STRUCTURAL STABILITY AND Na-Ca EXCHANGE SELECTIVITY OF SOILS UNDER SUGARCANE TRASH MANAGEMENT

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December, 2001

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Abstract

Good structure is an important property for sustaining crop production on agricultural soils because it influences water status, workability, resistance to erosion, nutrient availability and crop growth and development. The influence of calcium sources (gypsum and lime) and molasses on the structure and structural stability of soils used for sugarcane production has received little attention. Information about the influence of cane trash management practices (in which crop residues are burned before harvest (burnt) or retained as a 'trash blanket' (green)) on sodification of soil under irrigation with saline and sodic water is scarce. The aims of this thesis were to determine 1) the influence of calcium sources (gypsum and lime) and molasses on the structural stability of soils, and 2) the influence of trash management practices on the resistance to sodification of irrigated soils used for cane production.

The first experiment was conducted to determine whether molasses, a by-product of sugar manufacture, alone or combined with gypsum, could improve the structural stability of sodic soils used for sugarcane production. Burdekin sandy clay loam and Proserpine loamy sand soils (both from Queensland) were incubated with molasses (0 and 10 t/ha) and gypsum (0 and 10 t/ha) for 12 weeks, during which time they were leached 5 times with water (0.5 pore volumes each time). In the Burdekin soil, molasses and gypsum, either alone or combined, decreased spontaneous and mechanical clay dispersion and exchangeable sodium percentage (ESP). Molasses and gypsum both increased electrical conductivity and wet aggregate stability, with the combined effect being greater. In the Proserpine soil, the amounts of dispersible clay were much less than in the Burdekin soil. The effects of molasses and gypsum in decreasing spontaneous and mechanical clay

dispersion were similar to those in the Burdekin soil, but less pronounced. There appeared to be an additive effect of molasses+gypsum in improving structural stability of soils. Molasses and gypsum, either alone or combined, improved the structural stability of both soils by decreasing dispersion and/or slaking.

A second, similar experiment was carried out using lime instead of gypsum, since gypsum is more expensive than lime in the sugarcane growing districts of Queensland. The aim of this experiment was to determine whether a combination of molasses and lime would increase the solubility of the applied lime and thus more effectively achieve a synergistic effect to reduce sodification of irrigated soils used for sugarcane production. Using materials and methods similar to those of the molasses and gypsum experiment, molasses and lime either alone or combined improved the structural stability of the Burdekin and Proserpine soils. However, there did not appear to be a synergistic effect of molasses+lime in improving structural stability. Furthermore, the rate of 10 t/ha molasses did not lower the pH of the soil sufficiently to dissolve the lime substantially in this experiment. Further experiments are needed to determine the best combination rate of molasses and lime to overcome problems associated with sodicity.

In the final experiment, sodium-calcium exchange selectivity of soils under different trash management practices and with different organic matter contents were examined. Three soil types were selected from different locations in Queensland (Ayr, Mackay and Tully) in which two long-term, sugarcane trash retention management regimes have been practiced (i.e. leaving cane harvest residues as a blanket (green) and burning cane residue prior to harvest (burnt)). Soil samples from the Waite Agricultural Research Institute, Urrbrae, South Australia from long-term permanent pasture and wheat-fallow plots were also included to extend the experiment to a red-brown earth from a Mediterranean zone. The reasons for including the Urrbrae soil in part of the study were it

represents an important, structurally vulnerable soil type in Southern Australia and that there were significantly different organic matter contents in both Urrbrae soil samples. One hundred grams of soil aggregates (0.5-2 mm) were placed on a sintered glass funnel, saturated slowly with $CaCl_2$, freed of excess electrolyte then equilibrated with solutions of different total cation concentration (TCC; 2 and 10 mmol(+)/L) and sodium adsorption ratio (SAR; 3 and 10). When equilibrium was attained, the solutions were analysed to calculate the Gapon selectivity coefficient (k_G). The value of k_G was influenced by soil type, trash management practices or organic matter, and by the combination of SAR and TCC. The green trash treatment had generally lower k_G values than the burnt trash treatment; suggesting that soil under the burnt trash management appeared to be more susceptible to sodification than under the green trash management. Total soil organic matter contents in the burnt and green trash management practices were not significantly different from each other, and this suggested that the nature of soil organic matter may influence the value of k_G. Further experiments are needed to investigate how the nature of organic matter influences the value of k_G. A method used for measuring Na-Ca exchange selectivity while maintaining the natural aggregate structure was developed. The method appeared to be successful in measuring the Na-Ca exchange selectivity of soils without disturbing soil aggregates. The method can also be used for inducing known levels of sodicity in natural soil aggregates. Further experiments are needed to validate and refine this method at high SAR and low TCC where the soil becomes more dispersive.

In conclusion, molasses, lime and gypsum improved the structural stability of sodic soil although there was no synergistic effect in their combination. Sodium leached during experiments was enhanced by these amendments, with the gypsum effect most pronounced. In the molasses+lime treatment, the rate of 10 t/ha molasses did not lower the pH of the soil sufficiently to dissolve the lime substantially in this experiment. Soil under

green trash management was more resistant to sodification than under burnt trash management. An implication of this work is that molasses may be a useful ameliorant for sodic soils, either alone or combined with gypsum and lime but with increased rates of application. The green trash management practice will increase the resistance of the soils to sodification.

Statement

This work contains no material, which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material published or written by another person, except where due reference is made in the text.

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Acknowledgements

This thesis could not be completed without the support I received from many people. Firstly, I am deeply indebted to my supervisors, Dr. R.S. Murray, Dr. C.D. Grant and Dr. P.N. Nelson for their constant encouragement, advise, guidance and generosity throughout my project. All their support and help during my candidature was invaluable.

I am grateful to Dr. G.J. Churchman from CSIRO land and water, who helped in determining clay mineralogy, and members of Soil Physics and Chemists Lab Group for valuable discussion and advice about my work.

Special thanks to Mr. C. Rivers, Mrs. A. Baklan and Mrs. T. Fowler for their assistance in the laboratory when required. I would like to thank other members of the Department of Soil and Water particularly Prof. S.E. Smith, Dr. D.J. Chittleborough (Head of Department), Dr. R.J. Smernik, Mr. J.F. Davey (Departmental Manager) and Mrs. T. Parish (Departmental Secretary) for their help.

This work was fully funded by the Australian Agency for International Development (AusAID).

Finally, my deep gratitude is extended to my wife, my children, and my parents for their continuous support, patience and encouragement.

CHAPTER 1

Introduction

Soil structure is an important factor affecting aeration, hydraulic properties and mechanical impedance of soil and nutrient uptake by plants (Oades, 1984; Dexter, 1988; Mullins *et al.*, 1990; Rengasamy and Olsson, 1991). The stability of both micropores and macropores depend on bond strengths between different structural units during wetting and also determine the aggregate size resulting from the mechanical action of tillage tools.

Structural stability of soil is strongly influenced by a number of factors including organic matter, exchangeable cations, microorganisms, roots, hyphae and the cropping system (Ball *et al.*, 1996; Chaney and Swift, 1984; Harris *et al.*, 1966; Oades, 1984;) and other factors such as wetting and drying cycles (Utomo and Dexter, 1981) and cultivation or management practices (Chan, 1989). The ability of soil structure to withstand stresses, especially those created by wetting, drying and cultivation is very important. A particular arrangement is rarely stable as particles move under the influence of these stresses. Cultivation can lead to reduced aggregate stability, increased surface sealing and reduced hydraulic conductivity of surface soil (Chan and Heenan, 1993; Alegre *et al.*, 1986; Naidu *et al.*, 1996)

Deterioration of soil structure due either to loss of organic matter via cultivation or to low inputs of organic matter leads to soil compaction, hardening and erosion. Soil compaction reduces porosity, plant root and shoot growth and microbial activity. Reduced permeability and water holding capacity of surface and sub-surface soil can limit the amount of soil water available for crop growth, thus reducing crop production (Edward, 1982; Freebairn *et al.*, 1986; Jayawardane and Chan, 1994). In saline and sodic soils,

exchangeable sodium also leads to the deterioration of soil structure and structural stability. Many researchers have studied physical, chemical and biological aspects of soil structure deterioration (Utomo and Dexter, 1981; Oades, 1993). However, the structure and structural stability of soils used for sugar production have received little attention.

Most sugar cane grown in Queensland is planted as a monoculture every 5-6 years then left for about 6 months before being planted back with cane. Every year, ratoon crops, which are regrown from the original sugar cane plant, are harvested. Nearly all farm operations including planting, fertilising, harvesting, tillage and herbicide application are now highly mechanised. Over the last 15 years, cane yields have declined at a rate of 0.5 ton per hectare per year (Wood, 1985), a phenomenon known as 'sugar yield decline'. Recent studies of the causes of declining sugar productivity have focussed on root infection by a range of pathogenic fungi (Magarey *et al.*, 1995). However, application of highly mechanised equipment to the management of sugar cane production may be one cause of soil structure and structural stability deterioration and for 'sugar yield decline'.

Since the late 1970s or early 1980s in some areas of sugar cane production, leaving green cane residue on harvested land has been adopted as a trash management strategy. In most cases, the trash is retained as a surface cover called 'green cane trash blanketing'. Other management practices include burning of the cane residue, which was introduced in Australia in the 1930s to reduce the incidence of Weil's disease amongst the cane cutters. Trash was raked and burnt which made harvesting much easier and the soil between cane rows was cultivated (Wood, 1991).

The effects of both green cane and burnt trash management practices on soil properties such as aeration, water content, bulk density, organic matter, nutrient availability and biological activity have been reviewed (Wood, 1985, 1991; Bramley *et al.*, 1996).

However, the influence of these management practices have not been studied in relation to the issue of sodification when soil is irrigated with saline and sodic water. The role of organic matter in improving soil structure and structural stability has been widely examined. However, the influence of organic matter on sodification under irrigation with saline or sodic waters has not been critically examined. Soil with relatively high organic matter content generally has a strong selectivity for Ca over Na and it may inhibit sodification processes (Pratt and Grover, 1964; Nelson and Oades, 1998). Therefore, it is important to investigate the role of organic matter in soil undergoing sodification processes (Gupta and Abrol, 1990, Rengasamy and Olsson, 1991; Sumner, 1993), particularly where new cane-growing lands are being developed (e.g. in Mackay, Burdekin, Proserpine and Mareeba districts), which contain large areas of naturally sodic soil (Nelson, 1997).

Irrigation with water having a high concentration of sodium relative to divalent cations (sodic waters) may cause high exchangeable sodium on soil colloids and might lead to clay dispersion, which results in low fertility, poor infiltration and water-air relations, low readily available water holding capacity and difficulties in timely and effective tillage all of which place serious constraints on crop production and plant growth (Shainberg and Oster, 1978; Rengasamy and Olsson, 1991). The sodicity of soil is determined by its selectivity for sodium when in contact with soil solution. Sodium adsorption ratio (SAR) is most often used for determining the sodicity hazard of irrigation water, in which its relation with exchangeable sodium ratio (ESR) involving the Gapon selectivity coefficient (k_G) is generally linear. The value of k_G is influenced by soil properties such as clay and organic matter contents, pH, CEC and soil solution properties (Frenkel and Alperovitch, 1984, Haroon et al., 1983; Pratt and Gover, 1964).

Although the relative merits of different methods of cane-trash management have been documented for some of the better soils in the higher rainfall regions of Queensland (*eg.* Wood 1985; 1991; Bramley *et al.*, 1996), little has been done to understand their effects in relation to sodification of soils in the lower rainfall regions of Queensland, which require irrigation, often with saline or sodic waters.

In these situations, calcium is generally added as gypsum to reduce clay dispersion. Gypsum can, for example, reduce surface crusting, ESP and bulk density, and can also increase permeability, friability, water stable aggregation and crop yield (Sumner, 1993; Sekhon & Bajwa,1993; Shanmuganathan & Oades, 1983a). The addition of calcium has the added advantage that it tends to stabilise organic matter in soils. The problem in Queensland, however, is that gypsum is considerably more expensive than lime, so lime is the preferred source of calcium for most growers; lime can also raise the pH of sodic soils. Furthermore in alkaline soils, which are common in Queensland, lime is insoluble at pH>8.5 and thus relatively ineffective as a source of calcium to resist sodification.

To overcome the problem of low lime solubility, it was suggested that large amounts of organic matter could be incorporated with lime to lower the soil pH out of the highly alkaline region and thus increase the solubility of the lime (Robbins, 1986; Ahmad *et al.*, 1989; Gupta and Abrol, 1990). With a large source of decomposable organic matter in the soil, the partial pressure of CO_2 would be expected to rise and any organic acids produced during decomposition might lower the pH and dissolve more lime.

One source of organic material available to Queensland cane growers in large quantities is molasses, which is produced as a waste product by the sugar refineries and disposed of mainly as a concentrate in stock-feed. In general, the industry produces

considerably more molasses than it can dispose of for this purpose, so its supply would not be a limitation, at least in the foreseeable future (P.N. Nelson, *personal communication*).

This thesis outlines the results of a series of experiments on how calcium sources (gypsum or lime) and molasses affect the structural stability of soils, and how the trash management practices (burning cane trash and returning green cane harvest residues) and soil organic matter contents inhibit sodification under irrigation with saline and sodic waters. Two questions were addressed with regard to the management of irrigated, sodic soils used for cane production:

1. To what extent does the management of cane trash (or organic matter) influence the resistance to sodification of irrigated soils used for cane production?

2. Could the combined addition of lime and organic material (in the form of molasses) increase the solubility of applied lime and thus achieve a synergistic effect to reduce sodification of irrigated soils used for cane production more effectively?

CHAPTER 2

Literature Review

2.1 Soil Structure and Structural Stability

Soil structure has been defined as the size, shape and arrangement of particles and pores in soil (Marshall and Holmes, 1988). To this definition can also be added the stability of the structure of the soil because structure is not static but changes with water content and other agents of stress such as cultivation and machinery traffic which may be applied to the system. In addition, structure occurs across nine orders of magnitude (Waters and Oades, 1991) and descriptions at any one scale need to be integrated into the properties of the whole soil. Kay (1990) discussed three separate aspects of soil structure; (a) soil structural form refers to the current arrangement of soil aggregates and pores, (b) soil structural stability measures the change in structural form occurring under an external stress such as tillage, and (c) soil structural resilience refers to the tendency of a soil to regain its previous structural form once that has been disrupted.

Many researchers have reviewed soil structure and its measurement and have addressed various aspects of soil structure (Dexter, 1988; Kay, 1990; Harris *et al.*, 1966; Russell, 1971; Oades 1993; Quirk, 1994). Desirable soil structural form depends on the use to which the soil is being put. For crop growth as an example, good structure involves aggregation of soil particles into compound units with a range of diameters which maintain a range of pores sizes promoting infiltration of water, aeration, root growth and provide a good physical environment for root systems and associated organisms. Thus a soil with

good structure exhibits aggregation, crumbles and is friable. By contrast, for the lining of a water supply dam, a massive, high density, low porosity and very low permeability is preferred. Soil management can be altered or special treatments applied to promote the appropriate soil structural form (Geeves et al., 2000).

The structure of surface soil is complex and subject to more change than subsoil structure. Wetting and drying cycles, mechanical manipulation, plant roots, wind and water action on the soil surface are stresses which rearrange, break down and reform aggregates. Many physical, chemical and biological aspects of soil are also affected both directly and indirectly by soil structure. These include plant root and shoot growth, water and nutrient movement, soil workability, soil aeration, hydraulic properties and erodibility (Aylmore and Sills, 1982; Oades, 1993; Dexter, 1988, 1991; Chan, 1989; Kay, 1990)

Soil structure is strongly influenced by a number of factors including organic matter, exchangeable cations, microorganisms, roots, hyphae and cropping systems (Ball et al., 1996; Chaney and Swift, 1984; Harris et al., 1966; Oades, 1984;) and other factors such as wetting and drying cycles (Utomo and Dexter, 1981) and cultivation or management practices (Chan, 1989). The formation of soil structure involves physical forces of shrinking and swelling created by change in water status, freezing, thawing and tillage or movement of particles by water or larger biota such as roots and worms. The larger shrink/swell capacity of soils, the greater the tendency to generate macroaggregates on wetting and drying.

Aggregate or structural stability refers to the ability of the aggregates and pores to remain intact or resist slaking or breakdown into smaller units when subjected to stress by cultivation or tillage or when aggregates are wetted quickly by intense rainfall (Kay, 1990; Quirk and Murray, 1991; Tisdall, 1996). The ability of soil structure to withstand stresses,

especially those created by wetting, drying and cultivation, is very important. Particular arrangements are rarely stable as particles move under the influence of these stresses. In the field, the stability of these aggregates and the pores between them affect the movement and storage of water, aeration, erosion, biological activity and crop growth.

2.2 Soil Aggregation and Aggregate Hierarchy

Aggregation of soil has been studied in at least two ways; the formation and stabilisation of aggregates in suspensions of pure clay, and the separation of aggregates from soil disrupted by different amounts of energy (Tisdall, 1996). Several authors have proposed models of aggregation which show that soils are not homogeneous, but are made up of aggregate of different size held together by different organic and inorganic materials (Harris et al., 1966; Tisdall and Oades, 1982; Chaney and Swift, 1984; Bartoli et al., 1988; Oades and Waters, 1991).

The concepts of microaggregates (<250 μm diameter) and macroaggregates (>250 μm diameter) was proposed by Edwards and Bremner (1967) and supported by Tisdall and Oades (1982), Elliot (1986) and Miller and Jastrow (1990). Microaggregates are bound into macroaggregates and bonds within microaggregates are stronger and more stable than those between macroaggregates. In non-sodic soils, microaggregates are only dispersed by high energy such as ultrasound or by mechanical disturbance such as tillage or heavy rainfall. On the other hand, macroaggregates are easily disrupted by rapid wetting or end-over-end shaking. In the field, macroaggregate stability depends on management and can be stabilised or disrupted by agricultural management (Tisdall, 1991).

The hierarchy of soil aggregates refers to the way in which aggregates of different sizes breakdown in a stepwise fashion as the magnitude of an applied disruptive force increases (Tisdall and Oades, 1982; Oades and Waters, 1991; Oades, 1993). It is essential to describe precisely the scale at which soil structure or aggregation is being studied. The conceptual model for aggregate hierarchy has been presented by Tisdall and Oades (1982) and supported by Dexter (1988) with particular emphasis on implications for the bulk density and mechanical strength of aggregates. The larger aggregates have a greater porosity than the smaller ones because they contain the pores between the smaller aggregates, which are more dense. The larger aggregates will be weaker and have lower tensile strengths because they contain larger pores, which are the planes of weakness or failure planes when the aggregate is stressed.

Tisdall and Oades (1982) proposed that microaggregates were formed free within the soil and subsequently became the building block for macroaggregate formation. Hadas (1987) measured tensile strengths of air-dried aggregates with different diameters and found that the aggregates broke down in a stepwise fashion. The concept of aggregate hierarchy in which the primary particles (ie sand, silt, and clay) are attached to each other, was considered to be the lowest hierarchal order. With biotic (bacterial, fungal, and plant debris) and abiotic phenomena, the minerals tend to form domains, clusters, microaggregates, and macroaggregates, which comprise the hierarchal order of soil structure (Dexter, 1988; Tisdall and Oades, 1982; Oades, 1993). Figure 2.1 shows the scale of particles, aggregates, pores and biota, which range across about nine orders of magnitude in size. Recently experiments have been reported by Anger *et al.* (1997), Beare *et al.* (1994), Jastrow *et al.* (1996), and Six *et al.* (1998) supporting a more recent model of aggregate formation proposed by Oades (1984). Anger *et al.* (1997) conducted an

experiment in a field with ^{13}C- and ^{15}N-labeled wheat (*Triticum aestivum* L.) straw and observed an initial increase of labeled C and N in macroaggregates because of incorporation of new C and N therein. After further incubation, labelled C and N decreased in macroaggregates and increased in microaggregates.

Oades and Waters (1991) fractionated three types of soil (ie Alfisol, Mollisol and Oxisol) into different particle sizes after a range of disaggregating treatments and found that aggregate hierarchy existed in the Alfisol and Mollisol but not in the Oxisol. Aggregate hierarchy occurred in the Alfisol and Mollisol because organic materials such as roots and hyphae were the dominant stabilising agents in larger aggregates and fragments of roots acted as nuclei in smaller aggregates. The aggregates of the Oxisol were stabilised by cementing agents such as Fe and Al and hence most particles were compounded into a single, stable aggregate size.

2.3 Sodicity and Its Influence on Soil Structure and Structural Stability

2.3.1 Sodic Soil

Sodic soils are found in large areas of land both in arid and semi arid regions of the world that are dominated by the clay minerals montmorillonite and illite (Shainberg and Levy, 1992; Szabolcs, 1989). Sodic soils occur both naturally and as result of irrigation practices that permit the mobilisation of soluble salt within the soil body and its transport to other locations.

Scale (m)	Particles	Aggregations	Pore (functions)	Biota	Scale (m)
10^{-10}	Atoms		MICROPORES		10^{-10}
10^{-9}	Molecules	Amorphous minerals	(Adsorbed and intercrystalline water)	Organic molecules	10^{-9}
10^{-8}	Macromolecules			Poly-saccharides	10^{-8}
				Humic substances	
10^{-7}	Colloids	CLAY MICRO-STRUCTURE		Viruses	10^{-7}
			$\psi > -15$ bar	Bacteria	
	Clay particles	Quasicrystals	MESOPORES		
10^{-6}		Domains	(Plant available water)	Fungal hyphae	10^{-6}
10^{-5}	Silt	Assemblages		Root hairs	10^{-5}
10^{-4}	Sand	Micro-aggregates	$\psi < -0.1$ bar	Roots-Mesofauna	10^{-4}
			MACROPORES AND CRACKS		
10^{-3}		Macro-aggregates	(Aeration)		10^{-3}
10^{-2}	Gravel		(Fast drainage)	Worms	10^{-2}
10^{-1}		Clods		Moles	10^{-1}
	Rocks				
10^{0}					10^{0}

Figure 2.1 Scale in soil structure and different components of soil (Oades cited by Kay, 1990)

Exchangeable sodium in soil is usually expressed in relation to other cations. The most commonly used parameter is the exchangeable sodium percentage (ESP) which is defined as:

$$ESP = Na_{ex}100/CEC \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2.1)$$

or $\quad ESP = 100\ Na_{ex}/\Sigma(\ Ca_{ex} + Mg_{ex} + K_{ex} + Na_{ex} + Al_{ex}) \dots\dots\dots\dots\dots (2.2)$

where $[_{ex}]$ denotes amounts of exchangeable cations (mmol(+)/kg soil). When dealing with the sodicity of irrigation water or soil solution, the parameter sodium adsorption ratio (SAR) is also important (Shainberg and Oster, 1978):

$$SAR = [Na^+]/([Ca^{2+}]+[Mg^{2+}]/2)^{0.5} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2.3)$$

where [] refers to concentrations in mmol(+)/L; therefore, SAR has units of $(mmol/L)^{0.5}$.

The SAR of the soil solution is more easily and accurately measured than the ESP. Hence, for logistic rather than theoretical reasons, the SAR is often preferred over ESP as an index of sodicity (Sumner, 1993); SAR is related fairly directly to ESP. SAR is approximately numerically equivalent to ESP for saturation extracts (Richards, 1954) and approximately half the value of ESP for 1:5 soil:water extracts (Rengasamy et al., 1984). However, Cook and Muller (1997) reported that sensitivity to ESP varies across soil types. Soils with clay fractions dominated by illites tend to be more dispersive at a given ESP than soil with other clay minerals, and the sensitivity to ESP is greater in soil with higher clay contents (Churchman et al., 1993). The sensitivity to ESP also depends on soil pH,

particularly where the colloidal fraction has variable charge (Churchman *et al.*, 1993; Suarez *et al.*, 1984). Furthermore, Sumner *et al.* (1998) highlight the issues and problems associated with estimating the SAR of soil solution. The use of equation 2.3 may be misleading, as it gives Mg^{2+} rating equal to Ca^{2+} in countering negative attributes of sodium. Some studies have shown that magnesium may not contribute to soil stabilisation in the same way as calcium (Curtin at al., 1994). The use of magnesium in the equation may give an incorrect depiction of potential soil behaviour. Therefore, Cook and Muller (1997) proposed the alternative parameter exchangeable sodium content (ESC) in which levels of sodium are expressed on an oven-dried soil basis in the same way as CEC rather than relative to the cation exchange capacity.

Exchangeable Na generally has a detrimental influence on soil physical behaviour. However, the extent of this influence varies according to soil properties and composition, climate, plant species and management factors. Therefore, the classification of a soil as sodic also varies. The different classifications of sodic soils are summarised (Gupta and Abrol, 1990) in Table 2.1. In general, soils with an ESP in the root zone greater than approximately 6 are considered sodic, and those with an ESP > 15 are considered highly sodic (Northcote and Skene, 1972; Chartres, 1993; Richards, 1954).

The use of widely accepted threshold ESP values for sodic soils, however, does not necessarily mean that the effects of exchangeable Na are not evident at lower ESP values. The adverse physical properties usually attributed to sodicity are in fact also dependent on other soil conditions such as electrolyte concentration, pH, other exchangeable cations, clay mineralogy, organic matter content (and possibly its nature) and particle size distribution. The effect of these properties will also differ depending on whether surface soils or subsoils are being considered (Isbell, 1996). For Australian saline and sodic soils, Rengasamy and

Table 2.2 Classification of salt-affected soils (Gupta and Abrol, 1990)

Subcommission on Salt-affected Soils classification		Soil Map of the World (Soil Map of Europe) FAO/UNESCO project (ECA working party) classification	USDA classification (1967)	USSR classification (1967)
Basic grouping (1967)	Saline and sodic soils Map of Australia legend (1971)			
Saline soils	Saline soils	Solonchak:	Salorthids	Fluffy solonchak
Alkali soils without structure in B horizon		Orthic solonchak		(nonsteppic) Crust solonchak
	Alkaline sodic soils AS1 AS2 AS3	Mollic solonchak	Salorthidic Calcuiustolls Salorthidic Haplustolls	Soda solonchak (nonsteppic) Fluffy solonchak (steppic) Soda solonchak (steppic)
		Takyric solonchak gleyie solonchak	Halaquepts (pp)	Takyrs Meadow solonchak
	Nonalkaline sodic soils NS1 NS2	Solonetz:		
Alkali soils with structural B horizon		Orthic solonetz	Nadurargids Natrargids Natriboralfs Natrustalfs Natrixeralfs	Desert-steppe and desert solonetz
		Mollic solonetz	Natrallxolls Natriborolls Natrustolls Natrixerolls	Steppe solonetz
		Gleyic solonetz	Natraquolls Natraqualfs	Meadow solonetz
		Solodic planosols	Argiabolls (pp)	Solod

Olsson (1991) have proposed a classification shown in Figure 2.2 based upon key soil properties such as SAR, electrolyte concentration (measured as electrical conductivity, EC) and pH of 1:5 soil:water extracts. These key properties were selected since they are the major factors involved in the deleterious effects of sodicity on soil structure.

The main influence of sodicity on soil is on structure and structural stability. Accumulation of sodium in the exchange phase promotes dispersion at low electrolyte concentrations and affects soil properties such as structural stability, hydraulic conductivity and infiltration rate, which consequently affect crop production.
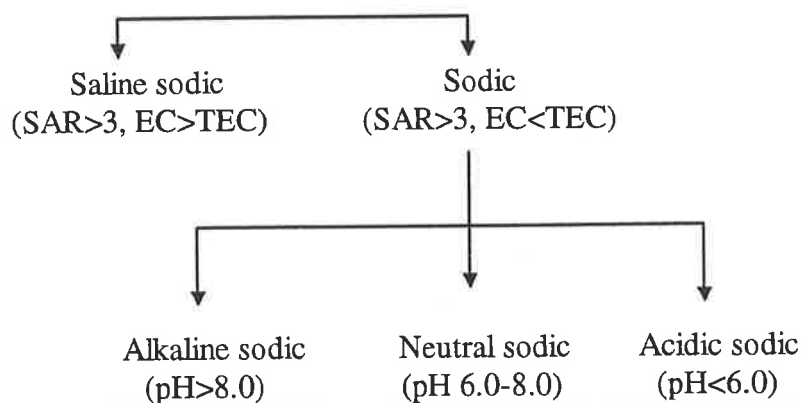
Figure 2.2 Proposed classification of sodic soils by Rengasamy and Olsson (1991), SAR, EC and TEC denote sodium adsorption ratio, electrical conductivity and threshold electrolyte concentration respectively in 1:5 soil:water extracts.

Soil aggregate stability at the larger scales (and hence that of the pore system) depends on aggregations at smaller scales, which are, to a large extent, a result of the attractive and repulsive forces arising from intermolecular and electrostatic interactions between soil particles. The balance between the opposing forces of attraction and repulsion between individual clay particles largely govern soil behaviour. Therefore, the formation

and stability of microaggregates and macroaggregates depend on dispersion and flocculation at the scale of colloidal particles (Quirk and Aylmore, 1960). In colloidal systems, the two layers represented by the negatively charged colloidal surfaces and the positively charged ions are referred to as the electrical double layer. In a liquid continuum, both electrostatic attractive forces and ion-related Brownian motion influence the spatial distribution of these counter ions in relation to the colloidal surface, resulting in a diffuse double layer (DDL) (Bear, 1964). This distribution of counter ions is important in influencing the effectiveness of the attractive and repulsive forces between particles and hence the stability of colloidal systems.

When dry soil aggregates are placed in contact with water, interactive forces lower the potential energy of the water molecules (Iwata *et al.*, 1988). This releases energy from the aggregates, which is used partly for structural transformation of the clay surfaces in the aggregate while the rest is released as heat. Slaking and clay dispersion are the major mechanisms by which the aggregates are damaged during these transformations and have been recognised as causes of degradation of soil structure (Abu-Sharar *et al.*, 1987; Frenkel, *et al.*, 1978; Rhoades and Ingvalson, 1969). Both slaking and dispersion are discussed in the following sections.

2.3.2 Slaking

Slaking refers to the breakdown of macroaggregates into microaggregates upon wetting. This leads to clogging of pores, reduced permeability and low infiltration rates and hence overland flow and erosion. On drying, this process causes hardsetting and crusting (Agassi *et al.*, 1981; Emerson, 1991), which results in poor plant establishment and

production (Rengasamy and Olsson, 1991). During wetting and drying processes, slaked aggregates are reduced to microaggregates which are closely packed and aggregates become denser as soil structure slumps (Mullins *et al.*, 1990).

Slaking results in microaggregates from which clay particles may or may not be dispersed depending on factors described in double layer theory, and some that are not including particle size, shape, packing and energy input (Oades, 1984). Slaking depends on swelling, entrapped air and heat of wetting. These parameters are influenced by organic matter, amount and type of clay minerals and exchangeable cations (Oades, 1984; Rengasamy *et al.*, 1984). Slaking of aggregates has been found to increase with rate of wetting (Emerson, 1984). The tendency of a soil to set hard is low when the degree of slaking can be minimised (Aylmore and Sills, 1982) although slaked particles may not necessarily be considered as microaggregates (Chan and Mullins, 1994).

The slaking phenomenon may be important in the regeneration of friable aggregates in Vertisols (Grant and Blackmore, 1993). Under field conditions, during rainfall or flood irrigation, the surface layers are subjected to rapid wetting. Soil aggregates are disrupted by slaking and disperse to some degree because of the mechanical action of rain or the heat of wetting. The aggregates below the soil surface (subsoil) are wetted slowly by capillary action, and may remain relatively unchanged. On drying, the dispersed materials may bind aggregates together, which in turn results in higher soil strength.

2.3.3 Clay Dispersion

Clay dispersion refers to the release of individual clay particles into suspension. Dispersible clay and aggregate stability in soils are of tremendous importance from

agricultural, environmental and engineering points of view. When individual particles become detached from aggregates, dispersion begins and results in soil structure, which is unstable and undesirable.

Dispersion of inorganic and organic colloids in soils results in the collapse of large pores and closer packing of particles. Reduced pore volume and closer packing leads to problems associated with poor permeability to water and air such as water logging, runoff and poor aeration (Dexter, 1988). When soil dries, high bulk density and strength lead to poor root penetration and seedling emergence, and difficulties in timely and effective tillage (Dexter, 1988; Mullins *et al.*, 1990). Dispersed colloids also move out of the soil and can cause problems with water quality (Oades, 1995). Therefore, the tendency of clay to disperse is an important property of soil, and should probably be routinely measured for assessing the impact of soil, crop and water management practices (Shanmuganathan and Oades, 1983b; Rengasamy *et al.*, 1984; Kay and Dexter, 1990).

The amount of clay dispersed depends on the amount of energy applied and soil properties (Rengasamy *et al.*, 1984). In undisturbed soil, the amount of dispersion is governed by clay content, the surface area from which clay is able to disperse and by the intrinsic dispersibility of the clay. Disturbance of the soil increases surface area by breaking up aggregates thereby increasing the potential for dispersion. It may be possible that clay on newly exposed surfaces differs in dispersibility to that on the previously exposed surfaces (Kay, 1990).

Stability of aggregates during wetting and when wet is an important soil property. Soils with aggregates that break down when wet, either as a result of compaction by raindrops or as a result of dispersion or slaking, have smaller pores, reduced pore continuity and increased soil strength upon drying (Connolly, 1998). When sodic soils are

wetted, continuous hydration of adsorbed sodium results in osmotic swelling and, as the water content increases beyond saturation, the clay particles bound by electrostatic forces involving sodium are separated. The repulsive forces in the diffuse double layer push the clay particles into suspension.

Spontaneous clay dispersion from soil aggregates depends on the proportion of sodium in relation to other cations involved in electrostatic bonding and electrolyte concentration of soil solution which opposes the repulsive hydration force (Quirk and Schofield, 1955; Rengasamy *et al.*, 1984). Spontaneous dispersion occurs if the clay swells to such an extent that the attractive forces between the particles are no longer strong enough to hold them together (Emerson, 1977). The particles of clay are released slowly and appear as a spreading cloud around the aggregate (Arnold, 1978).

Clay dispersion in soil is also influenced by water content at the time of measurement and by water content history. A positive relationship between clay dispersion and antecedent water content was demonstrated by Kay and Dexter (1990) and Caron and Kay (1992). The stabilising effect of drying shown by Caron and Kay (1992) was attributed to non-microbial mechanisms such as cementation. The sensitivity of clay dispersion to previous water contents was greater in less stable soils with low organic matter and low clay content (Rasiah *et al.*, 1992). Wetting and drying cycles tend to reduce wet aggregate stability, which is inversely correlated with dispersible clay (Caron and Kay, 1992) in both sterilised and unsterilised soils and increased hardsetting (Utomo and Dexter, 1982).

Hardsetting occurs when soil packs hard after several wetting and drying cycles without any externally applied load. Hardsetting is common in soils with a high percentage of fine sand and/or sodic soils. The hardest soils have low porosity, low permeability or

hydraulic conductivity and high strength when dry. This leads to reduced infiltration and problem with plant emergence and root growth (Chan and Heenan, 1993).

When disturbed soils are kept wet over a period of time, tensile strength, compressive strength and wet aggregate stability tend to increase, and dispersible clay decreases. This is probably due to rearrangement and cementation of particles (Utomo and Dexter, 1981, Dexter *et al.*, 1988; Caron and Kay 1992). In a recent study, Nelson *et al.* (1998) investigated clay dispersibility as influenced by incubation of sodic soils under different water content regimes. They found that clay dispersion was greater when measured on wet rather than on dry soils, irrespective of water contents during the prior incubation, while electrical conductivity increased, and sodium adsorption ratio (SAR), pH and organic carbon content decreased as a function of the time for which the soils were wetted. The dispersible clay decreased moderately under the wetting/drying regimes, which were not related to electrolyte composition and were attributed to particle rearrangement and cementation. The decreases in clay dispersibility with time occurred despite net losses of carbohydrate and aliphatic materials.

Dispersible clay not only affects soil strength but also influences soil erosion. Clay dispersion can increase soil erosion in three ways; first, dispersed clay is easy transported during runoff; second, clay dispersion in surface soils induces crust formation on drying and hence reduces infiltration; and third, the dispersed clay particles clog soil pores and reduced infiltration resulting in ponding and runoff. Agassi *et al.* (1985) studied the effect of electrolyte concentration and sodicity on infiltration rates in loamy soils with different raindrop energies. They found that when solutions of high electrolyte concentration were applied, the impact energy of the drop was the main cause of breakdown of the soil aggregates. Shainberg *et al.* (1992) compared erodibility of soil using different energy input

and water quality and concluded that the extent of rilling increased with ESP. Under the dispersive conditions, runoff was sufficient to initiate rilling, and soil losses increased sharply with slope.

In general, clay dispersibility is influenced by: (a) the amount of clay and the absence of clay domain formation; (b) particle size, clay mineralogy and surface charge characteristics; (c) exchangeable cation, electrolyte concentration and pH; (d) the presence of dispersing agents such as anions and cementing or aggregating agents such as organic matter, carbonates (Ca and Mg) and (hydro)oxides of Si, Fe and Al; (e) the strength of edge-to-face attractions; and (f) the interaction between these factors (Oades, 1984; Dong *et al.*, 1983; Suarez *et al.*, 1984; Chorom *et al.*, 1994; Emerson, 1983; Shanmuganathan and Oades, 1983; Shainberg and Letey, 1984; Hardcastle and Mitchell, 1976; Goldberg *et al.*, 1990; Churchman *et al.*, 1993; Greene *et al.*, 1978).

2.4 Organic Matter

2.4.1 Sources of Soil Organic Matter

The state of organic matter in soil is dynamic. Plant and animal materials, such as dead roots, straw and seeds are important components of organic matter and continually add to soil biota. These materials may be regarded as the parent materials for soil organic matter (Oades, 1989), and these are frequently named the 'light' or 'macroorganic' fractions. The light fraction of organic matter is often retained in cultural practices designed to reduce erosion and is mixed with the top soil through the activities of macrofauna (Stevenson, 1994). It can be separated from soil using sieving and density techniques following dispersion. Microorganisms convert the carbon in organic material to CO_2 and

thereby complete the biological carbon cycling that was initiated during photosynthesis. Thus, the amount of organic matter retained in soils is a balance between production of carbon compounds by biota and loss of carbon dioxide through microbial decomposition.

2.4.2 Influence of Organic Matter on Soil Structure and Structural Stability

The amount of organic matter in soils is often very small; approximately 1-5% of soil mass. This includes microbial biomass, plant remains, microbial/fauna products and remains, and occasionally charcoal. Organic carbon content in the top 10 cm ranges from < 5 g C/kg soil for desert loams (Aridisols) to > 130 g C/kg soil for alpine humus soils (Histosols and Mollisols) in Australia (Spain *et al.*, 1983). In other parts of the world, (eg. Sombroek *et al.*, 1993), organic carbon ranges from 0.5-3 g C/kg soil for Yermosols up to 310-555 g C/kg soil. A typical agricultural soil may contain organic matter of 2-5% in the top 15 cm (Schnitzer, 1978).

Although organic matter often constitutes only a minor proportion of the total mass of mineral soils, it is intimately associated with inorganic particles and can exert a profound influence on soil properties. Organic matter is considered important in the maintenance of soil structural stability and influences pore size distribution and soil water retention. Organic matter is usually porous and can absorb and hold substantial quantities of water, up to twenty times its mass (Stevenson, 1994). An increase in organic matter content generally increases the amount of plant-available water (Heinonen, 1985). However, its influence depends on the morphological structure of the organic materials and will not impart any beneficial effect to the soil unless it serves to enhance the ability of soil to hold water at potentials within the plant-available water range. Kay *et al.* (1997) assessed the

sensitivity of soil structure to change in organic content by prediction using pedotransfer functions, which also predict pore-size distribution. They predicted that when organic carbon content was increased by 0.01 kg/kg, the available water holding capacity of soils ranging in clay content from 7 to 35% increased by 0.02-0.04 m^3m^{-3} and increased the least limiting water range by 0.01-0.05 m^3m^{-3}. However, the magnitude of the increase found to decrease with increasing clay content.

Organic matter also plays an important role in the structural stability of soil. Different components of organic matter act to stabilise structure at different scales. Figure 2.3 shows the role of organic matter in stabilising soil structure. At large scale, plant roots, and mycorrhizal and saprophytic fungal hyphae enmesh macroaggregates, thus inhibiting slaking and dispersion. Plant roots and fungal hyphae (especially mycorrhizal) are transient binding agents which are only present when plants are growing and fresh organic materials are being returned to the soil. These organic materials are also easily disrupted by desiccation or mechanical disturbance and rapidly decomposed by microorganisms. At the smaller scale, mucilages and colloidal organo-mineral complexes play an important role in binding microaggregates through a variety of mechanisms, and their effects tend to be more persistent (Tisdall and Oades, 1982).

There are three consequences of the model aggregation of soil by organic matter in Figure 2.3: (1) macroaggregates gradually break down into microaggregates before they dissociate into primary particles when increasing dispersive energy is applied to soil (Oades and Waters, 1991); (2) an increase in C concentration occurs with increasing aggregate-size classes because large aggregate size classes are composed of small aggregate size classes plus organic binding agents (Elliott, 1986); and (3) younger and more labile organic

matter occurs in macroaggregates rather than in microaggregates (Elliott, 1986; Puget *et al.*, 1995; Jastrow *et al.*, 1996).
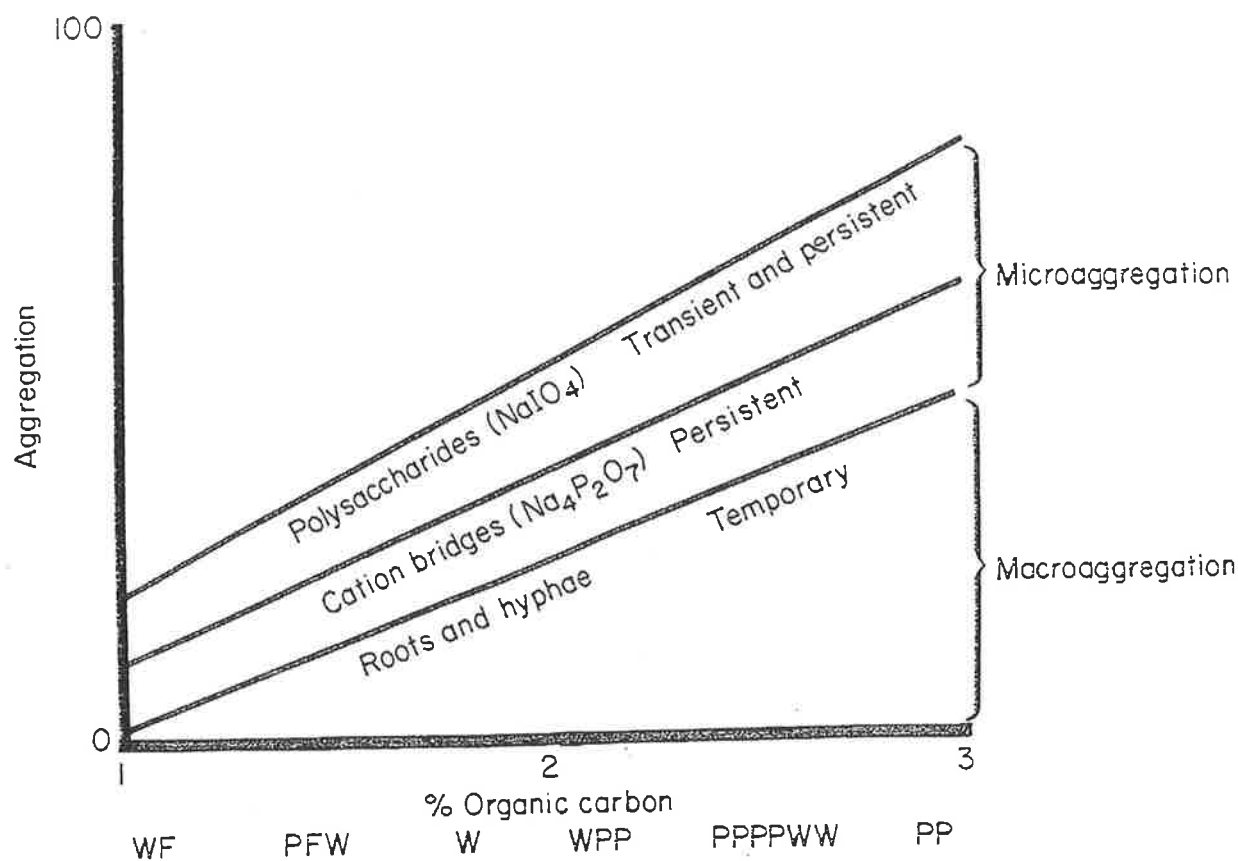
Figure 2.3 Effect of crop-rotation on stable macroaggregation, W = Wheat, F = fallow P = pasture (Tisdall and Oades, 1982)

2.4.3 Influence of Cultivation and Trash Management on Soil Organic Matter

Different techniques for preparation of seedbeds or in the production of crops include conventional cultivation, direct drilling and minimum tillage. The purpose and the scale at which they are used for tilling the soil depends on some variables such as soil properties, plant to be grown, and climatic zone. Furthermore, cultivation may be as simple as punching or digging a hole in a soil to plant seeds, tubers or other means of plant propagation, then controlling competing plants by hoeing or slashing; it may be an intensive

cultivation system involving primary tillage, several subsequent tillage operations, application of fertilisers, pesticides and planting operations. Thus, after plant establishment, additional cultivation may be used to control weeds, erosion or break surface crusts and to enhance soil aeration or water infiltration. However, untimely tillage can result in a compacted layer at the base of the ploughed zone which impedes water flow. Primary tillage usually inverts the soil, mainly to incorporate residues or bury weeds, and secondary tillage provides the seed-bed. These differing systems vary considerably in the way they modify the soil structure and the extent to which they do so. They differ in the amounts of energy put into the soil. These differences have an impact on the activity of microorganisms and soil animals which bring about mineralisation as they metabolise organic carbon and nitrogen (Addiscott, 2000).

One of the objectives in tillage operations is to maintain the upper layer or surface soil in an aggregated state and good porosity for the purpose of facilitating adequate aeration and water infiltration for crop development. However, when soils are cultivated, aggregates are exposed to physical disruption by rapid wetting or by rain drop impacts as well as to shearing by implements. It has been proposed that soil aggregates physically protect certain soil organic matter fractions, resulting in pools with longer turnover times (Adu and Oades, 1978). Since soil aggregates are sensitive to management practices, an increase in aggregate disruption by tillage or cultivation may lead to increased decomposition of soil organic matter. Tillage may expose organic matter that was previously inaccessible to microorganisms, resulting in loss of organic matter, which may reduce inter-aggregate bonding leading to further loss of soil stability. This loss of organic matter reduces the proportion of macroaggregates in cultivated soil.

The effects of cultivation in decreasing soil organic matter levels are well documented (Tisdall and Oades, 1982; Elliott, 1986; Dalal and Mayer, 1986; Cerri *et al.*, 1991; Paustian *et al.*, 1997; Six *et al.*, 1998; Six *et al.*, 1999). Dalal and Mayer (1986) showed that in the wheatbelt of southern Queensland, soils which had been cropped for 20-70 years suffered a decline in soil organic matter, with particular reductions in total organic carbon, organic C in light fractions, total nitrogen and mineralisable nitrogen. Mann (1986) estimated that a considerable proportion of organic matter is lost during cultivation. Elliott (1986) also reported that cultivation resulted in a loss of labile organic matter which binds microaggregates into macroaggregates.

Microbial biomass and enzyme activity, which are important parts of the organic matter in soil, are reduced by cultivation in both microaggregates and macroaggregates but mainly in macroaggegates (Gupta and Germida, 1988).

The decline of organic matter in cultivated soils is primarily due to change in soil temperature, moisture fluxes, aeration and exposure of organic materials within aggregates, reduced addition of organic materials and frequently, to increased soil erosion (Dalal and Mayer, 1986). The loss of soil organic matter by cultivation is usually exponential, with loss being rapid during first 10-20 years of cultivation, followed by continuous loss at a slower rate with a new equilibrium finally approached after 30-60 years (Arrouays *et al.*, 1995; Schlesinger, 1986; Mann, 1986). However, the time scale varies with climatic zone, management of crop residue and soil type. Oades (1993) suggested that repeated cultivation of soils, combined with limited soil organic matter inputs, would eventually lead to deterioration of soil and leaving the soil vulnerable to erosion and compaction. Karlen and Cambardella (1996) contended that changing management practices such as retention of plant residues, reduced and no-tillage techniques, the use of green manure crops and

pasture leys, or the application of organic materials resulted in numerous beneficial effects on soil properties.

There are two trash management practices commonly used in sugarcane growing areas in Queensland, Australia including burning trash (burning) and returning trash as a blanket (green). In general, the amount of crop residue removed or returned, its placement and the use of burning, all affect the level of soil organic matter. Blair *et al.* (1995) reported that the continuous cultivation and burning crop residues have led to reduce level of soil organic matter. Similar results were reported by Ball *et al.* (1993) in sugarcane growing districts, northeast Brazil. Blair *et al.* (1998) investigated the dynamics of soil carbon at two long-term plot experiments in Queensland (Ayr and Tully) and in Brazil (Pernambuco State) by comparing the effects of sugarcane burning with green trash management relative to a reference forest area. Their measurements of total carbon and labile carbon in the top 1 cm indicated that there was more loss from burning cane trash than from "green cane trash management" in Queensland. In Brazil, total carbon did not change over 12 months but labile carbon increased under green cane trash management. They suggested that sustainable sugarcane cropping systems must include crop residue without burning in order to maintain an active C cycle in the system. In another study, Skjemstad *et al.* (1999) found substantial amounts of charcoal, of pre-cane origin, in both uncropped and cropped soil for sugarcane production in Queensland.

2.5 Cation Exchange Selectivity of Soil

The selectivity coefficients of soil can be measured when soils are equilibrated with mixed-cation solutions. Equilibrium is reached when the rate of the forward reaction equals the rate of the reverse reaction (Bear, 1964).

When two kinds of cation are present in soil solution, clay surfaces will adsorb these cations in different amounts. The proportion of adsorbed cations is determined by the composition of the soil solution and by the properties of the solid surface. The proportion of exchange sites on clay surfaces or organic materials occupied by each ion and the proportion of each ion in solution can be used to express the exchangeable cation selectivity of the soil. There are many factors which influence this selectivity, including 1) type of cation, 2) ion concentration, 3) the nature of anions associated with cations or accompanying anions, 4) the type of clay, and 5) amount and type of organic matter (Toth, 1964; Ji and Li, 1997).

Many studies in the past have quantitatively evaluated the extent of ion exchange reactions from theoretical bases such as adsorption equations, mass-action equations and kinetic equations, each of which describes the distribution and selectivity of cations between adsorption and solution (Bresler *et al.*, 1982; Sposito, 1977, 1989). Because of problems such as measuring cation activity on the exchange complex, exchange complex characteristics and the variety of cations, none of the parameters used to express selectivity for different ions are satisfactory for all soil conditions. Therefore, Nelson and Oades (1998) argued that the Gapon equation is still useful.

The amount of cation that will be taken up by an exchange complex will be proportional to the surface charge of the clay. Between cations of different valency, the equilibrium reaction can be written, for simple system containing only Na and Ca, as:

$$Ca_{1/2}X + Na^+ \longleftrightarrow 1/2Ca^{2+} + NaX \quad \dots\dots\dots(2.4)$$

where X is a single exchange site (charge). From this reaction, the Gapon constant can be formulated as:

$$k_G = \frac{[Ca^{2+}]^{1/2}(NaX)}{[Na^+](Ca_{1/2}X)} \quad \dots\dots\dots(2.5)$$

in which $Ca_{1/2}X$ and NaX are the equivalent fraction of calcium and sodium ions on the exchange complex and the square brackets refer to concentrations in solution rather than activities. In sodic soils, the exchange behaviour of Ca^{2+} compared with Na^+ is important, because of the influence on soil dispersive behaviour. When we consider the proportion of Na and Ca ions on exchange sites as ESR (exchangeable sodium ratio) and in solution as SAR (sodium adsorption ratio), the Gapon constant can be written as:

$$ESR = k_G (SAR) \quad \dots\dots\dots(2.6)$$

where:

$$ESR = (NaX)/(Ca_{1/2}X) \quad \dots\dots\dots(2.7)$$

and

$$SAR = [Na^+]/([Ca^{++}]/2)^{0.5} \quad \dots\dots\dots(2.8)$$

Over the concentration ranges common to salt-affected soils, the ratio of ion concentrations is of similar magnitude to the corresponding ratio of ion activities although ion activities can be quite different from ion concentration (Shainberg and Letey, 1984).

An important characteristic of clay is surface charge density. Surface charge density is usually calculated from CEC (cation exchange capacity) and surface area derived from ethylene glycol adsorption measurements (Pratt and Grover, 1964). The CEC of clay minerals generally decreases in the order of: vermiculite > montmorillonite > illite > kaolinite. However, the surface charge density of clay minerals is not necessarily correlated with CEC. Relative adsorption of divalent cations compared to monovalent cations on the exchange sites of clay minerals increases proportionally to surface charge density. The selectivity and bonding strength of all cation exchange sites in soil is greater for cations of higher valence (Toth, 1964; Pratt and Grover, 1964). This means that the selectivity and binding strength of divalent cations on exchange sites is generally greater than that of monovalent cations so that their replacement is more difficult. The average of the bonding energies of divalent cations is twice as high as for monovalent cations (Marshall, 1964). Amongst cations of equal valence, the replacing power tends to increase with the size of ions and with reduced hydration of the ion (Toth, 1964). Curtin et al. (1994) also reported that soils which they examined had a stronger tendency to accumulate exchangeable Na when Mg rather than Ca was present as the complementary cation, indicating that the exchange sites of clay surfaces have a preference for Ca over Mg.

2.5.1 Cation Exchange Selectivity of Soils as Affected by Organic Matter

Schachtschabel (1940) found that organic material adsorbed more Ca than clay minerals. He was the first to put forward the idea that cations are present in different proportions on different types of colloids in soil. Pratt and Grover (1964) investigated the influence of organic matter and clay type on monovalent-divalent exchange equilibria in

soil. They found that soil with relatively high organic matter content had strong preferential adsorption of Ca over Na; but this preference was weaker when the organic matter was removed from the soils. Nelson and Oades (1998) argued similarly that soils with higher organic matter contents may inhibit sodification under irrigation with saline or sodic water more so than soils with lower organic matter contents. This idea, however, has not yet been critically evaluated.

When soils are leached with salt solutions containing a mixture of monovalent and divalent cations until equilibrium is attained, a linear relation is obtained between ESR and SAR involving the Gapon constant (equation 2.6) (Shainberg and Oster, 1978). The value of the Gapon constant depends on soil characteristics, and solution composition. Curtin *et al.* (1995) investigated variables influencing k_G in a group of 16 Canadian soils. They found that k_G for Na-Ca exchange ranged from 0.0063 to 0.013 $(mmol/L)^{-1/2}$. The magnitude of k_G was negatively correlated with organic carbon content (r=-0.90), with pH (r=-0.90) and with CEC (r=-0.95). When the pH of a soil of high organic matter content was raised from 5.2 to 7.3, k_G decreased from 0.009 to 0.0065 $(mmol/L)^{-1/2}$. Girdhar (1996) and Kachoui *et al.* (1996) reported that the Gapon selectivity coefficient increased with an increase in salinity and sodicity. The highest value of k_G was observed at high SAR, high residual sodium carbonate (RSC) and high EC of the equilibrium solutions.

2.6 Amelioration of Sodic Soils

Reclamation of sodic soils requires that part or most of the exchangeable sodium is replaced by calcium ions at least in the root zone. The reclamation processes of sodic soils are reasonably well understood, and the addition of a variety of both organic and inorganic

ameliorants is widely recognised and practiced. Some reclamation processes that have been practiced in the past include the use of gypsum (Khosla *et al.*, 1973; Loveday, 1976, 1984; Qadir *et al.*, 1998), lime (Naidu *et al.*, 1990), organic matter (Chorom and Rengasamy, 1997; Boyle *et al.*, 1989; Qadir *et al.*, 1997; Wahid *et al.*, 1998); molasses (Weber and Van Rooyen, 1971; Van Rooyen and Weber, 1977). The reclamation of sodic soil can be accomplished in many ways; the best being dictated by local conditions, available resources and the kinds of crops to be grown during reclamation. For quick results, cropping must be preceded by the application of a chemical ameliorant followed by leaching to remove soluble salts and other reaction products of amendment.

2.7.1 Chemical Amelioration

2.7.1.1 Gypsum

Gypsum has been widely accepted as an ameliorant of sodic soils. Application of gypsum to sodic soils, either incorporated into the soil or left on the surface, is known to increase removal of Na in drainage water, decrease exchangeable Na content (Figure 2.4), reduce soil pH, prevent excessive swelling and dispersion, reduce surface crusting, decrease bulk density, increase permeability and porosity, increase structural stability, reduce dry soil strength, improve crop production, increase the stability of soil organic matter and increase soil faunal activity (Rengasamy, 1983; Shanmuganathan and Oades, 1983, Wallace, 1994; Sumner, 1993; Keren and Shainberg, 1981; Sekhon and Bajwa, 1993; Ellington *et al.*, 1997; Qadir *et al.*, 1996). Surface crust strength is very largely dependent on water content and, because gypsum treatment slows the rate of surface drying, it reduces the strength (Loveday and Scotter, 1966). With regard to soil tilth, gypsum-induced improvements

include a wider range of water content at which tillage can be performed, and greater ease
and effectiveness of tillage for seedbed preparation and for weed control.
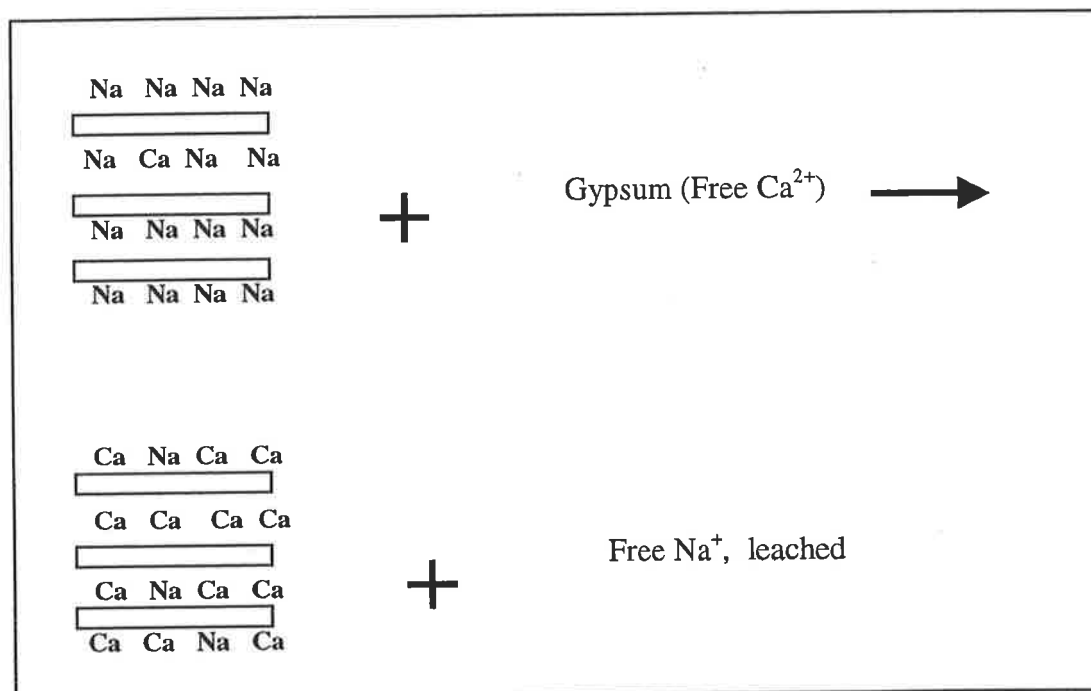
Figure 2.4 Schematic amelioration of sodic soils via the addition of gypsum

Gypsum added to a sodic soil can improve permeability by increasing electrolyte
concentration and by exchanging Na with Ca (Loveday, 1976; Keren and Shainberg, 1981;
Keren *et al.*, 1983). The relative significance of the two effects is of interest for several
reasons. If the electrolyte effect is sufficient to prevent swelling and clay dispersion, surface
application of gypsum may be worthwhile. In this case, the amount of gypsum required
depends on the amount of high-quality water applied and the rate of gypsum dissolution
(Shainberg *et al.*, 1989). This is somewhat independent of the amount of the exchangeable
Na in the soil. If, on the other hand, the effect of electrolyte concentration is less significant
with respect to preventing clay dispersion and swelling than cation exchange reactions, the
amount of gypsum required will depend more upon the amount of exchangeable Na in the

soil. However, the amount of exchangeable sodium to be replaced during reclamation depends on the initial exchangeable sodium, CEC, bulk density, the desired final level of exchangeable sodium and the depth of soil to be reclaimed (Keren, 1995).

The rate of gypsum dissolution is an important parameter affecting its efficiency as an amendment. Gypsum ($CaSO_4.2H_2O$) and its dehydration products are slightly soluble in aqueous solution (approximately 2.5 g/L or 15 mmol/L). However, this level of solubility is influenced by ESP, SAR, ionic strength, ion-pair associations, and Ca/Mg ratio (Hira and Singh, 1980; Gupta and Abrol, 1990).

The acceptance of gypsum as an ameliorant to most soils has several drawbacks, including cost when applied at high rates, suitability for use in certain soil types such as acidic soil, and long-term availability. As gypsum requirement for sodic soil reclamation increases with increasing soil pH (Gupta and Abrol, 1990), the amount required for total reclamation is too expensive for most farmers. They therefore, only purchase enough gypsum to temporarily change the soil Na^+/Ca^{2+} balance to a small degree or, more usually, to exploit the "electrolyte effect", so repeated application is needed. Sometimes they apply less gypsum or low-grade gypsum containing high concentrations of NaCl, leading to soil salinity in the long-term. Gypsum is used for a wide variety of purposes, including the manufacture of Plaster Board and Plaster of Paris. It is important to realise that gypsum is a limited resource, therefore it is important to find alternate resources such as lime in the reclamation of sodic soils.

2.7.1.2 Lime

Lime has been extensively used in Australia to overcome soil acidity and some sodicity problems (Offiah and Fanning, 1994; Heenan et al., 1998, Wang et al., 1999).

Lime acts as an aggregate cementing agent (Rimmer and Greenland, 1976; Emerson, 1983; Rengasamy *et al.*, 1984) and, depending on soil pH, may improve soil structure by releasing calcium ions (Shainberg and Levy, 1992; Naidu and Rengasamy, 1993). Carbonate from the lime reacts with H^+ in the soil, which raises soil pH (Singer and Munns, 1987). The rate of reaction of the lime is related to several factors, including the soil CEC, the finesses of the lime (Barber, 1984) and the initial soil pH (Peveril *et al.*, 1999). The amount by which soil pH increases is related to soil buffering capacity, which is influenced by organic matter content, clay content and type, CEC and the initial soil pH. A soil that has well buffered (significant 'reserve acidity') requires greater amounts of lime to increase pH than a soil with a low buffering capacity (Aiken *et al.*, 1998).

The beneficial effects of lime as an ameliorant are reasonably well understood. However, lime is relatively insoluble in soils having pH > 8.5 and therefore contributes little to the exchange of sodium by calcium. In alkaline sodic soils, the total quantities of Ca are usually more than sufficient for desodification, but the Ca is present as $CaCO_3$, which is insoluble at high pH, therefore the ESP and SAR of soil solution remain high.

Lime may dissolve slowly to release Ca ions, especially in the reclamation of saline sodic soils in which its solubility is enhanced (Oster, 1982). However, it has generally been considered of doubtful value to add lime to nonsaline sodic soils because its dissolution rate is too small to provide much Ca to replace sodium unless an acid or acid-former is applied concurrently.

The pH of alkaline soils is a function of the activity of $CO_3^{2-} + HCO_3^-$, P_{CO2} and ionic strength as shown in equation 2.9 (Mashhady and Rowell, 1978). The presence of Na increases the pH of calcareous soils by increasing the activity of CO_3^{2-} and HCO_3^-. The relationship between pH, P_{CO2} and $CaCO_3$, $NaHCO_3$ and Na_2CO_3 concentrations has been

described by Nakayama (1970). $NaHCO_3$ and Na_2CO_3 salts are relative soluble and their removal by leaching with high quality water can substantially reduce pH and ESP in alkaline sodic soils. However, because of the high pH and ESP, permeability is low enough to make leaching impractical. Therefore, the addition of acid is the favoured technique for amelioration.

$$pH = 7.82 - \log P_{CO2} + \log X - 0.5\sqrt{I} \qquad (2.9)$$

(where X = activity of CO_3^{2-} and HCO_3^{-} and I = ionic strength)

To overcome the problem of low lime solubility, it was suggested that large amounts of organic matter could be incorporated with lime to lower the soil pH out of the highly alkaline region and thus increase the solubility of the lime (Robbins, 1986; Ahmad *et al.*, 1990; Gupta and Abrol, 1990). With a large source of decomposable organic matter in the soil, the partial pressure of CO_2 would be expected to rise and any organic acids produced during decomposition might lower the pH and dissolve more lime (Robbins, 1986; Gupta *et al.*, 1989; Puttaswamygowda and Pratt, 1973; Sadana and Bajwa, 1985). The calcium ions from lime may then exchange with sodium ions adsorbed by clay particles, allowing sodium ions to be leached into the soil profile, thus decreasing the ESP (Lehrsch *et al.*, 1993).

2.7.2 Biological Amelioration

Addition of a variety of organic materials as ameliorants to reclaim sodic soils is widely recognised and practised. The addition of animal manures and plant residues has been applied extensively, but of all the approaches to biological amelioration, the most generally useful involve stimulating sufficient plant growth to build up and maintain organic matter in the soil. Crops grown during reclamation must tolerate both poor soil physical properties and sodium-induced calcium deficiency (Gupta and Abrol, 1990; Carter *et al.*, 1979). Moreover, the high electrolyte concentration in saline-sodic soil increases the osmotic pressure in the soil solution and hinders the uptake of ions by the plant root systems, this phenomenon is one of the major causes of reduced fertility in saline and sodic soils (Szabolcs, 1989).

The main purpose of any biological amelioration program is to produce the maximum amount of biomass per unit area and time. The soils must be continuously cropped and not left fallow. While cropping generally brings the best economic return in the short term, pastures and green manures can also play an important role in reclamation of sodic soils (Singh *et al.*, 1991).

Many studies have made comparisons between the effectiveness of inorganic and organic amendments and results have depended on the situation. However, it is clear that the combinations of inorganic and organic amendments (eg. gypsum + wheatstraw) may be the most efficient means of reclamation. Combinations of Ca-ameliorants with organic matter have been found to further reduce dispersion of sodic soils. In some cases (Baldock *et al.*, 1994), greater level of macro-aggregation may result from combination of gypsum and wheatstraw than from either gypsum or wheatstraw acting alone on a sodic soil.

One source of organic material available to Queensland cane growers in large quantities is molasses, which is produced as a waste product by the sugar refineries and disposed of mainly as a concentrate in stock-feed. In general, the industry produces considerably more molasses than it can dispose of for this purpose, so its supply would not be a limitation, at least in the foreseeable future. Weber & Van Rooyen (1971) found its application to soils increased aggregate stability and infiltration, and reduced the modulus of rupture and bulk density of saline-sodic soils. Molasses was more effective within five months than other common soil ameliorants such as gypsum, sulfur, potassium sulphate, manure - and with no increase in pH or total salt content, despite the high content of total calcium in molasses. By incorporating molasses and lime (section 2.7.1.2), it may be possible to increase the solubility of the lime to levels not otherwise expected.

2.8 Summary of Literature Review

The factors that influence the structural stability of soil and its relationship with organic matter are complex. They depend on the amount of organic matter added, properties of soil such as particle size distribution, clay mineralogy, EC, pH, nature of the anions and exchangeable cations and the presence of Al, Fe and Si oxides.

Two processes, namely slaking and dispersion, are responsible for the structural instability of soil. These processes are influenced by various factors such as the amount of clay, particle size distribution, clay mineralogy and surface charge characteristics, exchangeable cation, electrolyte concentration, pH, organic matter, carbonates (Ca and Mg) and (hydro)oxides of Si, Fe and Al, and the interaction between these factors.

The role of organic matter in improving soil structure and structural stability in soils has been widely examined. However, the influence of organic matter on inhibition of sodification under irrigation with saline or sodic water has not been intensively evaluated. It is important to investigate the role of organic matter on soil undergoing sodification processes.

It is also frequently economical to ameliorate sodic soils by biological amendments or organic matter. Molasses, a waste product of sugar refineries, is composed largely of polysaccharides. Incorporating molasses with lime might be expected to lower the soil pH out of the highly alkaline region. The partial pressure of CO_2 and any organic acids produced during decomposition might then increase the solubility of the lime.

CHAPTER 3

Structural Stability of Sodic Soils as Influenced by Gypsum and Molasses

3.1 Introduction

Stable structure and structural stability are essential for a fertile soil. These soil properties arise from the presence of macro-and micro-aggregates. Macroaggregation is very sensitive to change in land use and cultivation practices (Chaney and Swift, 1984; Roberson et al., 1991; Anger, 1992; Oades, 1984), whereas microaggregation is much less so (Oades, 1984; Elliott, 1986; Besnard et al., 1996). One of the measures of stable structure is stability of soil aggregates in water. Such changes in water-stable aggregation have generally been correlated with the quality and quantity of organic matter in the soil (Tisdall and Oades, 1982; Piccolo, 1996; Puget et al., 2000) At least two processes have been recognised in the deterioration of soil structure; these are slaking and dispersion (Section 2.3.2 and 2.3.3).

Gypsum ($CaSO_4.2H_2O$) and organic materials are commonly used as ameliorants to overcome sodicity and related problems. In the sugarcane growing districts of Queensland, gypsum is available at about \$90/ton and a substantial source of organic material is available as molasses at about \$45/ton. Molasses, a by-product of sugar production, contains carbohydrates (62%), protein (3-4%) and ash (8.6%) (data from Weber and Van Rooyen, 1971) as well as cations (calcium, 0.07%; magnesium, 0.08%; potassium, 0.5%; sodium, 0.03%), nitrogen (0.39%) and water (20% w/w), and has a pH of about 5.5 (data from this work). The aim of this work was to determine whether molasses alone or

combined with gypsum, could improve the structural stability of two sodic soils used for sugarcane production.

3.2 Materials and Methods

3.2.1 Soils

The soils used in the present study originated from two sugarcane producing areas in Queensland, Proserpine (20°30'S, 148°30'E) and Burdekin (19°30'S, 147°20'E). The soil from the Burdekin area is a Mesonatric Brown Sodosol and from the Proserpine area a Natric Brown Kurosol (Isbell, 1996). The soils were sampled at 0-15 cm depth. Each soil sample was air-dried and passed through a 5 mm sieve by hand. Table 3.1 shows some of the physical and chemical properties of the soils, including particle size distribution, pH, electrical conductivity (EC), organic carbon, exchangeable sodium percentage (ESP), cation exchange capacity (CEC) and exchangeable cations. Particle size distribution was determined by sedimentation after sodium saturation using methods described by Gee and Bauder (1986). EC and pH of soils were measured (1:5 soil:water) after shaking for 2 h and allowing to stand overnight. Clay mineralogy was determined by XRD on <2 μm fractions (Riley, 1993). Both soils contained a range of clay minerals; the Burdekin soil is dominated by illite and illite-smectite, and the Proserpine soil by illite and kaolinite.

3.2.2 Experimental Design and Treatments

The experiment had a factorial design with 3 factors (gypsum, molasses, and soils) and 4 replicates. The gypsum and molasses factors consisted of an application of either 10 t/ha gypsum, 10 t/ha molasses, or 10 t/ha each of both gypsum and molasses in the Burdekin and Proserpine soils and an untreated control for each soil. Applications of

Table 3.1 Selected properties of soil used in this study.

Soil	pH^A	EC^A	Cations (cmol(+)/kg)				CEC
		dS/m	Ca	Mg	K	Na	cmol(+)/kg
Burdekin	8.0	0.2	6.5	3.9	0.5	0.9	10.9
Proserpine	4.9	0.1	0.9	0.4	0.4	0.4	2.3

	ESP	O C	Particle size (%)			Texture
		%	clay	silt	sand	
Burdekin	7.9	0.8	21.7	25.4	52.8	scl^B
Proserpine	18.8	0.7	5.0	12.8	82.2	ls^B

^{A}1:5 soil:water extracts.
^{B}scl and ls, sandy clay loam and loamy sand respectively.

molasses and gypsum were calculated on an areal basis (10 t/ha = 0.1g/cm^2), which meant that appropriate pots received 6.08 g of each treatment. Each experimental unit was a pot of soil, kept at 25°C for a period of 12 weeks.

For the molasses treatments, molasses was dissolved in deionised water and sprayed uniformly onto soil, which was spread out on a plastic sheet; the soil was then dried and mixed before being placed in pots. These treatments were based on oven dried weights of molasses (75°C, θ=0.25g/g). For the gypsum treatments, gypsum was thoroughly mixed with soil samples spread on a plastic sheet.

Pots, made from PVC tubing (8.8 cm i.d., 10 cm long) were filled with 500 g treated soil, which produced bulk densities in the range of 1.4-1.5 g/mL. Fine mesh was placed over a funnel at the base of each pot to retain soil but to allow leachate to pass. All the pots were wetted to 85% of field capacity (FC) and maintained in this state for 7 days to provide time for dissolution, diffusion and microbial activity. Pots were leached with 0.5 pore-volumes of distilled water (88 mL or equal to 14.5 mm rainfall for the Burdekin soil and 72 mL or equal to 11.8 mm rainfall for the Proserpine soil). This water was

applied as a spray over a period of 2.5-3 hours. Leachate was collected and analysed for

dissolved organic carbon (DOC), cations (Ca^{2+}, K^+, Mg^{2+} and Na^+), pH and EC. The

sodium adsorption ratio (SAR) of solutions was calculated from:

$SAR = [Na^+]/([Ca^{2+}] + [Mg^{2+}])^{0.5}$, where cation concentrations are expressed in mmol/L.

DOC was measured using a DC-180 Automated Total Organic Carbon Analyzer. Between

leaching events, pots were allowed to dry for 7-10 d, which was long enough to bring

them to their original air-dry water contents. At this point, they were again leached with

water, during which leachate was collected for analysis. These wetting and drying cycles

were conducted to simulate the changes in soil solution concentration that occur in the

field and to promote the migration of solutes and colloids that may impact on soil

structural stability. A schematic of the leaching events and water status of the soils is

presented in Figure 3.1. Leaching events were conducted a total of 5 times and all pots

were then air-dried for soil analysis after the last leachate had been collected.
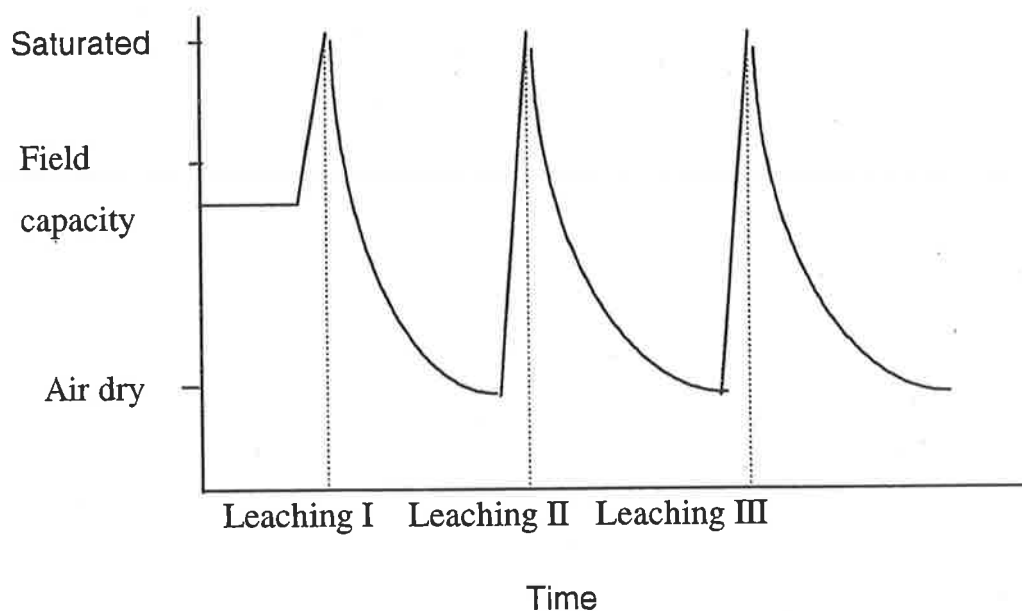
Figure 3.1 Schematic of leaching events and soil water contents

3.2.3 Soil analyses

Air-dried soil from pots was passed through a 2 mm sieve for chemical analyses. The pH and EC were determined using 1:5 soil:water extracts. Exchangeable cations and CEC were determined using methods described by Rayment and Higginson (1992). Exchangeable cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) were extracted with 1 M NH_4Cl at pH 7 and concentrations were measured using Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES). The CEC of the leached samples was then measured by displacement of NH_4^+ with K-Ca displacing solution (15% KNO_3 and 6% $Ca(NO_3)_2.4H_2O$) and subsequent measurement of NH_4^+ by auto-analyser. The organic carbon content was measured in a Leco furnace (Wang and Anderson, 1998) and the ESP was calculated from exchangeable sodium concentrations and the measured CEC.

Wet aggregate stability. 25g of soil aggregates (5-10 mm) were wet-sieved for 10 minutes on a set of 2 sieves (0.25, 0.125 mm) following the method described by Kemper and Rosenau (1986). The fraction remaining on each sieve was collected, oven dried at 105°C and weighed. The fraction <0.125 mm was calculated by difference.

Spontaneous and mechanical dispersion. Spontaneous dispersion was measured as follows: 20 g of sieved soil (<2 mm) was placed in a 150 mL vial and 100 mL of deionised water was poured gently down the side of a vial, which was then allowed to stand for 24 hours. The vial was then slowly inverted once and returned upright, giving just enough agitation so that the aggregates simply slid down the side of the vial. This single inversion step is a modification of the method proposed by Rengasamy *et al.* (1984), which addresses our concern that the method relies heavily on slow diffusion of dispersed clay

into suspension. This is, however, a relatively minor matter in so far as measurements of dispersion are always 'relative' rather than 'absolute' and were made here to assess the changes wrought by treatments. The supernatant was then stirred slowly and gently to allow the suspended matter to mix without further disturbance to the soil sediment in the container. After allowing an appropriate sedimentation time for particles >2 μm, the supernatant containing dispersed clay was drawn off and its concentration measured by turbidimetry. An individual calibration curve for each soil type was used to convert turbidity to clay concentration (Rengasamy *et al.*, 1984). A similar procedure was used to measure mechanical dispersion. The 1:5 soil:water suspension was agitated on an end-over-end shaker for one hour at 60 r.p.m. The top 2 cm of suspension containing <2 μm material was drawn off after allowing an appropriate sedimentation time and measured by turbidimetry. Data was analysed using the Genstat V Statistical Package (Genstat 5 Committee, 1987).

3.3 Results

3.3.1 Leachate Properties of Treated Soil.

Figures 3.2 and 3.3 show the effects of molasses and gypsum on the properties of successive leachates from the Burdekin and Proserpine soils respectively. The first leaching was conducted on soil, which had been slowly wetted to 85% of field capacity; subsequent leachings were conducted on air-dried soil. After five leachings, there were significant changes in leachate properties imposed by molasses and gypsum treatments for both soils. As the fourth leachate was only analysed for EC and pH, data for this leaching is not presented. However, as the pH and EC values in the fourth leachate were

intermediate between those of leachates 3 and 5, it is probable that SAR and DOC values were also intermediate between those of leachates 3 and 5.

In the Burdekin soil (Figure 3.2), pH and SAR were generally reduced when molasses and gypsum were added. However, in the case of the lighter-textured, more acid Proserpine soil (Figure 3.3), molasses tended to increase pH and SAR whereas gypsum did the opposite. Molasses and gypsum increased the EC of leachate in both soils. For the Burdekin leachate, the EC was generally greatest in the gypsum-only treatment compared with either molasses-only or molasses+gypsum. The highest EC was found in the second leachate of the gypsum-only treatment and the lowest EC was found in the fifth leachate of the control. For the Proserpine soil, the EC was greatest for the molasses+gypsum treatment. The lowest EC was found in the first leachate of the control and the highest EC was found in the third leachate of the molasses+gypsum treatment. The average EC of Burdekin leachates ranged between 0.5 and 6.5 dS/m for all treatments and for the Proserpine soil, between 0.3 and 5.5 dS/m.

Dissolved organic carbon (DOC) concentrations were high in molasses treatments. For the Burdekin soil, the highest DOC was found in the second leachate of the molasses-only treatment and the lowest DOC was found in the fifth leachate of the gypsum-only treatment. DOC generally decreased as leaching proceeded except in the control. For the Proserpine soil, the lowest DOC was found in the first leachate of the gypsum-only treatment and the highest was found in the second leachate of the molasses-only treatment. In general, DOC was less in molasses+gypsum than in molasses-only treatments in both soils as calcium presumably immobilised some organic carbon.
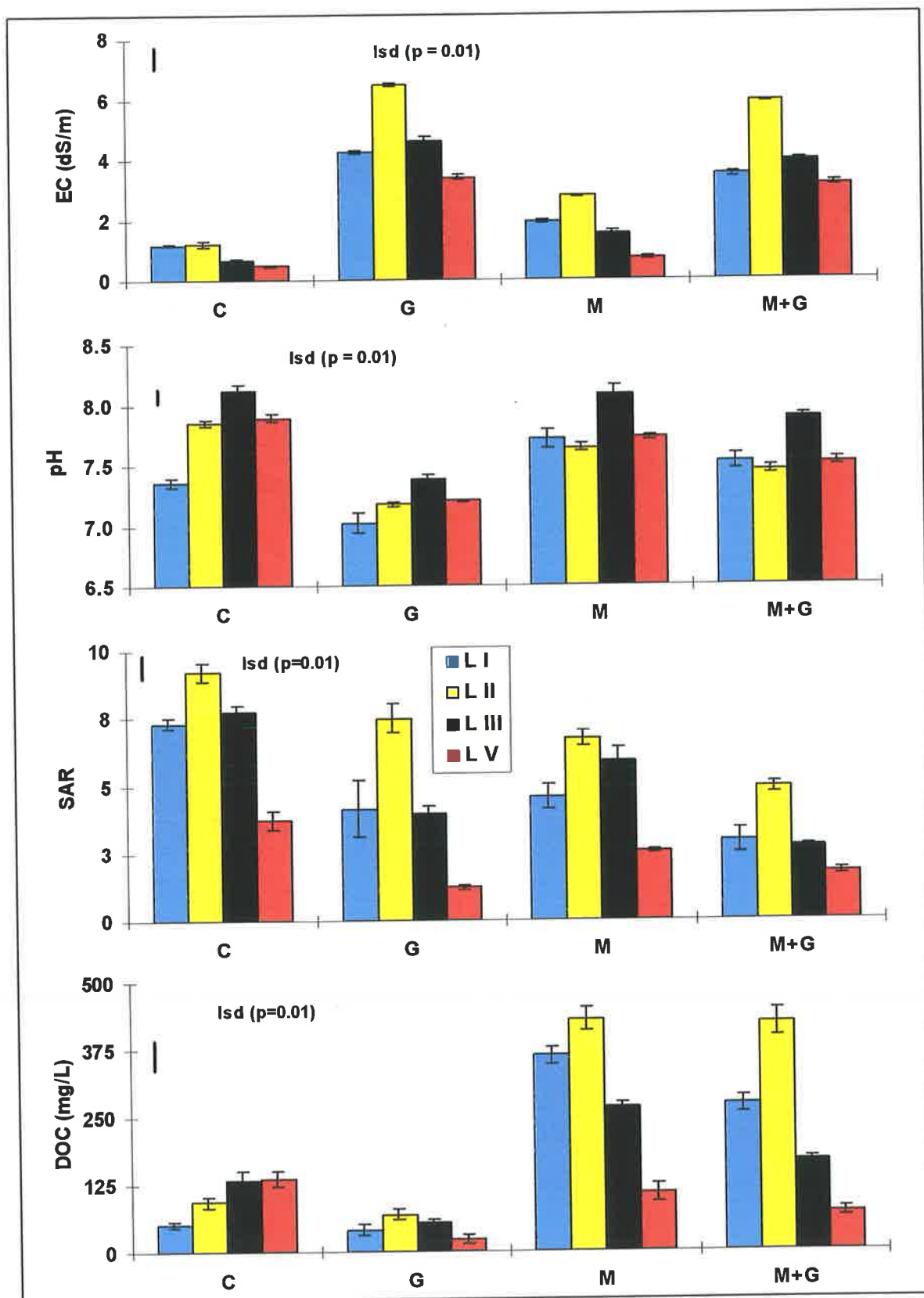
Figure 3.2 Burdekin soil: Electrical conductivity (EC), pH, sodium adsorption ratio (SAR), dissolved organic carbon (DOC) in 4 of 5 successive leachates after molasses and gypsum treatments. C, M, G, M+G refer to control, molasses, gypsum and molasses+gypsum (each 10 t/ha) respectively. L I-V are leachates of leaching events I-V.
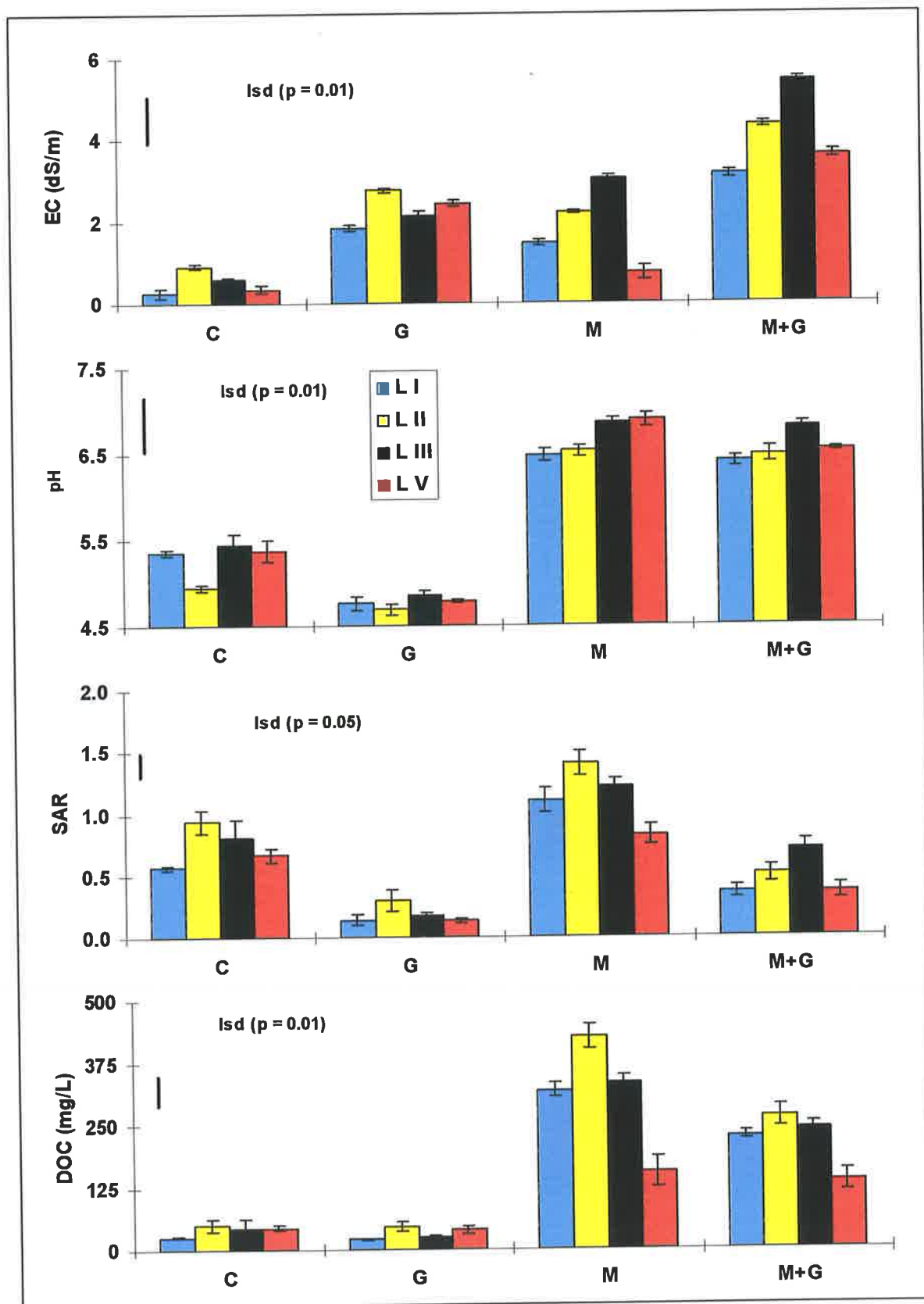
Figure 3.3 Proserpine soil: Electrical conductivity (EC), pH, sodium adsorption ratio (SAR), dissolved organic carbon (DOC) in 4 of 5 successive leachates after molasses and gypsum treatments. C, M, G, M+G refer to control, molasses, gypsum and molasses+gypsum (each 10 t/ha) respectively. L I-V are leachates of leaching events I-V.

3.3.2 Physical Properties of Treated Soil

Clay Dispersibility.

Both gypsum and molasses reduced spontaneous and mechanical dispersion substantially in the both soils (Figure 3.4 and 3.5). In the Burdekin soil, the reduction in spontaneously dispersed clay compared with the control was dramatic when gypsum or molasses were added alone or in combination. The lowest spontaneously dispersed clay was found in the molasses+gypsum treatment, although this was not significantly different from the gypsum-only and molasses-only treatments and the highest one was found in the control. When the soil was mechanically dispersed, gypsum, alone or combined with molasses, dramatically reduced clay dispersion, whereas the effect of molasses alone was much less pronounced. The highest mechanically dispersed clay was found in the control and the lowest one was found in the gypsum-only treatment.

In the coarser-textured Proserpine soil (Figure 3.5), the amount of spontaneously and mechanically dispersed clay was generally much less than in the Burdekin soil. Spontaneous dispersion was reduced by all treatments, with molasses+gypsum being the most effective. The lowest spontaneously dispersed clay was found in the molasses+gypsum treatment and the highest one was found in the control. When soil was mechanically disturbed, gypsum treatments produced a dramatic reduction in dispersed clay compared with the molasses-only treatment. The lowest mechanically dispersed clay was found in the gypsum-only treatment and the highest one was found in the control.
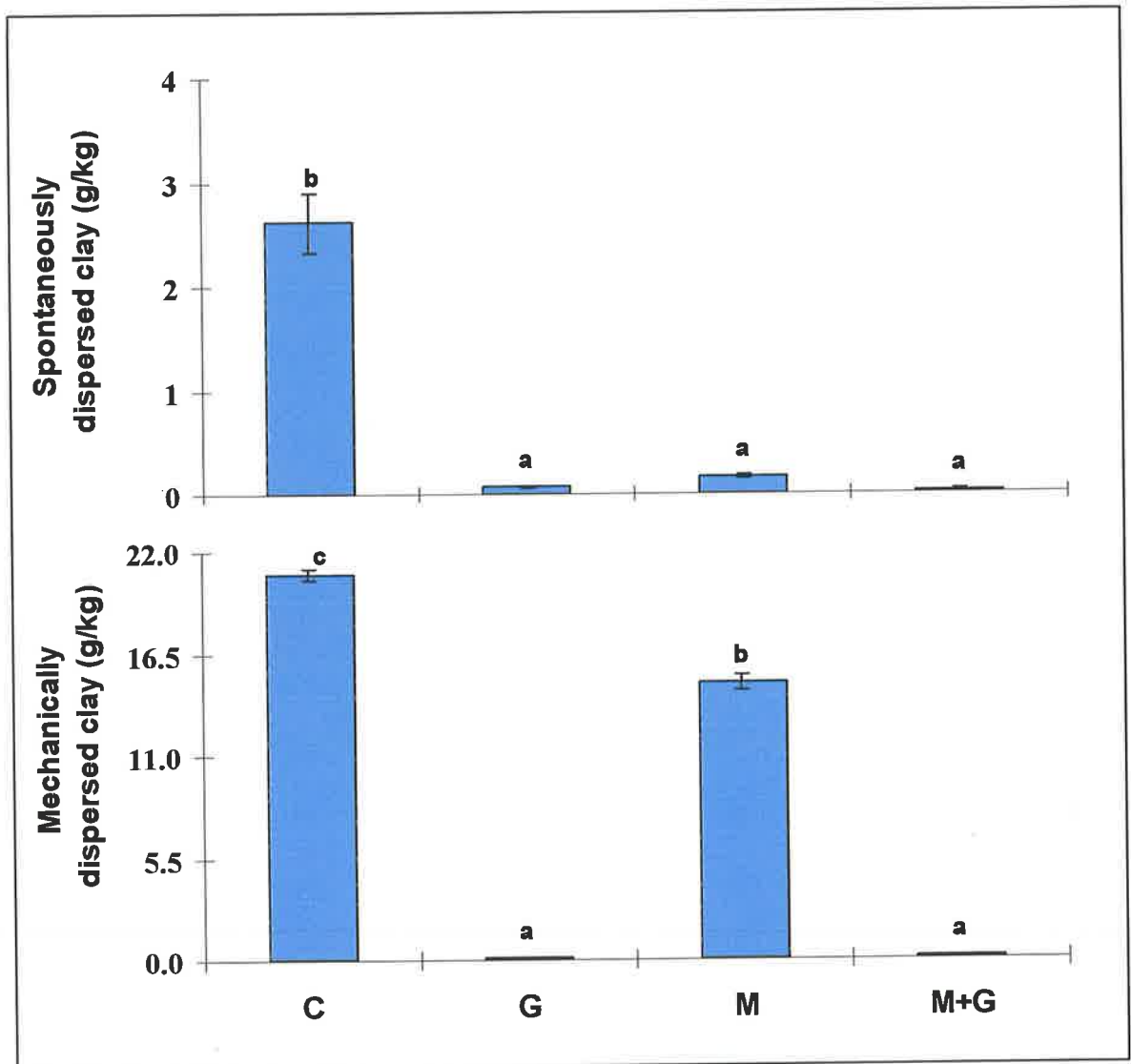
Figure 3.4 Spontaneous dispersion and mechanical dispersion of the Burdekin soil after gypsum and molasses treatments. C, M, G, M+G refer to control, molasses, gypsum and molasses+gypsum (each 10 t/ha) respectively. Letters show which results are significantly different (p =0.001).
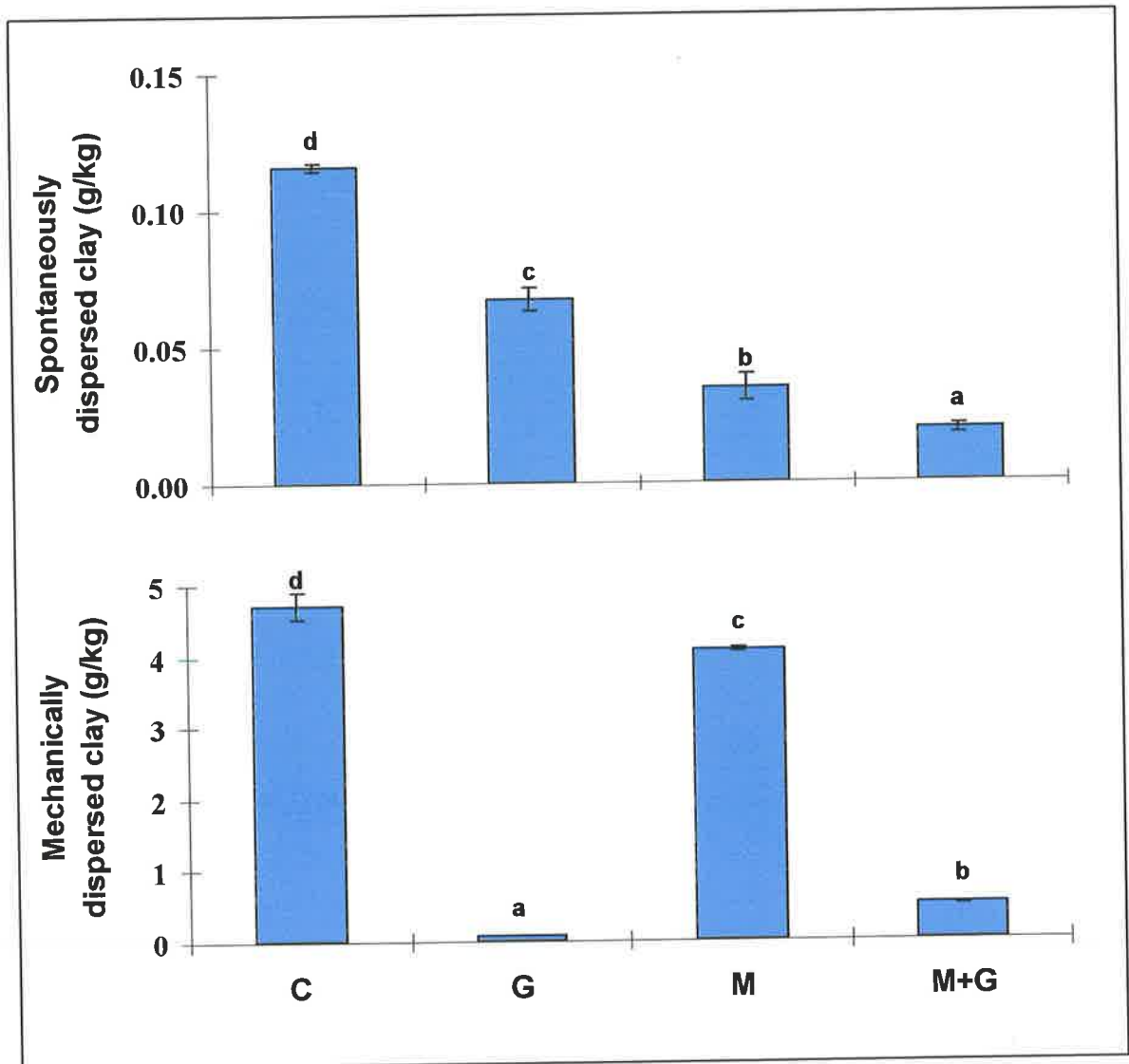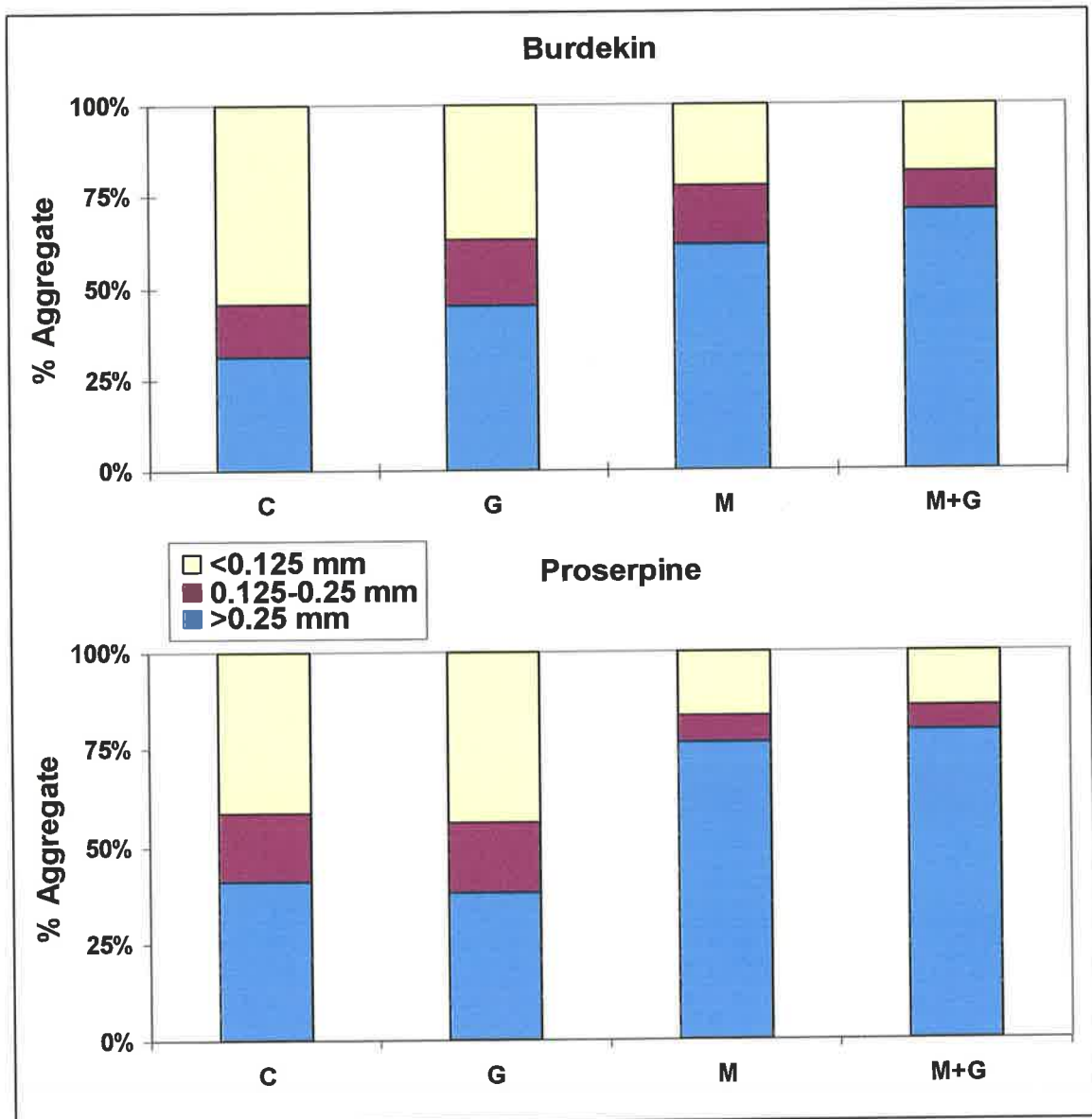
Figure 3.5 Spontaneous dispersion and mechanical dispersion of the Proserpine soil after gypsum and molasses treatments. C, M, G, M+G refer to control, molasses, gypsum and molasses+gypsum (each 10 t/ha) respectively. Letters show which results are significantly different (p =0.001).

Wet Aggregate Stability

The effects of molasses and gypsum on wet aggregate stability of the Burdekin and Proserpine soils are shown in Figure 3.6. In the Burdekin soil, molasses and gypsum treatments either alone or combined, provided significant increases in aggregate stability. Molasses and gypsum increased the proportion of macro-aggregates (> 250 μm) and decreased the proportion of aggregates < 125 μm, with the combined effects being greatest; aggregates in the range of 125-250 μm were relatively unaffected except by the combined treatment. In the Proserpine soil, gypsum had no significant effect on aggregate stability, either alone or combined with molasses. Molasses significantly increased the proportion of macro-aggregates while decreasing the proportion of both aggregate fractions < 250 μm.

3.3.3 Chemical Properties of the Treated Soil

Table 3.2 shows the chemical properties of the two soils treated with gypsum and molasses and then leached five times. Leaching alone decreased pH for the control treatment in the Burdekin soil but the effect was reversed in the Proserpine soil. In the Burdekin soil, the decrease in pH was enhanced by the addition of both treatments with the gypsum-only treatment was being greatest. However, molasses increased pH in the Proserpine soil, while gypsum did the opposite. The lowest pH was observed in the gypsum-only treatment for both soils and the highest pH was observed in the control and in the molasses-only treatment for the Burdekin and Proserpine soils respectively.

The EC of both soils was significantly increased by gypsum but not by molasses (Table 3.2). In the Burdekin soil, the EC of the soil treated with molasses+gypsum was slightly greater than that treated with gypsum alone. The EC values of the gypsum-treated

Figure 3.6 Wet aggregate stability of the Burdekin and Proserpine soils after molasses and gypsum treatments. C, M, G, M+G refer to control, molasses, gypsum and molasses+gypsum (each 10 t/ha) respectively

soils indicated that gypsum remained in the soil after 5 leaching events. The highest EC was observed in the molasses+gypsum treatment and this was significantly different for all other treatments; the lowest EC was observed in the molasses-only treatment although this was not significantly different from the control. In the Proserpine soil, the highest EC was observed in the gypsum-only treatment although this was not significantly different from the molasses+gypsum treatment. The lowest EC was observed in the control although this was not significantly from the molasses-only treatment.

Table 3.2 pH and electrical conductivity (EC) in 1:5 soil:water extracts, exchangeable sodium percentage (ESP), cation exchange capacity (CEC) and organic carbon content of the Burdekin and the Proserpine soils after molasses and gypsum treatments and 5 leaching events. C, G, M and M+G refer to control, gypsum (10 t/ha), molasses (10 t/ha) and molasses+gypsum (both 10 t/ha) respectively.

Soil	Treatment	pH	EC dS/m	ESP	CEC cmol(+)/kg	Org. C %
Burdekin	Initial	8.0	0.2	7.9	10.9	0.8
	C	7.7c	0.1a	4.1c	10.6a	0.8a
	G	7.1a	1.6b	0.4a	10.4a	0.7a
	M	7.6b	0.2a	2.4b	11.6b	1.0b
	M+G	7.1a	1.9c	0.2a	11.2b	1.0b
	Significance	*	*	**	**	**
Proserpine	Initial	4.9	0.1	18.8	2.3	0.7
	C	5.4b	0.1a	3.4c	2.1a	0.6a
	G	4.6a	2.2b	0.3a	2.2a	0.7a
	M	6.4d	0.1a	2.1b	2.5b	0.8b
	M+G	6.1c	2.1b	0.2a	2.5b	0.9b
	Significance	**	**	**	**	**

Letters (a, b, c, d) show which results are significantly different at p=0.05 (*) and p=0.01 (**)

Exchangeable sodium percentage (ESP) was determined to investigate the changes in sodicity after addition of molasses and gypsum; both treatments reduced the ESP substantially. Leaching alone decreased the ESP for the control in both soils; this effect was more pronounced in the Proserpine soil. This is expected as dilution of soil solution by water of high quality reduces SAR and, therefore, ESP. In the coarser textured soil (Proserpine) this effect is largely un-buffered and dramatic compared with the finer textured soil (Burdekin) in which the CEC is much greater. In both soils, gypsum reduced ESP more than molasses because of the high concentration of calcium in solution. The lowest ESP was observed in the molasses+gypsum treatment although this not significantly different from those of gypsum-only. Cation exchange capacity (CEC) and organic carbon were significantly increased by molasses treatment in both soils, whereas the gypsum had no effect.

The concentrations of organic carbon in leachate and in soil were used to calculate the percentage of carbon lost in respiration, presumably released as CO_2 or leached as DOC during experiments (Table 3.3). In general, a substantial proportion of the molasses added was lost in respiration (CO_2) but a small proportion was leached as DOC. In the molasses-only and molasses+gypsum treatments of both soils, the percentages of carbon released as CO_2 and leached as DOC were similar at 31-36% and 1-2% respectively. DOC was higher in molasses-only than in the molasses+gypsum treatments as observed above.

The concentrations of cations in the leachate and on the exchange sites of soil were used to calculate the abundances of cations in the system at the beginning and at the end of experiments (Table 3.4). Molasses and gypsum affected the proportion of cations in the leachate and on the exchange sites of both soils. In the Burdekin soil, when gypsum was added, Ca in the leachate and in the soil increased as expected. The displacement of other

exchangeable cations by Ca can be seen in Table 3.4. In general, the proportions of Na, Mg and K cations in the leachate were higher than in the soil when gypsum was added.

Molasses also facilitated removal of Na, but not to the extent that gypsum treatment. The proportions of Ca, Mg and K were generally higher in soil than in leachate for the molasses-only treatment in both soils; molasses contains considerable amounts of these cations. In the Burdekin soil, when molasses+gypsum was added, 95% of Na was removed in the leachate; in the Proserpine soil, a lower proportion of Na was found in the leachate. Adding molasses+gypsum partially compensated for the loss of K through leaching; this loss of plant available-K might be a negative effect of adding gypsum alone.

Table 3.3 Percentage of carbon lost in respiration (CO_2) and dissolved organic carbon (DOC) leached in the control (C), gypsum (G), molasses (M) and molasses+gypsum (M+G) treatments in the Burdekin and Proserpine soils.

Soil/	Organic carbon (mg/kg)				% CO_2	% DOC
Treatment	Initial	Leachate (DOC)	Soil (final)	DOC+final	released	leached
Burdekin						
C	8000	73	8050	8123	-1	0.9
G	8000	33	7225	7258	9	0.5
M	14222	205	9525	9730	32	2.1
M+G	14222	164	9700	9864	31	1.7
Proserpine						
C	7000	23	6200	6223	11	0.4
G	7000	19	6700	6719	4	0.3
M	13222	175	8300	8475	36	2.1
M+G	13222	123	8625	8748	34	1.4

Table 3.4 Cation abundance in control (C), gypsum (G), molasses (M) and molasses+gypsum (M+G) treatments

| | Cations in (cmol(+)/kg) | | | | | | | |
| | Initial | | | Final | | | | |
	Soil	Addition	Total	Leachate	Soil	Total	Leachate (%)	Soil (%)
Ca								
Burdekin								
C	6.5	0.0	6.5	0.1	7.1	7.2	1	99
G		14.4	20.9	1.9	17.9	19.8	9	91
M		0.04	6.6	0.2	7.2	7.4	3	97
M+G		14.4	20.9	1.9	19.9	21.7	9	91
Proserpine								
C	0.9	0.0	0.9	0.1	0.8	0.8	10	90
G		14.4	15.3	1.8	13.7	15.5	11	89
M		0.0	0.9	0.2	1.4	1.6	11	89
M+G		14.4	15.3	2.0	17.3	19.4	10	90
Mg								
Burdekin								
C	3.9	0.0	3.9	0.1	4.8	4.9	3	97
G		0.0	3.9	3.0	1.3	4.3	69	31
M		0.1	4.0	0.3	4.7	5.0	6	94
M+G		0.1	4.0	3.4	1.6	4.9	68	32
Proserpine								
C	0.4	0.0	0.4	0.1	0.3	0.4	19	81
G		0.0	0.4	0.2	0.2	0.4	52	48
M		0.1	0.5	0.1	0.4	0.5	24	76
M+G		0.1	0.5	0.3	0.2	0.5	64	36
Na								
Burdekin								
C	0.9	0.0	0.9	0.51	0.53	1.0	49	51
G		0.0	0.9	1.01	0.09	1.1	92	8
M		0.01	1.0	0.66	0.33	1.0	67	33
M+G		0.01	1.0	0.99	0.05	1.0	95	5
Proserpine								
C	0.4	0.0	0.4	0.26	0.16	0.4	62	38
G		0.0	0.4	0.35	0.05	0.4	87	13
M		0.01	0.4	0.31	0.14	0.5	69	31
M+G		0.01	0.4	0.33	0.10	0.4	76	24
K								
Burdekin								
C	0.5	0.0	0.5	0.02	0.5	0.5	5	95
G		0.0	0.5	0.3	0.01	0.3	96	4
M		0.2	0.7	0.1	0.8	0.9	7	93
M+G		0.2	0.7	0.7	0.1	0.8	89	11
Proserpine								
C	0.4	0.0	0.4	0.03	0.4	0.4	7	93
G		0.0	0.4	0.4	0.0	0.4	93	7
M		0.2	0.7	0.3	0.4	0.7	46	54
M+G		0.2	0.7	0.4	0.4	0.8	54	46

3.4 Discussion

The questions addressed in this study were whether molasses alone or combined with gypsum could improve the structural stability of sodic soils. The results of leachate analysis show that additions of molasses and gypsum significantly changed the properties of sodic topsoils. For the soil leachates, gypsum increased EC and decreased pH immediately. The effect of the gypsum on pH was due to the displacement of adsorbed protons by calcium. Similar results were found by Sekhon and Bajwa (1993), and by Chorom and Rengasamy (1997). However, this effect may be temporary and progressively lost as the gypsum is leached.

In the Burdekin soil, the EC of leachate in the molasses+gypsum treatment was generally lower than of the treatment with gypsum alone (Figure 3.2). This may indicate that some soluble calcium is complexed by organic matter and immobilized in the soil. Conversely, organic matter may have been protected from leaching by the presence of soluble Ca in the soil. This can be seen in Figure 3.2 and Table 3.3 where DOC was generally lower with molasses+gypsum than with molasses alone. Muneer and Oades (1989) also found that DOC decreased when gypsum and glucose were added to soil. When gypsum was applied, the concentration of DOC decreased; soluble calcium from gypsum inhibited decomposition of organic matter by microorganisms and reduced the release of the DOC by leaching. Calcium tends to block and protect functional groups in organic matter that represent sites of initial decomposition and also cross-links flexible polymers to create more dense, rigid molecules that are more stable to both chemical and biological degradation (Oades, 1989). However, in the Proserpine soil the EC after molasses+gypsum treatment was higher than after gypsum alone (Figure 3.3). This may be because the clay content of the soil was too low to protect cations in the soil solution from

leaching so that the effects of molasses and gypsum on EC were simply additive in this case.

The small decrease in pH of the Burdekin soil brought about by addition of molasses is most likely due to the pH of the molasses (5.5), and to the CO_2 and organic acids produced during incubation. However, in the less buffered, more acidic Proserpine soil, addition of molasses increased soil pH to a higher value than that of either the soil or the molasses. This may have been due to reactions such as the mineralisation of cations or nitrogen in the molasses, or to the uptake of nitrate by microorganisms.

Cation exchange capacity (CEC) in both soils increased significantly with molasses but not with gypsum treatment. This was presumably due to the decomposition products of the carbohydrates in molasses having high CEC. The data in Table 3.2 suggest that this additional organic matter in the Burdekin soil had a CEC of approximately 300 cmol(+)/kg C whereas that in the Proserpine soil had a CEC of about 160 cmol(+)/kg C; these values were calculated from the increases in soil CEC in relation to increases in organic carbon (Table 3.2). Organic exchange sites may have a higher selectivity for Ca than mineral exchange sites (Nelson and Oades, 1998).

The water stability of aggregates and the clay dispersibility of the soils were significantly affected by molasses and gypsum. In the Burdekin soil, both molasses and gypsum treatments increased macro-aggregation at the expense of micro-aggregates (Figure 3.6). Organic matter from molasses, probably mostly carbohydrate, was able to stabilise micro-aggregates into macro-aggregates while the gypsum effect was mainly due to the flocculation of clay resulting in the aggregation of clay particles into domains and reduced dispersion (Chorom and Rengasamy, 1997; Nelson and Oades, 1998). In the Proserpine soil, molasses increased wet aggregate stability to an even greater degree than

in the Burdekin soil, but, as with the Burdekin soil, had a far less dramatic effect on mechanical dispersion, indicating that molasses was unable to stabilise aggregates under these more destructive conditions. The resistance to slaking afforded by increased organic matter is probably insufficient to withstand the rigours of mechanical dispersion in which the preliminary destruction of macro-aggregates provides opportunities for extensive dispersion. On the other hand, gypsum was able to prevent clay from dispersing but unable to maintain macro-aggregates. The extents of both spontaneous and mechanical dispersion in both soils generally reflect the ESP and EC data in Table 3.2 with higher ESP and lower EC promoting dispersion. It is significant that treatment of both soils with molasses alone resulted in substantial reductions in ESP and spontaneous dispersion.

3.5 Conclusions

Molasses and gypsum both increased the structural stability of sodic soils used in this study, but the effects depended to some extent on clay content. The effects of gypsum were more pronounced in the Burdekin soil (higher clay content), particularly in relation to reducing clay dispersion. On the other, molasses alone increased macroaggregation in the both soils regardless of soil texture. On the basis of this laboratory work, it is therefore likely that the addition of molasses alone or in combination with gypsum may beneficial for overcoming problems with sodic soils, particularly those of higher clay content used for either sugarcane production or in regions where molasses is available relatively cheaply.

CHAPTER 4

Structural Stability of Sodic Soil as Influenced by Molasses and Lime

4.1 Introduction

The addition of gypsum to soil can increase the stability of aggregates by lowering the exchangeable sodium percentage (ESP), increasing the electrolyte concentration and thereby reducing dispersion. These effects were observed in Chapter 3. However, gypsum additions are lost relatively quickly when water infiltrates through soil because gypsum is far more soluble than other sources of calcium such as lime. Furthermore, gypsum is more expensive than lime per unit calcium in the Queensland sugarcane-growing districts. Due to its low solubility, the action of lime in improving the soil physical conditions is likely much less dramatic than that of gypsum, particularly in soils of high pH, where its is relatively insoluble.

The water stability of soil macroaggregates mainly depends on the presence of organic material (section 2.4). The beneficial effects of organic matter on soil aggregation are usually attributed to an enhanced growth of microorganisms (bacteria, fungal, mycelia etc.) and the production of microbial metabolites. The soil organic matter content is governed by its rates of loss and of addition. Organic materials are added, either by growing plants and their residues, or by the addition of organic amendments. The major loss is by decomposition, although erosion may be a significant cause in some cases. In general, the more readily available an organic substance is to microbial activities, the greater is its aggregating effect on soil structure. Increased microbial activity can also result in the loss of organic matter, especially when soils are cultivated (section 2.4.3). The

balance between aggregation and disaggregation is related to the resistance and availability of the aggregating agents to microbial decomposition.

Organic acids and CO_2 are produced by microbial decomposition of organic matter, and under certain circumstances may reduce soil pH (Baldock *et al.*, 1994). Therefore in soils of high pH, the addition of large quantities of organic matter in the form of molasses might be expected to lower pH out of the alkaline range. The increased partial pressure of CO_2 and any organic acid might then aid the dissolution of the lime, freeing Ca^{2+} ions (Robbins, 1986) and lowering the soil pH. The Ca^{2+} ions may then exchange with Na^+ ions adsorbed to clay particles, allowing Na^+ ions to be leached, thus eventually decreasing the ESP (Lehrsch *et al.*, 1993). In this chapter, an assessment of the influence of molasses and lime on the structural stability of soils is presented.

4.2 Materials and Methods

The materials and methods for this experiment are virtually identical to those described in section 3.2 except that the treatments in this experiment were molasses and lime rather than molasses and gypsum. The amount of calcium added to the soils as lime was similar to that added as gypsum described in Chapter 3, and the application rate of molasses was also the same as in Chapter 3. The reader is referred to Table 3.1 for a description of some of the properties of the soils used here.

4.3 Results

4.3.1 Leachate Properties of Treated Soils

Figures 4.1 and 4.2 show the effects of molasses and lime on the properties of 5 successive leachates from the Burdekin and Proserpine soils. The first leaching was conducted on soil, which had been slowly wetted to 85% of field capacity and kept for 7 d.; subsequent leaching events were conducted after soil had been air-dried from the previous leaching event.

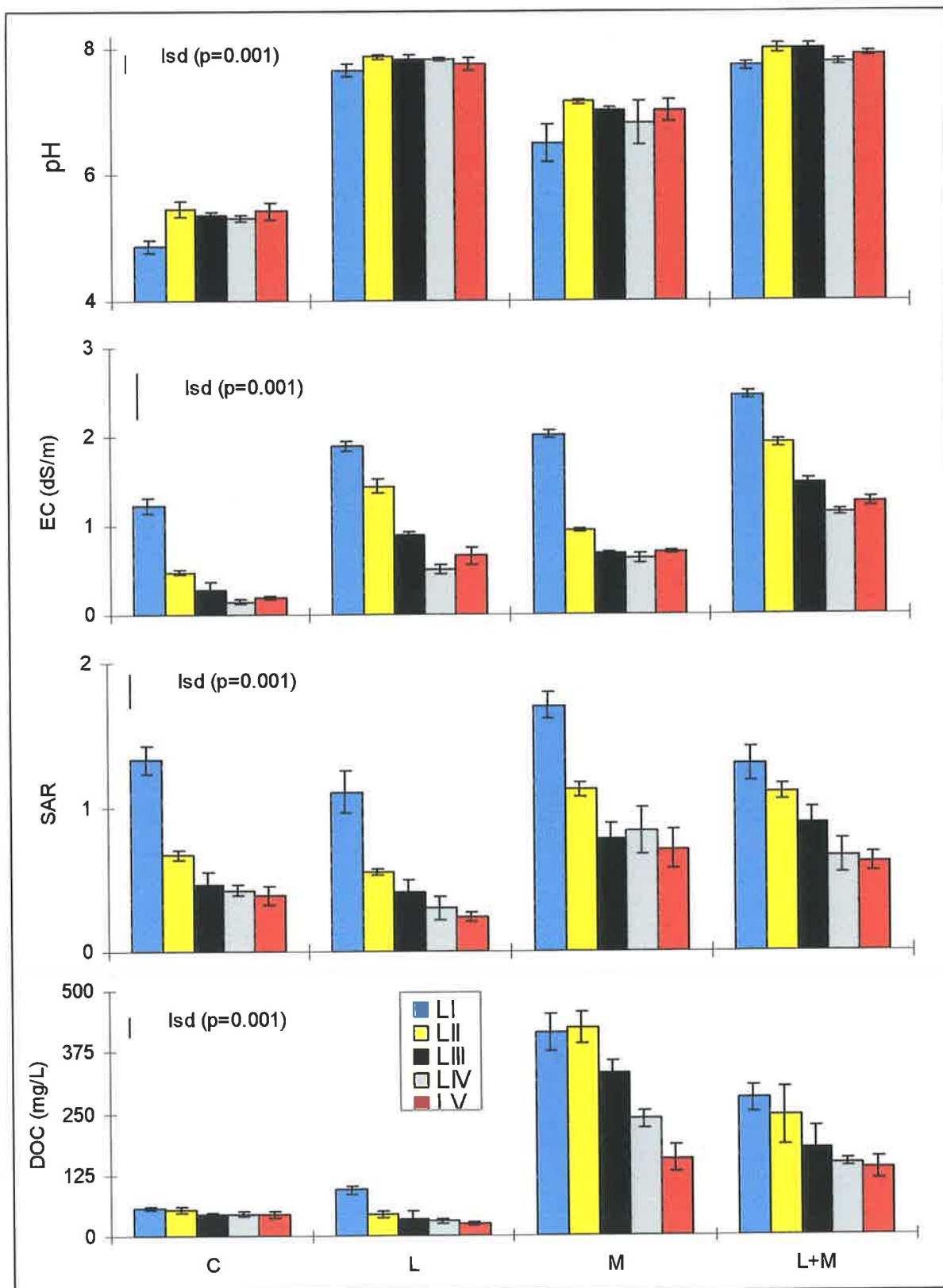There were significant changes in leachate properties related to molasses and lime treatments. In general, pH, electrical conductivity (EC), sodium adsorption ratio (SAR) and dissolved organic carbon (DOC) decreased as leaching proceeded, although the magnitude of reductions fluctuated. In the Proserpine soil, the pH of the first leachate was lower than that of the second leachate in all treatments, even though these were not significantly different for the lime-only and the molasses+lime treatments. In the Burdekin soil, by contrast the pH was lower in the first leachate of the control and the molasses-only treatments. This may simply be an experimental artifact caused by the first leaching being conducted on moist soil, while subsequence leachings were conducted on air-dried soil. Similar results were found by Nelson *et al.* (1998), where the pH of soil is lower under moist conditions than dry. The average pH of the Burdekin leachates ranged between 7.2 and 8.2 in all treatments, while for the Proserpine soil, the range was 4.8 to 8.0. In the Burdekin soil, the highest and the lowest pH were observed in the first leachate of the lime-only and the control treatments respectively and in the Proserpine, the highest and the lowest pH were observed in the second leachate of the molasses+lime and the first leachate of the control respectively.
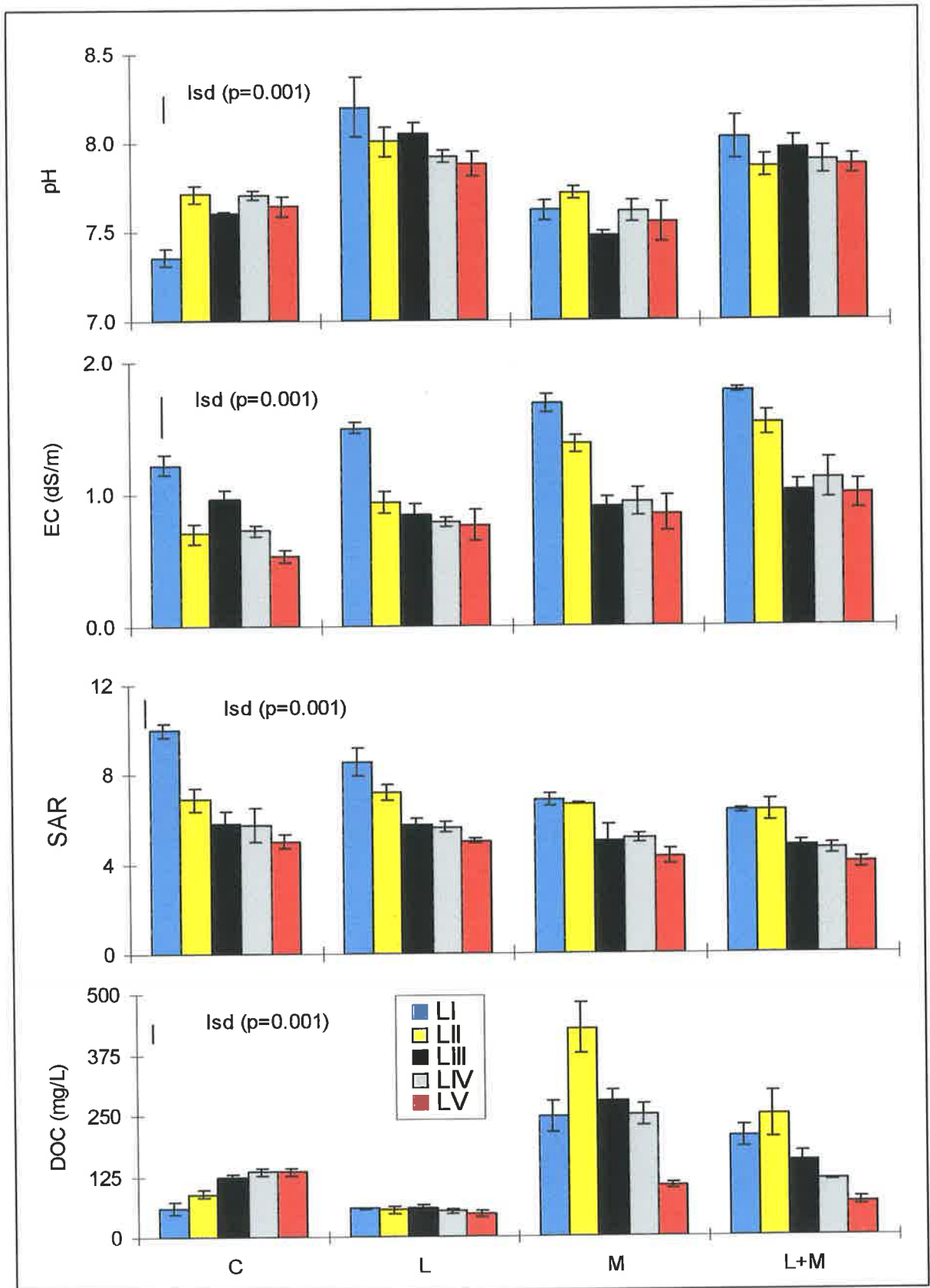
Figure 4.1 Burdekin soil: Electrical conductivity (EC), pH, sodium adsorption ratio (SAR) and dissolved organic carbon (DOC) of 5 successive leaching events (LI- LV) after molasses and lime treatments. C, L, M and M+L refer to control, lime, molasses, molasses + lime. Letters show results are significants different l.s.d (p = 0.01). Error bars represent standard deviation.

Figure 4.2 Proserpine soil: Electrical conductivity (EC), pH, sodium adsorption ratio (SAR) and dissolved organic carbon (DOC) of 5 successive leaching events (LI- LV) after molasses and lime treatments. C, L, M and M+L refer to control, lime, molasses, molasses + lime; Letters show results that are significantly different (p = 0.01). Error bars represent standard deviation.

Electrical conductivity (EC) of leachates decreased from the first to the fifth leachate in virtually all treatments for both soils. In the Burdekin soil, EC was greatest in the initial leaching and lowest in the last leachate in all treatments including the control. This indicates that cation dissolution was greater in the early stages and diminished as successive leaching proceeded. In the Proserpine soil, the trend of EC to decrease as leaching proceeded was similar to the Burdekin soil. The EC of each leachate in the molasses+lime treatment was almost invariably significantly higher than for the leachates of all other treatments at the same leaching events. Minor, but consistent reduction in the EC occurred for all leaching events.

Sodium adsorption ratio (SAR) of leachates decreased as leaching proceeded in all treatments for both soils. In the Burdekin soil, the lowest SAR was observed in the fifth leachate of the molasses+lime treatment, although this was not significantly different ($p < 0.01$) from the last leachate of all the other treatments. The highest SAR was observed in the first leachate of the control, although this was not significantly different ($p = 0.01$) from the first leachate of the lime-only treatment. The SAR was not significantly different from the third to the fifth leachate for each treatment. In the Proserpine soil, the lowest SAR was observed in the fifth leachate of the lime-only treatment, although this was not significantly different ($P = 0.01$) from the last leachate of the control. The SAR was not significantly different for last 3 leachates of the molasses-only and the control treatments and the last 2 leachates of lime-only and molasses+lime treatments. The highest SAR was observed in molasses-only treatment and this was significantly different from all the other leachates in all other treatments.

In all leaching events, dissolved organic carbon (DOC) concentration was higher in the molasses-only treatment than in all the other treatments in both soils. In the Burdekin soil, the lowest DOC in all 5 leachates was observed in the lime-only treatment, although

this was not significantly different from the first leachate of the control and the last leachate of molasses+lime treatment. In the molasses-only and molasses+lime treatments, DOC decreased as leaching proceeded for both soils. The highest DOC was observed in the second leachate of molasses-only treatment and this was significantly different from all the other leachates in all other treatments. In the Proserpine soil, the DOC invariably decreased with leaching. The lowest DOC was observed in the lime-only and the control treatments in all 5 leachates.

4.3.2 Physical Properties of Treated Soils

Clay Dispersibility

Figure 4.3 and 4.4 present the change in spontaneous and mechanical dispersion of the Burdekin and Proserpine soils respectively as a result of molasses and lime application. In the Burdekin soil, molasses, lime and the combination of molasses+lime treatments decreased spontaneous dispersion (Figure 4.3). The reduction in spontaneous dispersion amongst these treatments did not differ significantly, but the reduction in dispersed clay compared with the control was dramatic. The magnitude of dispersed clay for each treatment was markedly greater when the soil was mechanically dispersed. Mechanically dispersed clay in all treatments was dramatically higher than that of spontaneously dispersed clay. Lime, molasses and lime+molasses treatments significantly reduced (p=0.01) the dispersed clay compared with the control.

In the coarser-textured Proserpine soil, as was observed in the previous experiment (Chapter 3), the amount of dispersed clay in spontaneous and mechanical dispersion was much less than that in the Burdekin soil (Figure 4.4). The spontaneously dispersed clay was significantly higher in the control than those in the other treatments. However, when
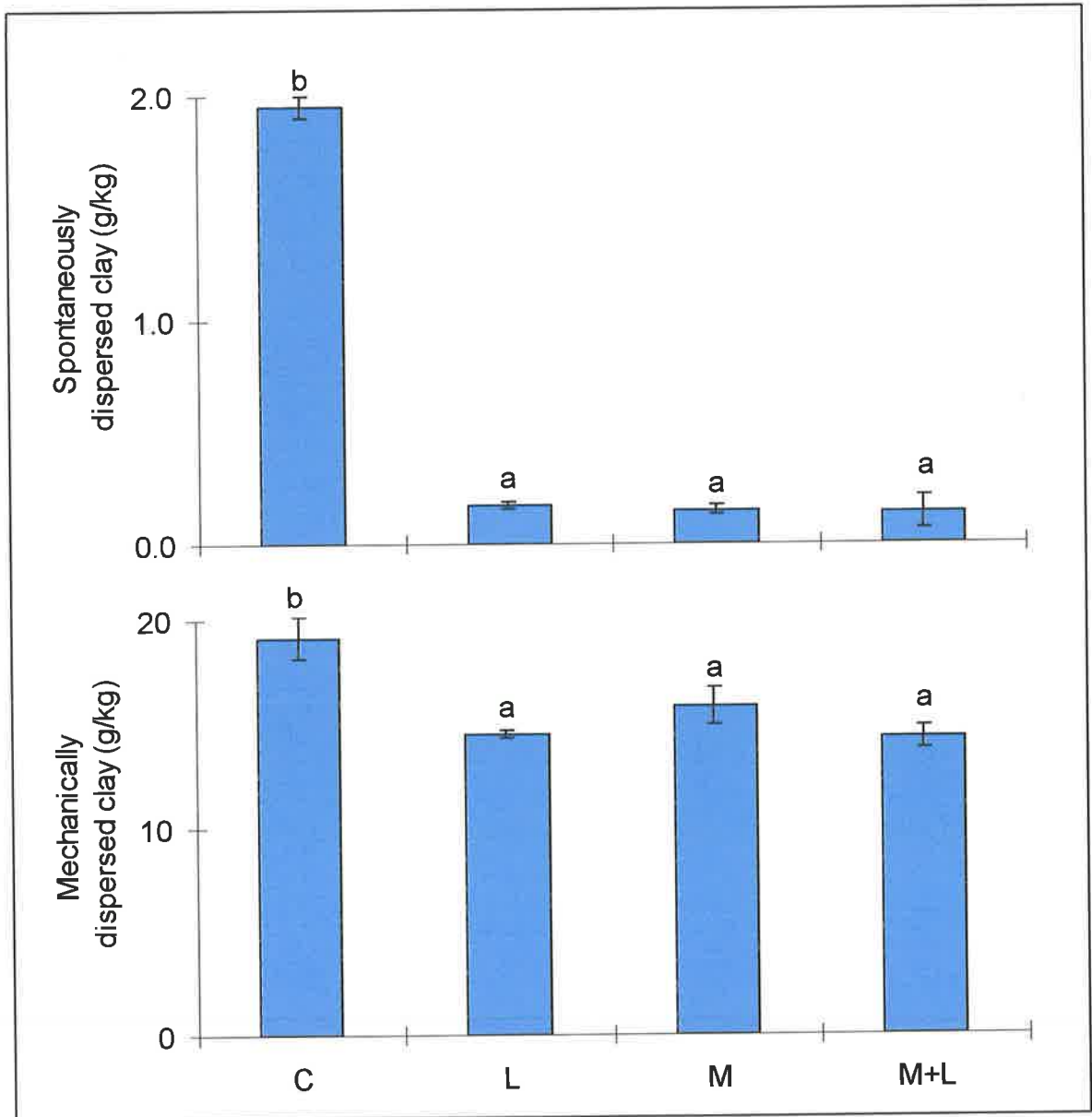
Figure 4.3 Spontaneous and mechanical dispersion of the Burdekin soil as influenced by molasses and lime. C, L, M, M+L represent control, lime-only, molasses-only and molasses+lime treatments respectively. Letters show results that are significantly different (p = 0.01). Error bars represent standard deviation.
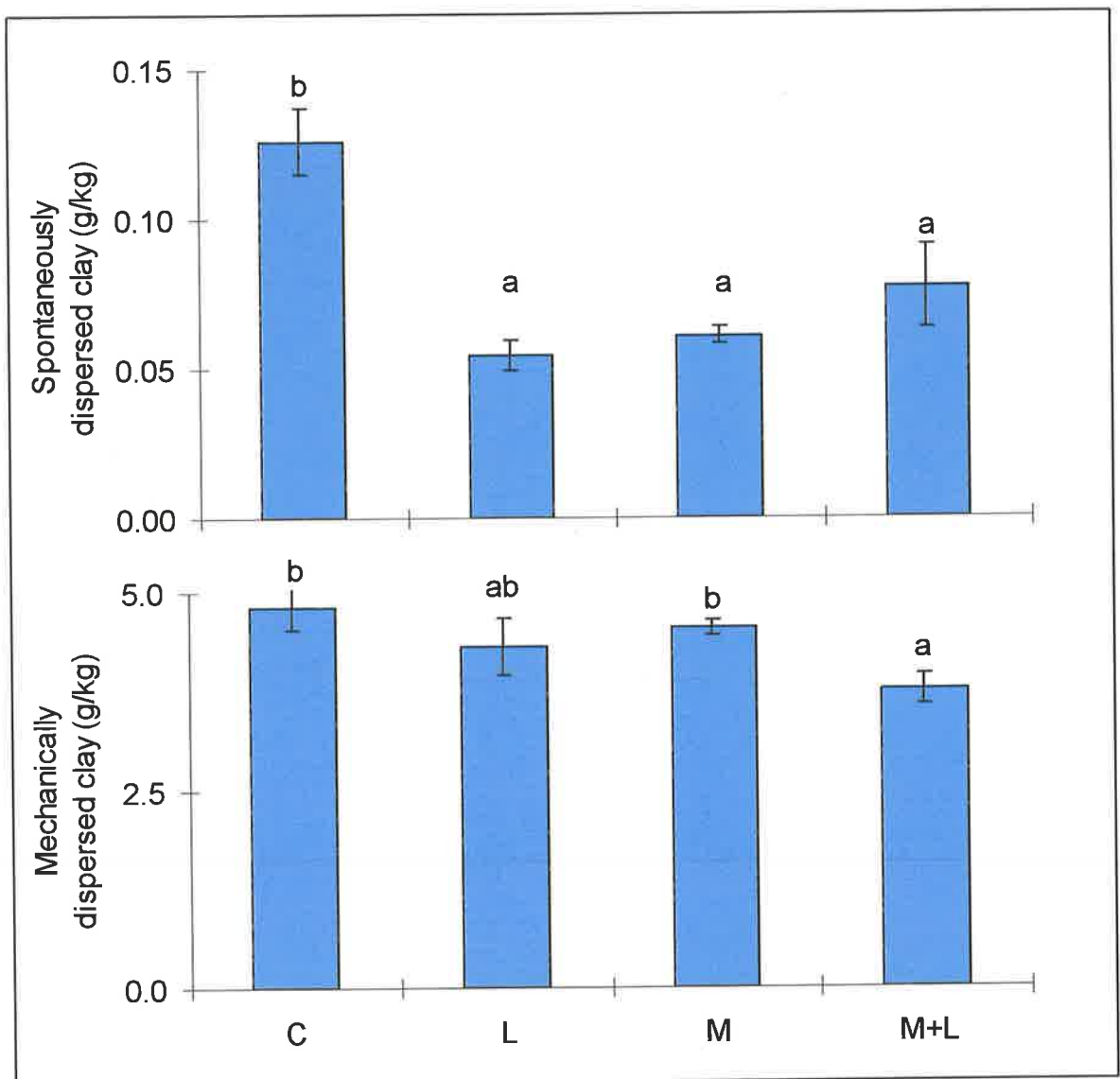
Figure 4.4 Spontaneous and mechanical dispersion of the Proserpine soil as influenced by molasses and lime. C, L, M, M+L represent control, lime-only, molasses-only and molasses+lime treatments respectively. Letters show results that are significantly different (p = 0.01). Error bars represent standard deviation.

the soil was mechanically dispersed, the amounts of the dispersed clay in the molasses-only and lime-only treatments were not significantly different from the control.

Wet Aggregate Stability

Figure 4.5 shows the influence of molasses and lime application on wet aggregate stability of soils. In the Burdekin soil, molasses-only, lime-only and molasses+lime treatments all increased the proportion of macroaggregates (>250 μm) largely at the expense of aggregates fraction <125 μm, which indicates an increase in water stability of aggregates. The greatest proportion of macroaggregates (or the smallest proportion of aggregates <125 μm) was observed in the molasses+lime treatment, although this was not significantly different (p=0.01) from the molasses-only treatment, yet significantly different from the lime-only treatment. The proportion of 125-250 μm aggregates was relatively constant in all treatments. In the Proserpine soil, the proportion of macroaggregates increased at the expense of both smaller aggregate fractions in both molasses-only and molasses+lime treatments. In the lime-only treatment, the proportion of aggregates <125 μm appears to have increased marginally with a complementary decrease in aggregates 125-250 μm while the proportion of macroaggregates remained unchanged.

4.3.3 Chemical Properties of Treated Soils

Table 4.1 presents the change in chemical properties of the Burdekin and Proserpine soils after molasses and lime treatments. In the Burdekin soil, pH decreased after five leaching events whereas in the Proserpine soil, the effect was reversed. The molasses-only treatment significantly decreased soil pH in the Burdekin soil, whereas the lime-only treatment increased soil pH to its maximum possible value. In the Proserpine
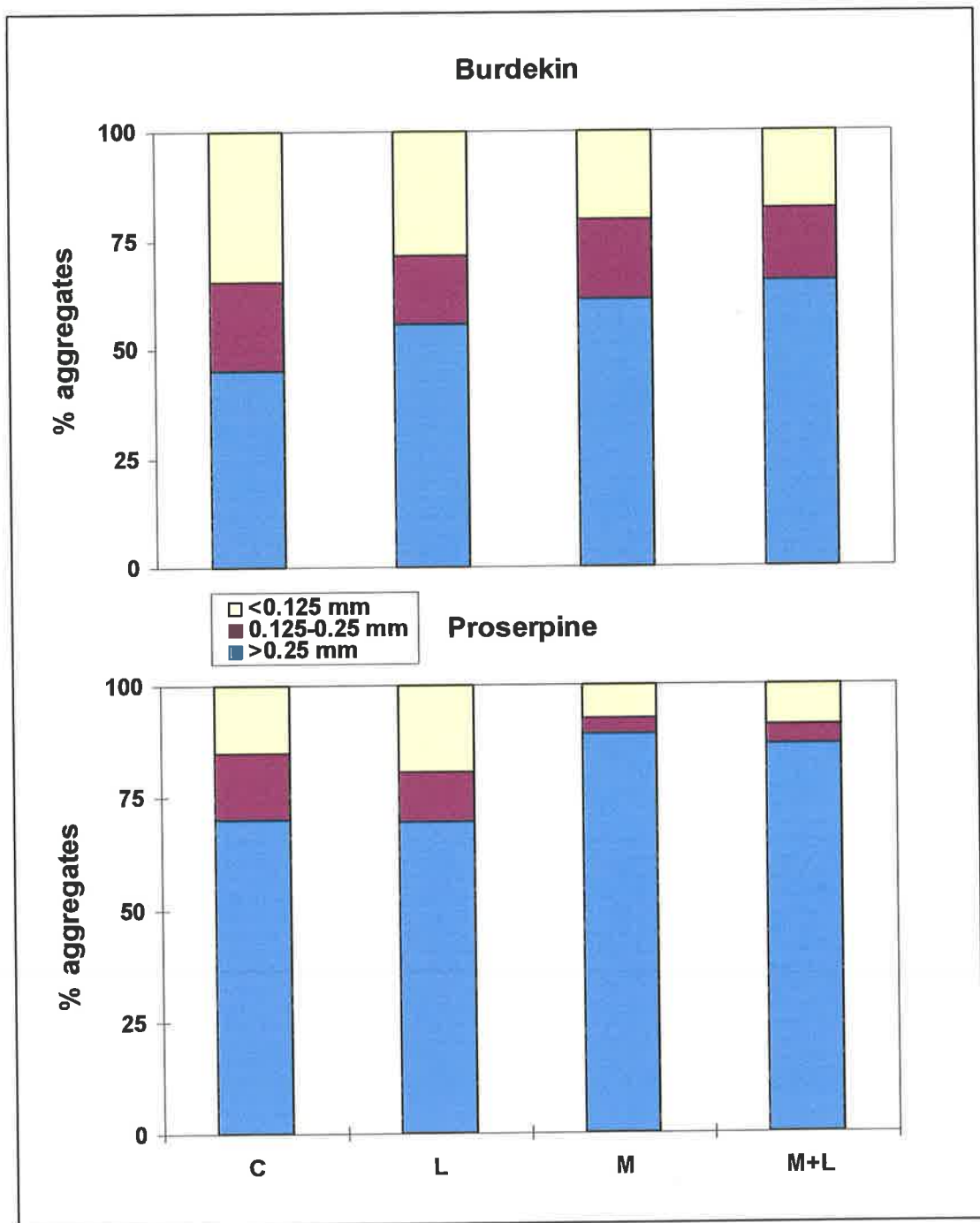
Figure 4.5 Wet aggregate stability of soils as influenced by molasses and lime treatments. C, L, M, M+L represent control, lime-only, molasses-only and molasses+lime treatments respectively.

soil, all treatments significantly increased the soil pH. The highest and the lowest soil pH were observed in the lime-only and in the control treatments respectively.

The EC of both soils was generally increased by molasses and lime applications and was maintained at a significantly higher level in the molasses+lime treatment than in all the other treatments with their effect being additive rather than synergistic. Leaching alone reduced the EC for both soils with the effect being more pronounced in the Proserpine soil. In the Burdekin soil, the EC in the molasses-only treatment was not significantly different from that the EC in the lime-only treatment while in the Proserpine soil, the EC resulting from each treatment was significantly different. The EC for both soils increased in the order of treatments control<lime<molasses<molasses+lime.

Table 4.1 pH and electrical conductivity (EC) in 1:5 soil:water extracts, exchangeable sodium percentage (ESP), cation exchange capacity (CEC) and organic carbon content of the Burdekin and the Proserpine soils after molasses and gypsum treatments and 5 leaching events. C, L, M and M+L refer to control, lime (10 t/ha), molasses (10 t/ha) and molasses+lime (both 10 t/ha) respectively.

Soil	Treatment	pH	EC(dS/m)	ESP	CEC	Carbon
		(1:5 soil:water)			cmol(+)/kg	%
Burdekin	initial	8.0	0.16	7.9	10.9	0.8
	C	7.7*b*	0.06*a*	4.3*c*	10.6*a*	0.81*a*
	L	8.5*d*	0.14*b*	2.0*a*	10.4*a*	0.83*a*
	M	7.5*a*	0.16*b*	3.4*b*	11.6*b*	0.95*b*
	M+L	8.1*c*	0.27*c*	1.5*a*	11.2*b*	0.91*b*
	Significance	**	**	**	**	**
Proserpine	initial	4.9	0.12	18.0	2.3	0.7
	C	5.4*a*	0.06*a*	7.3*c*	2.1*a*	0.62*a*
	L	8.1*d*	0.10*b*	0.9*a*	2.2*a*	0.71*a*
	M	6.0*b*	0.13*c*	4.6*b*	2.5*b*	0.83*b*
	M+L	7.5*c*	0.21*d*	1.0*a*	2.5*b*	0.86*b*
	Significance	**	**	**	**	**

Letters (a, b, c, d) show results significantly different at p=0.01 (**)

The exchangeable sodium percentage (ESP) was generally reduced by molasses and lime treatments in both soils. Leaching alone (with distilled water) reduced the ESP by nearly half for the Burdekin soil and more than half for the Proserpine soil. This result was consistent with the previous experiment (Chapter 3). The lime-only and molasses+lime treatments reduced the ESP more than the molasses-only and the control treatment. The effect of lime-only treatment in reducing the ESP appears to be more pronounced in the Proserpine soil than that in the Burdekin soil. In general, the ESP decreased for both soils in the order of treatments control>molasses>lime≥molasses+lime.

The cation exchange capacity (CEC) and organic carbon content were significantly increased for both soils after addition of molasses while the lime-only treatment did not influence the CEC and organic carbon content of either soil. The CEC and organic carbon in the Burdekin soil was higher than that of the Proserpine soil.

The abundance of cations in the system at the beginning and at the end of the experiment is shown in Table 4.2. In general, molasses and lime increased the proportion of cations in the leachate and on exchange sites of both soils. The cations in the leachates for each treatment were higher in the Proserpine soil than that in the Burdekin soil except for sodium. This reflects the coarser texture of Proserpine soil relative to that of the Burdekin soil. It should be noted, however, that the volume of water leached during each event was greater in the Burdekin soil than in the Proserpine soil (88 mL versus 72 mL). The proportion of cations in leachate was small compared with those on the exchange phases of soil in all treatments except sodium in the Burdekin soil. In the Burdekin soil, it appeared that Ca from lime displaces exchangeable Na but not for exchangeable Mg and K which good for plant nutrients.

Table 4.2 Cation abundance (cmol(+)/kg) in control (C), lime (L), molasses (M) and molasses+lime (M+L) treatments

	Initial cation abundance			Final cation abundance			Leachate (%)	Soil (%)
	Soil	Addition	Total	Leachate	Soil	Total		
Burdekin				**Ca**				
C	7.9	0.0	7.9	0.1	7.4	7.5	1.2	98.8
L		17.9	25.8	0.1	23.3	23.4	0.6	99.4
M		0.04	7.9	0.2	7.5	7.7	2.4	97.6
L+M		17.9	25.8	0.2	14.5	14.7	1.5	98.5
Proserpine								
C	0.9	0.0	0.9	0.1	0.8	0.9	9.1	90.9
L		17.9	18.7	0.5	15.8	16.3	3.3	96.7
M		0.04	0.9	0.1	0.9	1.0	11.2	88.8
L+M		17.9	18.8	0.5	15.0	15.5	3.2	96.8
Burdekin				**Mg**				
C	4.7	0.0	4.7	0.1	4.8	4.9	1.9	98.1
L	4.7	0.0	4.7	0.1	4.3	4.4	2.4	97.6
M		0.1	4.8	0.2	4.7	4.9	4.3	95.7
L+M		0.1	4.8	0.2	4.2	4.4	5.0	95.0
Proserpine								
C	0.4	0.0	0.4	0.1	0.3	0.4	28.3	71.7
L	0.4	0.0	0.4	0.1	0.3	0.4	26.0	74.0
M		0.1	0.4	0.1	0.6	0.7	18.1	81.9
L+M		0.1	0.4	0.2	0.6	0.8	25.6	74.4
Burdekin				**Na**				
C	1.4	0.0	1.4	0.5	1.2	1.7	30.1	69.9
L	1.4	0.0	1.4	0.6	0.6	1.2	49.6	50.4
M		0.01	1.4	0.6	0.5	1.2	54.4	45.6
L+M		0.01	1.4	0.6	0.4	1.0	61.2	38.8
Proserpine								
C	0.7	0.0	0.7	0.1	0.7	0.7	8.0	92.0
L	0.7	0.0	0.7	0.1	0.7	0.8	11.4	88.6
M		0.01	0.7	0.1	0.7	0.8	11.6	88.4
L+M		0.01	0.7	0.1	0.7	0.8	16.6	83.4
Burdekin				**K**				
C	0.5	0.0	0.5	0.01	0.5	0.5	1.3	98.7
L	0.5	0.0	0.5	0.01	0.5	0.5	1.1	98.9
M		0.2	0.8	0.05	0.9	0.9	5.1	94.9
L+M		0.2	0.8	0.05	0.8	0.9	5.3	94.7
Proserpine								
C	0.4	0.0	0.4	0.03	0.4	0.4	6.7	93.3
L	0.4	0.0	0.4	0.04	0.4	0.4	9.3	90.7
M		0.2	0.7	0.3	0.6	0.9	31.8	68.2
L+M		0.2	0.7	0.4	0.5	0.9	42.2	57.8

The proportion of carbon lost in respiration, presumably released as CO_2 and leached as DOC was calculated to show the balance of organic carbon in the system during the period of experiment (Table 4.3). The different amounts of carbon in the soil (before and after incubation) and in the leachate was assumed to be due to carbon lost in respiration, presumably released as CO_2. In general, a substantial proportion of molasses added was presumably lost in respiration (CO_2) and only a small proportion was leached as DOC. In the molasses-only treatment, the proportion of CO_2 was higher in the Proserpine soil than that in the Burdekin soil. In both soils, the proportions of carbon lost in respiration and leached as DOC in the molasses-only and molasses+lime treatments were in range of 30-36% and 1-2% respectively. DOC was higher in the molasses-only than in the molasses+lime treatments, which is consistent with what was observed in Chapter 3. In the lime-only and control treatments, the proportion of carbon lost in respiration was very small compared with molasses-only and molasses+lime treatments.

Table 4.3 Percentage of carbon lost in respiration (CO_2) and dissolved organic carbon (DOC) leached in the control (C), lime (L), molasses (M) and molasses+lime (M+L) treatments in the Burdekin and Proserpine soils.

Soil/	Organic carbon (mg/kg soil)				%CO_2	% DOC
Treatment	Initial	Leachate(DOC)	Soil(final)	DOC+final	released	leached
Burdekin						
C	7800	96	8050	8146	-4	1.2
L	7800	48	8303	8351	-7	0.6
M	14022	230	9525	9755	30	1.6
M+L	14022	141	9146	9287	34	1.0
Proserpine						
C	7000	35	6200	6235	11	0.5
L	7000	33	7136	7169	-2	0.5
M	13222	227	8300	8527	36	1.7
M+L	13222	140	8621	8761	34	1.1

4.4 Discussion

Lime and molasses added at the rate of 10 t/ha each resulted in a number of changes in the leachate, physical and chemical properties of the two soils studied. The results of leachate analysis showed that the addition of molasses and lime significantly influenced the leachate properties of both soils in different ways. When lime was applied to soil, the leachate pH increased immediately while the molasses had the reverse effect in the Burdekin soil.

The EC of soils was increased by adding molasses and lime because both treatments provided an increase in electrolyte concentration. When lime+molasses was applied to the soil, the increase in EC was not significantly higher than that of molasses-only. This indicates that the application rate of molasses (10 t/ha) may be too small to affect the solubility of lime and that either the rates may need to be increased to enhance the solubility of lime or that more time is required to observe the desired effect. Further experiments are needed to answer this question.

DOC of the leachates increased markedly in the molasses treatments. However, when molasses+lime was applied to the soils, the DOC was lower than that of the molasses-only treatment. This may indicate that some dissolved organic matter was protected from leaching by the presence of calcium in the soil, as was found and discussed in Chapter 3.

The increase in pH of both soils brought about by addition of lime is most likely due to CO_3^{2-} produced when lime was applied to the soils. However, the increase in pH of both soils may induce the soils to become more alkaline and, therefore, more sodic as solubility of calcium is suppressed; this was proposed by Rengasamy and Olsson (1991). In arid and semi-arid climates, the soluble Ca and Mg become low and Na and K ions

accumulate in soil solution when the concentrations of CO_3^{2-} and HCO_3^- increase (Rengasamy and Olsson, 1991). Organic acids and CO_2 produced during incubation of molasses might reduce pH in the Burdekin soil. However, the magnitude of this decrease brought about by 10 t/ha of molasses did not lower the pH of the soils sufficiently to influence lime solubility. Further experiments are needed to determine the best combination rates of molasses and lime to overcome problems associated with sodicity. In the Proserpine soil, the pH was increased when molasses was added as was observed and discussed in Chapter 3.

Wet aggregate stability and clay dispersibility of soils were influenced by molasses and lime. An increase in macroaggregation occurred at the expense of microaggregates (Figure 4.5), which may have been due to carbohydrate production after molasses addition plus fungal hyphae produced during incubation. Observations made during the experiments indicate that fungal hyphae were abundant in the soils to which molasses was added. However, macroaggregates are easily disrupted and broken into microaggregates when increasing dispersive energy was applied to soil. This can be seen in Figure 4.3 especially in the light-textured Proserpine soil; when molasses was added, the amount of spontaneously dispersed clay was significantly lower than that of the control. There was no significant difference in the amount of dispersed clay between the molasses-only treatment and the control when dispersive energy was applied to soil (mechanical dispersion). However, the dispersed clay from lime treatments was significantly lower than that of the molasses treatments and its combination with molasses resulted in the lowest dispersed clay. In the Burdekin soil, which had a clay content 4 times higher than the Proserpine soil, the amount of spontaneously and mechanically dispersed clay brought about by the molasses and lime treatments were significantly lower than that of the control. This probably results from strong binding of mucilages and colloidal organo-

mineral complexes, which may have induced less clay to disperse even though the higher dispersive energy was applied to soil (Tisdall and Oades, 1982).

4.5 Conclusions

Molasses and lime either together or alone improved the structural stability of sodic soil. For the leachate properties, molasses-only addition reduced pH and SAR in the Burdekin soil whereas they increased pH in the Proserpine soil, and increased EC and DOC in both soils. The lime-only treatment increased pH and EC but decreased DOC. The DOC was higher in molasses alone than in molasses+lime in both soils, which may indicate that some of the organic matter in the molasses was protected from leaching by the presence of soluble calcium in the soil. Application of molasses together with lime increased macroaggregation and EC, and decreased ESP, spontaneous dispersion and mechanical dispersion. Molasses alone increased CEC and macroaggregation in both soils but had little effect on mechanically dispersed clay in the Proserpine soil. Lime alone decreased spontaneously and mechanically dispersed clay in both soils but had little effect on mechanically dispersed clay in the Proserpine soil. In this experiment, the rate of 10 t/ha molasses did not lower the pH of the soil sufficiently to dissolve the lime substantially. Further experiments are needed to determine the best combination rates of molasses and lime to overcome problems associated with sodicity.

CHAPTER 5

Sodium-Calcium Exchange Selectivity of Soils Under Trash Management Practices

5.1 Introduction

Cation selectivity coefficients relate adsorbed cations to their activities in the soil solution. Knowledge of the factors influencing cation selectivity is central to the understanding of processes in soil such as cation leaching, fertilizer-soil interactions, nutrient supply to plants, and reclamation of saline and sodic soils (Thomas, 1974; Robbins *et al.*, 1980; Gaston *et al.*, 1993).

Although the sodicity hazard in soils is associated with exchangeable sodium status, sodium adsorption ratio (SAR) is most often used as the principal diagnostic tool for determining the sodicity hazard of irrigation water. The reason is that SAR can be more easily and accurately measured than exchangeable sodium percentage (ESP; section 2.3.1). The SAR relationship with exchangeable sodium (Na_{ex}) in soil, involving the Gapon selectivity coefficient (k_G), is generally linear (Section 2.5).

$$ESR = k_G(SAR) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 5.1$$

Where, for a Na-Ca system, $ESR = (Na_{ex})/(CEC-Na_{ex})$, $SAR = [Na^+]/([Ca^{2+}]/2)^{0.5}$. CEC is cation exchange capacity and [m] refers to concentration in solution (mmol(+)/L).

The value of k_G may vary with soil properties such as clay content and type, organic matter content, surface charge density, solution composition, pH, CEC, ionic strength and method of determination (Nelson and Oades, 1998; Haroon *et al.*, 1983; Frenkel and Alperovitch, 1984; Curtin *et al.*, 1995; Stehouwer *et al.*, 1993; Clark and Turner, 1965; Jensen and Babcock, 1973; McBride, 1979; Ross and Bartlett, 1992; Mansell *et al.*, 1993; McBride, 1980; Gaston and Selim, 1991; Gaston *et al.*, 1993; Sauve and Hendershot, 1995). The relationship between k_G and organic matter content has been reviewed by Nelson and Oades (1998). The selectivity of exchange sites for Ca over Na is proportional to organic matter content where it varies due to cultivation history, depth, or treatment with H_2O_2. Evaluation of the quantity of calcium amendment needed to reclaim a sodic soil or the effect of irrigation water on the ESP requires knowledge of k_G under the pertinent conditions. The value of k_G indicates how vulnerable a soil is to sodification. Large values of k_G indicate that a soil is vulnerable to sodification.

Most methods of measuring Na-Ca exchange selectivity use adaptations of batch equilibration techniques consisting of repeated shaking, centrifuging, and decanting which significantly disrupt soil aggregate structure (Helfferich, 1962; Rhue and Mansell, 1988; Gaston and Selim, 1990). The effects of aggregate disruption on Na-Ca exchange selectivity are unknown and there is little information about methods either for measuring Na-Ca exchange selectivity or for inducing known levels of sodicity in soil while maintaining the natural aggregate structure. Miller *et al.* (1989) argued that flow-through methods may be preferable to batch methods when studying certain surface reactions. For Na-Ca system, the flow-through method is closer to field conditions in which soil aggregates remain stationary relative to the mobile solution.

The aims of this study were to develop a method for measuring Na-Ca exchange selectivity of natural soil aggregates and to determine whether k_G is influenced by soil type, trash management practices or organic matter content in some Queensland soils used for sugar production and in a Red-brown earth from South Australia. The main question addressed in this chapter was whether soil with different management practices inhibits sodification under irrigation with saline and sodic water.

5.2 Materials and Methods

5.2.1 Soil

Soils were sampled at 3 locations in northern Queensland (Ayr, Mackay and Tully) in which two long-term, sugarcane trash retention management regimes have been practiced (i.e. leaving cane harvest residues as a blanket; hereafter referred to as 'green' and burning cane residue prior to harvest; hereafter referred to as 'burnt'). Soil samples from the Waite Agricultural Research Institute, Urrbrae, South Australia from long-term permanent pasture and wheat-fallow plots were also included to extend the experiment to a Red-brown earth from a Mediterranean zone.

Ayr Site

The Ayr site, which has an average annual rainfall of approximately 1100 mm (Clewett *et al.* 1994), was sampled in 1998 from the long-term green and burnt cane-trash blanket trial on a Ustropept (Soil Survey Staff, 1989) at the Burdekin Sugar Experiment Station, Queensland. This trial was planted with sugarcane in 1988 and has followed the crop cycle: cane planting followed by 3 ratoon crops, cane replanting, and 2 ratoon crops. In both

burnt and green trash management treatments, samples were collected as follows: 10 cores (5 cm diameter x 5 cm depth) were taken in a line across the furrow, from one mound to the next (approximately 1.5 metres), in the middle furrow of the plot. This sampling was repeated 5 times in evenly spaced intervals along the plot in the middle furrow. The cores for each plot were then bulked and air-dried.

Mackay Site

The Mackay site, which has an average annual rainfall of 1681 mm, was sampled in 1997 from the long-term green and burnt cane-blanket trial on a Chromic Luvisol (Stace *et al.*, 1972) at the Mackay Central Sugar Experiment Station. The trial was planted with sugarcane in 1992 on a site that had previously grown sugarcane for more than 20 years and followed by cane-crop cycles and 4 ratoon crops harvested. Soil samples were taken in the same way as the Ayr soil. In the green treatment, the soil had less cultivation than that in the burnt treatment.

Tully Site

The Tully soil is a Dystropept (Soil Survey Staff, 1989) with an average annual rainfall of 4074 mm (Clewett *et al.*, 1994); the dominant soils are deep, poorly to freely drained and derived from granite and acid volcanics (Canon *et al.*, 1992). The Tully site was sampled in 1997 from the long-term green cane trash blanket and burnt cane trial at the Tully Experiment Station, Queensland. This trial was planted in 1991 and has followed the crop cycles of cane planting and 4 ratoon crops harvested. The samples were collected by an excavation of 5 cm deep, approximately 40 cm wide and 40 cm long on the side of mounds in

the burnt and green treatment plots. Soil samples from each plot were then bulked and air-dried.

Urrbrae Site

Soil at the Waite Agricultural Research Institute, Urrbrae, South Australia was sampled at a permanent pasture trial and a wheat-fallow rotation. Soil samples were taken using an auger of 10 cm diameter from 0-10 cm depth. Details of these experimental plots have been described by Grace and Oades (1994).

Some properties of soil aggregates used in this study including organic carbon, cation exchange capacity (CEC), particle size distribution and clay mineralogy are presented in Table 5.1.

Table 5.1 Selected properties of soil used in this experiment

Soil sites and management	OC g/kg	CEC cmol(+)/kg	pH[A]	EC[A] dS/m	Particle size (%) clay	silt	sand	Mineralogy
Ayr (B)	14.4	8.0	7.04	0.04	10	11	79	Q*, I#, K#, F*
Ayr (G)	17.5	9.5	6.91	0.04				
Tully (B)	12.3	7.3	5.53	0.05	34	35	31	K#, S#, I*, Q*, F*
Tully (G)	18.1	11.0	5.23	0.07				
Mackay (B)	13.1	7.7	5.49	0.03	18	25	57	Q*, I*, K#, F#
Mackay (G)	14.3	7.7	5.35	0.04				
Urrbrae (WF)	11.4	9.9	5.85	0.13	11	27	62	K*, RIM#, I#, Q*
Urrbrae (PP)	31.1	10.3	5.65	0.36				

[A] = 1:5 soil:water extract, K = Kaolinite; RIM=Randomly Interstratified Minerals, I = Illite, Q = Quartz, S = Smectite, F = Feldspar B = burnt, G = green, WF = wheat fallow and PP = pasture. * and # = minor and major clay mineral

5.2.2 Methods

5.2.2.1 Calcium Saturation

Three plot-replications of soil samples were air-dried and sieved to collect 0.5-2 mm aggregates. One hundred grams of these soil aggregates were placed on a sintered glass funnel of porosity = 4 (10 cm inner diameter, 8 cm depth from rim to sintered plate), connected to 125 cm vinyl tubing ($\emptyset$ = 16 mm). The soil aggregates were equilibrated slowly with 0.1M $CaCl_2$ at 10 kPa (100 cm) suction to minimise slaking. To minimize evaporation, the sintered glass funnels were covered with plastic film which was punctured to avoid any air pressure buildup. The soil was gradually brought to zero suction by raising the tubing slowly for period of 2 hours until the position of the meniscus in the tubing was level with the bottom of the soil aggregate bed on the sintered funnel. The soil aggregates were then totally immersed in the solution overnight and then drained. This immersion and draining was repeated three times and the solution was discarded. The whole process was repeated with fresh 0.1M $CaCl_2$ to ensure saturation of exchange sites with Ca^{2+}.

Following the same procedure, the soil aggregates were immersed in distilled water several times to remove excess electrolyte. After 2 hours of immersion, the soil aggregates were drained and the electrical conductivity (EC) of the solution was measured. It had been found previously that 2 hours immersion of aggregates of this size was sufficient to reach EC equilibrium with the solution. The solution was then replaced with distilled water and the process continued until the EC of the solutions was about the same as that of the "blank" funnels (i.e. those with no soil; < 10 μS/cm). The final EC of the soil aggregates was used to calculate calcium left in the soil solution before the following treatment to adjust total cation concentration (TCC) and sodium adsorption ratio (SAR) were applied. Soil aggregates

without Ca saturation, SAR and TCC treatments immersed in distilled water only (hereafter referred to as the control treatments), were also included to monitor cation dissolution (weathering) during the applied treatments. These were observed by measuring the EC of the solution (distilled water) of the control treatment before TCC and SAR treatments were applied to Ca-saturated aggregates and at the end of the experiment (Table 5.2). Mercury chloride (1 mg/L) was added to all solutions to prevent microbial activity.

Table 5.2. Electrical conductivity (EC) of control treatments (soil aggregates without Ca saturation, TCC and SAR treatments) before SAR and TCC treatments were applied to Ca saturated aggregates (before) and at the end of the experiment (after).

Site	Trash management	EC (μS/cm)	
		before	after
Ayr	burnt	8.58	10.40
	green	10.06	14.62
Tully	burnt	4.55	4.58
	green	6.13	6.44
Mackay	burnt	5.32	5.40
	green	5.02	5.65
Urrbrae	wheat-fallow	6.92	6.96
	permanent-pasture	9.51	13.95

In Table 5.2, The EC of the control treatment at the end of experiment (after) was higher than before SAR and TCC treatments were applied to Ca-saturated aggregates. Furthermore, the EC of the green and the permanent pasture management practices (high
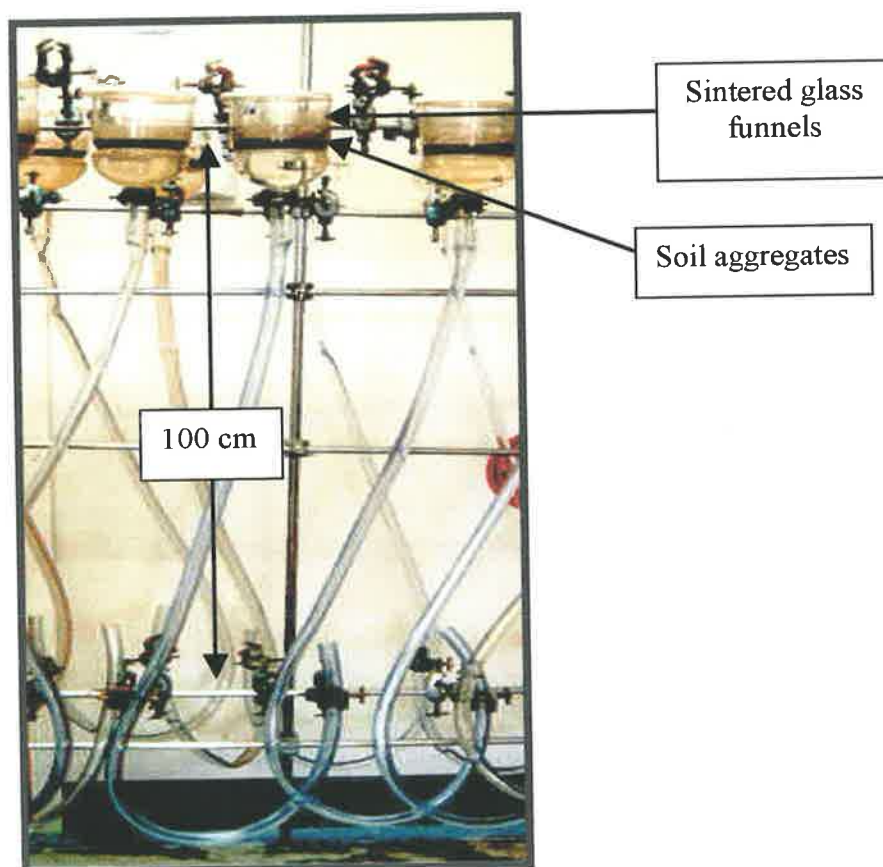
Figure 5.1 Arrangement of the experiment with sintered glass funnels

organic matter) at the end of experiment was higher than those of burnt and wheat fallow management practices. This is presumably due to dissolution (weathering), which has occurred during the treatment and was more pronounced with higher soil organic matter contents. However, the difference between EC value before and after experiments was quite small (< 5 μS/cm) and it is assumed that these would not significantly affect the outcome of these experiments.

5.2.2.2 SAR and TCC Treatments

When the EC of the solutions was about the same as that for blank samples (funnels with no soil; < 10 μS/cm), the aggregates were equilibrated with Na^+ at two chosen concentrations. The Na^+ concentrations and the ratio of solution:soil were chosen (3.5:1 solution:soil) to produce two equilibrium TCC (2 and 10 mmol(+)/L) and SAR values (3 and 10) (Table 5.3). The concentrations of sodium and calcium chloride required for each combination of TCC and SAR treatments were calculated by initially assuming a Gapon constant of 0.008 (mmol/L)$^{-0.5}$ and solving a series of simultaneous equations using the Excel$^®$ program to produce the total sodium in solution and held on the exchange sites. The premise of the calculations was that the soil was calcium-saturated and using the Gapon equation, conservation of calcium, sodium and exchange capacity, the initial concentration of sodium required to produce the target ESR was calculated. The soil aggregates were gently immersed in treatment solutions and drained (as during calcium saturation). Immersion and draining cycles were conducted several times for 5 days and then left overnight to drain at 100 cm suction. The solution was then removed for analysis and the soil samples were left to dry sitting in the sintered glass funnels. Each treatment combination was replicated three times.

5.2.3 Soil and Solution Analyses

Thoroughly mixed equilibrium solutions from each treatment were collected and analysed for Na^+ and Ca^{2+} using flame photometry and atomic absorption spectrophotometry (AAS) to calculate k_G. By assuming that Na^+ "missing" from solution was now held as exchangeable Na^+, k_G could be calculated from equilibrium solution properties alone.

Table 5.3 Calculated initial NaCl and CaCl$_2$ concentrations used to achieve each treatment combination of TCC and SAR

SAR	TCC	NaCl mmol(+)/L	CaCl$_2$
3	2	2.0	0.0
3	10	5.41	4.59
10	2	2.0#	0.0
10	10	10.0	0.0

#: A two stage treatment was needed for SAR10/TCC2. The first solution applied was 10 mmol(+)/L NaCl and the 2nd solution was 2 mmol(+)/L NaCl.

For validation of the method, a treated soil sample from the sintered glass funnels with a k_G value close to the average of k_G for each treatment-combination was chosen, remoulded and analysed for exchangeable Na and Ca by ammonium chloride displacement (section 3.3) based on methods of Rayment and Higginson (1992).

5.2.4 Statistical Analysis

Data were analysed using Genstat 5 (Genstat 5 Committee, 1987). The values of k_G calculated from solution properties alone and from soil and solution properties were analysed using simple linear regression and correlation. A close correspondence between these two k_G values was sought to confirm that the method described here of solution analysis alone can be used for measuring Na-Ca exchange selectivity of soils.

5.3 Results

5.3.1 Validation and Appraisal of the Method

Figure 5.2 shows the relationship between k_G values derived from soil and solution properties and from solution properties alone. There is a strong (1:1) linear relationship between the two values of k_G, and this indicates that the method appears to be useful in measuring Na-Ca selectivity of soil without disturbing the aggregates. An alternative way to demonstrate this is to plot ESR calculated from solution properties alone against the measured ESR (Figure 5.3). The results in Figure 5.3 also confirm that there is a strong linear relationship (1:1) between the two values of ESR.

Most methods used to study Na-Ca exchange selectivity of soil are batch equilibrium methods. However, the main problem with these methods is that there is massive disturbance of soil aggregates. The flow-through method using sintered glass funnels, which is described here can be used to eliminate disturbance. Furthermore, this method is much closer to field conditions in which soil samples remain stationary relative to the mobile solution. However, this funnel flow-through method was time consuming; it took about 30 days overall to complete the experiment but this depends on soil aggregates size and whether the sintered funnel is very permeable; some of those used here were not. However, the critical stage of the method is when Na solution treatment was imposed on soil aggregates, which took 3-4 days.
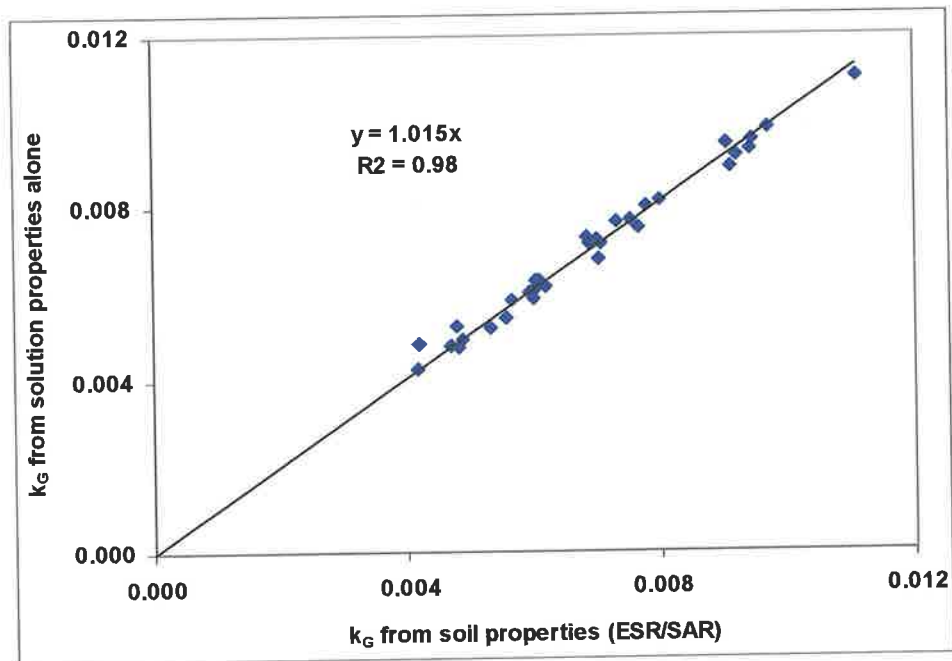
Figure 5.2 Relationship between k_G from soil and solution properties (ESR/SAR) and from solution properties alone
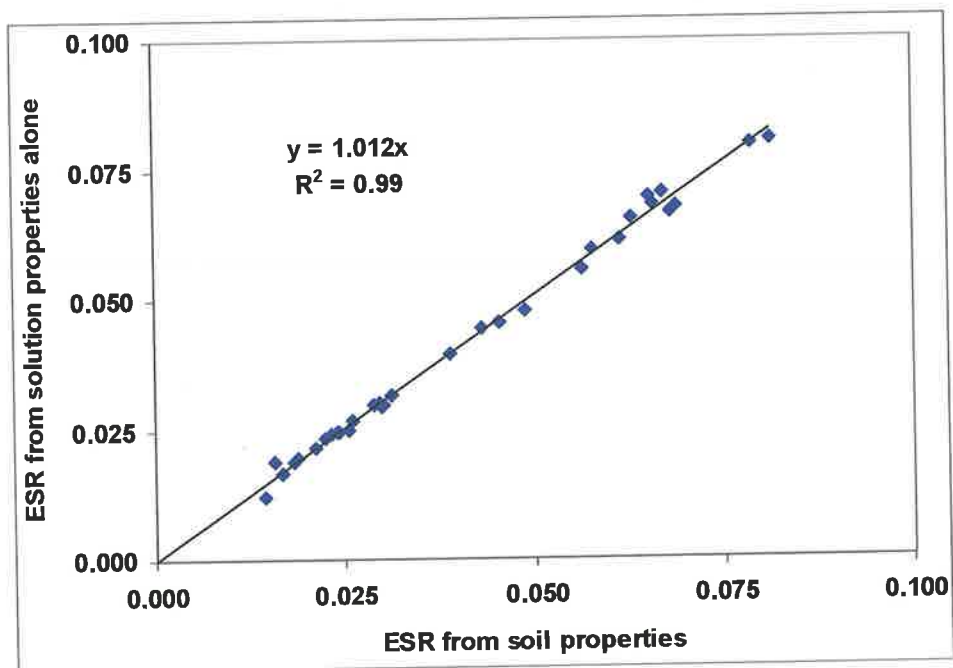
Figure 5.3 Relationship between ESR from soil properties and calculated from solution properties alone.

5.3.2 Effects of Management Practices (Organic Matter) and Soil Type on k_G

Figure 5.4 shows the effect of soil type and management practices (organic matter content) on the average value of k_G (irrespective of TCC and SAR). Analysis of variance showed that there was a highly significant effect ($p<0.001$) of soil type and management practices on values of k_G (Table 5.4). There was also a significant interaction effect ($p = 0.05$) between soil type and management practices on the value of k_G.

Soil type had a highly significant ($p=0.001$) effect on the value of k_G (Table 5.4). Clay content of the soils increases in the order of Ayr≤Urrbrae<Mackay<Tully (Table 5.1). Notwithstanding management practices, clay mineralogy, TCC and SAR, the highest overall average value of k_G was observed in the Ayr soil, which has the lowest clay content, although this was not significantly different from Mackay soil and the lowest overall average value of k_G was observed in the Tully soil which has the highest clay content, although this was not significantly different from that of the Urrbrae soil. The overall average values of k_G for the soils decreased in the order of Ayr (0.0084), Mackay (0.0076), Urrbrae (0.0070) and Tully (0.0064 $(mmol/L)^{-1/2}$).

Management practices strongly ($p=0.001$) influenced the value of k_G (Table 5.4). Figure 5.4 shows that the green treatment generally resulted in lower k_G values than the burnt treatment, even though the organic matter contents resulting from these management practices were not significantly different except for the Urrbrae site (Table 5.1). Further statistical analysis showed that the total organic carbon content in burnt and green trash management practices was not significantly different in the Mackay soil. The interaction between management practices (organic matter) and soil type (clay content) showed that the soil with the highest clay content and organic matter had the lowest value of k_G.
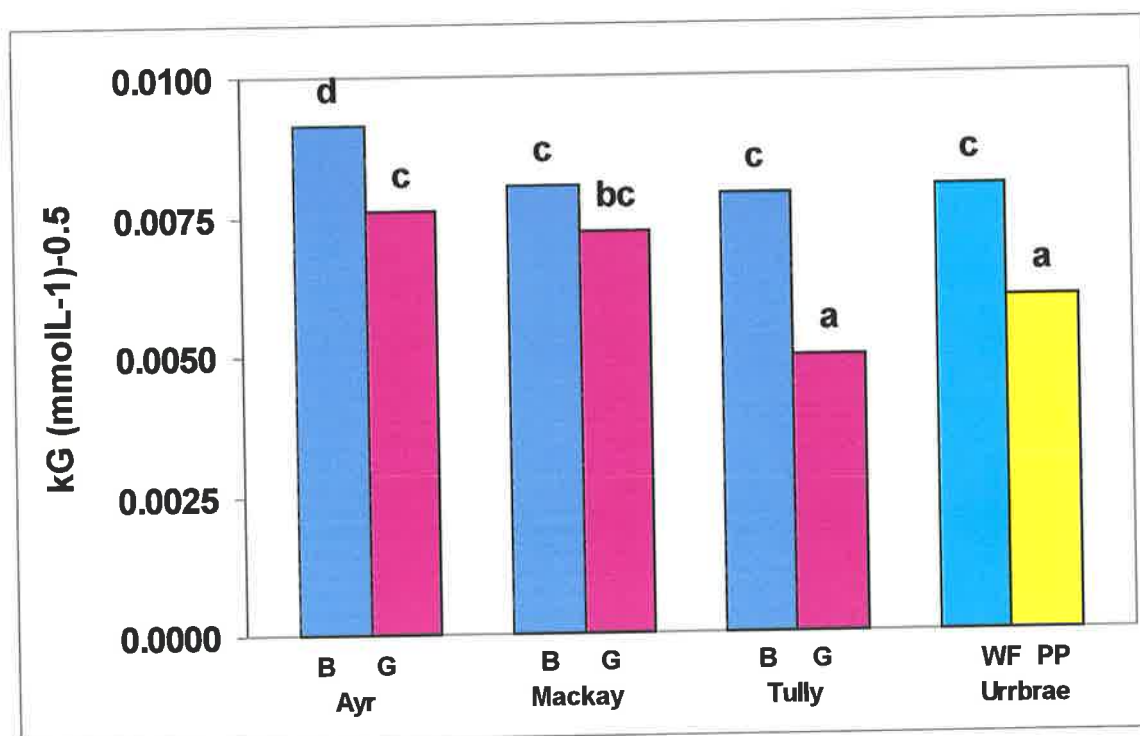
Figure 5.4 The effects of soil type and management practices (organic matter) on the average value of k_G (notwithstanding TCC and SAR treatments). B, G, WF and PP refer to burnt, green, wheat fallow and permanent pasture management treatments respectively. Lower-case letters indicate which results are significantly different ($p = 0.001$).

Table 5.4 Significance of the treatments as indicated by analysis of variance

Treatment	k_G
Management (C)	**
SAR (N)	*
TCC (T)	ns
Soil (S)	**
C x N	ns
C x T	ns
N x T	**
C x S	*
N x S	*
T x S	ns
C x N x T	*
C x N x S	ns
C x T x S	ns
N x T x S	ns
C x N x T x S	*

* and ** indicates significant at p = 0.05 and p = 0.001 respectively
ns denotes non significant at p = 0.05.

5.3.3. Effect of Salinity and Sodicity on k_G

SAR significantly (p = 0.05) affected the value of k_G while TCC did not (Table 5.4). The average values of k_G were 0.0073 and 0.0074 $(mmol/L)^{-1/2}$ for TCC 2 and 10 respectively, and 0.0076 and 0.0071 $(mmol/L)^{-1/2}$ for SAR 3 and 10 respectively. However, the interaction between SAR and TCC significantly influenced (p = 0.001) the value of k_G. Notwithstanding soil types, TCC and management practices, the average value of k_G decreased as SAR increased. The average values of k_G at SAR 3 and 10 were 0.0076 and 0.0071 respectively. At low SAR (3) or TCC (2), the value of k_G increased as TCC or SAR increased, while at high SAR (10) or TCC (10), the value of k_G decreased as TCC or SAR increased (Figure 5.5).
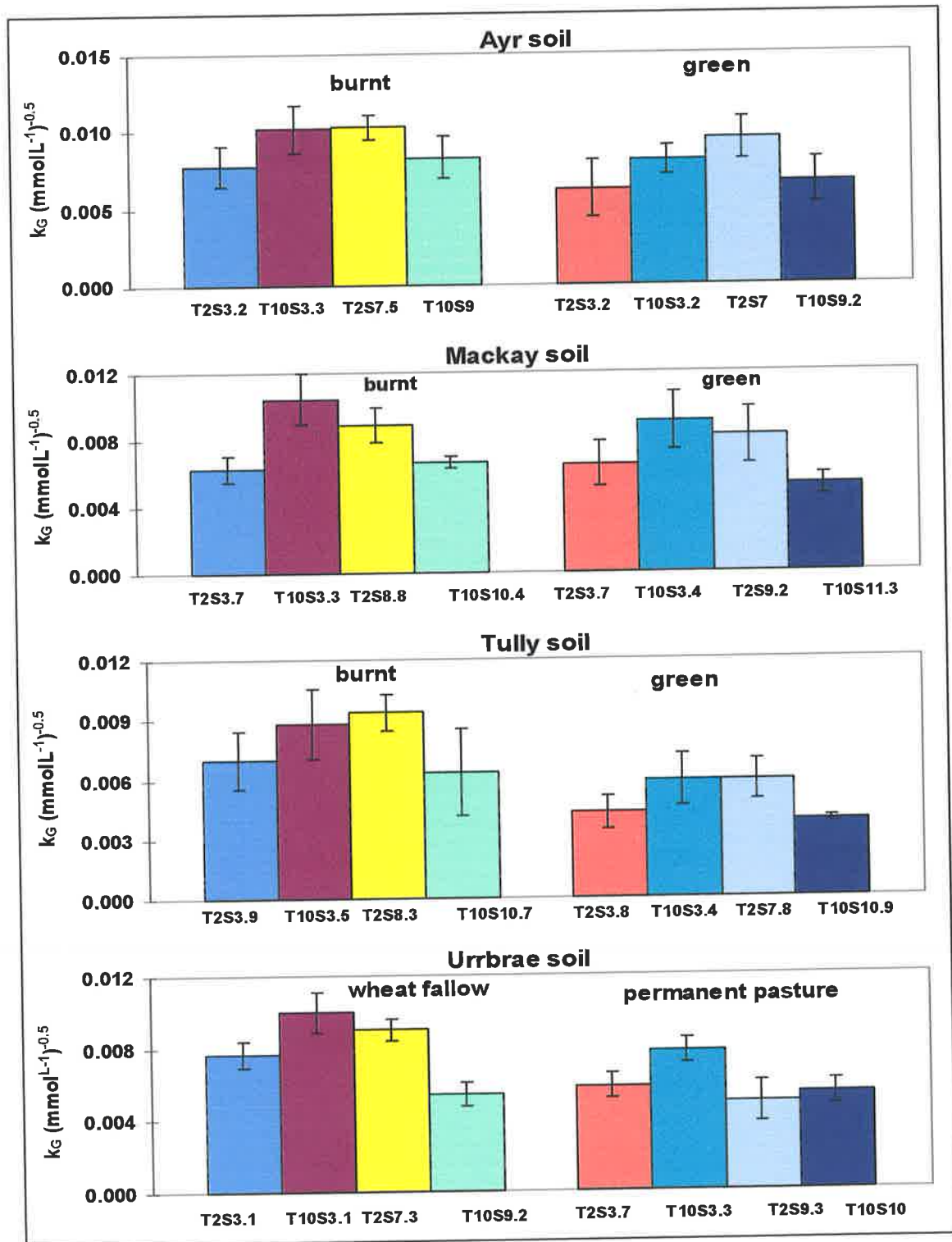
Figure 5.5 Effects of total cation concentration (TCC) and sodium adsorption ratio (SAR) on the value of k_G for different trash management practices in each soil. T2, 10 and SX denotes TCC = 2, 10 mmol(+)/L and SAR = X respectively. Error bars represent +/- standard deviation from the mean.

Table 5.5 The effects of TCC, SAR and trash management practices (organic matter) on the mean value of k_G and exchangeable sodium ratio (ESR) of soils based on solution properties alone. Parentheses denote standard deviations. Expected SAR denotes the SAR value calculated by assuming the k_G of 0.008 $(mmol/L)^{-0.5}$ and observed SAR denotes the SAR value measured at equilibrium.

Sites	Trash management	TCC	SAR expected	SAR actual	ESR	k_G from solution properties
	burnt	2	3	3.2 (0.2)	0.025 (0.005)	0.0078
		10	3	3.15 (0.05)	0.032 (0.004)	0.0102
		2	10	7.5 (0.5)	0.075 (0.008)	0.0103
Ayr		10	10	9.0 (0.1)	0.074 (0.006)	0.0083
(loamy sand)	green	2	3	3.2 (0.3)	0.020 (0.005)	0.0062
		10	3	3.2 (0.1)	0.026 (0.003)	0.0081
		2	10	7.0 (0.1)	0.066 (0.009)	0.0094
		10	10	9.2 (0.2)	0.062 (0.013)	0.0067
	burnt	2	3	3.9 (0.2)	0.030 (0.005)	0.0070
		10	3	3.5 (0.1)	0.031 (0.01)	0.0088
		2	10	8.3 (0.1)	0.078 (0.008)	0.0093
Tully		10	10	10.7 (0.2)	0.068 (0.02)	0.0063
(clay loam)	green	2	3	3.8 (0.4)	0.016 (0.004)	0.0043
		10	3	3.4 (0.1)	0.020 (0.004)	0.0059
		2	10	7.8 (0.3)	0.046 (0.007)	0.0059
		10	10	10.9 (0.2)	0.042 (0.002)	0.0039
	burnt	2	3	3.9 (0.3)	0.024 (0.001)	0.0063
		10	3	3.3 (0.1)	0.034(0.005)	0.0104
		2	10	8.8 (0.4)	0.077 (.007)	0.0088
Mackay		10	10	10.4 (0.4)	0.068 (0.003)	0.0066
(sandy loam)	green	2	3	3.7 (0.4)	0.024 (0.005)	0.0065
		10	3	3.4 (0.03)	0.031 (0.006)	0.0090
		2	10	9.2 (0.4)	0.074 (0.01)	0.0081
		10	10	11.3 (0.2)	0.059 (0.007)	0.0052
	wheat fallow	2	3	3.1 (0.1)	0.024 (0.001)	0.0077
		10	3	3.1 (0.05)	0.031 (0.003)	0.0100
		2	10	7.3 (0.4)	0.065 (0.005)	0.0090
Urrbrae		10	10	9.2 (0.1)	0.05 (0.006)	0.0054
(sandy loam)	permanent pasture	2	3	3.7 (0.1)	0.021 (0.001)	0.0058
		10	3	3.3 (0.1)	0.025 (0.001)	0.0076
		2	10	9.3 (0.4)	0.045 (0.005)	0.0049
		10	10	10.0 (0.2)	0.054 (0.005)	0.0054

These trends were generally the same for all soils within each trash management practice; an exception was that of the permanent pasture in the Urrbrae soil, although the value of k_G was not significantly different for SAR and TCC treatments.

5.4 Discussion

The sodicity of soil is determined by its selectivity for sodium when in contact with soil solution of a given electrolyte concentration and SAR. The range of soil properties used in this experiment demonstrates that different soils may differ considerably in Na-Ca selectivity. Although the influence of clay type and content on the value of k_G was not the main aim of this study, the value of k_G differed significantly between soils. Similar observations were made by Amrhein and Suarez (1991). The difference was probably due to clay content rather than clay type. The Ayr soil, which has the lowest clay content, has the highest k_G and the Tully soil, which has the highest clay content, has the lowest k_G; suggesting that selectivity of soil for Na over Ca decreases as clay content increases. Curtin *et al.* (1995) also found the selectivity of soil for Ca over Na increases as clay content increases. Thus, based on these data, the susceptibility of soil to sodification is lower in heavier textured soils. Amrhein and Suarez (1991) reported that there was no trend in Na-Ca selectivity preference as a function of clay mineralogy, even though the soils and minerals studied represented a wide variety of clay minerals and surface charge densities. Apparently, the effect of pH on Na-Ca selectivity for variable-charge minerals and organic matter can be attributed to specific competition between H^+ and Ca^{2+} rather than to a change in surface-charge density. Shainberg *et al.*, (1987) reported no effect of surface charge density on Na-Ca selectivity on four different smectite minerals. It has also been found that soil high in

variable-charge materials exhibits an increased preference for Ca^{2+} with increasing pH (Pratt *et al.*, 1962; Rhue and Mansell, 1988; Curtin *et al.*, 1995).

Organic matter influences the value of k_G. The results from this study confirm that the value the k_G was low in soil with high organic matter content. This is shown in Table 5.1 and Figure 5.4 where the Ayr soil has almost the same clay content as the Urrbrae soil but the value of k_G for the Urrbrae soil was significantly lower, possibly because the organic matter contents of these soils were markedly different (17.5 and 31.1 g/kg for Ayr and Urrbrae soils respectively). This suggests that soil with lower organic matter is more susceptible to sodification because organic matter has strong preferential adsorption for Ca over Na. The results are consistent with other researchers who found that k_G was lowest for the highest organic matter contents, effective cation exchange capacity and clay content (Curtin *et al.*, 1995; Nelson and Oades, 1998).

Different management practices may influence the amount and nature of soil organic matter. Table 5.1 shows that green sugarcane trash management retention has higher organic matter than burnt trash management, although this was not significantly different. This is possibly because plot trials of these management practices have been conducted for only relatively short periods of time (approximately 10 years). By contrast, compared with those described by Graham and Haynes (2000) reported that long-term (60 years) green trash retention caused a major increase in total and labile soil organic matter content and microbial activity in the surface soil compared with burnt trash management. Vallis *et al.* (1996) presented a model to simulate soil organic matter levels in long-term sugarcane trash management and found that the adoption of green trash management on old cultivated soil would lead to increases in soil organic matter of approximately 40% after 60-70 years and

that about half of this increase would occur in the first 20 years. However, the results of this experiment confirm that the value of k_G in the green trash management was significantly lower than that of burnt trash management. This suggests that there are two important implications of these results: (i) Soils with burnt trash management practices may be more susceptible to sodification than those with green trash management practices and that (ii) because the amount of organic matter in burnt and trash management was not significantly different, the nature of organic matter in soil might play an important role in influencing the value of k_G, because different functional groups have different selectivities (Nelson and Oades, 1998). Skjemstad et al. (1999) found substantial amounts of charcoal in soils used for sugarcane production, which may result from burnt trash management practices. Even in the case of Mackay soil where the value of k_G and organic matter contents in the green and burnt trash management practices was not significantly different, the value of k_G in the burnt trash management appears to be higher than that in green trash management. The similar organic matter content of burnt and green trash management practices in the Mackay soil may result from cultivation in the green treatment. The effects of cultivation in decreasing soil organic matter levels are well documented and have been discussed in the section 2.4.3. In contrast, Blair (2000) found that total organic carbon contents of burnt treatments were higher than those of green ones, although these was an 11% reduction of labile organic carbon in the burnt treatment in the Mackay soil (same soil as used in this study). The labile organic carbon is very important in maintaining soil structure and fertility (Skjemstad et al., 1999). However, previous researchers reported that returning crop residues (either incorporated, or retained on the soil surface) increased soil organic carbon compared to the burning of residues (Ladd et al., 1994; Blair et al., 1998; Weir, 1998).

The average value of k_G of soil used in this study was not significantly influenced by total cation concentration (TCC) alone but was influenced by SAR alone in which k_G generally decreased as SAR increased. Similar results were also reported by Pratt *et al.* (1962), and Jurinak *et al.* (1984). Bower (1959) found that the k_G of a montmorillonitic clay soil was not significantly affected by solution concentration (50-200 mmol(+)/L) but increased with increasing exchangeable sodium; that is, he found that Na^+-preference increased with increasing exchangeable Na, which contrasts with what was found here. Pratt *et al.* (1962) also reported that k_G was not significantly affected by solution concentration in the range of 50-330 mmol(+)/L on a soil high in amorphous clays and kaolinite. They also found that the selectivity coefficient of this soil was strongly pH-dependent. However, the interaction of SAR and TCC had a highly significant effect on the value of k_G. The value of k_G increased with TCC at low SAR, and decreased with TCC at high SAR, indicating that the selectivity for Na over Ca of soil tended to increase with TCC at low sodicity and decrease with TCC at high sodicity. This may result from the non-uniform distribution of cations on clay particles similar to the 'demixing' phenomenon described by Shainberg and Letey (1984), where Na^+ concentrates on external, and Ca^{2+} on internal surfaces of clay domains or quasi-crystals. The decrease in the values of k_G as salinity or SAR increased was in agreement with the results described by Jurinak *et al.*, (1984), Frenkel and Alperovitch (1984) and Doering and Willis, (1980). In contrast, other researchers reported that k_G increased with increasing salinity and sodicity level (Girdhar, 1996; Kachoui *et al.*, 1996).

In the group of soils included in this study, the value of k_G varied from 0.0036 to 0.0131 $(mmol/L)^{-0.5}$ and was always less than the average value of 0.0147 $(mmol/L)^{-0.5}$ determined by Richards (1954).

5.5 Conclusions

The method used in this study appears to be successful in measuring the Na-Ca exchange selectivity of soil without disturbing the aggregates. Further experiments are needed for validation of this method at low TCC and high SAR, because soil aggregates often disperse with increasing SAR, causing pores of sintered funnels to become blocked and impermeable and also leading to aggregate collapse. The value of k_G was influenced by soil type alone, management practices alone, and SAR alone, and interaction of all treatments. The green trash treatments had generally lower k_G values than the burnt trash treatment; suggesting that soil under burnt trash management was more susceptible to sodification than that under green trash retention. The difference in soil organic matter content between burnt and green trash management practices was not significantly different, which suggests that the nature of soil organic matter may influence the value of k_G. The extent to which various fractions of soil organic matter may influence Na-selectivity of soils over other cations (and thus k_G) deserves attention.

CHAPTER 6

General Discussion and Conclusions

6.1 General discussion

This study has addressed some important issues relating to the structural stability of sodic soils used for sugarcane production as influenced by molasses, lime and gypsum, and the way in which sugarcane trash management practices and organic matter affect sodification when soil is irrigated with saline and sodic waters. This final chapter of the thesis will integrate the conclusions drawn from each experiment and identify future research needs.

6.1.1 Molasses, Gypsum and Lime Influence on the Structural Stability of Sodic Soils

Sodic soils tend to have poor physical and chemical properties particularly when soil electrolyte levels are inadequate to compensate for the dispersive effects of exchangeable sodium. Increasing sugarcane production on sodic soils requires an understanding of the adverse impacts of sodicity on soil properties. Swelling and dispersion are two processes responsible for deterioration of physical properties of soil. The tendency to swell and disperse increases as electrolyte concentration (salinity) decreases and exchangeable sodium increases.

In Chapter 3, an experiment was conducted to assess the influence of molasses and gypsum on the structural stability of soils. Leaching events during this experiment were conducted to remove sodium by a process similar to that which might be used in the field. The results of this experiment indicate that addition of molasses and/or gypsum improved the physical and chemical properties of soils. When gypsum and molasses were applied

together, the concentration of dissolved organic carbon (DOC) decreased from that observed with molasses-only. This may indicate that soluble calcium from gypsum inhibited decomposition of organic matter by microorganisms and reduced the release of the DOC by leaching. Calcium tends to block and protect functional groups in organic matter that represent sites of initial decomposition, and also cross-link flexible polymers to create more dense, rigid molecules that are more stable to both chemical and biological degradation (Oades, 1989). In the coarser-textured Proserpine soil, this effect was not evident because the clay content of the soil was too low to protect cations and DOC in the soil solution from leaching. In the Burdekin soil, molasses and gypsum, either alone or combined, decreased spontaneous and mechanical clay dispersion and ESP. Molasses and gypsum both increased electrical conductivity and wet aggregate stability, with the combined effect being greatest. In the coarser-textured Proserpine soil, the amounts of dispersible clay were much lower than in the Burdekin soil but the effects of molasses and gypsum in decreasing spontaneous and mechanically dispersible clay were similar to those in the Burdekin soil. Molasses and gypsum reduced slaking and dispersion, and their effects either alone or combined improved the structural stability of both soils.

Since gypsum is more expensive than lime in the sugarcane growing districts in Queensland, a similar experiment was conducted using molasses and lime (Chapter 4). This experiment focused on whether the combination of molasses and lime could increase the solubility of applied lime and thus achieve a synergistic effect to reduce sodification of irrigated soils more effectively. Molasses and lime either together or alone improved the structural stability of both the Burdekin and Proserpine soils. In the Burdekin soil, it appeared that Ca from lime displaces exchangeable Na but not, unlike gypsum, exchangeable Mg and K which are plant nutrients. However, there appears to be no synergistic effect of molasses+lime in improving the structural stability of sodic soils.

Furthermore, the rate of 10 t/ha molasses did not lower the pH of the soil sufficiently to dissolve the lime substantially in this experiment. Further experiments are needed to determine the best combination rates of molasses and lime to overcome problems associated with sodicity or to follow the process for longer periods of time to establish if there is any sustained effect.

6.1.2 Sodium-Calcium Exchange Selectivity of Soils

The literature indicates that calcium selectivity of soil increases as soil organic matter content increases. In this work (Chapter 5), the value of the Gapon coefficient selectivity (k_G) was seen to be influenced by soil type, trash management practices or organic matter, and both SAR and TCC. The green trash treatment generally had lower k_G values than the burnt trash treatment, suggesting that soil under burnt trash management was more susceptible to sodification than that of green trash retention. Soil organic matter contents between burnt and green trash management practices were not significantly different, suggesting that the nature of soil organic matter may influence the value of k_G. Further experiments are needed to determine how the nature of organic matter influences the value of k_G. A method developed for measuring Na-Ca exchange selectivity of soil without physically disturbing the natural soil aggregates appears to be successful. The method can also be used for inducing known levels of sodicity in natural soil aggregates. Further experiments are needed to refine this method at high SAR and low TCC where the soil becomes more dispersive and thus difficult to manage.

6.2 General Conclusions

Molasses, lime and gypsum improved structural stability of sodic soils, but there were no synergistic effects of their combinations. The extent of sodium leaching was

enhanced by these amendments, particularly by gypsum. In the molasses+lime treatment, the rate of 10 t/ha molasses did not lower the pH of the soil sufficiently to dissolve the lime substantially in this experiment. Soil under green trash management was more resistant to sodification than soil under burnt trash management. An implication of this work is that molasses may be a useful ameliorant for sodic soils, either alone or combined with gypsum and lime. Green trash management practices appears to increase the resistance of soil to sodification.

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