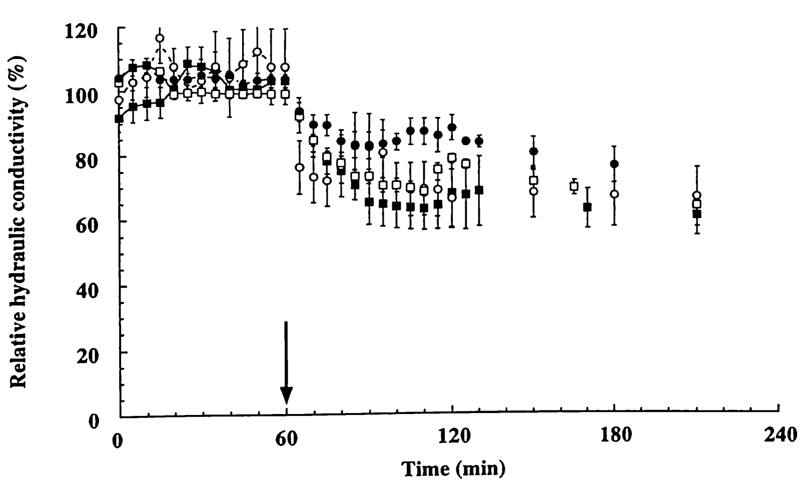


Table 4. Final relative saturated hydraulic conductivity (K_s/K_{si}) using distilled water on soil cores previously leached with 0.003 M NaCl, 0.003 M KCl, 0.3 M NaCl, or 0.3 M KCl for three soil types.

Values presented are means of triplicate analyses (± standard error of mean)

Soil type	Previous leaching solution		Final relative K_s ($\% K_{si}$)
	Type	Concentration (M)	
	NaCl	0.003	29.1 (10.3)
Hopai	NaCl	0.3	9.1 (2.4)
	KCl	0.003	31.0 (0.9)
	KCl	0.3	6.5 (2.8)
	NaCl	0.003	20.2 (6.0)
Wairua	NaCl	0.3	4.6 (0.3)
	KCl	0.003	27.8 (1.8)
	KCl	0.3	3.4 (0.4)
	NaCl	0.003	66.8 (9.2)
Horotiu	NaCl	0.3	61.0 (6.1)
	KCl	0.003	76.6 (5.5)
	KCl	0.3	64.2 (3.5)

Table 5. Organic carbon (%) measured in the upper 1 cm of three soils (Hopai, Wairua, and Horotiu) after leaching with 0.3 M NaOH and NaCl influent solutions.

Values represent means of triplicate analyses.

	Influent solution	Organic carbon (%)	Standard error
Hopai silty clay	0.3 M NaOH	8.0	0.2
	0.3 M NaCl	10.9	0.3
Wairua silty clay	0.3 M NaOH	1.2	0.0
	0.3 M NaCl	4.4	0.0
Horotiu silt loam	0.3 M NaOH	4.3	0.1
	0.3 M NaCl	7.9	0.0

Discussion

Our results indicate that hydroxide solutions dramatically weaken aggregates and decrease K_s in soil. We suggest that these adverse effects are mainly a result of dissolution of organic carbon by hydroxide solutions, as previously described (Lieffering and McLay, 1995).

Organic matter acts as a binding agent throughout a wide range of aggregate size classes in soils, from clay coatings to >250 μm macro-aggregates (Tisdall and Oades, 1982; Oades, 1984). Therefore any dissolution of organic carbon may seriously weaken aggregates, and may ultimately lead to their complete collapse. This study showed that aggregate stability decreased as the concentration of hydroxide solution increased. Strong NaOH (0.3 M) weakened the aggregates of the Horotiu silt loam and Wairua silty clay more than KOH, and this is consistent with our earlier results

(Lieffering and McLay, 1995): NaOH dissolved more organic carbon than KOH initially. Lieffering and McLay (1995) also showed that subsequent additions of fresh hydroxide solutions continued to dissolve organic carbon: approximately 75% of the initial organic carbon dissolved after 5 shakings with 0.3 M hydroxide solution. It would therefore be expected that additional treatment of soil aggregates with hydroxide solutions would result in weaker aggregates at all concentrations.

A two-stage process is proposed to explain the decrease of K_s when soils are leached with strongly alkaline solutions. First, organic carbon is dissolved at the surface of the soil (i.e. the upper 1 cm) where the solution is in contact with soil aggregates. The time required for dissolution to weaken aggregates (α) appears to depend on concentration. Second, aggregate instability causes clays and other fine particles to be dislodged and transported into pores, thereby blocking the pores and subsequently decreasing K_s. The rate of decrease in K_s (β) appears to depend less on hydroxide concentration, indicating that once organic carbon has dissolved, the rate at which pores are blocked is similar for all hydroxide treatments. In addition, the increase in pH of the soil solution increases the amount of negative charge on colloid surfaces which possess variable charge properties such as organic matter, oxides, and edge sites of clay minerals (van Olphen, 1977). The amount of negative charge (i.e. CEC) of the soils used in this study increases markedly as solution pH increases (Lieffering and McLay, unpublished data). It is probable, therefore, that the increase in negative charge would encourage the clay to swell, disperse, and deflocculate, and these would further increase the movement of dislocated particles into pores. The surface crust which developed in cores leached with hydroxides contained substantially less organic carbon than the upper 1 cm of cores leached with chlorides. It is likely, therefore, that organic carbon dissolution of only a very shallow layer of soil at the surface is sufficient to invoke a marked decrease in K_s.

This two-stage process differs from those suggested previously (e.g. Suarez *et al.*, 1984; Chiang *et al.*, 1987; Nakagawa and Ishiguro, 1994) that clay swelling and subsequent deflocculation is the main cause of decreased hydraulic conductivity in strongly alkaline soil. However, the soils used in those studies contained less organic carbon (all less than 2.8% organic carbon) than those we used (between 4.2-9.2%

organic carbon), which may explain why organic carbon dissolution had not been reported to be important in the decrease of K_s.

The effect of aggregate collapse through dispersion has been well documented for soils saturated with monovalent cations, particularly Na^+ (e.g. Quirk and Schofield, 1955; McNeal and Coleman, 1966; Rowell *et al.*, 1969; Frenkel *et al.*, 1978; Agassi *et al.*, 1981; Cass and Sumner, 1982). However, our results indicate that the hydroxide anion, and not the presence of monovalent cations on exchange sites, is the main cause of decreased K_s when strongly alkaline solutions which contain large concentrations of monovalent cations are leached through soil. Diffuse double layer theory suggests that K_s should not be affected, and should actually increase, when soils are leached with strong electrolyte solutions (Quirk and Schofield, 1955; Shainberg and Lety, 1984; Sumner, 1993). However, using NaOH and KOH as influent solutions does not conform to diffuse double layer theory, as both these solutions substantially decreased K_s.

The effects of NaCl and KCl solutions on K_s in the soils used in this study were, however, consistent with diffuse double layer theory (Shainberg and Lety, 1984; Sumner, 1993). The maintenance or increase in K_s which was observed when cores were leached with either a weak or strong NaCl or KCl solution is probably due to compression of the diffuse double layers surrounding soil colloids at the larger concentrations. However, the introduction of distilled water as the influent solution (i.e. decreased electrolyte concentration) would result in expansion of the diffuse double layer, causing clay swelling and deflocculation, and therefore a decrease in K_s. There was visual evidence for clay swelling and deflocculation occurring in chloride preleached cores. When the influent solutions were NaCl or KCl, the leachate collected remained clear (i.e. when K_s remained $\geq$100%). However, the introduction of distilled water as influent solution (which resulted in decreases in K_s) caused the leachate to become cloudy with visible suspended material, presumably dispersed clay. This was in contrast to the dark brown to black leachate collected from the cores during leaching with hydroxide solutions. The dark leachate had no visible suspended material (i.e. it appeared as a solution) and we attribute the dark colouration to the presence of dissolved organic carbon. This interpretation is supported by previous studies (Lieffering and McLay, 1995) which showed that soils treated with hydroxide solutions (NaOH and KOH) cause considerable discolouration of the hydroxide solution and contain substantially more dissolved organic carbon than non-hydroxide solutions (e.g. chlorides). Further evidence for the dissolution of organic carbon dissolution in the cores leached with hydroxide solutions was the smaller organic carbon contents in the surface crusts of cores leached with hydroxide solutions than in those in the upper 1 cm of soil cores leached with chloride solutions. It seems that dissolution of organic carbon was the main factor causing aggregate instability and consequent decreases in K_s in the soils leached with hydroxide solutions.

It also seems that K^+ on the exchange sites has the same detrimental effects in decreasing K_s as Na^+, irrespective of concentration or dominant clay type. Previous studies have reported that exchangeable K^+ may either increase or decrease K_s (e.g. Quirk and Schofield, 1955; Ahmed *et al.*, 1969; Chen *et al.*, 1983), the conflicting results possibly being due to differences in clay mineralogy and sample preparation (Levy and van der Watt, 1990).

In summary, the present study shows that hydroxide concentrations typically found in strongly alkaline industrial liquid wastes (pH 10 to >13.2) can diminish the hydraulic conductivity of soil and should not be applied to soil without prior investigation of the effects on soil properties, especially infiltration. Neutralization of the liquid wastes with acid would decrease the effects on the soils reported here, but may not minimize adverse effects resulting from accumulation of monovalent cations on exchange sites.

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Chapter 6
Cation Exchange Properties

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Cation exchange properties

6.1 Introduction

The results from experiments conducted in Chapter 4 showed that significant amounts of organic carbon are dissolved from soils in the presence of hydroxide solutions. The dissolution of organic carbon would, in theory, remove many exchange sites from the soil. However, the increase in pH due to the presence of the hydroxide solutions would also increase the number of negative sites on remaining surfaces which possess variable charge characteristics (i.e. pH dependent charge surfaces). It was unknown, therefore, the effect that the presence of hydroxide solutions would have on the net charge of the soil system and a series of experiments were therefore conducted to quantify the changes in cation exchange properties of four New Zealand soil types when treated with a range of concentrations of both NaOH and KOH solutions. Exchangeable cations were measured to compare monovalent cation concentrations which occurred when soil was treated with the hydroxide solutions and those when the soil was treated with chloride solutions (applied as NaCl and KCl).

The following chapter is a copy of a manuscript entitled "The effects of high monovalent cation concentration and high pH solutions on cation exchange properties" which is currently under review by *Australian Journal of Soil Research.* The manuscript has been slightly reformatted from the original manuscript to maintain consistency throughout the thesis. Reference made in this manuscript to Lieffering and McLay (1995) corresponds to Chapter 4 (Organic carbon dissolution).

The reader is also referred to Appendix C: Supplementary information and data for Chapter 6, for additional information pertaining to the experiments conducted for this manuscript.

The Effect of High Monovalent Cation Concentration and High pH Solutions on Cation Exchange Properties

Abstract

The effect of solutions with high monovalent cation concentrations and high pH on cation exchange properties was investigated in four New Zealand soils with different clay mineralogies. The soils were shaken with a range of concentrations (0-0.3 M) of NaOH, KOH, NaCl, and KCl and cation exchange capacity (CEC) and exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) were measured following shaking and washing procedures. Although the hydroxide solutions dissolved significant amounts of organic matter from all soils, there was still a net increase in CEC measured at all hydroxide concentrations. The magnitude of the CEC increase was dependent on hydroxide concentration. The increase in CEC is attributed to newly generated negative charge on surfaces which possess variable charge (i.e. pH dependent) characteristics such as sesquioxides, edge sites of clay minerals, and the undissolved organic matter remaining in the soil. In contrast to hydroxide solutions, no increase in CEC was measured in chloride-treated samples. Increasing the concentration of all treatment solutions resulted in increases in the exchangeable ion concentration of the index cation used in the treatment solution (either Na^+ or K^+) and decreases in concentration of the other three exchangeable cations.

In general, higher exchangeable sodium percentage (ESP) values were measured in samples treated with NaOH than samples treated with NaCl at all concentrations. Similarly, higher exchangeable potassium percentage (EPP) was measured in samples treated with KOH than samples treated with KCl at all concentrations. The higher ESP and EPP values recorded when hydroxide solutions were used as treatments is attributed to the newly generated negative charges being counter-balanced by the monovalent index cation present in the treatment solution. It is suggested that existing equations commonly used to predict ESP and EPP values were unsuccessful for accurately predicting changes when soil were treated with hydroxide solutions due to their inability to account for the newly generated exchange sites. The equations did, however, adequately predict the effects of both chloride solutions on ESP and EPP.

Introduction

The use of soil as a medium for the treatment and disposal of industrial liquid wastes is becoming increasingly common. Some liquid wastes from industrial sources are characterized by high pH (in some cases exceeding pH 13) and high monovalent cation concentrations, especially where sodium hydroxide (NaOH) and/or potassium hydroxide (KOH) are used in processing or for cleaning purposes. Typically, high pH industrial liquid wastes tend to be in the range pH 10-12 in the meat processing/fellmongery (Keeley and Quin, 1979) and dairy manufacturing (Marshall, 1975; Barnett *et al.*, 1994) industries and can be as high as pH 13.2 (Marshall and Harper, 1984).

Few reports exist in the literature on the effects that high pH solutions have on cation exchange properties in soils. Some field studies have shown that both soil pH and exchangeable Na^+ tend to increase where liquid wastes with high pH and high Na^+ concentrations have been spray irrigated onto soil (e.g. Keeley and Quin, 1979; Barnett and Parkin, 1985). Very few workers have investigated the effect that hydroxide anions have on cation exchange processes. Sommerfeldt (1962) and Sommerfeldt and Peterson (1963) suggested a greater amount of Na^+ can be exchanged by soil materials when NaOH solutions were used than when NaCl were used as treatments due to the increase in measured cation exchange capacity (CEC) of the soil materials when in the presence of hydroxide anions.

It would be expected that application of hydroxide based solutions (i.e. high pH) to soil would increase CEC if the soil contained components which possess variable charge (i.e. pH dependent) properties. One of the main sources of pH dependent charge in soil is organic matter (Helling *et al.*, 1964), and it has been shown that a strong relationship exists between CEC and organic matter content for many soils (Sposito, 1989). However, hydroxide based solutions (particularly NaOH) are commonly used to dissolve organic matter from soils for characterization purposes (e.g. Kononova, 1966; Schnitzer and Skinner, 1968), and Lieffering and McLay (1995) recently showed that the amount of organic carbon dissolved from soils increased with increasing hydroxide concentration. Furthermore, a similar amount of organic carbon was dissolved by both NaOH and KOH solutions over a relatively wide range of concentrations (0.003 - 0.3 M).

Many studies have been conducted which investigate the potential Na^+ hazard when soils are irrigated with high Na^+ concentration waters, especially in arid areas where high Na^+ concentration water is commonly the only water available for irrigation purposes or the accumulation of soluble Na-salts occurs (e.g. Shainberg and Lety, 1984; Rengasamy and Olsson, 1993). The accumulation of Na^+ on exchange sites is often reported as the exchangeable sodium percentage (ESP) which is defined as (Sumner, 1993):

$$\mathrm{ESP} = \frac{\text{Exchangeable Na}}{\sum(\text{Exchangeable Ca} + \text{Mg} + \text{K} + \text{Na})} \times 100 \tag{1}$$

Prediction equations were developed by United States Salinity Laboratory Staff (Richards, 1954) to predict ESP values from the sodium adsorption ratio (SAR) of irrigation waters and soil solutions:

$$\mathrm{ESP} = \frac{100(-0.0126 + 0.01475\ \mathrm{SAR})}{1 + (-0.0123 + 0.01475\ \mathrm{SAR})} \tag{2}$$

where:

$$\mathrm{SAR} = \frac{[\mathrm{Na}^+]}{[\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}]^{\frac{1}{2}}} \tag{3}$$

and the values in [] refer to concentrations in $\mathrm{mmol_c\ L^{-1}}$ (Sumner, 1993). Similarly, the accumulation of exchangeable K^+ in soils is often reported as the exchangeable potassium percentage (EPP) which is defined as:

$$\mathrm{EPP} = \frac{\text{Exchangeable K}}{\sum(\text{Exchangeable Ca} + \text{Mg} + \text{K} + \text{Na})} \times 100 \tag{4}$$

Richards (1954) also presented a prediction equation to estimate EPP values from the potassium adsorption ratio (PAR) of irrigation waters:

$$\mathrm{EPP} = \frac{100(0.036 + 0.1051\ \mathrm{PAR})}{1 + (0.036 + 0.1051\ \mathrm{PAR})} \tag{5}$$

where:

$$PAR = \frac{[K^+]}{[Ca^{2+} + Mg^{2+}]^{\frac{1}{2}}} \tag{6}$$

The above prediction equations have been successfully used to predict accumulation of exchangeable Na^+ and K^+ worldwide. It would be expected that these equations would work well in soils used in this study when equilibrated with NaCl or KCl solutions as these are common soluble salts in irrigation waters and in soils found in arid areas which were used to derive equations 2 and 5. However, no workers appear to have investigated the ability of the equations to predict exchangeable Na^+ or K^+ concentrations of soils when hydroxide anions are present in irrigation waters or soil solutions.

The overall aim of this study, therefore, was to investigate the effects that solutions with high monovalent cation content and high pH have on exchange processes in soils. The objectives were to:

i) investigate changes to CEC and exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) that occur when soils are treated with a range of concentrations of NaOH, KOH, NaCl, and KCl solutions. The use of these solutions allows the effects of cations (Na^+ and K^+) and anions (OH^- and Cl^-) to be differentiated.

ii) establish whether existing prediction equations can be used to predict ESP and EPP values from soil solution SAR and PAR when hydroxide anions are present in the soil solution.

Material and Methods

Soils

The surface horizons (0-10 cm) of four New Zealand soils were used: Hopai silty clay (Aeric Fluvaquent, Soil Survey Staff, 1994), Horotiu silt loam (Vitric Hapludand), Wairua silty clay (Aeric Endoaquult) and Manawatu silt loam (Aquic Dystric Eutrochrept). Relevant properties of these soils are presented in Table 1.

Table 1. Relevant properties of soils used.

Chemical parameter	Hopai	Horotiu	Manawatu	Wairua
pH (H_2O)[1]	5.6	5.1	5.2	5.6
Organic carbon (%)	9.2	7.9	4.2	6.3
CEC ($cmol_c\ kg^{-1}$)[2]	22.3	6.2	13.6	15.8
Exchangeable cations ($cmol_c\ kg^{-1}$)[2]				
Ca	19.0	5.4	13.8	15.3
Mg	3.9	0.7	1.0	1.0
K	0.6	0.5	0.5	0.3
Na	0.4	0.1	0.1	0.2
% clay	58	20	38	32
Clay mineralogy[3]	M, K, I	A	K, V, I	I, C, V

[1] soil:water = 1:2.5

[2] unbuffered (silver thiourea method)

[3] clays: M=montmorillonite, K=kaolinite, I=illite, A=allophane, V=vermiculite, C=chlorite

Treatment solutions

Five concentrations (0.003, 0.01, 0.03, 0.1, and 0.3 M) and four solution types (NaOH, KOH, NaCl, and KCl) were used to investigate cation and anion effects of high pH solutions on cation exchange properties (Na^+ and K^+ are therefore defined in this study as index cations in the presence of two anions). An additional treatment, distilled water, was also used as a control and represented zero concentrations of each treatment solution. The pH of the five concentrations of hydroxide solutions were 11.5, 12.0, 12.5, 13.0, and 13.5 respectively. The pH of the chloride solutions ranged between 5.0 and 7.0. All treatments were replicated in triplicate.

The concentrations of hydroxide solutions were chosen to represent those typically found in high pH industrial liquid wastes. Pure hydroxide solutions were used because it is not possible to accurately simulate high pH industrial liquid wastes due to high natural variability (Marshall, 1975) and the site specific nature of the liquid wastes. However, in all industrial high pH liquid wastes, it is the hydroxide component which is mainly responsible for high pH.

Equilibration and washing procedure

Air-dry soil (0.8 g, <2 mm) was shaken with 40 mL of treatment solution in tubes using an end-over-end shaker for 18 h. After shaking, the tubes were centrifuged at 2000 r.p.m. for 10 min and the supernatant solution was discarded. Approximately 40 mL of 97% ethanol was then added and the soil shaken for a further 18 h to wash off excess salt solution from the soil. The tubes were then centrifuged and the supernatant solution discarded. The ethanol treatment was repeated until each soil had received a total of six washings. This is more washings than frequently reported (e.g. Blakemore *et al.*, 1987) for removing excess salts from soils, but preliminary studies indicated it was necessary. After six washings, the soils were allowed to air-dry in the tubes and the mass of the tube and soil was weighed to calculate the volume of entrained solution.

Measurement of exchangeable cations and CEC

Unbuffered silver thiourea (AgTU) was used to measure exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) and CEC of the soil after equilibration with the treatment solutions and washing with ethanol (Blakemore *et al.*, 1987). It was necessary to use an unbuffered salt solution to investigate the effects of the high pH (hydroxide) solutions on exchange properties. 40 mL of 0.01 M AgTU was added to the washed soil and the tubes were shaken for 18 h. After shaking, the tubes were centrifuged and exchangeable cations and Ag^+ were measured (following dilution) using atomic absorption spectrophotometry. The Ag^+ measured in the supernatant solution gives an inverse measure (by difference) of the CEC of the soil.

SAR and PAR calculations

SAR and PAR values were calculated according to equations 3 and 6, respectively, after measurement of: i) exchangeable cations on untreated soil; ii) exchangeable cations following equilibration with treatment solutions; and iii) concentration of index cation in the treatment solution.

ESP and EPP (measured and predicted)

The ESP and EPP were calculated according to equations 1 and 4 respectively. Measured ESP and EPP values were then compared to predicted ESP and EPP values using the two equations presented by Richards (1954) (equations 2 and 5) using calculated SAR and PAR values (see above).

Results

After analysis of exchangeable cations and Ag^+, it was noted that the sum of the exchangeable cations (i.e. $Ca^{2+} + Mg^{2+} + Na^+ + K^+$) for some of the treated samples was greater than the measured CEC of the sample (i.e. base saturation (BS) was >100%). The difference was attributed to excess index cations (either Na^+ or K^+) present in the soil solution and the data was therefore normalized, by decreasing either exchangeable Na^+ or K^+ concentrations (whichever was the index cation), so that BS equaled 100%.

The relative changes in CEC and exchangeable cations with various treatments were very similar in all four soil types used and, for the purposes of this paper, the results of only one soil type (Hopai silty clay) will be presented graphically to make interpretation of results easier. The data for the other three soils is presented in Table 2.

Table 2. Exchangeable cations (Ca, Mg, K, and Na) in three soils using different concentrations of four treatment solutions. Values represent means (n=3).

		Horotiu silt loam							Manawatu silt loam							Wairua silty clay						
		Concentration (M)						Max.	Concentration (M)						Max.	Concentration (M)						Max.
Parameter	Treatment solution	0	0.003	0.01	0.03	0.1	0.3	S.E.*	0	0.003	0.01	0.03	0.1	0.3	S.E.*	0	0.003	0.01	0.03	0.1	0.3	S.E.*
Exchangeable	NaCl	4.8	4.0	3.7	2.8	1.6	1.0	0.2	10.2	10.5	9.4	7.6	4.6	2.3	0.2	12.2	14.3	12.3	9.9	5.6	2.2	1.0
Ca	NaOH	4.8	3.5	1.0	0.5	0.7	1.1	0.1	10.2	9.3	5.6	4.7	5.1	5.5	0.2	12.2	11.2	7.0	6.5	6.4	6.2	0.4
(cmol$_c$ kg^{-1} soil)	KCl	4.8	3.9	2.9	2.1	1.3	0.8	0.1	10.2	8.9	7.1	5.3	3.1	1.6	0.2	12.2	10.0	7.5	5.0	3.4	1.5	0.7
	KOH	4.8	3.9	1.3	0.4	0.6	0.6	0.1	10.2	8.9	6.0	5.2	5.6	5.9	0.5	12.2	11.8	7.7	7.0	6.8	6.9	0.1
Exchangeable	NaCl	0.6	0.4	0.3	0.2	0.1	0.1	0.0	0.8	0.8	0.6	0.5	0.2	0.1	0.0	1.0	1.1	0.8	0.6	0.3	0.2	0.0
Mg	NaOH	0.6	0.6	0.2	0.1	0.1	0.1	0.0	0.8	0.6	0.2	0.1	0.1	0.1	0.0	1.0	0.8	0.2	0.2	0.2	0.1	0.0
(cmol$_c$ kg^{-1} soil)	KCl	0.6	0.4	0.2	0.1	0.1	0.1	0.0	0.8	0.6	0.4	0.3	0.1	0.1	0.0	1.0	0.7	0.5	0.3	0.2	0.1	0.1
	KOH	0.6	0.6	0.3	0.0	0.1	0.1	0.0	0.8	0.7	0.2	0.1	0.1	0.1	0.0	1.0	0.9	0.2	0.2	0.1	0.1	0.0
Exchangeable	NaCl	0.1	0.2	0.1	0.1	0.1	0.1	0.0	0.3	0.3	0.2	0.2	0.1	0.1	0.0	0.3	0.5	0.4	0.2	0.2	0.1	0.1
K	NaOH	0.1	0.5	0.3	0.2	0.1	0.1	0.0	0.3	0.3	0.3	0.2	0.2	0.2	0.0	0.3	0.4	0.3	0.3	0.3	0.2	0.0
(cmol$_c$ kg^{-1} soil)	KCl	0.1	1.7	3.0	3.7	5.7	6.2	0.6	0.3	1.5	4.1	5.8	9.1	10.3	0.7	0.3	3.9	7.1	9.6	11.7	13.9	0.8
	KOH	0.1	7.7	21.9	26.5	27.7	27.1	0.6	0.3	4.6	8.4	12.3	14.0	17.8	0.9	0.3	7.0	13.7	16.5	18.9	22.1	0.4
Exchangeable	NaCl	0.2	1.3	2.6	3.6	5.0	5.6	0.7	0.2	0.1	1.0	3.3	6.6	10.7	0.6	0.4	1.8	3.5	6.2	11.6	15.0	0.7
Na	NaOH	0.2	9.1	22.1	25.9	29.8	27.7	0.9	0.2	5.0	9.6	12.3	14.2	16.9	0.7	0.4	7.4	13.0	17.0	21.6	26.0	0.9
(cmol$_c$ kg^{-1} soil)	KCl	0.2	0.2	0.2	0.2	0.2	0.1	0.0	0.2	0.2	0.2	0.2	0.1	0.1	0.0	0.4	0.7	0.5	0.3	1.8	0.3	1.1
	KOH	0.2	0.3	0.3	0.3	0.2	0.3	0.0	0.2	0.2	0.2	0.2	0.2	0.3	0.1	0.4	0.4	0.4	0.4	0.3	0.3	0.1

* Max. S.E. = maximum standard error of mean within each treatment (0-0.3 M concentration range).

Cation exchange capacity

The CEC of all four soils increased when treated with either NaOH or KOH but was not affected by either NaCl, KCl or distilled water (Table 3). The CEC increased with increasing concentration of hydroxide solution, but concentration did not appear to affect CEC in chloride treated samples (Table 3). The relative effect of hydroxide solutions on CEC was greater in Horotiu silt loam (c. 4.5 times higher CEC when the highest concentration treatment was used than in untreated soil) than the other three soils (where only a twofold increase in CEC was measured between 0.3 M hydroxide-treated samples and untreated samples). Similar CEC values were recorded for both Na and K solutions at all concentrations.

Exchangeable cations

Exchangeable cation concentrations were affected by the type and concentration of index cation and anion used in the equilibration solution (Fig. 1 a-d). In untreated samples, Ca^{2+} was the dominant cation on exchange sites in all soils (Table 1). However, all treatments resulted in a decrease in exchangeable Ca^{2+} concentration. As the concentration of equilibration solution increased for all treatments, the concentration of exchangeable Ca^{2+} remaining in the soil decreased logarithmically (Fig. 1a-d).

The amount of exchangeable Mg^{2+} present in untreated soils of all soil types was low compared to Ca^{2+} (Table 2; Fig. 1 a-d). The effect of treatments was to decrease exchangeable Mg^{2+} concentrations as the cation or anion concentration increased in the treatment solution in all soils (Fig. 1 a-d).

When K^+ was used as the index cation in a treatment solution (KOH and KCl), the concentration of exchangeable K^+ increased logarithmically with concentration of treatment used, for both KOH and KCl solutions (Fig 1b,d). However, KOH-treated samples resulted in substantially higher exchangeable K^+ concentrations than in KCl-treated samples at all concentrations (Fig. 1b,d). In Horotiu silt loam, KOH resulted in c. 4.5x more exchangeable K^+ than KCl at the highest concentration used (0.3 M) (Table 2). However, a much smaller increase (1.5-2.5x) was recorded in the

Table 3. Cation exchange capacity (CEC) in four soils after treatment with different treatment solutions. Values represent means (n=3).

Soil type	Treatment solution	CEC ($cmol_c$ kg^{-1} soil) Concentration (M)						
		0	0.003	0.01	0.03	0.1	0.3	Max. S.E.*
Hopai silty clay	NaCl	22.5	20.7	21.1	20.8	22.0	24.1	0.5
	NaOH	22.5	27.2	31.8	36.4	47.7	51.4	0.9
	KCl	22.5	22.7	22.3	22.1	24.2	24.5	0.9
	KOH	22.5	24.4	31.8	36.6	47.4	51.7	0.9
Horotiu silt loam	NaCl	6.6	6.6	6.7	6.7	6.7	6.7	0.5
	NaOH	6.6	13.6	23.7	26.7	30.7	29.0	0.5
	KCl	6.6	6.5	6.4	6.1	7.3	7.2	0.5
	KOH	6.6	12.5	23.7	27.3	28.7	28.0	0.5
Manawatu silt loam	NaCl	11.4	11.6	11.2	11.6	11.6	13.2	0.6
	NaOH	11.4	15.3	15.6	17.3	19.6	22.7	0.7
	KCl	11.4	11.2	12.3	11.5	12.5	12.2	0.9
	KOH	11.4	14.4	14.8	17.7	19.8	24.1	1.5
Wairua silty clay	NaCl	16.4	17.7	16.9	17.3	17.7	17.7	0.5
	NaOH	16.4	19.8	20.5	24.0	28.5	32.6	1.2
	KCl	16.4	15.8	16.1	15.3	17.0	15.8	1.5
	KOH	16.4	21.0	21.9	24.0	26.1	29.4	0.8

* Max. S.E. = maximum standard error of mean for each treatment (0-0.3 M range).

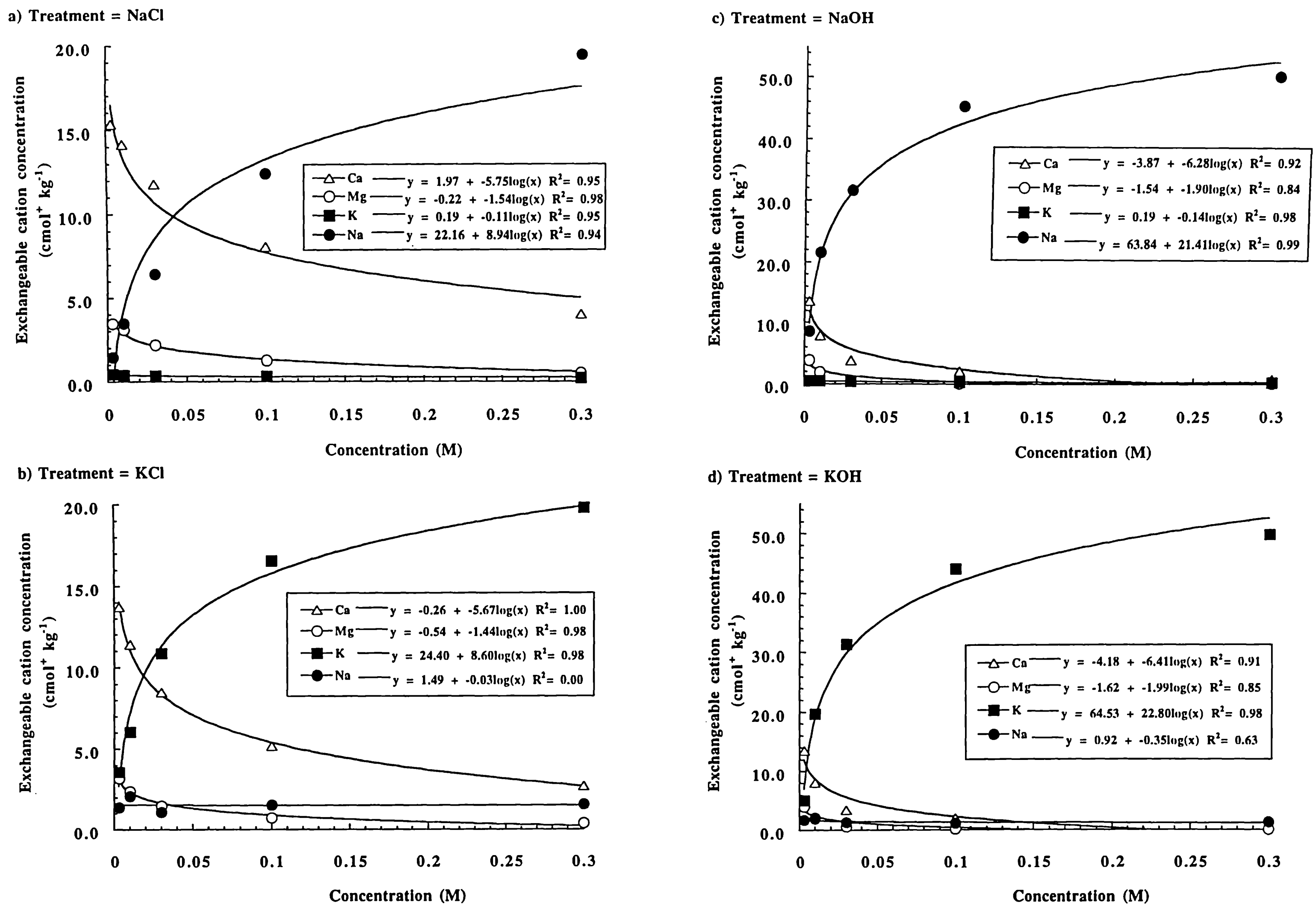

Fig. 1 Exchangeable cation concentrations (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) after treatment with different concentrations (0.003, 0.01, 0.03, 0.1, and 0.3 M) of: a) NaCl; b) KCl; c) NaOH; and d) KOH using Hopai silty clay. Symbols represent means (n=3). Most of the standard error of the means when plotted appear smaller than symbols used; maximum standard error is 1.2 $cmol_c\ kg^{-1}$).

other three soils (Table 2; Fig. 1b,d). When Na^+ was used as the index cation in the equilibration solutions, exchangeable K^+ concentrations either decreased with increasing Na^+ concentration (Fig. 1a,c) or were similar to initial concentrations (<0.5 $cmol_c\ kg^{-1}$).

Changes to exchangeable cations when Na^+ was used as the index cation (NaCl and NaOH) followed similar trends to those measured when K^+ was the index cation in treatment solutions. For example, exchangeable Na^+ increased logarithmically with concentration (Fig. 1a,c) and NaOH-treated samples resulted in a substantially higher exchangeable Na^+ concentration in the soil than NaCl-treated samples at all concentrations (Fig. 1a,c). In addition, similar trends to exchangeable K^+ concentrations were observed with respect to soil types. In Horotiu silt loam, NaOH-treated soil had c. 5x more exchangeable Na^+ than NaCl-treated soil at the highest concentration used (0.3 M) (Table 2). In the other three soils, exchangeable Na^+ concentrations were between 1.5-2.5x higher in NaOH-treated samples compared to chloride-treated samples when the highest (0.3 M) salt concentration was used (Table 2). However, when K^+ was the index cation present in equilibration solutions, exchangeable Na^+ concentrations either decreased with concentration (Fig. 1b,d) or remained close to (or the same as) initial concentrations (i.e. <0.5 $cmol_c\ kg^{-1}$).

SAR and PAR

Calculated SAR and PAR values of the soil solution after equilibration with treatments are presented in Table 4. SAR and PAR values were very similar when either chloride or hydroxide was the anion present in the equilibration solution, but differences existed between soils. The highest SAR and PAR values were recorded in the Horotiu soil at any given concentration (irrespective of cation or anion present) and the lowest values were recorded in the Hopai soil. Both the Manawatu and Wairua soils had similar (intermediate) SAR and PAR values at any given concentration of either chloride or hydroxide solution.

Table 4. Sodium adsorption ratio (SAR), exchangeable sodium percent (ESP), potassium adsorption ratio (PAR), and exchangeable potassium percent (EPP) in all four soils after different treatments. Values represent means (n=3).

Treatment	Concentration (M)	Hopai silty clay				Horotiu silt loam				Manawatu silt loam				Wairua silty clay			
		SAR	ESP	PAR	EPP	SAR	ESP	PAR	EPP	SAR	ESP	PAR	EPP	SAR	ESP	PAR	EPP
NaCl	0.003	4	7	-	-	7	20	-	-	5	1	-	-	9	10	-	-
	0.01	12	16	-	-	21	38	-	-	14	9	-	-	16	21	-	-
	0.03	31	31	-	-	52	54	-	-	36	29	-	-	38	36	-	-
	0.1	84	56	-	-	149	74	-	-	99	57	-	-	96	65	-	-
	0.3	218	80	-	-	423	82	-	-	268	81	-	-	252	85	-	-
KCl	0.003	-	-	3	16	-	-	7	25	-	-	4	13	-	-	3	25
	0.01	-	-	9	27	-	-	18	47	-	-	11	34	-	-	9	44
	0.03	-	-	25	49	-	-	47	59	-	-	30	50	-	-	27	63
	0.1	-	-	74	69	-	-	144	78	-	-	91	73	-	-	87	68
	0.3	-	-	210	81	-	-	413	86	-	-	261	85	-	-	245	88
NaOH	0.003	2	32	-	-	3	67	-	-	3	33	-	-	2	38	-	-
	0.01	5	68	-	-	8	93	-	-	8	62	-	-	8	64	-	-
	0.03	17	87	-	-	33	97	-	-	28	71	-	-	27	71	-	-
	0.1	63	95	-	-	129	97	-	-	99	73	-	-	97	76	-	-
	0.3	196	98	-	-	420	96	-	-	310	75	-	-	296	80	-	-
KOH	0.003	-	-	3	21	-	-	4	61	-	-	3	32	-	-	3	33
	0.01	-	-	5	62	-	-	8	92	-	-	9	57	-	-	8	62
	0.03	-	-	17	86	-	-	33	97	-	-	28	69	-	-	28	69
	0.1	-	-	63	93	-	-	129	96	-	-	102	70	-	-	99	72
	0.3	-	-	195	96	-	-	401	96	-	-	317	74	-	-	307	75

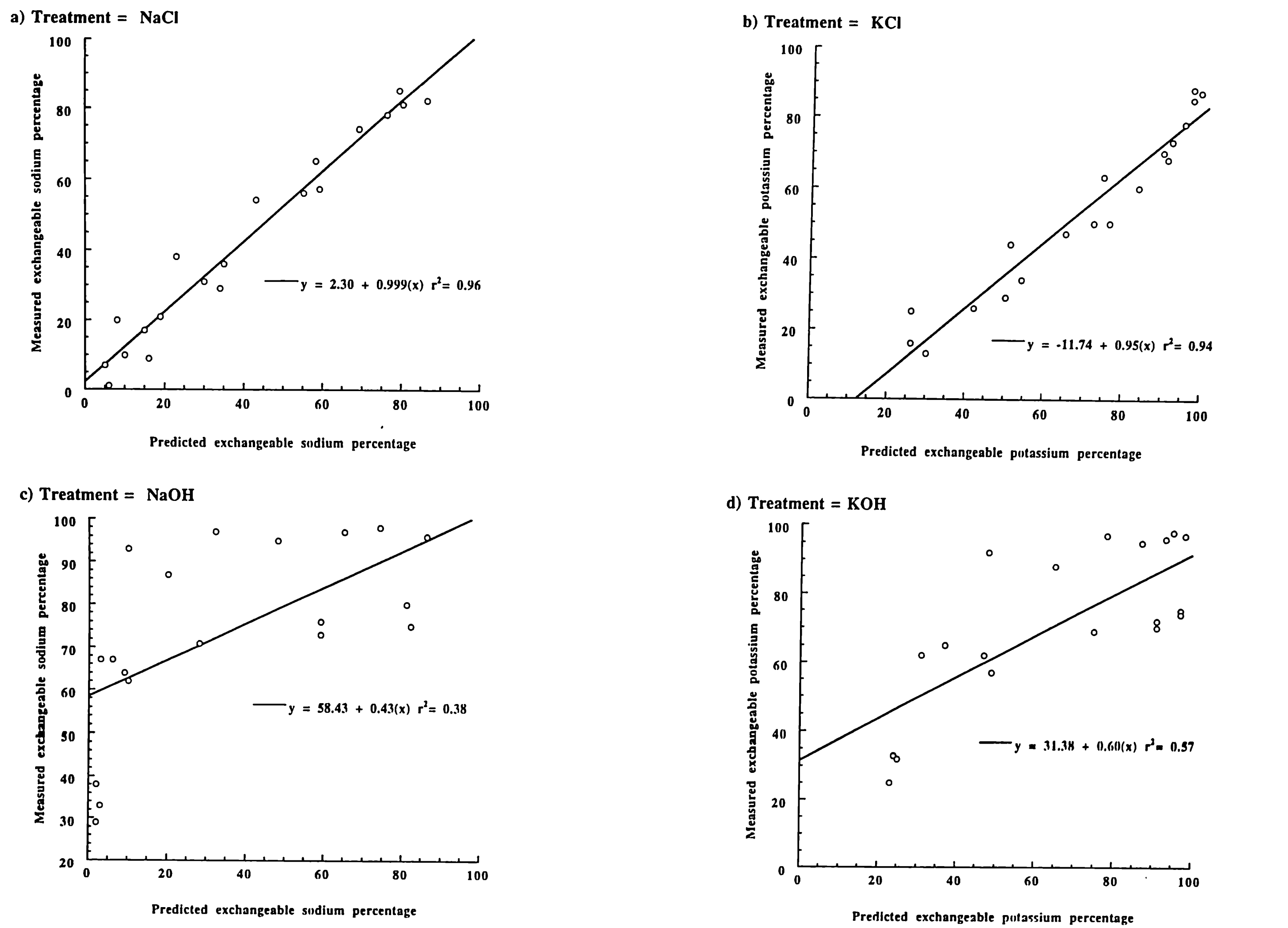

Fig. 2 Comparison between predicted and measured exchangeable sodium percent (ESP) and exchangeable potassium percent (EPP) values, using Richards (1954) equations, using data from all four soil types after treatment with: a) NaCl; b) KCl; c) NaOH; and D) KOH. Symbols represent means (n=3).

ESP and EPP (measured and predicted)

ESP and EPP increased with concentration and ranged from <10% in untreated soils up to 98% at the highest concentrations used (0.3 M). In most cases, hydroxide solutions resulted in a more rapid increase in ESP and EPP values with increasing concentration than chloride solutions (Table 4). The ESP and EPP values recorded when 0.3 M hydroxide solutions were used as treatments were higher than those measured in chloride treated samples for the Hopai and Horotiu soils (Table 4). In contrast to Hopai and Horotiu samples, ESP and EPP values were higher in chloride-treated samples (using 0.3 M) than hydroxide-treated samples in the Manawatu and Wairua soils (Table 4). However, in all soils, hydroxide-treated samples had higher ESP and EPP values than chloride solutions when all the other concentrations (i.e. <0.3 M) were used as treatments (Table 4).

The equation proposed by Richards (1954) to predict ESP values from SAR values in soil solution or irrigation water (equation 2) compared favorably with measured ESP values (i.e. slope of the best fit line in Fig. 2a is close to unity and the intercept is close to zero) for NaCl treatments using the data from all soil types (Fig. 2a). However, equation 5 tended to over-predict EPP values by c. 12% despite the slope of the line being close to unity (Fig. 2b). In addition, neither the ESP nor EPP prediction equation proposed by Richards (1954) accurately predicted ESP or EPP values when either NaOH or KOH were used as treatments (Fig. 2c,d).

Discussion

The presence of hydroxide anions in treatment solutions increased the negative charge (CEC) in all soils and the increase in CEC was concentration dependent (i.e. pH dependent). No increase in CEC was measured using chloride solutions. Higher ESP and EPP values were generally measured in hydroxide-treated soil compared to chloride-treated soil at each concentration used. The increase in exchangeable monovalent cation concentration with increasing anion concentration occurred at the expense of the other three exchangeable cations. ESP and EPP values were well predicted in chloride-treated soil using existing equations but these equations failed to accurately predict ESP and EPP values in hydroxide-treated soil.

It is well known that the charge characteristics of variable charge components in soil systems change according to solution pH. One of the major components in soil systems which displays variable charge characteristics is organic matter (Helling *et al.*, 1964). It has been shown previously that significant quantities of organic carbon are dissolved from the three soil types used in this study by both NaOH and KOH solutions (Lieffering and McLay, 1995). The previous study found that although less than 10% of the total organic carbon was dissolved at hydroxide concentrations ≤0.03 M, the amount dissolved increased substantially (up to c. 50% of total initial organic carbon) up to 0.3 M hydroxide in the same soil types used in the present study (Lieffering and McLay, 1995). The dissolution of any organic matter would, in theory, remove many of the cation exchange sites of the soil and any dissolution of organic matter could, therefore, result in a decrease in CEC of the soil. However, the results presented in this study and the study by Lieffering and McLay (1995) indicate that although hydroxide solutions cause considerable dissolution of organic carbon there is still a net increase in CEC.

The overall increase in negative charge (CEC) of all four soils in the presence of hydroxide solutions is attributed to the increased negative charges generated on variable charge surfaces of clay minerals (edge sites), sesquioxides, and the organic fractions which do not get dissolved by the hydroxide solutions. Alkali solutions have previously been shown to dissolve the humic and fulvic acid components of soil organic matter, with the humin fraction being alkali insoluble (Kononova, 1966; Stevenson, 1982; Oades, 1989). Schnitzer (1978) suggested that the humin fraction remains insoluble as it is firmly adsorbed on, or bonded to, the inorganic phase of the soil. Although the CEC of humins is less than that of both the fulvic and humic acid components, it has been reported to be up to 100 $cmol_c\ kg^{-1}$ (Oades, 1989), and can therefore still contribute significant negative charge with increasing soil solution pH. In addition, if the presence of hydroxide solutions in the soil solution only dissolves some of the humic and fulvic acid components, the remainder can, therefore, also contribute significantly to the increase in CEC with increasing pH. In contrast to hydroxide solutions, the presence of chloride anions did not cause significant changes to CEC, thereby implying that chloride and hydroxide anions have very different effects on charged surfaces of soils.

The differences in CEC between the different soils following treatment with hydroxide solutions may be attributed to differences in clay mineralogy and organic matter contents. Horotiu silt loam showed the greatest increase in CEC with increased concentration of hydroxide solution. Horotiu silt loam contains approximately 80% allophane (Singleton, 1991), a short range order clay mineral with marked variable charge properties (Parfitt, 1980), and it would therefore be expected that increases in solution pH would cause significant increases in CEC in this soil. Although it has been shown previously that the amount of organic carbon dissolved by hydroxide solutions in Horotiu silt loam was more than in the other three soils used in this study (Lieffering and McLay, 1995), the allophanic mineralogy plus the charge generated on the undissolved organic matter probably contributed to the higher CEC measured in this soil than the other three soils. Hopai silty clay had the second largest increase in CEC when using 0.3 M hydroxide solutions (c. 2.3x). Hopai silty clay contains significant amounts of montmorillonite, kaolinite, and illite, and also has higher organic carbon levels than the other three soils used (Table 1). It is suggested that the increase in negative charge is probably mainly on the edge sites of the kaolinite (Schofield and Samson, 1954) and undissolved organic matter. The other two soils, Manawatu and Wairua, showed smaller increases in CEC.

The adsorption of the (dominant) monovalent index cation onto newly generated exchange sites resulted in higher ESP and EPP values in the soils that had been treated with hydroxide solutions than chloride solutions in most instances. In the Hopai and Horotiu soils, the monovalent cations exchanged more readily for Ca^{2+}, the dominant divalent cation present in untreated soil, than the Manawatu and Wairua soils which retained more Ca^{2+} (as a percentage of CEC) with increasing hydroxide concentration. However, increasing the concentration of the treatment solution caused a decrease in exchangeable Ca^{2+} and Mg^{2+} and an increase in the index cation present in the treatment solution (either Na^+ or K^+) regardless of anion present.

High pH industrial liquid wastes can have pH values as high as pH 13.2 (Marshall and Harper, 1984) corresponding to a hydroxide concentration between 0.1 and 0.3 M. When liquid wastes of this composition are applied to soil it would be expected that the CEC of the soil in contact with this solution (particularly near the soil surface) would increase significantly. However, the newly formed negative sites will be balanced by the monovalent cations (normally Na^+ or K^+ in typical high pH industrial liquid wastes) present in the liquid waste. This study has shown that hydroxide and chloride concentrations between 0.1-0.3 M can lead to ESP and EPP values as high as 95%, however, exchangeable Na^+ or K^+ concentrations were much higher in hydroxide-treated soil than in chloride-treated soil. The accumulation of monovalent cations on exchange sites may in turn affect soil structure through clay dispersion and deflocculation processes. However, other factors, such as the presence of divalent cations in the liquid wastes, may decrease the exchangeable concentrations in the soil.

The equation presented by Richards (1954) for predicting ESP from SAR (equation 2) predicted measured ESP values very well when the soils were treated with NaCl but could not accurately predict ESP values in soils treated with NaOH. Similarly, the equation which predicts EPP values from PAR values (equation 5) predicted EPP values reasonably well when the soils were treated with KCl (however, the equation overestimated EPP values consistently by c. 12%) but could not accurately predict EPP values in KOH treated soil. Both equations presented by Richards (1954) assume that the CEC of the soils is unaffected by the salt present in the soil solution. This study has shown that hydroxide solutions cause significant increases in CEC and thus ESP and EPP values can not be accurately predicted by current equations as they do not take into account the newly generated negative sites which allows significantly higher concentrations of monovalent cations to accumulate.

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Chapter 7
Field Trial

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Field Trial

7.1 Introduction

Structural problems in the surface 0-10 cm depth of soil have been observed in soils spray irrigated with high pH dairy factory liquid wastes by the Northland Dairy Company at Kauri, near Whangarei. A field trial was conducted to examine the short term effects that surface applied gypsum had on selected soil chemical and physical properties at a field site where liquid waste with high monovalent cation concentrations and high pH was regularly spray irrigated. The field trial was conducted on an established and operating dairy farm to simulate "normal" farm management conditions. The trial started in June 1994 and gypsum was applied to two sites, one site which had a 3 year history of spray irrigation with high pH liquid wastes and where spray irrigation occurred during the trial period, and one site which had not been spray irrigated (which acted as a control). Selected soil physical and chemical properties were measured approximately every 3 months for a period of 12 months to examine the short term effects that gypsum had on soil properties.

The following chapter is a copy of a manuscript entitled "The effect of surface applied gypsum on soil properties in a soil irrigated with high pH liquid waste". This manuscript is intended for publication in *Soil Technology.* The manuscript has been slightly reformatted from the original manuscript to maintain consistency throughout the thesis. Reference made to Lieffering and McLay (1995) in this manuscript corresponds to Chapter 4 (Organic carbon dissolution), reference to Lieffering and McLay (in press) refers to Chapter 5 (Aggregate stability and hydraulic conductivity), and reference to Lieffering and McLay (unpublished data) refers to Chapter 6 (Cation exchange properties).

The reader is also referred to Appendix D: Supplementary information and data for Chapter 7, for additional information and photographs pertaining to the field trial.

The effect of surface applied gypsum on selected soil properties in a soil irrigated with high pH liquid waste

Abstract

The effectiveness of surface applied gypsum (5 t ha^{-1}) on remediation of selected soil physical and chemical properties was studied at a site where dairy factory liquid waste with high monovalent cation concentrations and high pH had been spray irrigated onto the soil for the past three years. The site was a farm used for dairy grazing and was under "normal" farm management throughout the study period. Soil infiltration rates, bulk density, organic carbon, pH, exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}), and cation exchange capacity were measured at 3 monthly intervals for 12 months after initial gypsum application. Gypsum had a positive effect on infiltration rates in irrigated soil but had no significant effect on infiltration rates in non-irrigated soil. Gypsum increased exchangeable Ca^{2+} concentrations, and decreased exchangeable Mg^{2+}, K^{+}, and Na^{+} concentrations in the irrigated soil (thereby also lowering the exchangeable sodium percentage and exchangeable potassium percentage) whereas very little change in soil chemistry was measured due to gypsum application in the non-irrigated soil. The differences recorded between irrigated and non-irrigated soils are attributed to lower initial exchangeable Ca^{2+} concentrations and higher initial exchangeable K^{+} and Na^{+} concentrations in the irrigated soil compared to the non-irrigated soil as a result of the 3 year history of spray irrigation with high monovalent cation concentration liquid waste which this soil has had. Soil bulk density, organic carbon, pH, and cation exchange capacity were generally unaffected by gypsum application in both irrigated and non-irrigated soil. Gypsum, therefore, had more effect on some soil properties in the shorter term, by increasing exchangeable Ca^{2+} concentrations in the irrigated soil whereas gypsum had little effect on soil properties in the non-irrigated soil because of the higher initial exchangeable Ca^{2+} concentrations. The application of soluble salts such as gypsum to increase divalent cation concentrations in the soil solution, which can lower exchangeable sodium percent and exchangeable potassium percent, is therefore recommended at sites where land treatment of liquid wastes with high monovalent cation concentrations and high pH is practiced.

Introduction

Liquid wastes which contain high monovalent cation concentrations and high pH are produced by many industries and land treatment of the wastes is a common method of disposal. The liquid wastes are typically characterised by high Na^+ and/or K^+ concentrations and high pH (which are often between pH 10-12 but can be as high as pH 13.2). The high monovalent cation concentration and high pH arises from the use of NaOH and/or KOH for processing or cleaning purposes. Industries which commonly produce these types of liquid wastes include dairy manufacturing (Barnett *et al.*, 1994), meat processing (Keeley and Quin, 1979), leather treatment, and wool scouring industries.

Few reports exist in the literature which have investigated the effects of spray irrigating liquid wastes with high monovalent cation concentrations and high pH on soil properties in the field. Barnett and Parkin (1985) reported that soil pH had increased from 5.8 to 7.2 and exchangeable Na^+ concentrations had increased in the soil profile to a depth of 60 cm in an allophanic soil spray irrigated with high pH dairy factory liquid wastes. Other workers (Keeley and Quin, 1979; Hart and Speir, 1992; Balks, 1990) have reported increased pH, exchangeable Na^+, exchangeable sodium percent (ESP), and cation exchange capacity (CEC) in different soils throughout New Zealand which have been spray irrigated with high pH and high monovalent cation concentration meat processing liquid wastes. At many sites where high pH liquid wastes are spray irrigated, structural deterioration has been observed in the upper 10 cm of the soil profile, often resulting in a surface crust which restricts the movement of either the applied liquid wastes and/or rainfall.

Previous laboratory studies have shown that NaOH and KOH solutions can cause: i) dissolution of organic carbon (OC) (Lieffering and McLay, 1995); ii) a decrease in aggregate stability and hydraulic conductivity (Lieffering and McLay, in press); and iii) higher CEC and exchangeable Na^+ and K^+ concentrations (Lieffering and McLay, unpublished data) in the topsoils of a range of New Zealand soils.

Some workers have investigated the effects of chemical amendments on soil properties where high pH liquid wastes are spray irrigated. Carter (1994) found that neither $CaCO_3$ nor $Ca(OH)_2$ application caused any improvements in chemical or physical properties of a soil which had been spray irrigated with high pH liquid wastes from a meat processing plant. Barnett and Upchurch (1992) showed that application of $CaCO_3$ (0-6 t ha^{-1}) resulted in higher soil pH and increased proportions of Na^+ and Ca^{2+} on exchange sites in soils spray irrigated by high pH dairy factory wastes. The same study found that soil bulk density (ρ_b) had decreased in one soil type (with clay mineralogy dominated by halloysite) but no difference was measured in another soil type (with clay mineralogy dominated by allophane). Surprisingly, the effects of gypsum ($CaSO_4.2H_2O$) on soil receiving high pH liquid wastes do not appear to have been studied.

A large amount of literature is available on the effectiveness of gypsum for the reclamation and remediation of sodic and saline soils or amelioration of subsurface acidity (reviewed in detail by Shainberg *et al.*, 1989). The effects of gypsum on soil physical properties is often attributed to either increasing the electrolyte concentration or increasing Ca^{2+} concentrations in the soil solution (thereby exchanging for monovalent cations on exchange surfaces) (Shainberg *et al.*, 1982). Both of these mechanisms have been suggested to promote structural stability and increase soil infiltration and hydraulic conductivity rates.

The objectives of the present study were to study the effect that surface applied gypsum has in the short term (i.e. 12 month period) on selected physical and chemical exchange properties in a soil which had been irrigated with liquid waste with high monovalent cation concentrations and high pH. It should be noted that this trial was conducted on a natural site (i.e. a working dairy farm) which had a 3 year history of spray irrigation with high pH dairy factory liquid wastes.

Materials and methods

Field trial location and design

The field trial was conducted on a dairy farm property which is owned and operated by the Northland Dairy Company, Whangarei, New Zealand (lat. 35°37' S, long. 174°16' E, and altitude 90 m). The annual average rainfall of the area is 1751 mm and the mean monthly temperatures vary from 11.2°C in July to 19.8°C in February (New Zealand Meteorological Service, 1980).

Two plots (25 m^2) were located in two pasture sites, one of the pasture sites having a three year history of spray irrigation with high pH liquid wastes and the other site (adjacent to the irrigated site) having never been irrigated with liquid wastes. One of the plots in each pasture site received a single gypsum application (equivalent to 5 t ha^{-1}) on 28/6/94 (hereafter referred to as +G plots) and the other plot received no gypsum (i.e. control plot; hereafter referred to as -G plots). Field measurements of infiltration rate and ρ_b were made at approximately three monthly intervals over a 12 months period. On each sampling date, 5 topsoil (0-10 cm) samples were collected from each plot for analysis of exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+), CEC, and soil pH. In addition, 5 samples of the soil surface (0-1 cm depth) in each plot were sampled on each collection date for OC analyses. The surface samples were analysed for OC because previous laboratory work had shown that soils leached with hydroxide based solutions develop a surface crust which have lower OC contents than untreated samples (Lieffering and McLay, in press).

The site which received liquid wastes was irrigated a total of 11 times by Northland Dairy Company over the 12 month duration of the trial with volumes of waste application varying throughout the trial period (Table 1). The spray irrigation rate was 6 mm h^{-1} and spray duration varied between 40 min to 5 h. The nature of the high pH liquid waste which was spray irrigated during the study was not determined for each irrigation, however, typical characteristics of the liquid waste are presented in Table 2. It should be noted that the farm on which the trial was conducted was an intensive dairy farm and both the irrigated and non-irrigated sites were periodically grazed (including intensive "strip grazing") throughout the duration of the trial. Therefore, the variable nature of the liquid waste applied and the presence of heavy livestock on the plots, represented the natural farm management system and the trial was therefore not conducted under controlled conditions.

Table 1. Dates when irrigated site received liquid wastes and volumes (mm) sprayed.

Irrigation date	Volume of liquid waste applied (mm)
26/8/94	54
28/9/94	36
16/10/94	30
6/11/95	24
21/11/95	33
2/1/95	22
2/3/95	33
16/3/95	21
17/4/95	36
Total volume applied	289 mm

Table 2. Typical composition of liquid waste applied to irrigated site.

Chemical parameter	Value
pH	10-12
Ca	82 g m^{-3}
Mg	37 g m^{-3}
Na	400 g m^{-3}
K	260 g m^{-3}
PO_4	220 g m^{-3}
NO_3	16 g m^{-3}

Soil type

The soil type of the field site has been mapped as Wairua clay (Sutherland *et al.*, 1981). The topsoil texture of soil in the field trial was silty clay and the name Wairua silty clay is therefore used in this study. Properties of Wairua silty clay (Aeric Endoaquult, Soil Survey Staff, 1994) have been presented elsewhere (Lieffering and McLay, 1995).

Field measurements

To investigate the effect that gypsum had on water movement and compaction, two soil parameters which are simple to measure and are good indicators of physical change in soils (infiltration rate and ρ_b) were measured. Measurement of infiltration rates were conducted using undisturbed soil cores collected in stainless steel cores (10 cm internal diameter x 10 cm long) and shallow (c. 2 cm depth) ponding. Each core was carefully inserted into the surface of the soil to a depth of c. 6 cm and excavated. The base of the soil core was then carefully cleared to expose any blocked or smeared pores. Petroleum grease was liberally applied around the inside of the cutting edge of the cores prior to insertion into the soil to minimise the possibility of edge flow and to assist insertion. The cores were wetted up for 1 h prior to infiltration rate measurements by maintaining the constant head of water (c. 2 cm). After 1 h, the volume of water required to maintain the constant head was measured over a period of 10 min, or until 1 L of water had passed through the core (in cases where the cores had very high infiltration rates). Ten measurements were made in the +G and -G plots within each site on every sampling date.

Measurements of soil ρ_b at the site were conducted by inserting and extracting brass cores (4.5 cm internal diameter x 3.5 cm long) from the 0-3.5 cm depth. Ten cores were collected per plot on each sampling date. However, during the second sampling date (December 1994) the soil at the field site was too hard and dry to accurately collect ρ_b samples and therefore no data is available for this date. Wairua silty clay is prone to swelling depending on the moisture status of the soil. In swelling soils, the ρ_b can vary with moisture content and the ρ_b obtained should be accompanied by the water content of the soil at the time of sampling (Blake and Hartge, 1986). Volumetric water contents (θ_v) were therefore also calculated for each of the collected ρ_b cores.

Laboratory analyses

Exchangeable cations and CEC were measured using a single-step extraction with unbuffered silver thiourea (AgTU) (Blakemore *et al.*, 1987). Sieved (<2 mm) air-dry soil was shaken with 0.01 M AgTU solution at a 1:50 soil to solution ratio. Exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) and Ag^+ ions (for CEC measurements) were measured using atomic absorption spectrophotometry. Exchangeable sodium percentages (ESP) were calculated from measured exchangeable cation concentrations according to equation 1,

$$\mathrm{ESP} = 100 \times \frac{\text{exchangeable Na}}{\sum \text{exchangeable Ca} + \text{Mg} + \text{K} + \text{Na}} \tag{1}$$

and exchangeable potassium percentages (EPP) were calculated from measured values according to equation 2,

$$\mathrm{EPP} = 100 \times \frac{\text{exchangeable K}}{\sum \text{exchangeable Ca} + \text{Mg} + \text{K} + \text{Na}} \tag{2}$$

Soil pH was measured at a 1:2.5 soil to distilled water ratio (Blakemore *et al.*, 1987). Organic carbon was measured using a slight variation of the Modified Mebius Method (Nelson and Sommers, 1982) using 0.5 g air-dry soil (<2 mm), 20 mL $K_2Cr_2O_7$ (50 g L^{-1}) solution, and 20 mL 98% H_2SO_4.

Results

Selected soil physical properties

Measured infiltration rates varied by over two orders of magnitude in some sites between winter and summer sampling dates due to the swelling nature of the clay minerals which resulted in large cracks appearing during summer months. Infiltration rates are therefore presented in this paper as relative infiltration rates. Relative infiltration rate within either the irrigated or non-irrigated site on any sampling date is defined as (also see Table 3):

$$\text{Relative infiltration rate} = \frac{\text{mean infiltration rate of } +\text{G plot}}{\text{mean infiltration rate of } -\text{G plot}} \qquad (3)$$

Measurements of water movement in soils is frequently reported to be lognormally distributed (Warrick and Nielson, 1980). Calculated standard deviations of measured infiltration rate means were proportional to the means which is indicative that the data were lognormally distributed (Gomez and Gomez, 1984) and measured infiltration rates were, therefore, log-transformed (using natural logarithms) prior to statistical analysis. Relative infiltration rates were always >1 in the irrigated soil (Table 3) but differences (P<0.10) between +G and -G plots were only recorded 3 and 6 months after gypsum application. Gypsum did not affect (P>0.10) infiltration rate in the non-irrigated soil (Table 3).

Table 3. Mean and relative[a] infiltration rate (IR) of gypsum (+G) and non-gypsum (-G) plots in irrigated (I) and non-irrigated (NI) sites. Values represent means (n=10).

Infiltration rate (IR)	Site and treatment	Months after gypsum application 3	6	9	12
	I+G	240.6 *	1193.5 *	79.9 ns	30.0 ns
Mean	I-G	57.9	523.7	57.1	4.3
IR ($mm\ h^{-1}$)	NI+G	8.2 ns	1928.6 ns	236.4 ns	7.1 ns
	NI-G	7.6	3104.7	289.7	3.0
Relative	I	4.2	2.3	1.4	7.0
IR[a]	NI	1.1	0.6	0.8	2.4

[a] relative IR = $IR_{(+G\ plot)}/IR_{(-G\ plot)}$; i.e. where relative IR>1, gypsum had a positive effect.

* denotes significant difference (P<0.10) between +G and -G plots within each site.

ns denotes no significant difference (P<0.10) between +G and -G plots within each site.

Gypsum did not affect (P>0.10) ρ_b in either the irrigated or non-irrigated soil throughout the trial (Table 4) and there was no apparent trend of ρ_b changes recorded over time.

Table 4. Bulk density (ρ_b) and volumetric moisture contents (θ_v) for soil collected 3, 9, and 12 months after gypsum application. Values in parentheses represent standard error of means (n=10).

Months after application	Irrigated site				Non-irrigated site			
	Non-gypsum		Gypsum		Non-gypsum		Gypsum	
	ρ_b	θ_v	ρ_b	θ_v	ρ_b	θ_v	ρ_b	θ_v
3	0.68 (0.01)	0.61	0.72 (0.02)	0.57	0.74 (0.02)	0.56	0.75 (0.03)	0.55
6*	-	-	-	-	-	-	-	-
9	0.77 (0.02)	0.47	0.75 (0.01)	0.45	0.81 (0.02)	0.41	0.77 (0.02)	0.43
12	0.80 (0.02)	0.61	0.76 (0.02)	0.60	0.76 (0.02)	0.64	0.81 (0.04)	0.62

* No data available (see text)

Selected soil chemical properties

Soil pH was affected by gypsum application in both irrigated and non-irrigated soil on some sampling dates, but no overall trend was measured over time (Fig. 1). Where differences (P<0.10) were measured between +G and -G plots, soil pH was always lower in the gypsum treated plots.

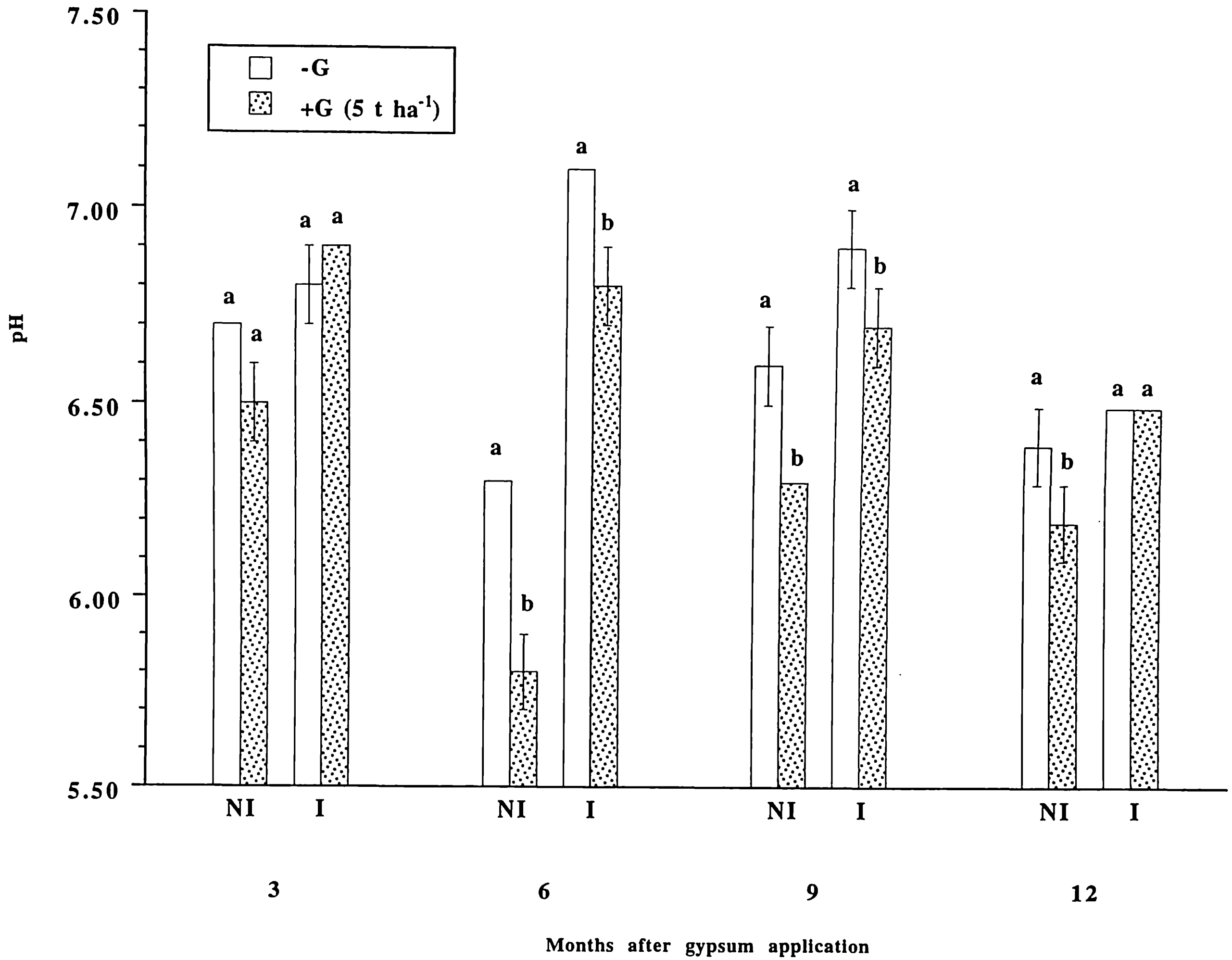


Fig. 1 Soil pH after gypsum application (5 t ha^{-1}) in an irrigated (I) and non-irrigated (NI) soil measured 3, 6, 9, and 12 months after application. Values plotted represent means (n=5) and error bars represent standard error of means. Bars with different letters (a or b) indicate a significant difference (P<0.10) occurred between gypsum (+G) and non-gypsum (-G) plots within each site on each sampling date.

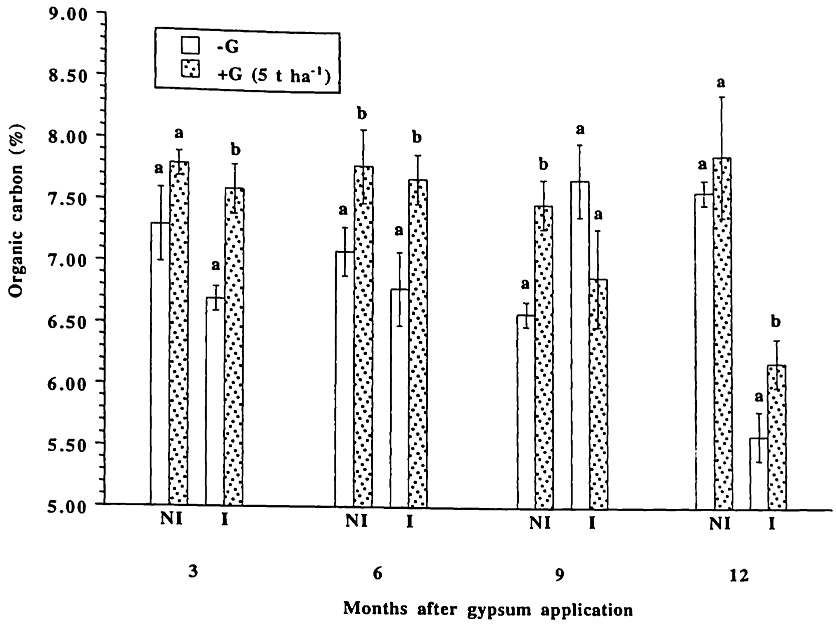
Soil OC contents in the 0-1 cm depth layer were affected by gypsum application in both irrigated and non-irrigated soil at various times throughout the trial (Fig. 2), but no definite trends were measured over time. Where differences (P<0.10) were measured between +G and -G plots, OC contents were always higher in the +G plots. In all plots throughout the trial, OC contents were between 6.5-8.0% except in the irrigated soil sampled 12 months after gypsum application when lower OC contents were measured (c. 5.5-6.5%).

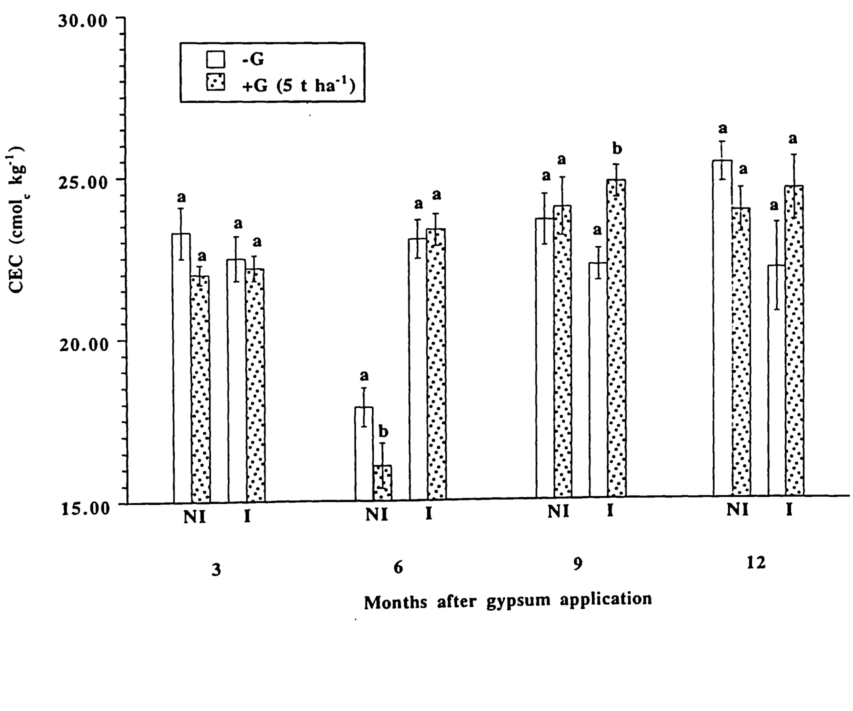
CEC was not generally affected by gypsum application throughout the 12 month period (Fig. 3). On all sampling dates, the CEC was between 22-25 $cmol_c\ kg^{-1}$ except those measured in the non-irrigated soil after 6 months where both the +G and -G plots had lower CEC values (Fig. 3). Gypsum increased (P<0.10) exchangeable Ca^{2+} concentrations in irrigated soil but had a variable effect in non-irrigated soil (Fig. 4a). Exchangeable Mg^{2+} concentrations were always higher in -G plots than in +G plots in both non-irrigated and irrigated soils on all sampling dates (Fig. 4b), however these differences were not always significant. Gypsum had no effect on exchangeable K^+ concentrations in the non-irrigated soil but resulted in lower (P<0.10) exchangeable K^+ concentrations in the irrigated soil 9 and 12 months after gypsum application (Fig. 4c). In irrigated soil, exchangeable K^+ concentrations increased to a maximum (c. 4 $cmol_c\ kg^{-1}$) after a period of 6 months after gypsum application. Thereafter, exchangeable K^+ concentrations decreased over time in both +G and -G plots. In the non-irrigated soil, exchangeable K^+ concentrations remained relatively constant (and relatively low compared to the irrigated soil) over time. Exchangeable Na^+ concentrations were lower (P<0.10) in the +G plot on all sampling dates in the irrigated soil but gypsum application had no effect on exchangeable Na^+ concentrations in the non-irrigated soil (Fig. 4d). In irrigated soil, exchangeable Na^+ concentrations increased to a maximum (c. 4 $cmol_c\ kg^{-1}$) after a period of 6 months after gypsum application and decreased thereafter.

In the irrigated soil, gypsum lowered both ESP and EPP values, with +G plots having approximately half the ESP values recorded in -G plots (Table 5). In -G plots, ESP values increased over the first 6 months and remained constant at c. 14% thereafter. In contrast, ESP in +G treated plots increased to nearly 10% after a period of 6 months after gypsum application and then remained fairly constant at c. 7%. Less difference between EPP values were measured between +G and -G plots (Table 5).

Fig. 2 Soil organic carbon after gypsum application (5 t ha^{-1}) in an irrigated (I) and non-irrigated (NI) soil measured 3, 6, 9, and 12 months after application. Values plotted represent means (n=5) and error bars represent standard error of means. Bars with different letters (a or b) indicate a significant difference (P <0.10) occurred between gypsum (+G) and non-gypsum (-G) plots within each site on each sampling date.

Fig. 3 Cation exchange capacity (CEC) after gypsum application (5 t ha^{-1}) in an irrigated (I) and non-irrigated (NI) soil measured 3, 6, 9, and 12 months after application. Values plotted represent means (n=5) and error bars represent standard error of means. Bars with different letters indicate a significant difference (P<0.10) occurred between gypsum plot and non-gypsum plot within each site on each sampling date.


-G
+G (5 t ha^{-1})
Organic carbon (%)
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
NI I NI I NI I NI I
3 6 9 12
Months after gypsum application


-G
+G (5 t ha^{-1})
CEC (cmol$_c$ kg^{-1})
30.00
25.00
20.00
15.00
NI I NI I NI I NI I
3 6 9 12
Months after gypsum application

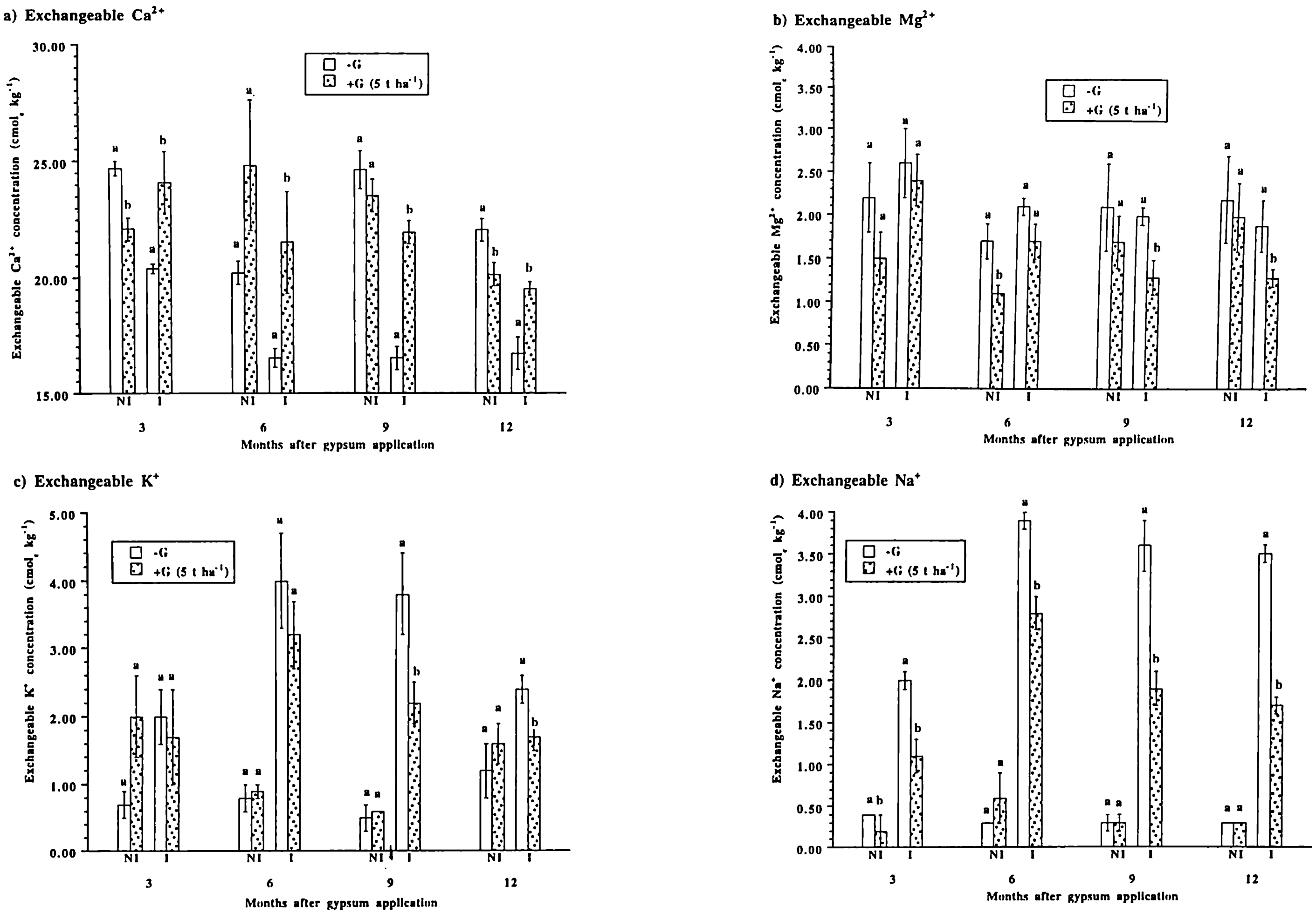


Fig. 4 Exchangeable cations, (a) Ca^{2+}, (b) Mg^{2+}, (c) K^{+}, and (d) Na^{+} after gypsum application (5 t ha-1) in irrigated (I) and non-irrigated (NI) sites measured 3, 6, 9, and 12 months after application. Values plotted represent means (n=5) and error bars represent standard error of means. Bars with different letters (a or b) indicate a significant difference ($P<0.10$) occurred between gypsum (+G) and non-gypsum (-G) plots within each site on each sampling date.

EPP values in -G plots increased to 15% after a period of 6 months after gypsum application and then decreased to 10% thereafter. EPP values in +G plots were always lower than those measured in -G plots and remained constant at c. 7% for the 12 month post-application period (Table 5).

Table 5. Exchangeable sodium percent (ESP) and exchangeable potassium percent (EPP) in irrigated soil in plots which received gypsum (+G) and plots which did not have gypsum (-G) application. Values represent means (n=5) and values in parentheses represent standard error of means.

Months after	ESP		EPP	
gypsum application	-G plot	+G plot	-G plot	+G plot
3	7.6 (0.3)	3.7 (0.6)	7.3 (1.2)	5.7 (2.4)
6	14.8 (0.2)	9.7 (0.9)	15.0 (2.3)	11.3 (1.9)
9	13.8 (0.7)	7.0 (0.8)	14.7 (2.2)	8.9 (0.8)
12	14.1 (0.4)	7.1 (0.5)	10.0 (1.2)	7.2 (0.8)

Discussion

The surface application of gypsum to soil which had been spray irrigated with the high monovalent cation concentration and high pH liquid wastes affected infiltration rates, exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}), ESP and EPP values but had little effect on other measured soil properties (soil ρ_b, OC, pH, and CEC) in the short term. In contrast to the irrigated site, gypsum had minimal effect on any of the measured soil properties in the non-irrigated soil.

The positive effect of gypsum on infiltration rates is similar to other reports of beneficial effects of gypsum, particularly in the reclamation of sodic and saline soils or other soils which are prone to dispersion (e.g. Keren and Shainberg, 1981; Shainberg *et al.*, 1982; Miller and Scifres, 1988; Zahow and Amrhein, 1992). However, the lack of improvement (i.e. no gypsum effect measured) in the non-irrigated soil may be explained by the fact that this soil had significantly higher initial exchangeable Ca^{2+} concentrations compared to the irrigated soil and no structural problems pre-existed in this soil. The lower initial exchangeable Ca^{2+} concentrations in the irrigated soil may be explained by the fact that three years of liquid waste application on the irrigated site had decreased the exchangeable Ca^{2+} concentrations, presumably as a result of increased exchangeable Na^+ and K^+ concentrations. Both these monovalent cations have previously been shown (in laboratory experiments) to cause structural problems in the Wairua silty clay soil (Lieffering and McLay, in press). The application of gypsum substantially increased exchangeable Ca^{2+} concentrations in the irrigated soil, which is consistent with previous reports of changes to soil chemical properties following gypsum application (Shainberg *et al.*, 1989; McCray *et al.*, 1991; Armstrong and Tanton, 1992).

Gypsum application did not affect ρ_b in either the irrigated or non-irrigated soil. The ρ_b of Wairua silty clay soil is naturally low (c. 0.70-0.80 Mg m^{-3}) and no significant compaction (as assessed by ρ_b measurements) had occurred in the irrigated soil despite 3 years of irrigation prior to this trial. Differences in ρ_b between +G and -G plots were not measured and is similar to the results of other workers (Hall *et al.*, 1994). However, it is also possible that differences between +G and -G plots may have been masked due to farm management practices during the trial. These practices included intensive grazing by large stock animals (both in irrigated and non-irrigated sites) which would cause significant artificial modification of the structure in the soil (especially in the surface horizon) during winter months or unseasonably wet periods through pugging and compaction.

The changes in exchangeable cations measured over a period of 12 months after gypsum application in the irrigated soil can be explained by cation exchange processes. In the irrigated soil, the applied gypsum would have increased the Ca^{2+} concentration in the soil solution and displaced other cations (particularly Na^+ and K^+) present on exchange sites in the soil over time. Loveday (1976) reported similar results with higher exchangeable Ca^{2+} concentrations at the expense of exchangeable Na^+ and Mg^{2+} following gypsum application. Syed-Omar and Sumner (1991) also found that gypsum application decreased concentrations of exchangeable K^+ and Mg^{2+} and that production yields of some crops were adversely affected at gypsum rates >5 t ha^{-1} due to lower plant availability of K^+ and Mg^{2+}. At the study site for the research reported in this paper, it would therefore be recommended that pasture Mg was regularly monitored to ensure that pasture and animal health was maintained. The general lack of change in exchangeable cations in the non-irrigated soil may be due to the relatively low initial concentrations of exchangeable Mg^{2+}, K^+, and Na^+ concentrations in this soil and the relatively high initial exchangeable Ca^{2+} concentrations (as discussed previously).

Both ESP and EPP were lowered by gypsum application in the irrigated soil due to higher exchangeable Ca^{2+} concentrations and lower exchangeable Na^+ and K^+ concentrations. In the irrigated soil, exchangeable Na^+ and K^+ accounted for over a quarter (c. 28%) of the exchangeable cations in the -G plot, but less than 15% in +G plots. This has important implications with respect to clay dispersion, as increased concentrations of both Na^+ and K^+ on exchange sites have previously been shown to adversely affect hydraulic conductivity through clay swelling, dispersion, and deflocculation processes when water with low total electrolyte concentration is leached through the soil (Ahmed *et al.*, 1969; Lieffering and McLay, in press).

Previous laboratory studies using Wairua silty clay soil have shown that NaOH and KOH solutions can cause considerable dissolution of OC (Lieffering and McLay, 1995). However, lower OC concentrations in the irrigated soil compared to the non-irrigated soil were only recorded at the last sampling date, despite 3 years previous irrigation history with high pH liquid wastes. It is possible that substantial mixing of topsoil occurs due to extensive pugging by livestock during wet periods, causing large variability, and may have masked differences in the upper 1 cm of soil at the site. It is also probable that pH buffering mechanisms in the field may lower the pH of the high pH liquid wastes within the top 10 cm of soil, thereby decreasing the effectiveness of the hydroxides to dissolve OC. The application of gypsum had little effect on OC in the surface 0-1 cm depth of soil within the first 12 months after application in either irrigated or non-irrigated soil, this is similar to results found in the study by Hall *et al.*

(1994). If pasture production increases in the longer term due to the positive effects of gypsum on infiltration rates and soil structure, soil OC contents may increase slightly.

Soil pH was slightly higher in the irrigated soil than the non-irrigated soil throughout the trial and is attributed to the 3 year history of high pH liquid waste application to the site. The magnitude of the increase is affected by the buffering capacity of the soil. In general, soil pH was not affected by gypsum application. Where differences were observed, gypsum plots always had lower soil pH values than non-gypsum plots. The increase in Ca^{2+} in the soil solution due to dissolution of the gypsum may result in an exchange of H^+ ions from exchange sites into soil solution thereby decreasing the pH.

Lime ($CaCO_3$) has been used at a few sites in New Zealand as a soil amendment where liquid wastes with monovalent cation concentrations and high pH are spray irrigated onto soil. In New Zealand, lime was chosen for its source of Ca^{2+} and preferred to gypsum on an economic basis. However, Barnett and Upchurch (1992) found that lime application caused soil pH to rise in a soil spray irrigated with high pH dairy factory wastes. Gypsum may be a more suitable alternative to lime because of its higher solubility (gypsum solubility, 14 mmol L^{-1}; lime, 0.14 mmol L^{-1}), which will result in higher concentration of Ca^{2+} in the soil solution (which would decrease exchangeable Na^+ and K^+).

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Chapter 8
Synthesis, Conclusions, and Recommendations

Chapter 8
Synthesis, conclusions, and recommendations

8.1 Overview and synthesis of results

8.1.1 Introduction

Disposal of liquid wastes with high monovalent cation concentrations and high pH using land treatment systems poses unique soil problems due to the combined effects of: i) the presence of monovalent cations (Na^+ and K^+) in the liquid waste which can accumulate on cation exchange sites in the soil; and ii) the presence of hydroxide anions (i.e. solution pH) which can dissolve organic carbon (OC) and result in increased repulsion between soil particles. Although some reports exist in the literature which quantify changes in soil physical and chemical properties under field conditions where high pH liquid wastes are spray irrigated, there is a distinct lack of literature available on the processes involved. A large amount of literature is available on the effects of Na^+, and to a lesser extent K^+, on soil properties, but many previous studies investigating the effects of monovalent cations on soil properties have not considered the effects of the accompanying anion.

It is widely acknowledged that structural deterioration, particularly in the surface horizon (0-10 cm) of the soil profile, occurs at many sites throughout New Zealand where liquid wastes with high monovalent cation concentrations and high pH are spray irrigated. The surface horizon is often a structureless mass (i.e. single-grained) which is very soft when wet (during winter months or periods of intense irrigation) and extremely hard when dry (during summer months). Prior to this study, the observed structural deterioration of surface horizons were considered by many workers (i.e. people involved with design and monitoring of land treatment systems) to occur due to dispersion and deflocculation processes because of the presence of high concentrations of Na^+ and K^+ in the liquid wastes. However, this study has shown that other factors may play a more important role in the deterioration of the soil physical properties and that substantial changes can occur to soil chemical exchange properties when high pH liquid wastes are applied to soil.

8.1.2 Proposed conceptual model

A conceptual model is proposed in Fig. 8.1 which illustrates the possible reactions which can occur in soils when liquid wastes which contain high monovalent cation concentrations and high pH are applied to the surface of the soil. The model also illustrates the effect that lowering the pH (either by neutralisation or through pH buffering by the soil) has on soil reactions.

8.1.2.1 High pH liquid wastes directly applied to soil

When high pH liquid wastes are applied directly to the soil surface, a two-stage process occurs (at the 0-1 cm depth). Firstly, OC dissolution occurs and leads to aggregate instability (Box A, Fig. 8.1); and secondly, the increased pH of the soil solution increases the negative charge on variable charge components in the soil which leads to increased repulsion between particles (Box B). These two processes combine to induce aggregate collapse (Box C) which results in decreased hydraulic conductivity through pore blockage (Box D) and finally surface crust formation occurs (Box E).

8.1.2.2 Lowering the pH of the liquid waste

The pH of liquid wastes which contain high monovalent cation concentrations can be lowered either by acid dosing (prior to land treatment) or by the natural pH buffer capacity of the soil. When the pH is lowered, the monovalent cations present in the liquid waste will accumulate on exchange sites resulting in increased exchangeable sodium percent (ESP) and exchangeable potassium percent (EPP) in the soil (Box F). The hydraulic conductivity of the soil will be unaffected as long as the electrolyte concentration (EC) of the percolating solution (i.e. the liquid waste) remains high. The high EC of the soil solution effectively compresses the diffuse double layer (DDL) surrounding soil particles (Box H) allowing the particles to remain close to each other and the soil stays flocculated. However, when low EC solutions are

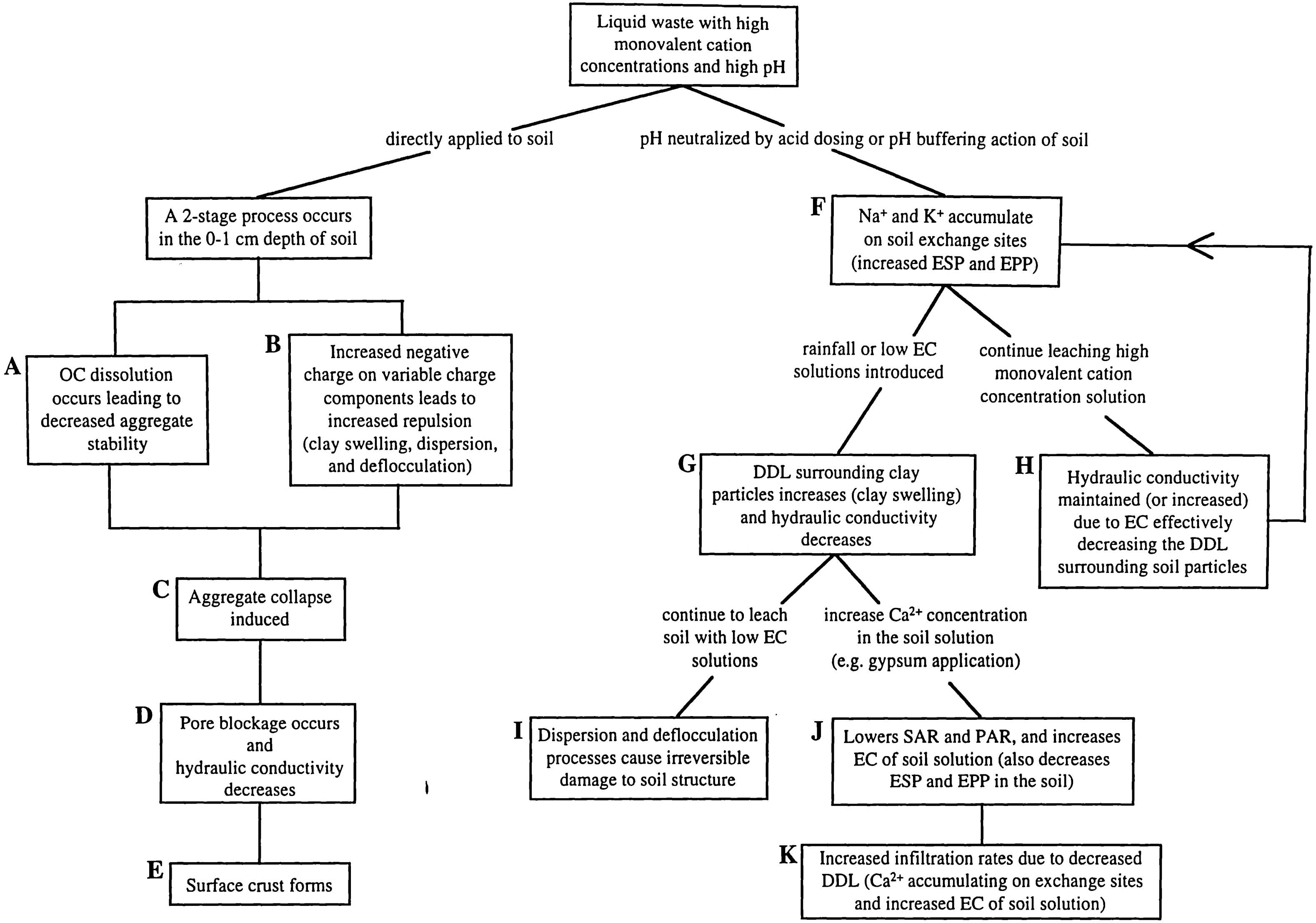

Fig. 8.1 Conceptual model of the processes involved when high monovalent cation concentration, high pH solutions are applied to soil

introduced (i.e. rainfall or high quality irrigation water), the DDL surrounding soil particles increases causing clay swelling to occur and the hydraulic conductivity of the soil will decrease (Box G). Continued leaching with low EC solutions will result in irreversible damage to soil structure through dispersion and deflocculation processes (Box I). However, increasing the EC and Ca^{2+} concentration in the soil solution (i.e. through gypsum application) has a two-fold effect on the soil. Firstly, increasing the EC of the soil solution compresses the DDL surrounding soil particles which will increase the hydraulic conductivity of the soil as long as clay swelling (which is a reversible process) is the dominant mechanism responsible for the initial hydraulic conductivity decrease (Boxes J and K). Secondly, increasing the Ca^{2+} concentrations in the soil solution lowers the sodium adsorption ratio (SAR) and potassium adsorption ratio (PAR) which results in lower ESP and EPP in the soil (Boxes J and K).

The following sections discuss the results of the different experiments conducted during the research for this thesis and relates the results to the processes shown in Fig. 8.1

8.1.3 Effects of high pH solutions on organic carbon in soil

When solutions with high pH are in contact with the 0-1 cm depth of the soil (i.e. the surface layer), OC dissolution will occur if the pH of the solution remains relatively high (at pH values >10.5). The pH of the soil solution following application of high pH solutions will depend on the pH buffer capacity of the soil (see Appendix C) which will naturally lower the pH, thereby decreasing the amount of OC which is dissolved. The pH of the soil solution probably changes rapidly with depth and therefore OC dissolution would only likely to occur in the upper 1 cm of soil. The field trial (Chapter 7) showed that soil pH had not increased despite 3 years of irrigation with high pH solutions and illustrates that there is sufficient pH buffer capacity in the soil to minimise pH changes, at least in the 0-10 cm sampling depth. Therefore, the nature of the soil solution probably changes dramatically over a very small vertical distance in the soil.

The experiments conducted in Chapter 4 (Organic carbon dissolution) showed that the chloride solutions dissolved minimal OC from soils whereas OC dissolution increased with increasing concentration when hydroxide solutions were used as treatments. This result shows that it is the hydroxide anion which is responsible for OC dissolution in soil and that lowering the pH of the soil solution (i.e. the liquid wastes) will result in lower amounts of OC dissolution occurring. It was also shown that although NaOH initially dissolved more OC than KOH, similar amounts of OC were dissolved by both solutions in the longer term. Therefore, it would be expected that KOH and NaOH would react similarly with OC where repeated irrigation of these hydroxides occurs in the field situation. Although the soil to solution ratio (1:25) used in the laboratory experiments in this study was quite large and cannot necessarily be directly related to field conditions, OC dissolution would be expected to occur where the soil is in contact with high pH solutions (i.e. the 0-1 cm depth). Dissolution of OC in the upper 1 cm of soil was also shown to occur in the hydraulic conductivity experiments conducted in Chapter 5 (Aggregate stability and hydraulic conductivity) where the surface crust (0-1 cm depth) in hydroxide-leached cores (see Fig. B4, Appendix B) had significantly lower OC contents than untreated samples.

On the basis of these laboratory results, it was expected that lower OC contents would have been measured in the 0-1 cm depth of soil at the irrigated site than the non-irrigated site in the field trial (Chapter 7). However, significantly lower OC contents in the irrigated soil were only measured on the final sampling date (12 months after gypsum application). The lack of an observed difference between irrigated and non-irrigated sites may have been due to the problems of measuring soil properties at sites where active, intense management occurs. For example, presence of large stock on the soil during wet periods can cause severe pugging with considerable mixing of soil in the 0-10 cm depth by hooves (especially where intensive “strip grazing” is practiced). Also, natural spatial variability of soil properties and uneven returns of animal wastes makes it very difficult and to pick up differences using collected samples. The mixing of the 0-1 cm depth (where OC dissolution is hypothesised to occur) with soil from lower horizons could mask any differences between the irrigated and non-irrigated site, not only in OC measurements but also differences in some of the other parameters measured (e.g. bulk density and pH).

8.1.4 Effects of high pH solutions on soil physical conditions

Very few workers have investigated the effect of hydroxide solutions or increased soil pH on either aggregate stability or saturated hydraulic conductivity (especially using high pH solutions as influent solutions) in soils, and those who have (e.g. Chiang *et al.*, 1987; Nakagawa and Ishiguro, 1994), used soils with OC contents which were considerably lower than the OC contents often found in New Zealand soils.

Aggregate stability decreased when soil aggregates were treated with hydroxide solutions whereas the chloride treatments had no effect on aggregate stability (Chapter 5). The decrease in aggregate stability measured in hydroxide-treated soil was attributed to the hydroxide solutions dissolving OC (Box A, Fig. 8.1) which is usually considered to be a very important binding and cementing agent in soil aggregates (Oades, 1989). Aggregate stability decreased with increasing hydroxide concentration (solution pH) and the degree of aggregate collapse appeared to be directly related to the amount of OC dissolution which occurs. No studies appear to have previously reported the effect of hydroxide anions on aggregate stability and the results presented in Chapters 4 and 5 identify the processes involved in explaining why aggregate stability decreases in the presence of hydroxide solutions. Although it is proposed that OC dissolution is the main mechanism responsible for decreased aggregate stability in hydroxide-treated soil, it was shown in Chapter 6 (Cation exchange properties) that there was still a net increase in CEC (i.e. increased negative charge) despite the possible removal of significant numbers of negative sites through the dissolution of OC. The increased negative charge on the surfaces of soil constituents which possess variable charge characteristics could also result in increased repulsion of particles and further encourage clay swelling, dispersion, and deflocculation processes and contribute the decrease in aggregate stability (Box B, Fig. 8.1).

The saturated hydraulic conductivity of soils decreased rapidly when hydroxide solutions were used as influent solutions (Box D, Fig. 8.1). The time taken to effect the dramatic decrease appeared to be concentration dependent. It was proposed that the decrease in hydraulic conductivity is caused primarily by aggregate collapse (through dissolution of OC) and, to a lesser extent, clay swelling, dispersion, and deflocculation processes due to the increased pH of the soil environment (as discussed above; Box A + Box B $\rightarrow$ Box C, Fig 8.1). The two stage process proposed to explain the decrease in hydraulic conductivity when soils are leached with high pH solutions (i.e. Box A + Box B, Fig. 8.1) differs from suggestions made previously (e.g. Suarez *et al.*, 1984; Chiang *et al.*, 1987; Nakagawa and Ishiguro, 1994), that clay swelling and subsequent deflocculation is the main cause of decreased hydraulic conductivity in high pH soil environments. However, the OC contents of soils used in those studies were relatively low compared to the soils used in this study. As mentioned earlier, surface crusts which were observed in the hydroxide-leached soil cores (Box E, Fig. 8.1; see also Fig. B4, Appendix B) had substantially lower OC contents compared to untreated soil, supporting the suggestion proposed in Chapter 4 that OC dissolution only the 0-1 cm depth of soil occurs. These results suggest, therefore, that OC dissolution and increased negative charge on soil components need only occur in the 0-1 cm depth of soil to induce aggregate collapse which can result in a substantial decrease in hydraulic conductivity (through pore blockage; Box D, Fig. 8.1) when soil is leached with high pH solutions.

8.1.5 Effects of high monovalent cation concentration solutions on soil physical conditions

The hydroxide anion appears to be the major component in high pH solutions which causes problems in soil (as discussed above). Ideally, therefore, the pH of the liquid wastes should be lowered (by acid dosing) prior to application to the soil which would decrease the hydroxide concentration. However, the presence of high concentrations of monovalent cations in the solution may still affect soil physical conditions if remediation measures are not taken. Although the pH of the applied liquid waste will be lowered as it migrates through the soil profile due to the pH buffering capacity of the soil (particularly the surface horizon), the presence of high concentrations of monovalent cations still exist.

It has been well established in the literature that soils can be continuously leached with high monovalent cation concentration solutions due to the high EC of the soil solution. The high EC effectively decreases the DDL surrounding soil particles (Box H, Fig. 8.1). However, hydraulic conductivity will decrease if low EC solutions are introduced (such as rainfall or high quality irrigation water in field situations) following the application of high monovalent cation concentration solutions. When NaCl or KCl were used as influent solutions in this study (Chapter 5), hydraulic conductivity increased according to DDL theory, and the introduction of distilled water (simulating rainfall or high quality irrigation water) caused significant decreases in hydraulic conductivity rates (Box G, Fig. 8.1), which is also consistent with DDL theory (i.e. increased DDL due to decreased electrolyte concentration). The leaching of NaCl and KCl also increases the ESP and EPP in the soil (Box F, Fig. 8.1). The processes involved in decreased hydraulic conductivity due to decreasing the EC of the soil solution in soils with high ESP and/or EPP are well known and have been shown by previous workers (e.g. Quirk and Schofield, 1955; Shainberg *et al.*, 1981; Cass and Sumner, 1982) to be due to clay swelling, dispersion, and deflocculation processes.

When clay swelling is the major process responsible for decreased water movement during leaching of low EC solutions through a soil with high ESP and/or EPP (Box G, Fig. 8.2), the hydraulic conductivity can increase if the electrolyte concentration of the soil solution is increased (thereby effectively decreasing the DDL; Box K, Fig. 8.1). However, if low EC solutions are continued to be leached through the soil and ESP and EPP values are high enough (>15% as suggested by Richards, 1954), dispersion and deflocculation processes will be induced which will lead to irreversible damage to the soil structure (Box I, Fig. 8.1). When Ca^{2+} is introduced into the soil solution (e.g. by the application of gypsum) in a soil where clay swelling is the dominant process affecting water movement, not only does the EC of the soil solution increase but the Ca^{2+} will exchange for both Na^{+} and K^{+}, thereby decreasing ESP and EPP in the soil and infiltration rates should increase (due to decreased DDL; Boxes J and K, Fig. 8.1). The field trial (Chapter 7) showed that gypsum application was effective in the short term at decreasing ESP and EPP and had positive effects on infiltration rates in a soil spray irrigated with liquid wastes which had high monovalent cation concentrations and high pH.

The inability of hydroxide solutions to be leached through soils is not predicted by DDL theory and there are, therefore, different processes involved in the observed decreases in hydraulic conductivity between hydroxide- and chloride-based solutions (i.e. OC dissolution and increased negative charge on soil particles causing aggregate collapse versus dispersion, deflocculation, and clay swelling, respectively).

8.1.6 The effects of high pH solutions on exchange properties in soil

High pH solutions were shown (Chapter 6) to increase the cation exchange capacity (CEC) of soils despite significant amounts of OC being dissolved (shown to occur in Chapter 4), the increase in CEC being concentration dependent. The increased number of negative sites are suggested to be generated on surfaces which possess pH dependent charge characteristics (i.e. the remaining organic matter, iron oxides, and edge sites of clay minerals). When NaOH is present in the soil solution, the increased negative sites are counter-balanced by Na^+ cations, thereby also increasing the ESP of the soil. Likewise, KOH caused the EPP to increase. Neither NaCl nor KCl caused changes in CEC at any concentration used. Although the experimental conditions (i.e. the high solution to soil ratio) cannot necessarily be directly related to field conditions, increased negative charge and high ESP and EPP values would at least be expected in the 0-1 cm depth of the soil where it is in direct contact with high pH solutions.

The increase in CEC may indicate that more exchange sites are available in the soil to hold plant essential nutrients, but in situations where NaOH based solutions are applied to soil, the majority of the new exchange sites will be occupied by Na^+ cations, to which many plant species have low tolerances. In contrast to NaOH, where KOH based solutions are applied to soils, the increased exchangeable K^+ concentrations may be less injurious to plants. However, in both cases the increased negative charge and increased exchangeable monovalent cation concentrations in the soil may cause increased repulsion between clay particles resulting in clay swelling, deflocculation, or dispersion to occur, thus deteriorating soil physical conditions which are important to plant growth.

This study found (Chapter 6) that current equations used to predict ESP and EPP values from the sodium adsorption ratio (SAR) and potassium adsorption ratio (PAR) of soil solutions (Richards, 1954) do not give accurate predictions when hydroxide anions are present in the soil solution. The equations do not take into account the new negative sites and assume the CEC of the soil remains constant. In contrast to hydroxide-treated soil, the prediction equations predicted ESP and EPP reasonably well in chloride-treated soils.

8.2 Recommendations for disposal of liquid wastes which contain high monovalent cation concentrations and high pH using land treatment systems.

From the results of this study, two major recommendations are suggested for the successful disposal of liquid wastes with high monovalent cation concentrations and high pH using land treatment systems:

1) the pH of the liquid waste should be carefully monitored and adjusted prior to application onto soils. This will decrease the hydroxide concentration and decrease the amount of OC dissolved at the surface of the soil. Lowering the pH of the liquid should prevent aggregate collapse and pore blockage and hydraulic conductivities should not be adversely affected.

2) divalent cations (Ca^{2+} <u>and</u> Mg^{2+}) should either be added to the liquid waste prior to disposal or be applied to the soil in a form which is both economical and relatively soluble. The addition of divalent cations will have a twofold effect on the soil system. Firstly, the presence of divalent cations will lower the SAR and PAR of the liquid waste (soil solution) and would decrease the accumulation of monovalent cations on exchange sites in the soil (decrease ESP and EPP). As long as ESP and EPP values remain low (<15% as suggested by Richards, 1954), the introduction of low EC solutions should not affect water movement. Secondly, the presence of Ca^{2+} and Mg^{2+} will be beneficial for plant health. The addition of Mg^{2+} to the soil is recommended to minimise the likelihood of Mg deficiency occurring in plants, especially where low natural exchangeable Mg^{2+} concentrations are present in the soil.

8.3 Some additional suggestions to alleviate current problems associated with land treatment of high pH liquid wastes.

Land treatment of liquid wastes with high monovalent cation concentrations and high pH has been practiced at some industrial sites in New Zealand for more than 15 years. However, problems have occurred due to factors such as: i) overloading the soil system with liquid wastes by applying hydraulic loading rates which exceed design limits and often result in surface ponding of liquid wastes; ii) problems in the manufacturing or processing plant which can result in increased volumes of liquid wastes being produced, all of which need to be disposed of (often resulting in (i) occurring); iii) the variable nature of the liquid wastes, short residence times, and poor mixing in storage silos which often lead to large differences in chemical composition being spray irrigated from hour to hour or day to day; iv) unseasonably wet winters which can cause the soil to be sufficiently wet that spray irrigation should not be practiced; v) poor stock management which leads to compacted and pugged topsoil, especially in wet soil; and vi) inadequate pretreatment of the liquid wastes which can result in increased fats or suspended solids which cause physical blockage of soil pores.

Ideally, if the nature of the liquid waste applied can be modified and controlled by addition of chemicals, the effects of the liquid waste on soil properties could be better predicted and managed. Currently, the liquid wastes from the dairy manufacturing industry are pumped to the disposal site and stored in silos (typically holding between 100-500 m^3 of liquid waste), however, the total storage volumes are often less than the volume of waste produced and the residence time in each silo is therefore relatively short. If the volume of liquid waste could be stored in large ponds or vessels equipped with mixing devices, the chemical composition of the liquid waste could be easily determined and modified by the addition of: i) acid, to decrease the pH of the liquid to the desired value (ideally pH 7.0); and ii) the addition of divalent cations (Ca^{2+} and Mg^{2+}) to overcome the problems associated with build-up of exchangeable monovalent cations (as discussed above). In addition, if land treatment systems were operated on the basis of the soil's and plant's water requirements (which would involve monitoring soil moisture status and plant health), the likelihood of spray irrigating a soil which is already wet would decrease and would therefore also ensure that the liquid waste is fully "treated" by the soil. It is also important that preliminary investigations be conducted on all the soil types to be irrigated to examine how effective it treats the liquid waste and its ability to receive the waste (i.e. measurements of infiltration rates using actual or simulated liquid waste) at different times throughout the year (to take into account seasonal effects on infiltration rates).

The discussion above relates to an ideal situation where no monetary constraints exist. However, some of the ideas could still be implemented in current systems to ensure the nature of the liquid waste was not too variable and that controlled pH correction occurred. This study has shown that one of the primary problems with land treatment of high pH liquid wastes is the presence of the hydroxide anion. Neutralisation of the liquid waste does not, however, solve the problems associated with the presence of monovalent cations in the liquid waste. The application of gypsum to soils irrigated with liquid wastes high in monovalent cation concentrations and high pH has been shown to decrease exchangeable Na^+ and K^+ and increase exchangeable Ca^{2+} concentrations without increasing the pH of the soil. Therefore, it is suggested that gypsum application, rather than lime application (used as an amendment at some sites where high pH liquid wastes are sprayed), occur because it has been shown by previous studies that lime application increases soil pH (Barnett and Upchurch, 1992) and is less soluble than gypsum.

The results of this study also appear to suggest that the use of KOH-based cleaning detergents may be less detrimental on soil properties than NaOH-based detergents. In most of the results obtained, KOH behaved slightly different to NaOH, at least initially, although increased exchangeable K^+ concentrations were also shown to be as detrimental on soil properties as increased exchangeable Na^+ concentrations. However, increased exchangeable K^+ concentrations would probably not be as injurious to plant growth as high exchangeable Na^+ concentrations.

8.4 Conclusions

The main conclusions from this thesis are:

1. High pH solutions can be very effective at dissolving organic carbon in soils, with organic carbon dissolution increasing with increasing hydroxide concentration (solution pH). Initially, NaOH dissolves more organic carbon than KOH though in the longer term no cationic difference exists. Neither NaCl nor KCl cause significant organic carbon dissolution to occur.

2. Hydroxide solutions decrease aggregate stability in soils with aggregate stability decreasing with increasing hydroxide concentration. The decrease in aggregate stability is attributed to dissolution of organic carbon (organic matter) which acts as a major binding agent in soil aggregates. The increased negative charge on soil particles also leads to increased repulsion with clay swelling, dispersion, and deflocculation processes also contributing to decreased aggregate stability. Neither NaCl nor KCl cause aggregate instability.

3. Hydroxide solutions result in rapid decreases in saturated hydraulic conductivity when used as influent solutions. The time required before a decrease in saturated hydraulic conductivity occurs decreases with increasing hydroxide concentration. The decrease in saturated hydraulic conductivity is caused by aggregate collapse in the 0-1 cm depth of the soil through organic carbon dissolution, clay dispersion, deflocculation, and clay swelling. In contrast to hydroxide solutions, chloride solution can be leached through soils and decreases in saturated hydraulic conductivity only occur when low electrolyte solutions (i.e. distilled water) are introduced (the decrease being attributed to clay swelling, dispersion, and deflocculation processes),

4. Hydroxide solutions increase the cation exchange capacity (CEC) of soils whereas chloride solutions do not affect CEC. CEC increases with increasing hydroxide concentration. Although organic carbon dissolution occurs, the number of exchange sites potentially removed by this process is compensated by the number of negative sites generated on components in the soil which possess variable charge

characteristics (i.e. remaining organic matter and pH dependent sites on clay minerals). The generated negative sites are balanced by the accompanying monovalent cation and decreases in the other exchangeable cations occur with increasing hydroxide concentration.

5. Surface applied gypsum has the potential to increase infiltration rates in soils irrigated with liquid wastes with high monovalent cation concentrations and high pH. The increased infiltration is due to increases in exchangeable Ca^{2+} and decreases in exchangeable K^+ and Na^+ resulting in decreased exchangeable potassium percent and exchangeable sodium percent in the soil over time. Generally, soil bulk density, organic carbon, CEC, and pH are all unaffected by gypsum application.

8.5 Recommendations for future research

Some recommendations for future research as a result of this study include:

- Study of long term changes to soil chemical and physical properties in field conditions. It is important to quantify changes in soil chemical and physical properties under field conditions using controlled conditions such as known composition of liquid waste, livestock and no livestock, and several amendments (including gypsum, lime, dolomite, and $CaCl_2$) at different application rates. In addition, it would be useful to establish the depth effects (down the soil profile) these amendments have at sites with different histories of liquid waste application.

- An investigation of high pH liquid waste movement through soils under unsaturated flow conditions. Although saturated hydraulic conductivity has been shown to decrease when hydroxide solutions are used as influent solutions, it would be useful to investigate how high pH solutions affect unsaturated hydraulic conductivity through the use of disc permeameters (i.e. K_{-40} measurements) using hydroxide solutions as influent solutions.

- A study of the effects that high pH solutions have on soil biology, particularly earthworm health and numbers, when spray irrigated onto soil. This would be useful to understand as earthworms and other soil fauna play very important roles with respect to soil aeration, permeability, and structure formation and stability. From field observations, earthworm numbers appear to be unaffected in spray irrigated sites, however, during irrigation periods, earthworms have been observed to migrate to the surface of the soil and congregate on the concrete spraying pads surrounding the spray nozzles where no liquid waste lands.

- An investigation of the response of pasture species to irrigation of liquid wastes with high pH would be useful if land treatment sites are to be used as economically viable enterprises. Overall management practices associated with the farming of land disposal sites should also be investigated to ensure the best returns are gained.

8.6 References

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Appendices

Appendix A
Supplementary information and data for Chapter 4

This section includes additional data and photographs related to the series of experiments conducted in Chapter 4 - Organic carbon dissolution.

Table A1 presents the organic carbon measured in all the untreated soil samples. Table A2 presents data of the amount of organic carbon dissolved from Horotiu silt loam after different shaking periods (i.e. data used in Fig. 1, pg. 97). Table A3 summarises the data used in Fig. 2 (pg. 98).

Also included are three photographs (Figs. A1, A2, and A3) which visually show the discolouration of the supernatant solutions after shaking for 18 hours with different treatment solutions. Note the difference in the nature of the colour between the KOH and NaOH treatments at each concentration (in particular the 0.03 M concentration), in every case the colour of the KOH solutions is lighter than that of NaOH. This colour difference may be due to slightly different organic fractions being dissolved by either solution or the fact that KOH dissolved slightly less organic carbon after 1 shaking.

Table A1 Organic carbon analyses for all four soil types used. Values represent means (n=6).

Soil type	Organic carbon (%)	Standard error
Hopai silty clay	9.20	0.05
Wairua silty clay	4.23	0.03
Horotiu silt loam	7.87	0.07
Manawatu silt loam	4.85	0.04

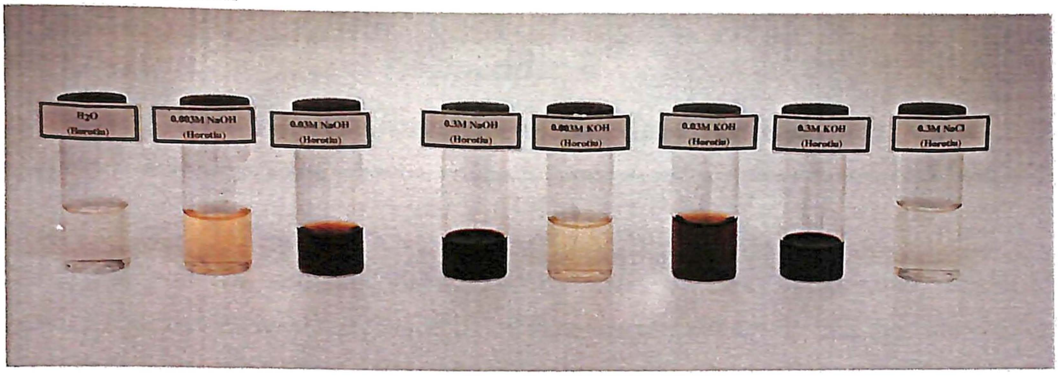
Table A2 Amount of organic carbon dissolved (mg OC g^{-1} soil) as a function of shaking time using 0.003 and 0.3 M NaOH on a Horotiu silt loam. Values represent means (n=3).

Shaking time (min)	Extraction solution			
	0.003 M NaOH		0.3 M NaOH	
	Organic carbon dissolved (mg OC g^{-1} soil)	Standard error	Organic carbon dissolved (mg OC g^{-1} soil)	Standard error
10	0.2	0.0	29.7	0.5
30	0.2	0.1	30.8	0.1
60	0.2	0.1	31.9	0.2
180	0.2	0.0	34.0	0.4
1080	0.4	0.1	39.0	0.4
2880	0.5	0.0	38.0	0.8

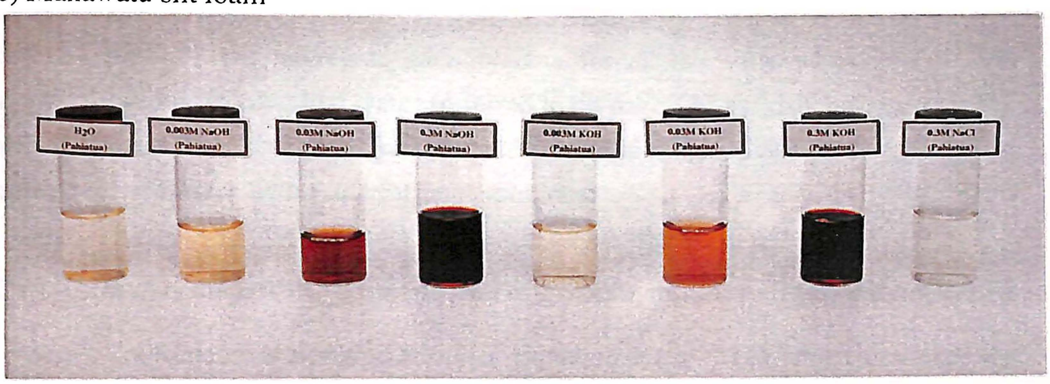
Table A3 Amount of organic carbon dissolved (mg OC g^{-1} soil) in all four soil types using different extracting solutions. Values represent means (n=3). Values in parentheses represent standard error of means.

Extraction solution	Concentration (M)	Soil type Hopai silty clay	Horotiu silt loam	Wairua silty clay	Manawatu silt loam
NaOH	0.003	0.8 (0.1)	0.4 (0.1)	0.4 (0.0)	0.0 (0.0)
	0.01	1.5 (0.3)	0.9 (0.1)	1.2 (0.2)	0.8 (0.1)
	0.03	3.7 (0.1)	3.5 (0.1)	3.4 (0.2)	3.4 (0.0)
	0.1	18.6 (0.4)	16.9 (0.2)	12.8 (0.3)	15.0 (0.2)
	0.3	35.3 (0.7)	39.0 (0.3)	15.7 (0.3)	19.2 (0.0)
KOH	0.003	0.8 (0.2)	0.0 (0.0)	0.3 (0.1)	0.0 (0.0)
	0.01	0.9 (0.1)	0.5 (0.1)	0.4 (0.1)	0.3 (0.0)
	0.03	1.8 (0.1)	2.0 (0.0)	1.4 (0.2)	1.3 (0.1)
	0.1	8.5 (1.5)	11.1 (0.2)	9.5 (0.0)	11.6 (0.6)
	0.3	31.3 (0.9)	36.4 (0.5)	14.2 (0.7)	17.2 (0.3)
NaCl	0.003	0.5 (0.1)	0.1 (0.1)	0.2 (0.1)	0.2 (0.1)
	0.3	0.1 (0.1)	0.5 (0.1)	0.6 (0.1)	0.3 (0.0)
KCl	0.003	0.3 (0.0)	0.2 (0.0)	0.1 (0.1)	0.2 (0.0)
	0.3	0.7 (0.1)	0.4 (0.1)	0.4 (0.1)	1.0 (0.3)
Distilled H_2O		0.5 (0.1)	0.0 (0.0)	0.1 (0.0)	0.0 (0.0)

a) Horotiu silt loam



b) Manawatu silt loam



c) Wairua silty clay

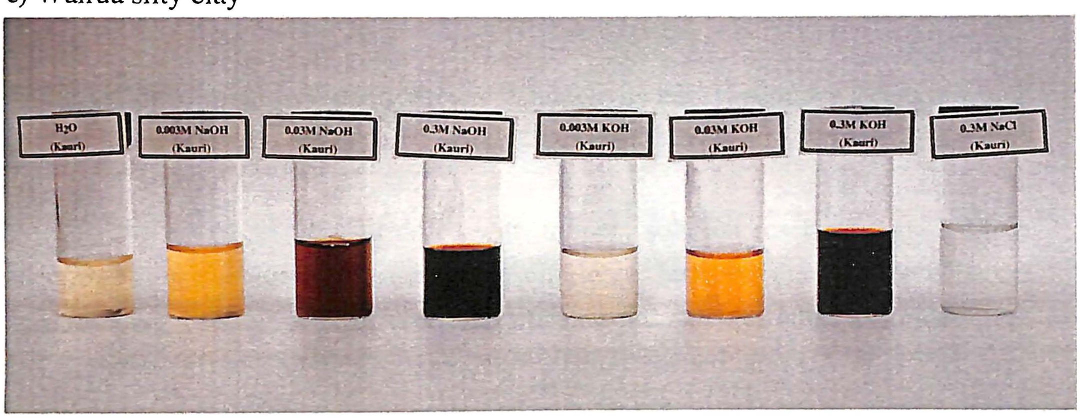


Fig. A1 Supernatant solutions after shaking three soils: (a) Horotiu silt loam; (b) Manawatu silt loam; and (c) Wairua silty clay with different treatment solutions for 18 hours. (Note: the labels on the vials in (b) and (c) refer to soil collection locations and not soil types).

Appendix B
Supplementary information and data for Chapter 5

This section includes additional data from the series of experiments conducted in Chapter 5 and also includes photographs of the experimental set up and the nature of the leachate collected during saturated hydraulic conductivity measurements using different influent solutions.

Table B1 presents the aggregate stability data for all the soils when treated with chloride solutions and distilled water (referred to on page 113 as "data not presented"). Table B2 presents the final relative saturated hydraulic conductivity of the soils when leached with different hydroxide influent solutions.

Also presented is the BASIC program used to generate the curve fitting parameters (α and β) and coefficients of determination for Equation 1 (pg. 116) which describes the reverse sigmoid shaped curves of decreasing saturated hydraulic conductivity over time when hydroxide solutions were used as influent solutions.

A series of photographs of the hydraulic conductivity experiment are included which show:

Fig. B1 - the set up of the soil cores with influent solution reservoirs and leachate collection. This photograph illustrates the difference between the leachate collected when hydroxide solutions were used as influent solutions and when chlorides were used. The core on the left (Wairua silty clay) is being leached with 0.3 M NaOH, note the dark brown-black colour of the collected leachate (dissolved organic matter). There is also discolouration of the reservoir solution which is due to some dissolved organic matter from the very surface of the soil migrating into the reservoir when the hydraulic conductivity has decreased to almost 0. In contrast to the hydroxide leached core, the core on the right had previously been leached with 0.3 M NaCl and the photograph shows the cloudiness of the leachate when distilled water replaced the NaCl as the influent solution. The cloudiness being attributed to dispersed clay.

Fig. B2 a and b - close up views of the leachates collected from leaching with 0.3 M NaOH (Fig. B2 a) and distilled water following NaCl leaching (Fig. B2 b).

Fig. B3 - the design of the feeder tubes used to maintain a constant head during hydraulic conductivity measurements. The slit openings at the bottom of the tube allow the reservoir solution to enter the constant head supply region via horizontal flow, thereby decreasing the likelihood of disruption of the soil surface. The slits at the top are the air-entry holes.

Fig. B4 a and b - dismantling of the soil cores after leaching with hydroxide solutions showed a distinct surface crust had formed in the upper 1 cm of soil (Fig. B4 a). In contrast to hydroxide-leached cores, no surface crust was observed in the upper 1 cm of the chloride-leached cores (Fig. B4 b). The surface crust in the hydroxide-leached cores had substantially lower organic carbon contents than those measured in the upper 1 cm of chloride-leached cores.

Table B1 Aggregate stability (expressed as mean weight diameter (MWD)) of three soil types after treatment with two concentrations of chloride (NaCl and KCl) solutions. Values represent means (n=3) and values in parentheses are standard error of means.

Treatment Solution	Concentration (M)	MWD		
		Hopai	Horotiu	Wairua
NaCl	0.003	256 (0)	286 (2)	276 (1)
	0.3	251 (3)	282 (1)	275 (9)
KCl	0.003	253 (0)	287 (3)	283 (3)
	0.3	254 (2)	287 (2)	270 (4)
Distilled H_2O		251 (3)	285 (5)	285 (2)

Table B2 Final relative saturated hydraulic conductivity (%) in three soil types using different hydroxides as influent solutions. Values represent means (n=3) and values in parentheses represent standard error of means.

		Soil type		
Influent solution	Concentration (M)	Hopai silty clay	Wairua silty clay	Horotiu silt loam
	0.003	0.4 (0.2)	0.5 (0.1)	2.2 (0.1)
NaOH	0.03	0.4 (0.1)	0.3 (0.1)	0.6 (0.0)
	0.3	0.0 (0.0)	0.1 (0.1)	0.4 (0.2)
	0.003	0.7 (0.0)	2.0 (0.1)	2.3 (0.1)
KOH	0.03	0.8 (0.3)	0.5 (0.1)	0.6 (0.1)
	0.3	0.0 (0.0)	0.0 (0.0)	0.2 (0.2)

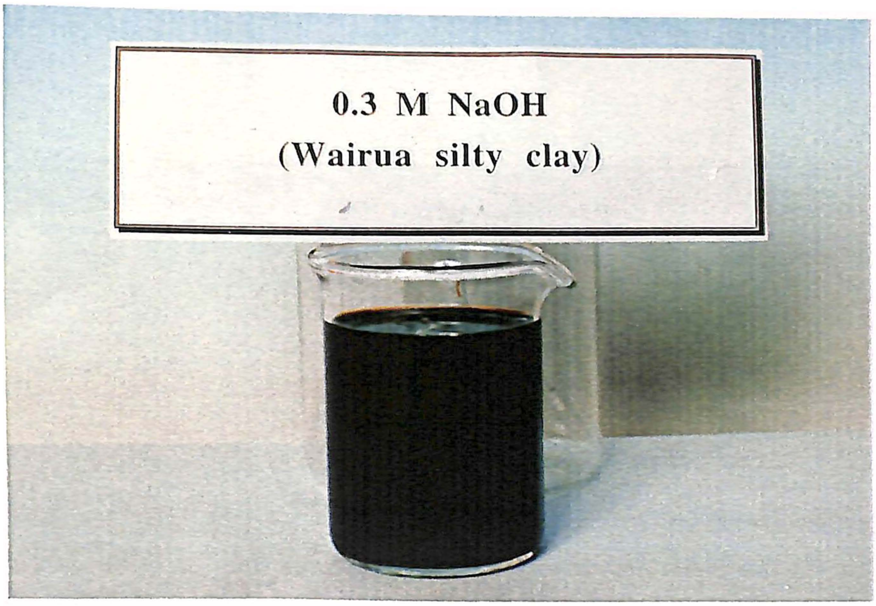
The following BASIC program was used to generate the curve fitting parameters (α and β) used in Equation 1 (pg. 116) which describes the hydraulic conductivity curves when hydroxide solutions were used as influent solutions:

```
'This program calculates the Alpha and Beta by least sum of squares method.
'The inputfile is `X.dat' and The outputfile is `X.out'

CLS
INPUT " Enter hydraulic conductivity data filename  : ", Inputfile$
INPUT " Enter hydraulic conductivity output filename: ", Outputfile$

OPEN Inputfile$ FOR INPUT AS #1
OPEN Outputfile$ FOR OUTPUT AS #2

'INITIAL SECTION
'm is the number of points for which computation is carried out
m = 26
alpha = 3.12305: beta = 1.039
DIM Time(m), HC(m), HCex(m, 3, 3), SumSq(3, 3)
LSumSq = 1E+10
TSS = 0
pi = 3.14159
p = .47047
a1 = .34802
a2 = -.09588
a3 = .74786
Ca = 100
delta = .001
Total = 0

FOR n = 1 TO m
    INPUT #1, Time(n), HC(n)
    Total = Total + HC(n)
    Average = Total / m
NEXT

FOR n = 1 TO m
    TSS = TSS + ((HC(n) - Average) * (HC(n) - Average))
NEXT


'DYNAMIC SECTION

DO UNTIL ABS(alpha - alpha(1)) = 0 AND ABS(beta - beta(1)) = 0
```

```
alpha(1) = alpha
alpha(2) = alpha + delta
alpha(3) = alpha - delta
beta(1) = beta
beta(2) = beta + delta
beta(3) = beta - delta

FOR u = 1 TO 3
FOR v = 1 TO 3
SumSq(u, v) = 0
FOR n = 1 TO m

i = 1
x = (LOG(Time(n)) - alpha(u)) / (SQR(2) * beta(v))
IF x < 0 THEN x = -x: i = -1
t = 1 / (1 + p * x)
erfx = 1 - (a1 * t + a2 * t * t + a3 * t * t * t) * EXP(-x * x)
erfx = erfx * i
HCex(n, u, v) = 100 - ((Ca) * 1 / 2 * (1 + erfx))

SumSq(u, v) = SumSq(u, v) + (HC(n) - HCex(n, u, v)) * (HC(n) - HCex(n, u, v))
NEXT

IF SumSq(u, v) < LSumSq THEN
      LSumSq = SumSq(u, v)
      alpha = alpha(u)
      beta = beta(v)
END IF

NEXT
NEXT
RSq = 1 - (LSumSq / TSS)
PRINT USING "#########.###"; LSumSq; alpha; beta
LOOP
'PRINT " Time "; " Measured HC "; " Predicted HC "
FOR n = 1 TO m
PRINT USING "###.##"; Time(n); HC(n); HCex(n, 1, 1)
PRINT #2, USING "#####.###"; Time(n); HC(n); HCex(n, 1, 1)
NEXT
PRINT USING "#######.#####"; LSumSq; alpha; beta; Rsq
```

Fig. B1 Experimental set up for saturated hydraulic conductivity measurements using constant head.

a)



b)

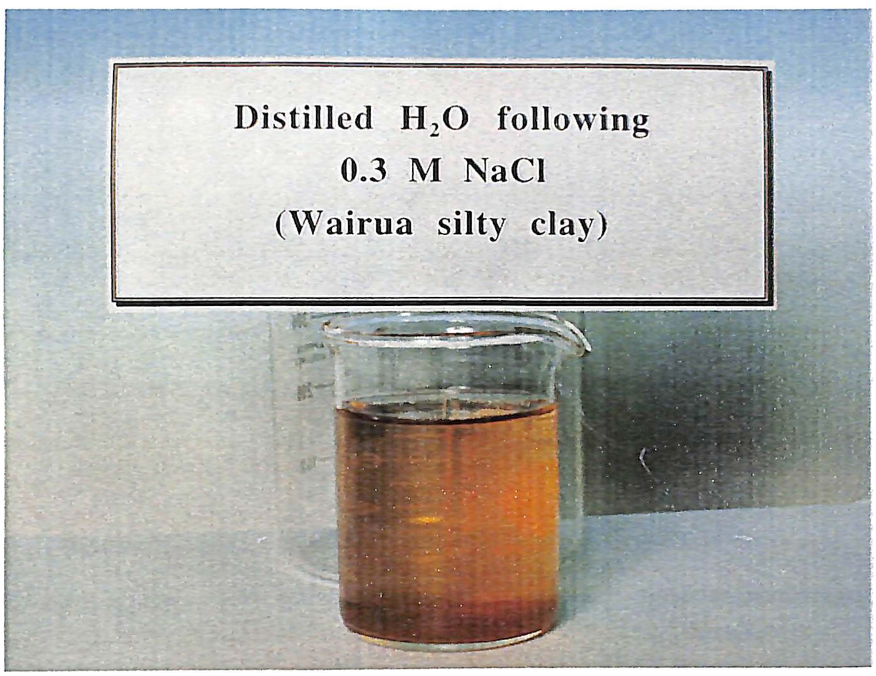


Fig. B2 Close up views of collected leachate during leaching with (a) 0.3 M NaOH; and (b) distilled water following leaching with 0.3 M NaCl. The dark colour in (a) is due to dissolved organic matter and the cloudy appearance in (b) is attributed to dispersed clay.

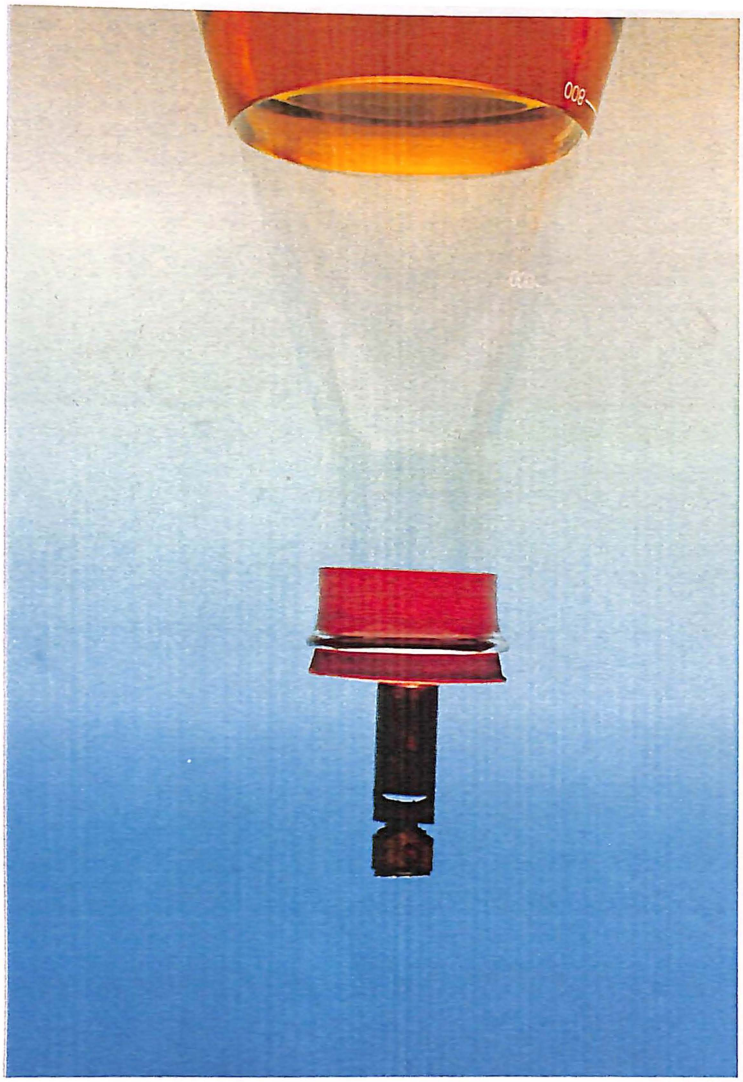
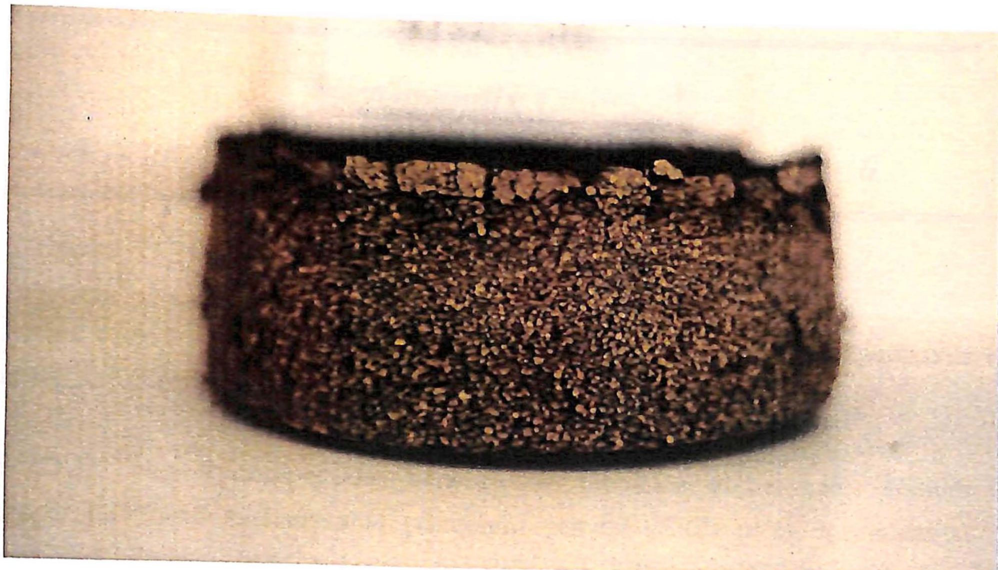


Fig. B3 Construction of feeder tube to maintain constant head of solution during measurement of saturated hydraulic conductivity. Bottom slits are solution supply holes and upper slits are air entry holes.

a)



b)

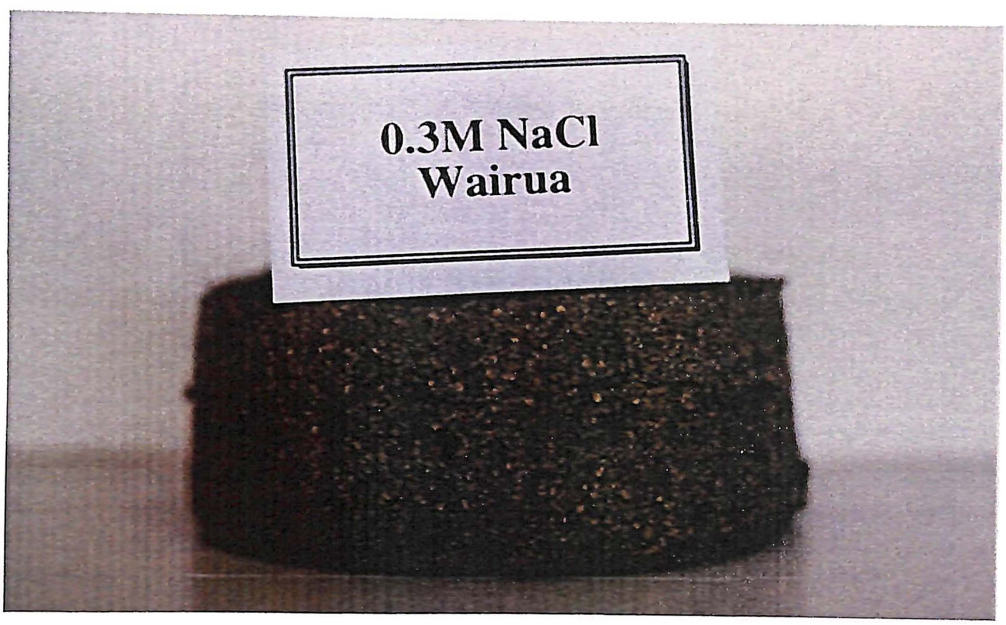


Fig. B4 Soil cores after leaching with (a) 0.3 M NaOH; and (b) distilled water following leaching with 0.3 M NaCl. Note the surface crust developed in the upper 1 cm of soil in (a) and the lack of surface crust in (b).

Appendix C
Supplementary information and data for Chapter 6

This section presents 4 tables and 3 pH buffer curves related to the experiments conducted for Chapter 6 - Cation exchange properties.

Tables C1-C4 present comparisons between the predicted exchangeable sodium percentage (ESP) and exchangeable potassium percent (EPP) using the equation proposed by Richards (1954) and measured ESP and EPP values in each of the four soil types when different treatment solutions were used.

Fig. C1 presents 3 pH buffer curves which were graphed using data obtained during the experiments in Chapter 4 (Organic carbon dissolution) but are better presented in this section.

Table C1 Measured and predicted exchangeable sodium percent (ESP) and exchangeable potassium percent (EPP) following treatment with different hydroxide and chloride solutions using a Hopai silty clay soil. Values presented represent means (n=3).

Treatment solution	Concentration (M)	Measured ESP	Predicted ESP	Measured EPP	Predicted EPP
NaCl	0.003	7	5	-	-
	0.01	17	15	-	-
	0.03	31	30	-	-
	0.1	56	55	-	-
	0.3	78	76	-	-
NaOH	0.003	29	2	-	-
	0.01	67	6	-	-
	0.03	87	20	-	-
	0.1	95	48	-	-
	0.3	98	74	-	-
KCl	0.003	-	-	16	26
	0.01	-	-	29	50
	0.03	-	-	50	72
	0.1	-	-	70	89
	0.3	-	-	85	96
KOH	0.003	-	-	25	23
	0.01	-	-	65	37
	0.03	-	-	88	65
	0.1	-	-	95	87
	0.3	-	-	98	95

Table C2 Measured and predicted exchangeable sodium percent (ESP) and exchangeable potassium percent (EPP) following treatment with different hydroxide and chloride solutions using a Horotiu silt loam soil. Values presented represent means (n=3).

Treatment solution	Concentration (M)	Measured ESP	Predicted ESP	Measured EPP	Predicted EPP
	0.003	20	8	-	-
	0.01	38	23	-	-
NaCl	0.03	54	43	-	-
	0.1	74	69	-	-
	0.3	82	86	-	-
	0.003	67	3	-	-
	0.01	93	10	-	-
NaOH	0.03	97	32	-	-
	0.1	97	65	-	-
	0.3	96	86	-	-
	0.003	-	-	26	42
	0.01	-	-	47	66
KCl	0.03	-	-	60	83
	0.1	-	-	78	94
	0.3	-	-	87	98
	0.003	-	-	62	31
	0.01	-	-	92	48
KOH	0.03	-	-	97	78
	0.1	-	-	96	93
	0.3	-	-	97	98

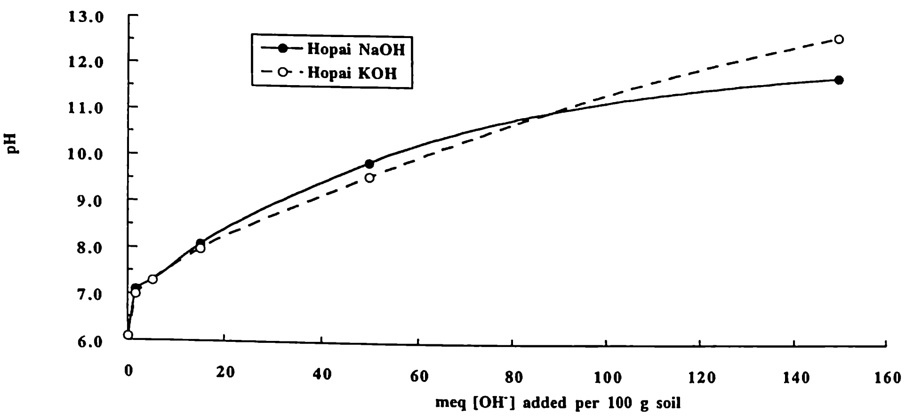
Table C3 Measured and predicted exchangeable sodium percent (ESP) and exchangeable potassium percent (EPP) following treatment with different hydroxide and chloride solutions using a Manawatu silt loam soil. Values presented represent means (n=3).

Treatment solution	Concentration (M)	Measured ESP	Predicted ESP	Measured EPP	Predicted EPP
	0.003	1	6	-	-
	0.01	9	16	-	-
NaCl	0.03	29	34	-	-
	0.1	57	59	-	-
	0.3	81	80	-	-
	0.003	33	3	-	-
	0.01	62	10	-	-
NaOH	0.03	71	28	-	-
	0.1	73	59	-	-
	0.3	75	82	-	-
	0.003	-	-	13	30
	0.01	-	-	34	54
KCl	0.03	-	-	50	76
	0.1	-	-	73	91
	0.3	-	-	85	96
	0.003	-	-	32	25
	0.01	-	-	57	49
KOH	0.03	-	-	69	75
	0.1	-	-	70	91
	0.3	-	-	74	97

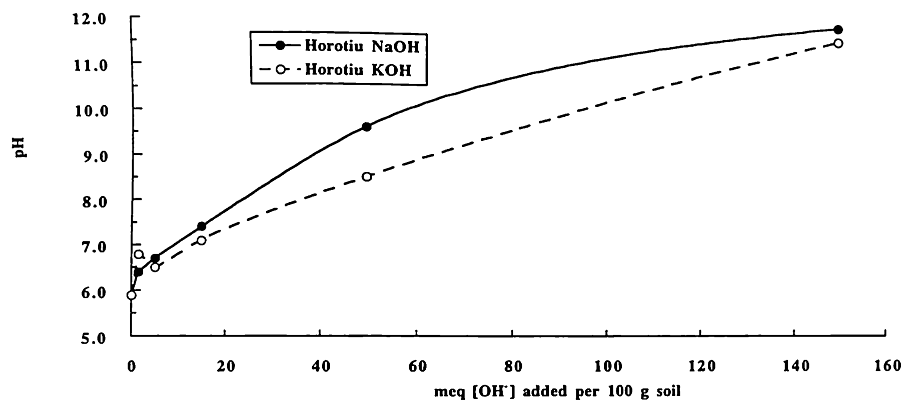
Table C4 Measured and predicted exchangeable sodium percent (ESP) and exchangeable potassium percent (EPP) following treatment with different hydroxide and chloride solutions using a Wairua silty clay soil. Values presented represent means (n=3).

Treatment solution	Concentration (M)	Measured ESP	Predicted ESP	Measured EPP	Predicted EPP
NaCl	0.003	10	10	-	-
	0.01	21	19	-	-
	0.03	36	35	-	-
	0.1	65	58	-	-
	0.3	85	79	-	-
NaOH	0.003	38	2	-	-
	0.01	64	9	-	-
	0.03	71	28	-	-
	0.1	76	59	-	-
	0.3	80	81	-	-
KCl	0.003	-	-	25	26
	0.01	-	-	44	51
	0.03	-	-	63	74
	0.1	-	-	68	90
	0.3	-	-	88	96
KOH	0.003	-	-	33	24
	0.01	-	-	62	47
	0.03	-	-	69	75
	0.1	-	-	72	91
	0.3	-	-	75	97

a)



b)



c)

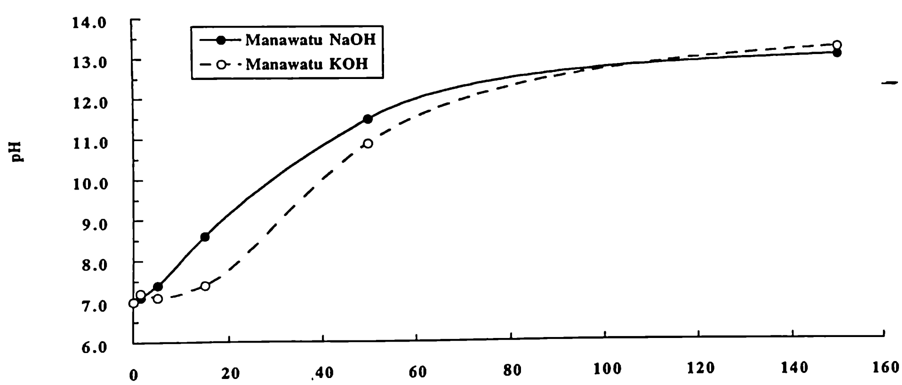


Fig. C1 pH Buffer curves for three soils: a) Hopai silty clay; b) Horotiu silt loam; c) Manawatu silt loam, using a 1:5 soil to solution ratio and adding NaOH solution to the soil.

Appendix D
Supplementary information and data for Chapter 7

This section contains additional data and information pertaining to the field trial conducted for Chapter 7 - Field trial.

Table D1 summarises some selected soil chemical parameters measured over the 12 month duration of the trial and form the basis for the graphs presented in Chapter 7.

Fig. D1 shows the equipment used for measurement of infiltration rates used in the field. The volume of water (recorded using plastic measuring cylinders) required to maintain a constant head of c. 2 cm was recorded over a period of at least 10 min. The cores were wetted up for at least 1 h prior to infiltration measurements.

Fig. D2 shows the surface horizon of soil from the irrigated site typically sampled for organic carbon analyses.

Table D1 Summary of selected physical and chemical properties measured in irrigated (I) and non-irrigated (NI) soil which was either gypsum treated (+G) or had no gypsum applied (-G) during the field trial. Values represent means (n=5) and values in parentheses are standard error of means.

Site and treatment	Months after gypsum application	pH	OC (%)	CEC ($cmol_c\ kg^{-1}$)	Exchangeable cations ($cmol_c\ kg^{-1}$) Ca	Mg	K	Na
	3	6.9 (0.0)	7.6 (0.2)	22.2 (0.4)	24.1 (1.3)	2.4 (0.3)	1.7 (0.7)	1.1 (0.2)
I+G	6	6.8 (0.1)	7.7 (0.2)	23.4 (0.4)	21.5 (2.2)	1.7 (0.2)	3.2 (0.5)	2.8 (0.2)
	9	6.7 (0.1)	6.9 (0.4)	24.9 (0.5)	21.9 (0.5)	1.3 (0.2)	2.2 (0.3)	1.9 (0.2)
	12	6.5 (0.0)	6.2 (0.2)	24.7 (1.0)	19.5 (0.3)	1.3 (0.1)	1.7 (0.2)	1.7 (0.1)
	3	6.8 (0.1)	6.7 (0.1)	22.5 (0.7)	20.4 (0.2)	2.6 (0.4)	2.0 (0.4)	2.0 (0.1)
I-G	6	7.1 (0.0)	6.8 (0.3)	23.1 (0.6)	16.5 (0.4)	2.1 (0.1)	4.0 (0.7)	3.9 (0.1)
	9	6.9 (0.1)	7.7 (0.3)	22.3 (0.5)	16.5 (0.5)	2.0 (0.1)	3.8 (0.6)	3.6 (0.3)
	12	6.5 (0.0)	5.6 (0.2)	22.2 (1.4)	16.7 (0.7)	1.9 (0.3)	2.4 (0.2)	3.5 (0.1)
	3	6.5 (0.1)	7.8 (0.1)	22.0 (0.3)	22.1 (0.5)	1.5 (0.3)	2.0 (0.6)	0.2 (0.0)
NI+G	6	5.8 (0.1)	7.8 (0.3)	16.1 (0.7)	24.8 (2.8)	1.1 (0.1)	0.9 (0.1)	0.6 (0.3)
	9	6.3 (0.0)	7.5 (0.2)	24.1 (0.9)	23.5 (0.7)	1.7 (0.3)	0.6 (0.0)	0.3 (0.1)
	12	6.2 (0.1)	7.9 (0.5)	24.0 (0.7)	20.1 (0.5)	2.0 (0.4)	1.6 (0.3)	0.3 (0.0)
	3	6.7 (0.0)	7.3 (0.3)	23.3 (0.8)	24.7 (0.3)	2.2 (0.4)	0.7 (0.2)	0.4 (0.0)
NI-G	6	6.3 (0.0)	7.1 (0.2)	17.9 (0.6)	20.2 (0.5)	1.7 (0.2)	0.8 (0.2)	0.3 (0.0)
	9	6.6 (0.1)	6.6 (0.1)	23.7 (0.8)	24.6 (0.8)	2.1 (0.5)	0.5 (0.2)	0.3 (0.1)
	12	6.4 (0.1)	7.6 (0.1)	25.5 (0.6)	22.0 (0.5)	2.2 (0.5)	1.2 (0.4)	0.3 (0.0)

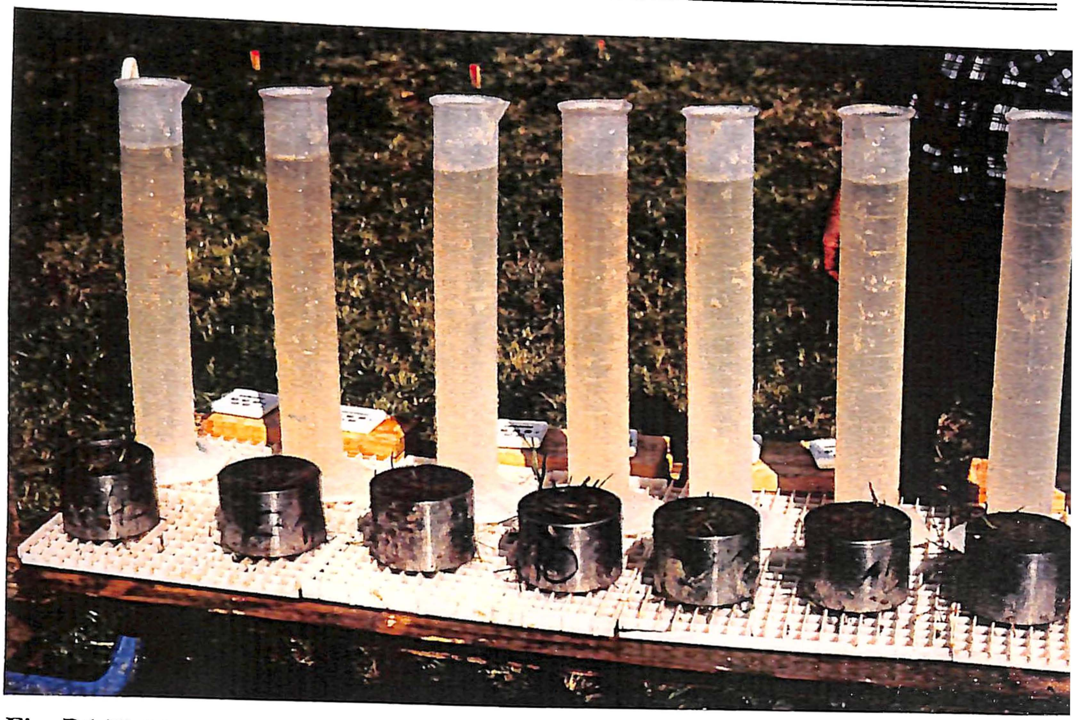


Fig. D1 Field equipment used for measurement of infiltration rates.

Fig. D2 Typical surface crust found in irrigated soil and sampled for organic carbon analyses.