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RESPONSE OF KIKUYU GRASS (*PENNISETUM CLANDESTINUM*) TO IRRIGATION WITH SALINE, SODIC WASTES AND NITROGENOUS, MANGANIFEROUS EFFLUENT

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This thesis is dedicated to my mother and father for their constant encouragement and enthusiasm for further study.

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ABSTRACT

The Manganese Metal Company (MMC) situated in Nelspruit, Eastern Transvaal, South Africa produces a manganiferous saline effluent from a manganese ore leaching process. The high NH_4 content of the waste has been identified as a possible nitrogen fertilizer source. Irrigation of the MMC waste over nearby kikuyu (*Pennisetum clandestinum*) pastures could thus potentially solve a waste disposal problem as well as provide fertilization of the pastures, although the high manganese content of the waste poses a risk of manganese toxicity or pollution.

The kikuyu pastures are presently used as a land disposal system for a saline waste from a pulp bleaching process. Due to process changes, the dominant salt type in the waste is anticipated to change from NaCl to Na_2SO_4. Pot experiments with kikuyu were undertaken to investigate NaCl versus Na_2SO_4 salinity effects, Mn toxicity threshold levels and MMC waste versus a standard nitrogen fertilizer (NH_4NO_3) yield response.

The results demonstrated that kikuyu grass is both salinity and Mn tolerant. Kikuyu salinity tolerance, using electrical conductivity as a salinity index, was significantly greater in NaCl than Na_2SO_4 salinity. This difference was attributed to the formation of SO_4 neutral ion pairs in Na_2SO_4 treatments which decreased cation uptake, increased osmotic stress relative to electrical conductivity and led to a possible SO_4-induced Ca deficiency. Cl adsorption in manganous sulphate and Na_2SO_4 treated soils was speculatively attributed to the formation of an undocumented ettringite-like mineral.

Kikuyu exhibited both a fertilization effect and a Mn toxicity effect with manganous sulphate applications. An increase in yield occurred between Mn applications of 800 and 1600 mg/kg soil. This effect was attributed to increased nutrient availability as a result of nitrogen mineralisation and soil desorption processes. Mn applications of 3200 and 8000 mg/kg resulted in severe Mn toxicity symptoms and reductions in yield.

Fertilization of kikuyu with NH_4NO_3 and MMC waste produced similar yield responses. Manganese toxicity did not manifest itself in MMC waste treated kikuyu, even at nitrogen loadings of 800 kgN/ha. Manganese attenuation in the soil by $MnCO_3$ precipitation, oxidation of Mn^{2+} and Mn adsorption are expected to prevent excess Mn^{2+} accumulation which would pose a Mn toxicity and water pollution risk.

The disposal of untreated MMC waste as a nitrogen fertilizer substitute for kikuyu pastures is thus in principle a feasible operation in terms of maintaining pasture sustainability and preventing pollution of water resources.

INTRODUCTION

The Manganese Metal Company (MMC) situated in Nelspruit, Eastern Transvaal, South Africa, produces a manganiferous saline effluent from a manganese ore leaching process. The waste is presently stored in a quarry and a means of disposal or treatment is under investigation.

The high NH_4 content of the MMC waste has been identified as a possible nitrogen fertilizer source. Irrigation of the MMC waste over nearby kikuyu (*Pennisetum clandestinum*) pastures could thus potentially solve a waste disposal problem as well as provide fertilization of the pastures.

A land disposal system does, however, pose a risk of manganese toxicity or pollution due to the high manganese content of the waste. A liming treatment of the waste was suggested as a means of precipitating out the Mn content. The raised pH of the treated waste would, however, result in ammonia volatilization with probable toxic consequences for plant growth.

This apparent deadlock was resolved with a review of Mn toxicity literature which revealed that kikuyu grass is extremely Mn tolerant. The use of MMC waste as a nitrogen fertilizer substitute for kikuyu pastures could thus be feasible. The current research was aimed at investigating this feasibility.

The present utilization of the kikuyu pastures as a land disposal system for a saline waste from a pulp bleaching process is an additional consideration. Furthermore, due to process changes, the dominant salt type in the waste is anticipated to change from NaCl to Na_2SO_4.

Pot experiments with kikuyu were thus undertaken to investigate the following effects:

- NaCl versus Na_2SO_4 salinity effects on yield and nutrient uptake;
- Mn toxicity threshold levels in kikuyu;
- MMC waste versus a standard nitrogen fertilizer (NH_4NO_3) yield response.

The conclusions set out at the end of this document suggest that there could be wide scope for MMC to utilize the waste product in a beneficial manner, offering not only substantial savings in disposal costs but also providing a fertilization of kikuyu pastures.

This research may serve as a base for further research into the utilization of waste products containing Mn and NH_4.

CHAPTER 1

PLANT AND SOIL RESPONSES TO SALINE MANGANIFEROUS IRRIGATION WITH PARTICULAR REFERENCE TO KIKUYU *(PENNISETUM CLANDESTINUM)*: A LITERATURE REVIEW.

1.1 PLANT RESPONSES TO SALINITY

Salinity is a problem limiting agricultural productivity in many parts of the world. Salinity problems exist if salts accumulate in the root zone to a concentration which results in yield reductions (Ayers & Westcot, 1985). Sposito (1989) defines a soil as saline if the electrical conductivity (EC) of a saturated paste extraction is >4 mS/cm. Irrigated land is susceptible to this salt accumulation from either a saline, high water table or salts in the applied water. Crop responses to this salinity stress vary between species, between cultivars within a species and during the life cycle of an individual plant. Consequently, growing salt tolerant plants or cultivars is one of the more cost effective strategies for coping with soil salinity (Curtin *et al.*, 1993).

1.1.1 Plant responses to salinity induced osmotic stress

Salinity reduces the osmotic potential of the soil solution and thus imposes an osmotic stress on plants. Yield losses occur when the osmotic stress in the root zone prevents the plant extracting sufficient water from the saline soil solution (Ayers & Westcot, 1985). The most common salinity effect is a general stunting of growth, usually more so in top growth than root growth. This decrease in growth occurs linearly as salinity increases above a critical threshold. Other salinity effects include wilting and scorching of leaves (Farooq *et al.*, 1989). Water stress at levels insufficient to cause visible damage may also slow plant growth through a decrease in photosynthesis (Shone & Gale, 1983).

Most plants respond to salinity as a function of the total osmotic potential of soil water without regard to the salt species present. In some cases, however, salinity induces nutritional imbalances or deficiencies causing decreased growth and plant injury for which osmotic effects alone cannot account (Maas & Hoffmann, 1977). Consequently, the response of plants to salinity depends not only on the total electrolyte concentration but also on the kinds of salts contributing to salinity (Curtin *et al.*, 1993).

1.1.2 Salinity tolerance mechanisms

Salt resistance depends on a variety of plant traits and involves the mechanisms of uptake, transport and excretion of ions (Malkin & Waisel, 1986). Water stress is predominantly overcome by osmotic adjustment within plant tissues, achieved by both decreasing tissue water content and solute accumulation (Marcum & Murdoch, 1990).

1.1.3 Plant responses to salt type

1.1.3.1 Effects of sodium and chloride

Both Cl and Na have the potential to affect plant growth adversely but there is evidence that Cl may have greater toxic effects than Na (Greub *et al.*, 1985). Soils do not adsorb chloride efficiently and it is usually freely bioavailable with the result that chloride toxicity is often cited as the most common toxicity in saline irrigation water. Cerda & Martinez (1988) note, however, that Cl is essentially a physiologically neutral anion tolerated over a wide range of concentrations by most plants and suggested that other processes such as Cl suppression of NO_3 uptake may cause the apparent Cl toxicity.

Sodium toxicity is not easily distinguished from chloride toxicity. Symptoms include leaf burn and dead tissue along the outside edges of leaves in contrast to Cl toxicity which usually manifests at the extreme leaf tip. Na toxicity is often alleviated if sufficient Ca or K is available in the soil. Chemical analysis of plant tissue is commonly used to diagnose either Cl or Na toxicity (Ayers & Westcot, 1985).

1.1.3.2 Sulphates

Irrigation with water high in sulphates results in an inevitable salt build up due to gypsum precipitation and consequently leaching is largely ineffective in controlling salinity derived from SO_4 (Papadopoulos, 1986). Osmotic stresses from gypsum salts are often greater than expected. Gypsum solubility in soils is greater than that predicted from pure water due to the higher ionic strength of the soil solution. Furthermore, the formation of ion pairs in sulphate waters is not accounted for in EC values but increases osmotic pressure and therefore decreases water availability to plants. The sum of cations or solute potential may therefore be a better measure for determining sulphate salinity effects on plants (Papadopoulos, 1986).

1.1.4 Fertilization and salinity

Ayers & Westcot (1985) state that fertilization has little effect on salt tolerance. Recent research by Cerda & Martinez (1988) shows, however, that plants grown in saline environments may be affected differently by the form of N fertilization. The impaired uptake of essential nutrients such as Mg and Ca as a result of salinity were found to vary according to N form. The antagonistic effect of NO_3 on Cl uptake may also affect plant salinity tolerance.

1.1.5 Plant tissue content and salinity

Ion concentrations in plant tissues vary in response to salinity. For example, Remison *et al.* (1988) noted a decrease in K with salinity in coconut while studies on Bermuda grasses (*Cynodon dactylon*) (Marcum & Murdoch, 1990) have resulted in increases of K with increasing salinity. Cation antagonism, (eg. Na substitution for K) is a common phenomena and may upset nutritional balances in the plant. Sodium is likely to slow down the translocation of the other cations into the plant as a result of its presence on the root absorption sites. Peacock *et al.* (1993) revealed that tissue K, Mg and Ca decreased non-linearly with increased salinity in St. Augustine grass (*Stenataphrum secundatum*). Anion antagonism was also evident in reductions of tissue P levels.

Sodium and chloride accumulation in plant tissues as a result of increased NaCl salinity varies between species and is not necessarily linked to yield reductions. Marcum & Murdoch (1990) demonstrated that even with a high accumulation of Na and Cl, St. Augustine grass maintained much higher tissue water levels and was deemed more salt tolerant than other grasses.

1.1.6 A comparison of sodium sulphate and sodium chloride salinity effects

1.1.6.1 Plant growth effects

Chloride is particularly effective in osmotic adjustment as it can be rapidly accumulated in high concentrations. For this reason, Cl salinity may be frequently less detrimental than sulphate salinity provided that the same osmotic potentials are compared and that the plant is not susceptible to Cl toxicity (Mengel & Kirkby, 1978). Tissue culture experiments with chinese cabbage (*Brassica campestris*) revealed Na_2SO_4 to be more than twice as inhibitory on growth as the same concentration of NaCl (Paek *et al.*, 1988). As this difference was also true as a function of Na concentration in the growth medium, excess sulphate ions appeared to exhibit a greater inhibitory effect than chloride. Manchanda *et al.* (1982) have shown, however, that certain plants are less tolerant of Cl than of SO_4 salinity, due to excessive accumulation of Cl in plant tissue.

In certain cases a high Na concentration may affect plant growth more than that of anions. Studies by Maas & Grieve (1987) and Lauter & Munns (1986) found Na shoot concentrations to be the best indicators of salt stress induced by both NaCl and Na_2SO_4 salinity. The overriding effect of Na may not, however, apply to plants that are efficient Na excluders or accumulators.

1.1.6.2 Nutrient uptake effects

Sulphate and Cl^- ions have different affects on nutrient uptake. Plants suffering SO_4 salinity may accumulate significantly more N than plants in Cl salinity due to greater Cl inhibition of NO_3 uptake. There is also evidence suggesting Cl antagonistic effects on P and K uptake (Manchanda & Sharma, 1989) while high Na concentrations may result in severe Ca deficiencies in species such as corn (*Zea mays*) (Maas & Grieve, 1987). The role of Ca in mediating salt responses in plants has been highlighted by a number of studies (Curtin *et al.*, 1993; Maas & Grieve, 1987). Calcium plays a critical role in controlling cell membrane permeability and selectivity and is thus involved in the salt economy of plants and may protect them against the deleterious effects of salinity (Curtin *et al.*, 1993). Available Ca may also be reduced in SO_4 soil solutions because of gypsum precipitation. Although gypsum has a relatively low solubility it is unlikely to cause a Ca deficiency unless the plant is an inefficient Ca absorber (Cooper, 1984). Indeed, gypsum is often used as a Ca source in soil amendment programmes (Shainberg *et al.*, 1989).

1.1.7 Irrigation management of saline waters

The three principal problems of water quality in saline irrigation practices are salinity hazard, sodicity hazard and toxicity hazard.

1.1.7.1 Sodicity

Excessive sodium in irrigation water can lead to soil dispersion and structural breakdown. Dispersion of soil can lead to serious water infiltration problems through plugging and sealing of surface pores. In sodic soils, clay sized particles will tend to disperse and reduce pore diameters through clogging (Ayers & Westcot, 1985). This effect of exchangeable sodium is, however, counteracted by soil salinity. The sodium adsorption ratio (SAR) is commonly used to evaluate the infiltration problem. Soon after irrigation, dissolution or precipitation of $CaCO_3$ or $CaSO_4$ may, however, occur which is not accounted for in the standard SAR. An adjusted SAR has been proposed which takes this error into account. A modified Ca value can be determined from a table presented by Ayers & Westcot (1985) and a new adjusted SAR value calculated. A high Na status in the soil arising from the application of sodic water is generally countered by use of a soil amendment such as gypsum (Shainberg *et al.*, 1989).

1.1.7.2 Salinity

High frequency, low volume irrigation is a recommended policy with saline water to maintain proper leaching requirements (Devitt, 1989). Such a practice minimises variation in soil water content and therefore minimises oscillations in soil salinity. Irrigating beyond evapotranspiration rate allows for a downward flux of salts from the root zone. Adequate drainage is necessary to achieve long term salinity control through these strategies (Ayers & Westcot, 1985). Furthermore, precipitation of sparingly soluble salts is an important consideration in assessing potential salinity problems, as it effectively decreases the EC of the applied water (Reichman & Trooien, 1993).

1.1.7.3 Toxicity

Salt accumulation not only poses a risk of crop damage due to osmotic stress but also a risk of toxicity. Toxicity hazard varies according to crop type and the salt type present. Leaching is a practical way to reduce and prevent accumulation of ions such as SO_4, Cl and Na to toxic levels within the root zone.

1.2 MANGANESE: SOIL REACTIONS AND PLANT RESPONSES

1.2.1 Manganese behaviour & speciation in soils

Mn is one of the most abundant elements in the lithosphere, with total concentrations in soils ranging from 10 to around 9000 mg/kg. It is an important soil constituent as it has considerable effect on soil properties, is an essential plant nutrient and controls the behaviour of several other micronutrients (Kabata-Pendias & Pendias, 1985). Mn accumulates in soil horizons enriched in Fe oxides or hydroxides and is usually concentrated in topsoils due to fixation with organic matter. Small shifts in Eh-pH conditions can greatly affect the Mn content of the soil solution due to rapid redox reactions (Schwab & Lindsay, 1983). Microbiological processes are known to catalyse many of these redox reactions (Ghiorse, 1988). Mn minerals commonly occurring in soils are presented in Table 1.1 below.

Table 1.1: Common Mn minerals in soils

Mineral	Formula	Reference
Birnessite	$(Na_{0.7}Ca_{0.3}) Mn_7O_{14}.2.8H_2O$	Gilkes & McKenzie (1988)
Vernadite	MnO_2	
Lithiophorite	$(Al,Li)Mno_2(OH)_2$	
Hollandite	$Ba_2Mn_8O_{16}$	
Todorokite	$(Na,Ca,k,Ba,Mn^{2+})_2 Mn_4O_{12}.3H_2O$	
Romanechite	$(Ba,K,Mn,Ca)_2 Mn_5O_{10}$	
Rhodochrosite	$MnCO_3$	Schwab & Lindsay (1983)

1.2.2 Manganese oxides

Mn in soils occurs largely in the form of complex oxides of Mn (III) and Mn (IV) as nodules and surface coatings in the sand and silt fractions. Mn concretions tend to accumulate Fe and several trace elements within the soil due to the high specific surface area and surface charge density. The Mn oxides possess a pH dependent surface charge with the ZPC (zero point of charge) being relatively low (eg 1.5 for birnessite). Consequently in the normal soil pH range the minerals develop a very high negative surface charge and a high cation exchange capacity (Norvell, 1988). Specific adsorption of heavy metal cations is enhanced and contributes to reduced Mn availability at pH>6. The role of Mn oxides in Mn availability is extremely important, serving as both a source of available Mn and as a sink for excess Mn (II) (Reisenauer, 1988).

1.2.3 Mn geochemistry

Soil pH and redox potential greatly influence the solubility, adsorption, desorption, and oxidation of Mn (II) and the reduction of Mn oxides (Bartlett, 1988). Solid phase $Mn_3(PO_4)_2.3H_2O$ and $MnCaCO_3$ complexes have been proposed as compounds controlling Mn solubility (Heintze, 1968; Boyle & Lindsay, 1986) below pe + pH =16. At high redox potential, Mn solubility is largely dependent on Mn oxides. Predictions of Mn levels in soil solutions from thermodynamic data (eg. Schwab & Lindsay, 1983) have, however, met with little success because of the mixed composition and metastable nature of Mn oxides, hydroxides and organic Mn complexes and variable soil Eh-pH.

The oxidation of Mn^{2+} by atmospheric oxygen is favoured thermodynamically through the pH range of soils except at very acidic pH values. The abiotic oxidation is largely a surface catalysed reaction with Mn and Fe oxides being among the most effective promoters of oxidation (Norvell, 1988).

Many mineral and organic surfaces adsorb Mn^{2+} and promote its oxidation. Soluble Mn^{2+} added to soils at common rates of fertilization (20-40 kg/ha) are commonly rapidly adsorbed and retain varying degrees of availability (Uribe *et al.*, 1988). Mn^{2+} has a relatively low adsorption specificity, however, and is often unable to compete for binding sites on humic acids or clay minerals except at high pH or in the presence of excess binding sites (Gilkes & McKenzie, 1988).

1.2.4 Manganese organic complexation

Soil organic matter plays a variable role in Mn availability through Mn humate complex formation, reduction reactions as an electron source, adsorption reactions and as a substrate for microbes (Bartlett, 1988). Generally the stabilities of Mn (II) organic complexes are too low for Mn (II) to compete successfully for organic ligands with other polyvalent metals, including the macronutrients Ca and Mg. High organic matter has, however, been reported to intensify Mn toxicity by increasing Mn availability through soluble Mn-fulvic acid complexation (Vega *et al.*, 1992).

1.2.5 Manganese bioavailability

Mn is an essential micronutrient and has a biochemical function involving enzymes controlling electron transfer in photosynthetic pathways (Houtz *et* *al.*, 1988; Nable *et al.*, 1988). Manganese differs from other micronutrients in three important ways: 1) the insoluble Mn oxides can serve along with the divalent free cation as a direct source to plants through a process known as contact reduction (Uren *et al.*, 1988); 2) the concentration of Mn^{2+} in the soil solution can vary by orders of magnitude within very short time frames; and 3) Mn may be accumulated by plants in amounts exceeding requirements by a factor of 50 or more (Reisenauer, 1988).

According to Clarkson (1988), the fractions of Mn known to contribute to available levels of the element are exchangeable Mn (exchanged on treatment with neutral salt solutions), specifically adsorbed forms, oxide-Mn and Mn precipitated with phosphate and as $MnCaCO_3$. The latter fraction includes Mn chemisorbed on calcite, present as rhodocrosite or as manganocalcite. Oxide-Mn is the principle source of available Mn in most soils, while in soils below pH 5.5 the more mobile Mn^{2+} is favoured.

1.2.6 Manganese solubility

The availability of Mn to plants depends largely on the solubility of soil Mn. Oxidising conditions may greatly reduce the bioavailability of Mn and associated micronutrients, while reducing and low pH conditions greatly increases the availability of these elements even up to toxic concentrations. Consequently acidifying N and P fertilizers can markedly increase Mn uptake (Siman *et al.*, 1971; Parker *et al.*, 1969). Solubility may also increase in the alkaline pH range due to formation of anionic complexes and complexation with organic ligands. Plant roots control Mn mobility to some extent through the release of reducing agents and exudates which complex with soluble Mn (Kabata-Pendias & Pendias, 1985).

1.2.7 Manganese uptake and accumulation in plants

Mn plant tissue content exhibits a wide variation among plant species, stage of growth, plant organs and soil types. Tissue levels generally show a negative relationship with increasing pH and a positive relationship with soil organic matter. The critical Mn deficiency level for most plants ranges from 15 to 25 mg/kg whereas the toxic concentration is more variable, with most plants being affected by a Mn concentration of 500 mg/kg. Mn tolerant species may accumulate up to 1000 mg/kg with no harmful effects (Sale *et al.*, 1992; Hannam & Ohki, 1988).

Interactions of nutrients and Mn affect both the growth of the crop and the uptake of the element of concern. Competition in the uptake of Mn by the major micronutrient cations, Zn and Fe are considered to be of major significance, while those with Cu and B are of lesser importance (Reisenauer, 1988; Goss & Carvalho, 1992). The form of N available for plant uptake exerts a strong influence on Mn uptake. Elamin & Wilcox (1986) demonstrated the effects of NO_3 and NH_4 on Mn uptake in watermelon (*Citrullus lanatus*) where NO_3 but not NH_4 nutrition induced Mn toxicity. NH_4 appears to have an antagonistic effect and NO_3 a synergistic effect on Mn uptake in watermelon.

The strong adsorption capacity of Mn oxides for metals may greatly reduce the availability of these elements to plants. Fe-Mn antagonism is particularly well documented and is observed mainly in manganiferous acid soils. Fe and Mn are interrelated in their metabolic functions and a Fe/Mn ratio range of 1.5 to 2.5 is necessary for healthy plant functioning. Fe or Mn toxicity in crops may often be alleviated by Mn or Fe applications respectively (Hiatt & Ragland, 1963). The interactions of Mn and other heavy metals are less clear. Mn has been recorded to have both antagonistic and synergistic effects on Cd and Pb uptake. Al may have an antagonistic effect on Mn uptake and have a protective effect against Mn toxicity. An Al rich soil may thus prevent the onset of Mn toxicity (Rees & Sidrak, 1961).

1.2.8 Manganese toxicity

The tolerance of a plant to Mn toxicity is dependent on two factors: the amount of Mn taken up by the plant and the ability of the plant to withstand high levels of Mn in the plant tissue (Morris & Pierre, 1949). Conditions that favour excessive Mn accumulation are as follows: high total soil Mn; soil reaction below pH 5.5; low soluble Ca in relation to Mn and low soil oxygen levels caused by poor drainage, compaction or excessive irrigation or rain (Siman *et al.*, 1974). Flooding may, however, increase the pH and therefore decrease Mn uptake thereby negating the Mn toxicity risk (Nelson, 1983; Whitehead, 1986).

Extreme climatic conditions may result in increased Mn availability. Siman *et al.* (1974) demonstrated that Mn toxicity developed in lucerne (*Medicago sativa*) under waterlogged conditions as well as during extended dry conditions. Under heat exposure the oxidation of Mn from the Mn^{2+} available form to unavailable higher oxides was restricted due to the inhibition of oxidising bacteria. The complicated interplay of environmental factors and variation in plant responses caused Horst (1988) to conclude that "a meaningful specification of a critical toxicity concentration for manganese is hardly possible".

1.2.8.1 Manganese toxicity symptoms

Mn accumulation is usually greater in older leaves than younger leaves and stems (Marsh & Peterson, 1990) and toxicity primarily affects plant shoots rather than roots (Burke *et al.*, 1990). The commonest symptom of Mn toxicity is Fe chlorosis - a result of induced Fe deficiency. Mn toxicity may also manifest itself in a form known as crinkle leaf disease, where symptoms include leaf crinkling, necrotic spots, interveinal chlorosis and malformation of pods (Foy *et al.*, 1969; Parker *et al.*, 1969; Marsh & Peterson, 1990). Severely injured plants may incur browning of roots. Diagnosis of Mn toxicity in plants is complicated by other potential toxicities (eg. Al) or deficiencies (eg. Mg, Ca or Fe) that exhibit similar symptoms. Hence, diagnosis by visual foliar symptoms alone is problematic (Hannam & Ohki, 1988).

1.2.8.2 Manganese toxicity tolerance and alleviation

Mn tolerance may operate by Mn exclusion, by tolerance of shoots to high Mn tissue content or by restriction of Mn transport to plant shoots (Burke *et al.*, 1990). Plants resistant to Mn excesses may have an ability to precipitate MnO_2, which is deposited mainly within the epidermis, or to accumulate Mn in root tissues. An increased Fe uptake has also been observed by Mn resistant plants (Loneragan, 1988).

Lime additions may be used for the remediation of Mn toxicity. Lime applications increase soil pH and lead to a marked reduction in available soil manganese (Siman *et al.*, 1971). Vega *et al.* (1992) note that liming to a soil pH of 5.8 - 6.2 is necessary to alleviate Mn toxicity, whereas Al toxicity is eliminated at pH 5.2 - 5.5.

1.2.8.3 Salinity effects on manganese tolerance

Salinity levels and salt composition of the soil solution affect Mn bioavailability. The application of $CaCO_3$ and Na_2CO_3 may prevent manganese toxicity by reducing the soil water soluble manganese content (Adams & Wear, 1957) whereas gypsum may induce manganese toxicity by increasing the water-soluble manganese of the soil (Morris, 1948). Cooper (1984) studied the tolerance of various salt marsh species to manganese under different salinity levels. Salinity had an alleviating effect on Mn toxicity for certain salt marsh species and this effect was attributed to the antagonistic effect of Na on manganese uptake. Synergistic effects of sodium on manganese uptake were recorded for other species.

1.3 MANGANESE AND SALINITY TOLERANCE IN *PENNISETUM CLANDESTINUM* (KIKUYU)

1.3.1 Manganese effects

Kikuyu is an extremely manganese tolerant grass species. Rayment & Verrall (1980) assessed kikuyu's response to variable Mn supply, lime and nitrogen applications in pot experiments with a krasnozem soil and demonstrated that kikuyu can tolerate a wide range of soil manganese, irrespective of nitrogen supply. Three soil Mn tests were undertaken (DTPA, NH_4OAc and H_2O extractions. No Mn toxicity leaf symptoms or significant reductions in kikuyu yield were recorded over the whole range of Mn tested ie. 0 to 1600 μg/g Mn as $MnCl_2$. A maximum yield occurred in pots treated with

1000 µg/g Mn. Kikuyu tops accumulated Mn up to 1537 mg/kg without any observed effects. Rayment & Verrall (1980) concluded that kikuyu growth in a krasnozem soil should not be limited by manganese toxicity at soil levels of up to 400, 600 and 220 mg/kg Mn for DTPA, NH_4OAc and H_2O extractions, respectively.

1.3.2 Pasture grass responses to salinity

There is great variation in responses to salinity among grass species and cultivars (Marcum & Murdoch, 1989; Dudeck, 1983; Francois, 1988). Experiments on St. Augustine grass by Peacock *et al.* (1993) showed that growth correlated better with solution conductivity than with leaf elemental content. This relationship suggests that the bulk of the growth reductions were largely due to osmotic effects and not a nutritional imbalance. This osmotic stress may be overcome if irrigation is frequent and consequently, yield and EC_w (applied water) may exhibit a greater correlation than EC_e (soil solution), as Devitt (1989) demonstrated in a study on Bermuda grass. Salt resistance of forage and fodder plants cannot be simply defined by their growth rates. Salt resistance in such plants must express their ability to survive under saline conditions combined with their ability to rejuvenate after exposure to multiple clippings (Malkin & Waisel, 1986).

Russell (1976) compared the salt tolerance of a number of tropical grasses and found kikuyu to be one of the most salt tolerant species. Fitting the data generated in pot experiments to a differential equation enabled the prediction of plant yield for a particular soil salinity. A zero yield at a soil salinity EC_e value of 29.4 mS/cm and half-maximum yield at 21.5 mS/cm

// dS/m

2940 mS/m

were predicted for kikuyu. These values place kikuyu in the category defined as salt tolerant species by Maas & Hoffman (1977). Rhodes grass (*Chloris gayana*) is defined as a halophytic forage grass and its growth is positively affected by low levels of salinity but inhibited by high salinity (Malkin & Waisel, 1986). Kikuyu exhibits similar salinity responses to Rhodes grass which suggests that kikuyu may be a halophyte.

CHAPTER 2

EXPERIMENT 1: KIKUYU YIELD RESPONSE TO Na_2SO_4, NaCl and $MnSO_4$.

2.1 INTRODUCTION

Kikuyu pastures near Nelspruit, eastern Transvaal, South Africa, are presently being utilised as a land disposal system for a saline waste from a pulp bleaching process. These pastures have been targeted as a potential site for the additional disposal of a manganiferous, nitrogenous effluent (MMC waste) from a manganese mining operation. Kikuyu is both salinity tolerant (Russell 1976) and manganese tolerant (Rayment & Verrall 1980) and is thus potentially a suitable grass species for the proposed co-disposal system. The dominant salt type in the pulp bleaching process is anticipated to change, due to process changes, from NaCl to Na_2SO_4. The effects of Cl versus SO_4 on plant growth are highly variable and species specific (Manchanda & Sharma 1988; Curtin *et al.* 1993). Kikuyu growth, foliar composition and soil chemical responses to the addition of NaCl, Na_2SO_4 and $MnSO_4$ were investigated in order to assess the environmental feasibility of the proposed co-disposal operation.

2.2 MATERIALS AND METHODS

2.2.1 Pot experiment

Kikuyu (*Pennisetum clandestinum*) was grown in 1 dm^3 pots (non-draining) in a phytotron unit to establish responses to various salinity and manganese treatments.

2.2.1.1 Experimental design

The individual effects of each salt and interactions between salt types were determined by a multifactorial experiment involving 24 treatments with two replications. Treatment levels were as follows:

Sodium sulphate salinity:	0, 5, 10 and 20 mS/cm
Sodium chloride salinity:	0, 5, 10 and 20 mS/cm
Manganese as $MnSO_4.H_2O$:	0, 800 and 1600 mg/kg

The sample codes for each experiment are presented in Appendix I.

2.2.1.2 Soil preparation

A clayey topsoil rich in organic matter was collected near the northern entrance to the University of Cape Town campus. The bulk soil was dried and sieved to 5mm. Basal fertilizers were applied for each experiment as follows:

Compound	Concentration
$NaH_2PO_4.H_2O$	100 mg P per kg soil
$MgSO_4.7H_2O$	31 mg Mg per kg soil
KCl	49 mg K per kg soil
NH_4NH_3	200 mg N per kg soil

The soil was thoroughly mixed to ensure uniform dispersion of the fertilizers. Soil treatments were carried out as follows:

- A pre-weighed amount of soil was added to each pot and a specific volume of treatment solution (see Table 2.1) was added to achieve the desired concentration.
- The treated soil was mixed thoroughly and a subsample of approximately 200g set aside for analysis.

Table 2.1: Soil treatments

Treatment	Solution (g/l)	Level	Volume added (ml per kg soil)
Na_2SO_4	14.2	5 mS/cm	125
	31.8	10 mS/cm	125
	33.6	20 mS/cm	250
NaCl	32	5 mS/cm	25
	70	10 mS/cm	25
	147	20 mS/cm	25
$MnSO_4.H_2O$	549	0.9 g Mn/kg	5
		1.8 g Mn/kg	10

2.2.1.3 Soil characterisation

A routine soil analysis for nutritional purposes was obtained from the Elsenburg Agricultural Development Institute as detailed in Table 2.2: below. This laboratory has a good reputation and is one of 300 members of the International Plant Analysis Scheme managed by Wageningen University. Major and minor elements were analysed by wavelength dispersive X-ray fluorescence spectrometry (XRF) in the UCT Geological Sciences Department, using a Siemens SRS 303 AS spectrometer. XRF results are presented in Appendix III.

Table 2.2: Outline of analytical procedures used in the Elsenberg laboratory

Property	Method
Acidity	K_2SO_4 extraction 0.1M NaOH titration
pH	KCl suspension; glass electrode
Resistance	Metrohm Konductermeter
Na P K Ca Mg	1% citric acid: 5g soil: 50 ml citric acid DCP analysis
Cu Zn Mn	EDTA extraction DCP analysis
B	$CaCl_2$ extraction DCP analysis

2.2.1.4 Saturated paste analysis

Extracts of saturated pastes were prepared from soil subsamples which were collected before planting. Distilled water was added to approximately 400g of soil, until the mixture showed the characteristics of a saturated paste (SSSA, 1990). The pastes were allowed to stand for 4 hours and then filtered by suction through 595 S&S filter paper.

Electrical conductivity and pH of extracts were determined by Crison micro CM 2201 and Crison micro pH 2001 instruments respectively. The extracts were stored in glass vials at 6°C for later analysis.

The extracts were subsequently filtered with an On Guard P filter and diluted by 100 or 200X to achieve an electrical conductivity of approximately 100 µS/cm for ion chromatography analysis.

Soluble cations and anions (Ca, Mg, Na, K, NH_4, Cl, SO_4 and NO_3) were analysed by a Dionex DX300 ion chromatography instrument using the eluents and columns detailed in Table 2.3 below.

Table 2.3: Ion Chromatography Analysis: Columns and Eluents

	Cations	Anions
Eluent	20mM methane sulfonic acid	1.7 mM sodium bicarbonate 1.8 mM sodium carbonate
Column	CS12 (4X250) CG12 guard column	Ionpac AS4A (4X250) AG4A guard column

Mn was analysed by Atomic Absorption Spectrometry using a Varian Spectr AA - 30 instrument. Matrix effects were checked by preparing standards with salt additions of NaCl.

2.2.1.5 Particle size analysis

A soil sample was oxidised with H_2O_2 to remove organic matter, dispersed using sodium hexametaphosphate (Calgon) and placed in a 1 litre cylinder. Clay and silt contents were determined by the pipette method (SSSA, 1990) after suitable sedimentation times.

2.2.1.6 Kikuyu preparation

Kikuyu sods of 1 dm^2 were cut from a monoculture field of kikuyu using a golf course pinhole corer. The sods were thoroughly washed to remove any soil and roots were cut to a length of 3cm. Soil was worked into the roots of each pre-weighed sod before planting.

2.2.1.7 Phytotron environmental parameters

Phytotron environmental parameters are presented in Table 2.4.

Table 2.4: Phytotron environmental parameters

Light	
Incandescent	06h00 - 08h00 17h00 - 19h00
Sodium halide	08h00 - 17h00
	08h00 - 09h00: gradual increase to full intensity
	16h00 - 17h00: gradual decrease to zero intensity
Humidity	50% mean (range: 47% - 70%)
Temperature	
28°C	9h00 - 18h00
20°C	18h00 - 9h00

2.2.1.8 Watering procedure

The saturation point of the soil was measured to be 430ml per kg soil. Field capacity was estimated at 170ml per kg soil. Pots were watered daily to field capacity, by mass.

2.2.1.9 Harvesting

The grass was harvested after 21 and 42 days growth, hereafter referred to as yields 1 & 2. The plant material was dried in an oven at 60°C for 5 days and subsequently weighed.

2.2.1.10 Plant analysis

The dried plant material was analysed for P, Ca, Mg, Na, K, Mn, Cu, Zn, Fe and B.

Plant digestion was achieved by - **dry ashing with uptake in HCl** as follows:

- Dried plant material was milled with a Falling Numbers mill to a fine consistency.
- Pre-weighed milled plant material was placed in covered porcelain crucibles and ashed in a high temperature oven at 480°C overnight.
- 5ml of 1:1 HCl was dispensed onto the pale grey ash in each crucible and allowed to equilibrate for 30 minutes in an oven at 50°C.
- 35ml of distilled H_2O was dispensed into each crucible.
- The solution was decanted into acid washed plastic bottles.
- Elements were analysed by direct current plasma optical emission spectrometry (DCP). The technique uses a direct current plasma created by initiating an electric discharge within a stream of argon gas. The solution is nebulised, the aerosol directed into the plasma and a spectrometer measures the optical emission.

2.2.1.11 Quality control of data analysis

Precision: Hidden duplicate samples were submitted with samples for analysis

Accuracy: Standard plant material samples were placed for analysis at regular intervals (every 10 samples)

2.2.2 Statistical analyses

Multiway factorial analysis of variance, two-factor analysis of variance and single factor analysis of variance were performed on Experiments 1, 2 and 3 yield and foliar data, respectively, using the statistical package Statgraphics 6.0 (Manugistics, 1993).

The ANOVAS were analysed as Model 1 ANOVAS, as all factors were fixed effects. Calculated F values were compared with critical F values to determine the level of probability. If $p<0.05$ the null hypothesis was rejected and a significant difference between levels was recorded. Least square deviations (LSD) (95% confidence interval) were recorded for ANOVA groups.

Discriminant analyses and correlation analyses were also performed on the yield and foliar data to establish variables accounting for variation between treatments and relationships between variables. Simple regression was performed on selected correlated variables.

2.2.3 MINTEQA2 speciation

An equilibrium ion speciation model (MINTEQA2) (USEPA 1991) was used for speciation of the soil solutions, calculation of activities and determination of saturation indices for various solid phases.

2.3 RESULTS

Detailed data are tabulated in appendices II, IV & VI and results are summarised in Figs. 2.1 - 2.11. The appearance of the plants is shown in Figure 2.2.

2.3.1 Yield

2.3.1.1 Salinity effect

Kikuyu yield showed a decreasing trend with an increase in salinity in yield 1 (Fig. 2.1). A significant difference between salinity levels was recorded in yield 1 ($p<0.01$). Differences recorded between yield 2 salinity levels were not significant.

2.3.1.2 Salt type effect

A significant difference between Na_2SO_4 and NaCl treatments was recorded in both yield 1 & 2 ($p<0.05$). The mean yield in the NaCl treatment block was significantly higher than the Na_2SO_4 block. Figure 2.1 illustrates the greater inhibitory effect of Na_2SO_4 salinity on kikuyu. The effect of salt type is particularly evident at high salinity (EC > 10 mS/cm), where Na_2SO_4 yields are without exception lower than NaCl yields in both yields 1 & 2.

2.3.1.3 Manganese effect

Manganese had a pronounced effect on kikuyu yield (see yield 1, Fig. 2.2). Presentation of the results is deferred to Chapter 3.

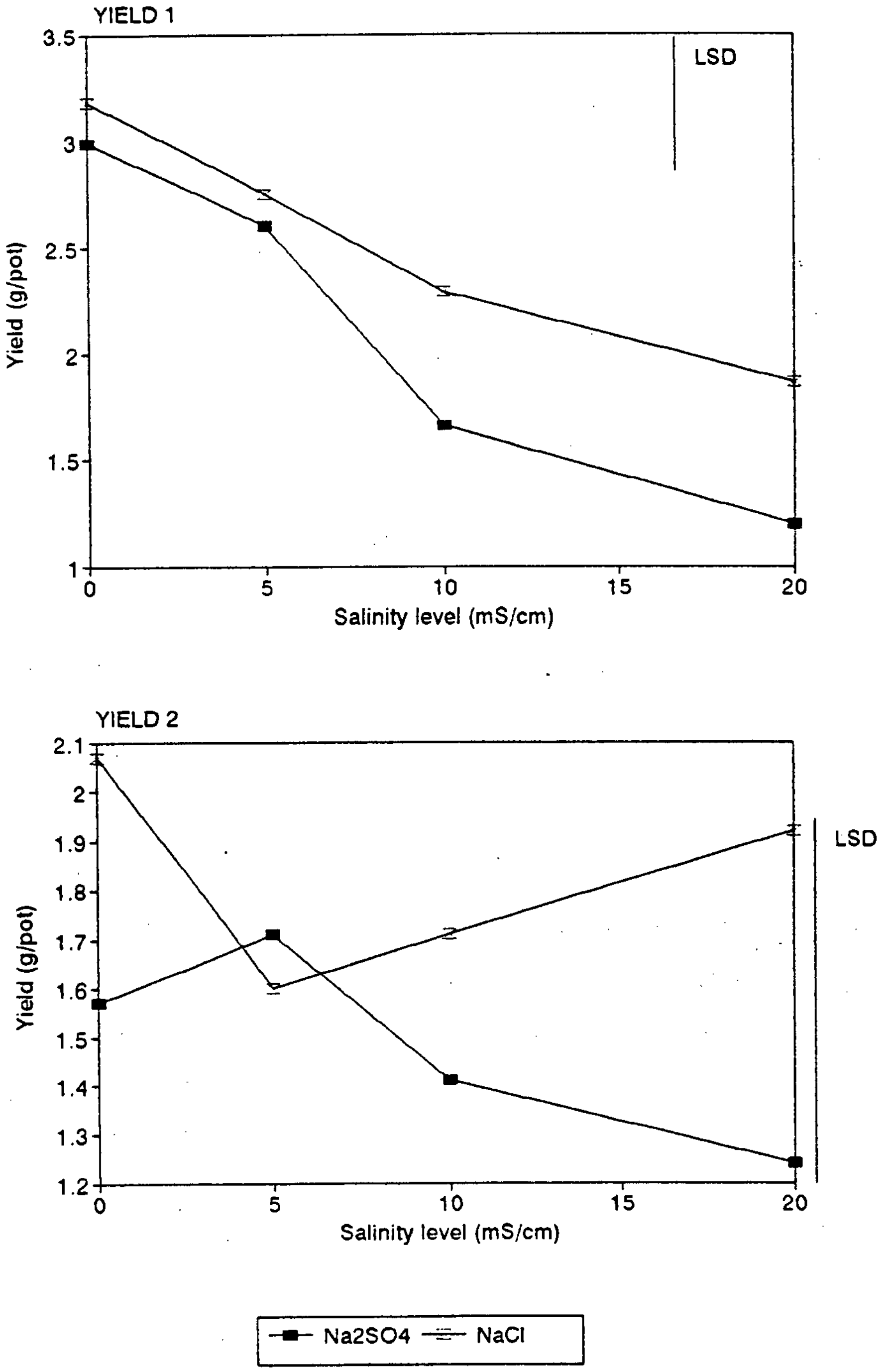


Fig. 2.1 The relationship between kikuyu yield and applied salinity of Na_2SO_4 and NaCl in yields 1 & 2 (pooled data for all Mn treatments).

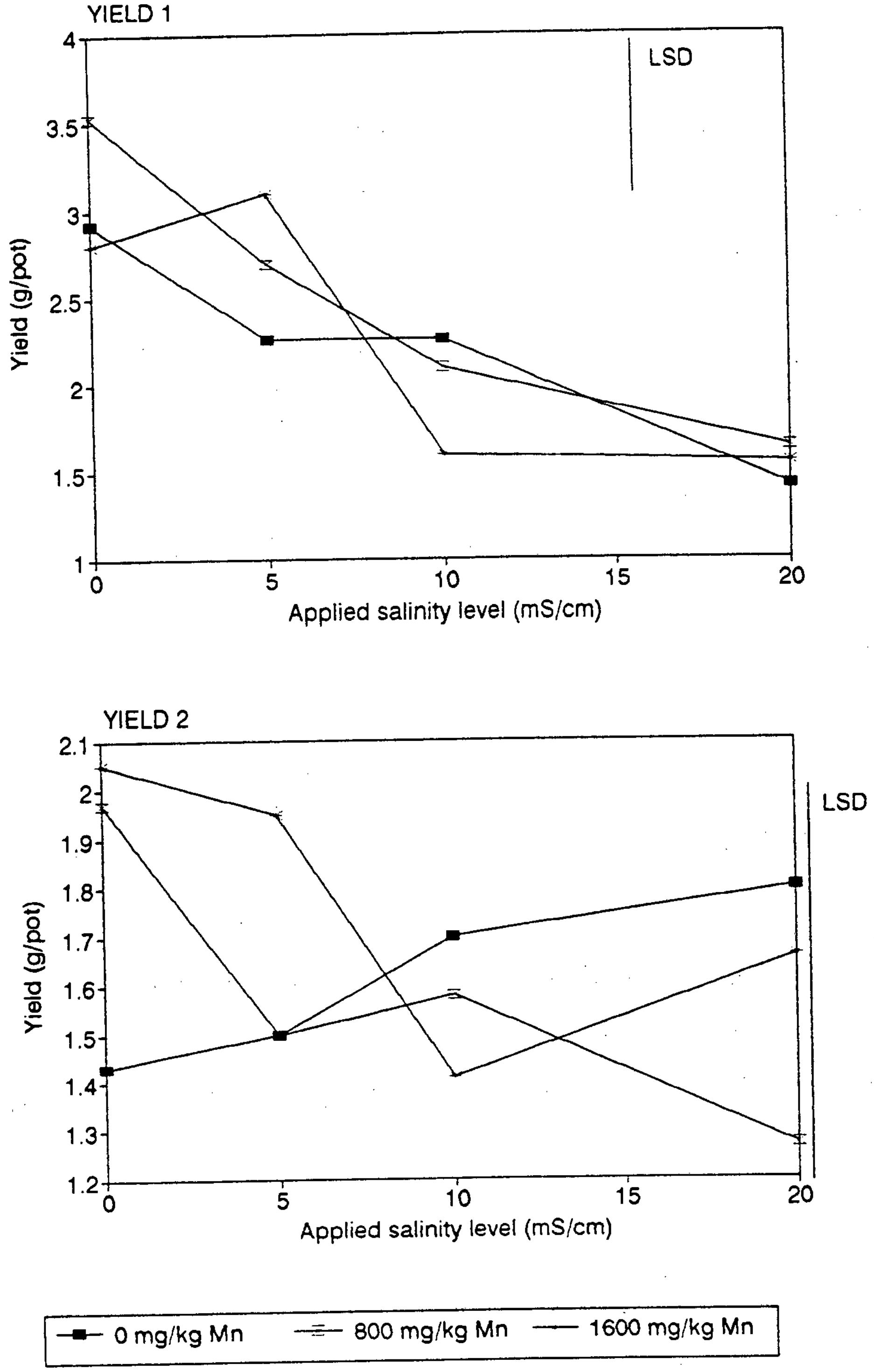


Fig. 2.2 The relationship between kikuyu yield and applied salinity (NaCl & Na_2SO_4 data pooled) at different levels of manganous sulphate in yields 1 & 2.

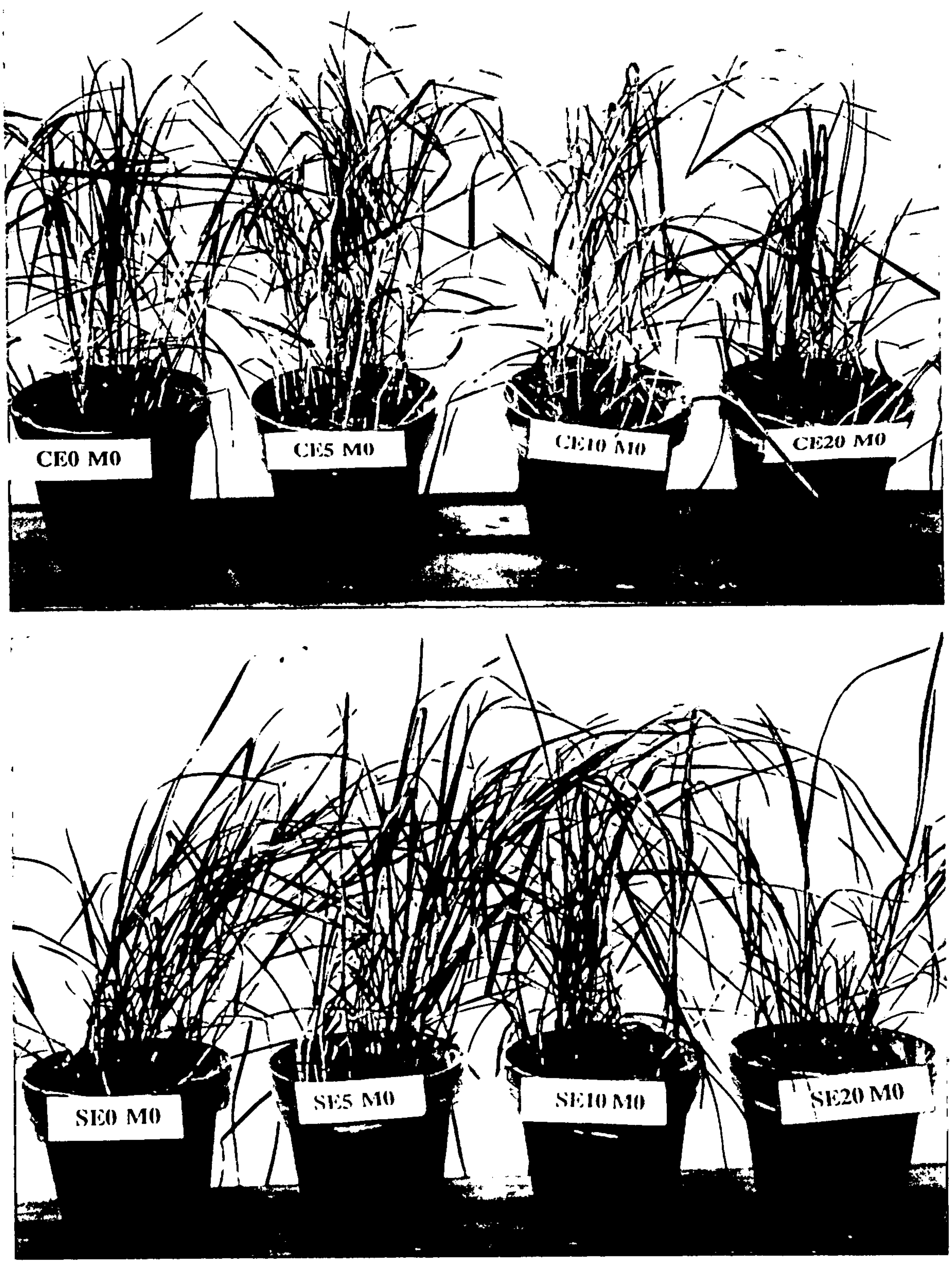


Fig. 2.3 Kikuyu response to four levels of NaCl (above) and Na_2SO_4 salinity (below).

2.3.2 Soil characterisation

Table 2.5 summarises the results obtained from Elsenburg Agricultural Development Institute and from particle size analysis.

Table 2.5: Soil characterisation

pH (KCl)	5.3
Resistance (ohms)	900
Na (mg/kg)	125
P (mg/kg)	9
K (mg/kg)	370
Ca ($cmol_c$/kg)	5.66
Mg ($cmol_c$/kg)	1.74
Cu (mg/kg)	2.42
Zn (mg/kg)	7.27
Mn (mg/kg)	31.3
B (mg/kg)	0.95
Acidity (H + Al)	0.72
Sand	33.1%
Coarse silt	12.1%
Fine silt	31.4%
Clay	23.0%
Organic matter	3.8%

2.3.3 Saturated paste analysis

The results of soil solution (saturated paste extract) analyses are presented in Figs. 2.4 - 2.7. Concentrations of Mn, Na, Cl and SO_4 ions in the soil solution increased according to the particular application of $MnSO_4$, Na_2SO_4 or NaCl. Data for C10M0 were not obtained due to laboratory error.

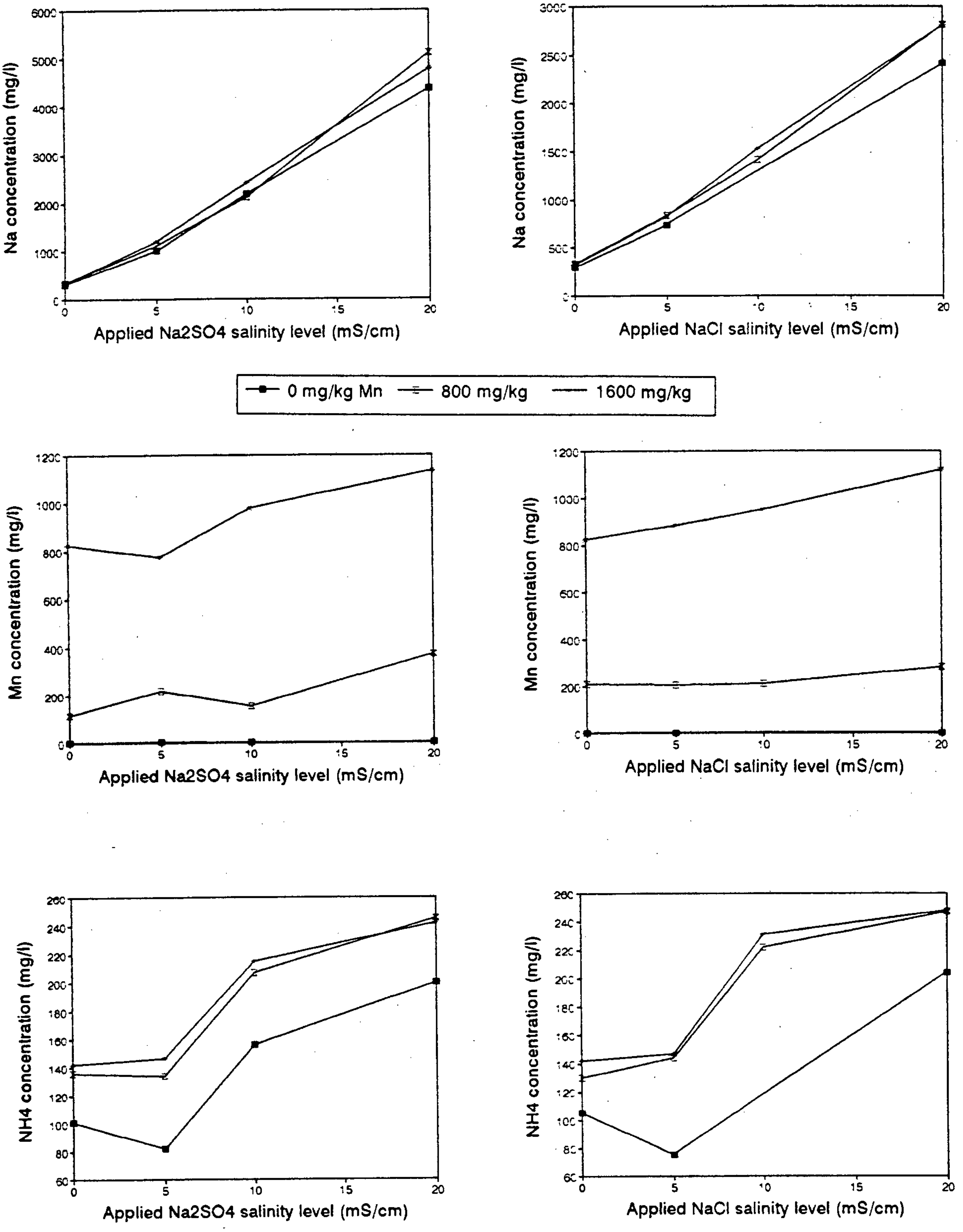


Fig. 2.4 The relationship between soil solution Na, Mn & NH_4 concentrations and Na_2SO_4/NaCl salinity at three levels of manganous sulphate.

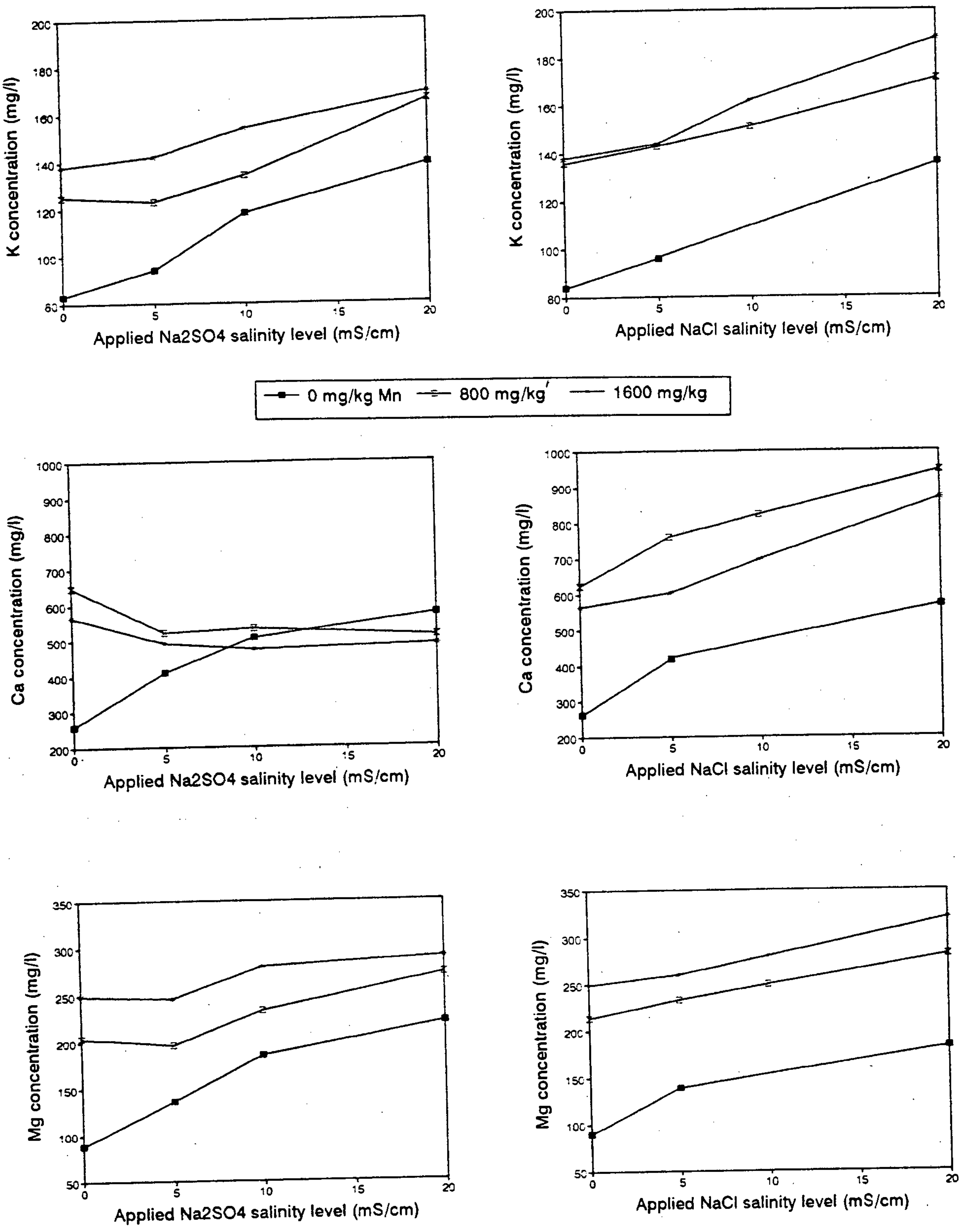


Fig. 2.5 The relationship between soil solution K, Ca & Mg concentrations and Na_2SO_4/NaCl salinity at three levels of manganous sulphate.

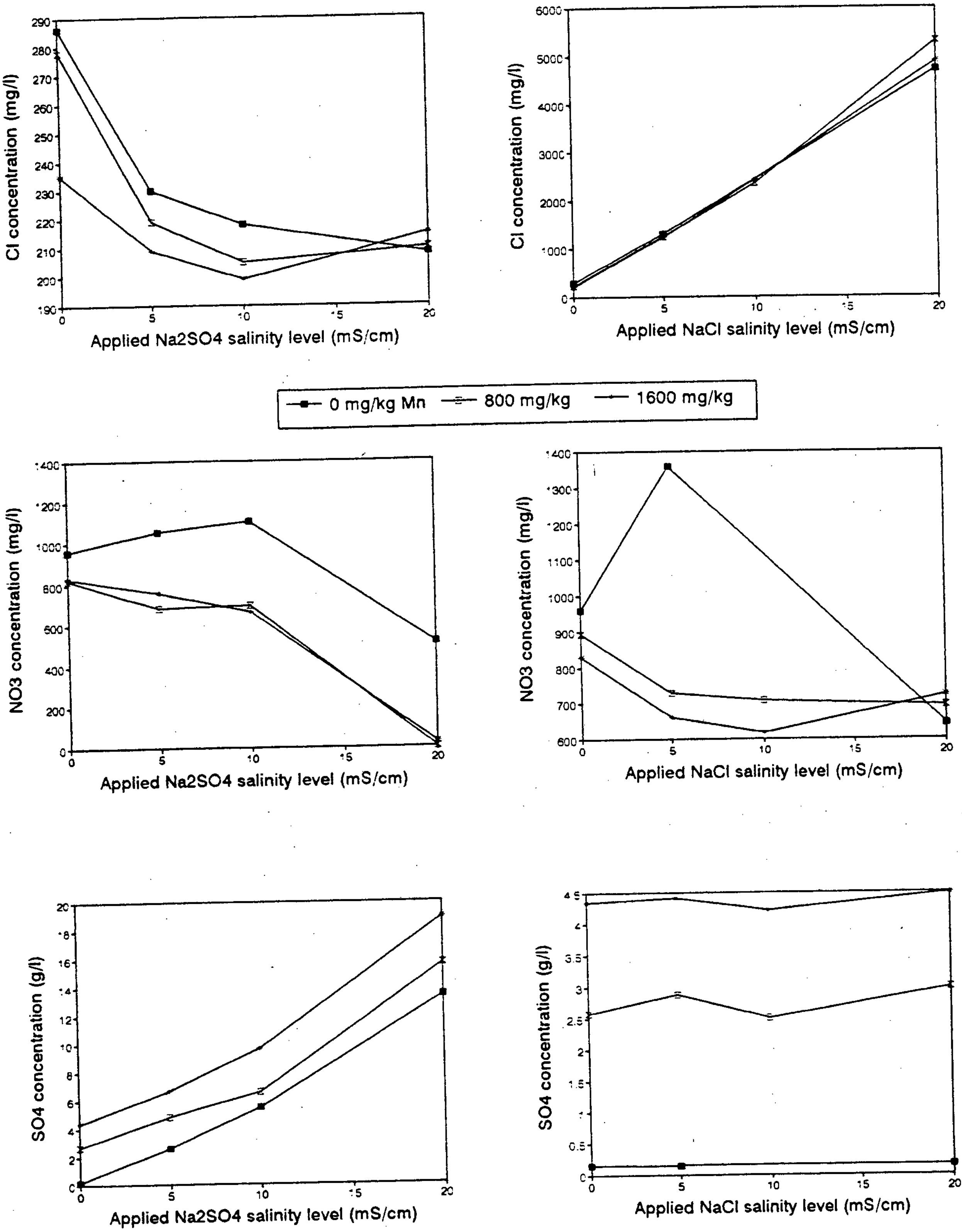


Fig. 2.6 The relationship between soil solution Cl, NO_3 & SO_4 and Na_2SO_4/NaCl salinity at three levels of manganous sulphate.

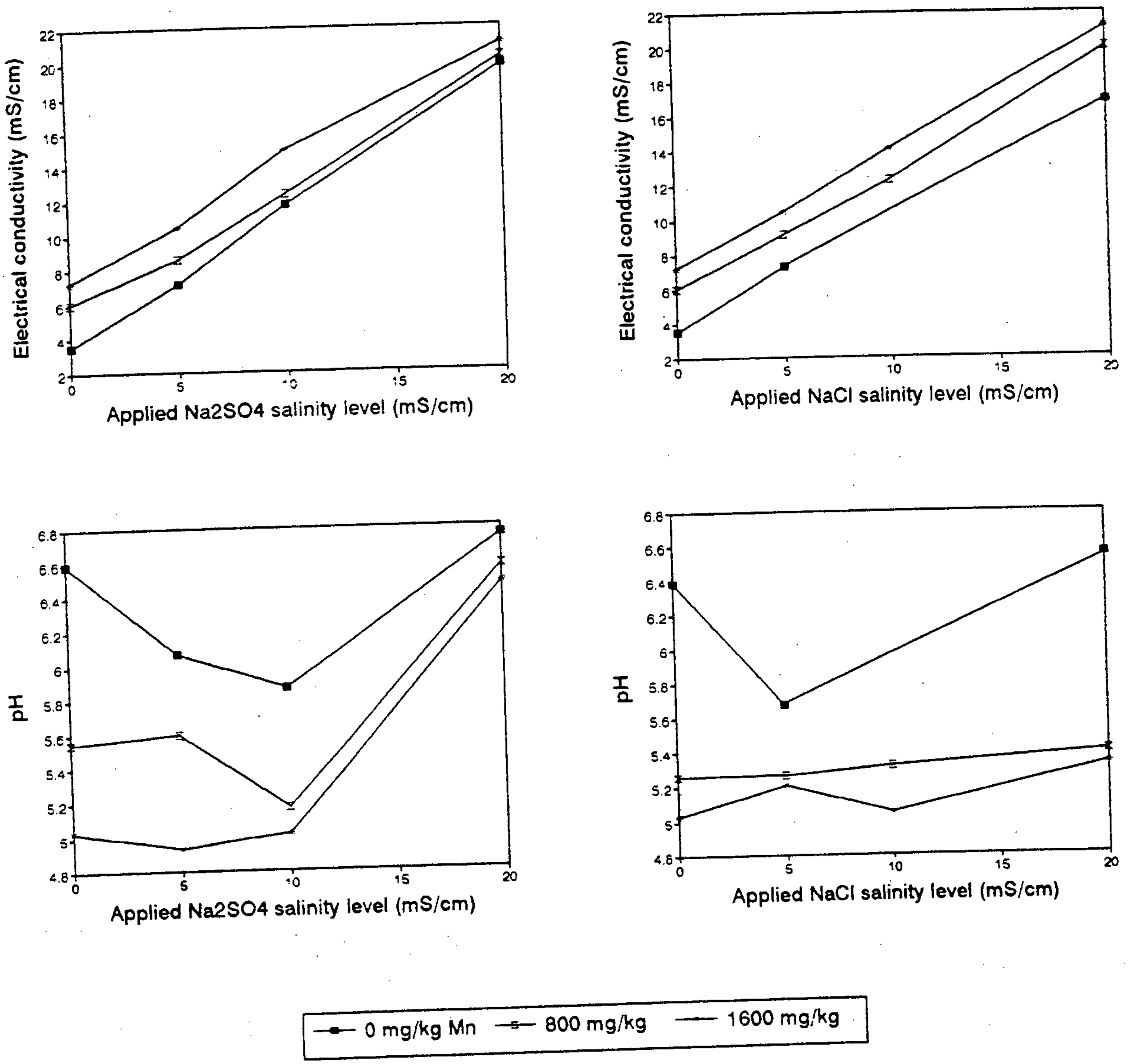


Fig. 2.7 The relationship between electrical conductivity; pH and applied salinity of NaCl and Na_2SO_4.

2.3.3.1 Salinity effect

K, Mg, Ca, NH_4 and EC increased with an increase in salinity (Figs 2.4, 2.5 & 2.7). NO_3 showed a trend of decreasing concentration with an increase in salinity (Fig. 2.6).

2.3.3.2 Salt type effect

Na and SO_4 concentrations were higher at the same salinity levels in Na_2SO_4 treated soils than NaCl treated soils (Fig. 2.4 & 2.6). Ca concentrations were markedly higher in NaCl treated soils than Na_2SO_4 treated soils (Fig. 2.5). Cl concentrations were an order of magnitude greater in NaCl treated soils than Na_2SO_4 treated soils (Fig. 2.6). Na_2SO_4 treatments and $MnSO_4$ treatments appeared to have a depressing effect on Cl in the soil solution, evident in Figure 2.6. The control (sample S0M0) Cl concentration was markedly higher than all treated soils. In addition, the lowest NO_3 concentrations occurred at the highest Na_2SO_4 salinity (Fig. 2.6)

2.3.3.3 Manganese effect

Manganese had a pronounced effect on soil solution chemical composition. Presentation and discussion of results is deferred to Chapter 3.

2.3.4 Foliar composition

Foliar analyses results are presented in Figs. 2.8 - 2.11. The Fe analyses in Experiment 1 were deemed inaccurate due to wide variation and have not been presented.

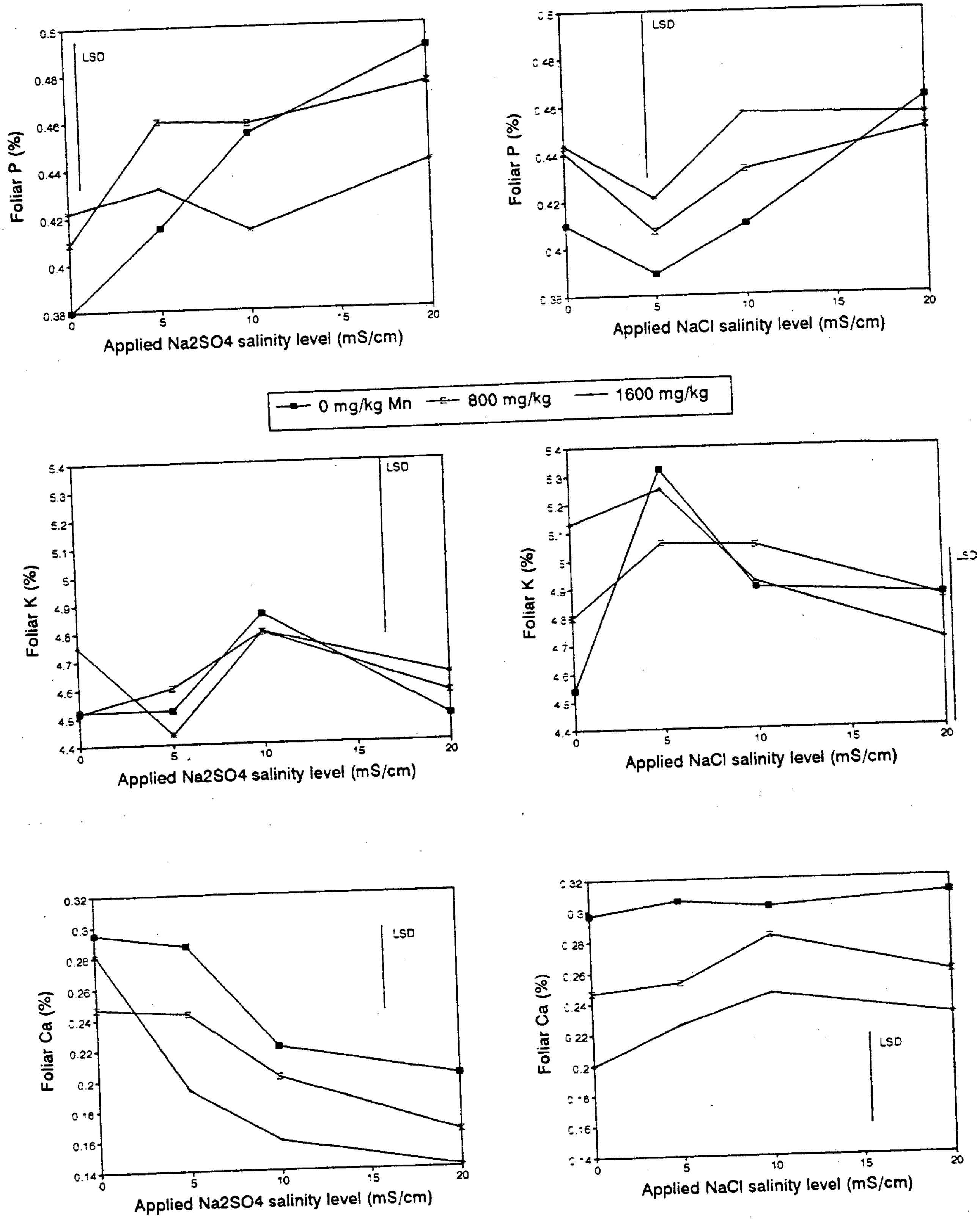


Fig. 2.8 The relationship between foliar composition and Na_2SO_4 and NaCl salinity at three levels of manganous sulphate.

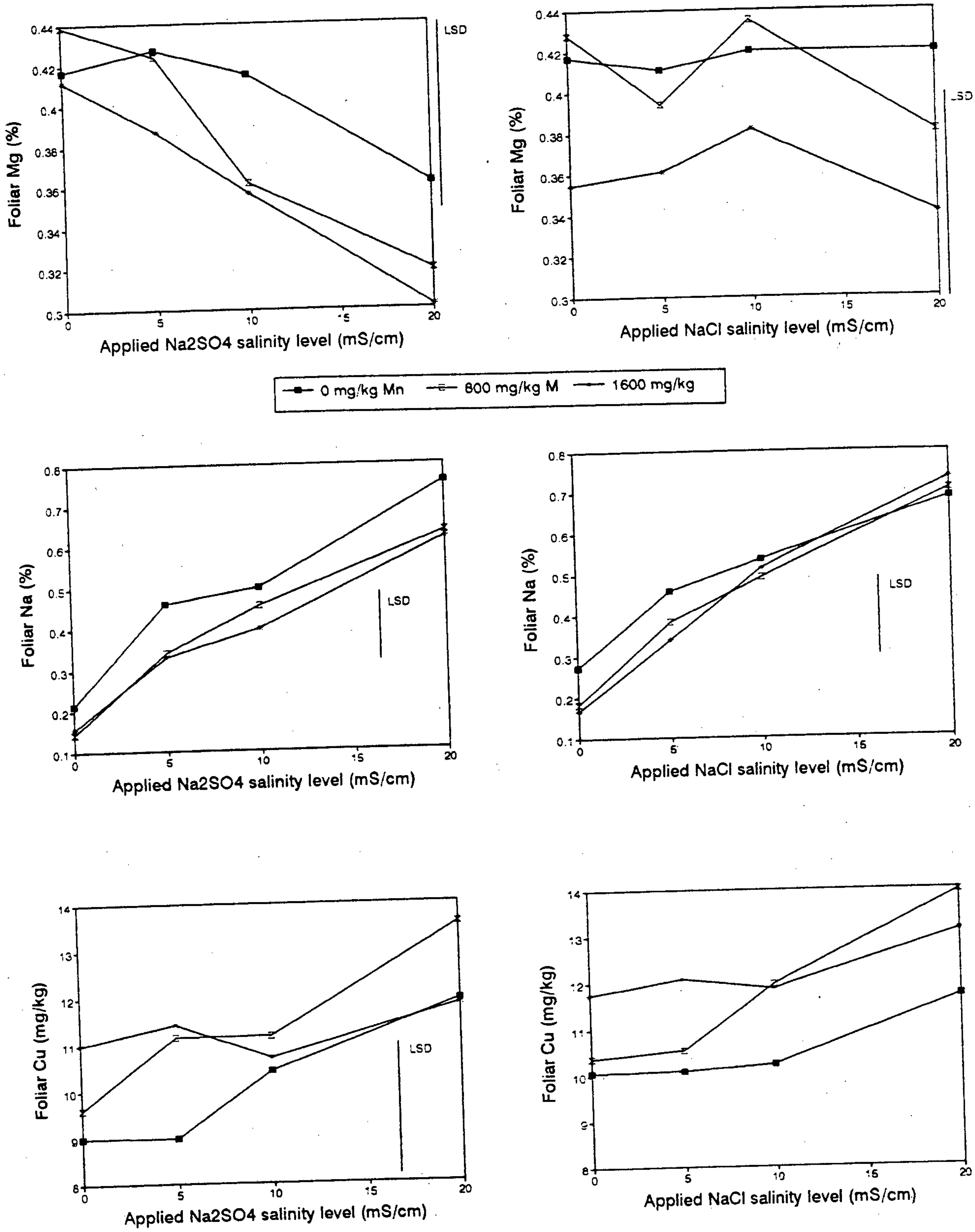


Fig. 2.9 The relationship between foliar Mg, Na & Cu and Na_2SO_4/NaCl salinity at three levels of manganous sulphate.

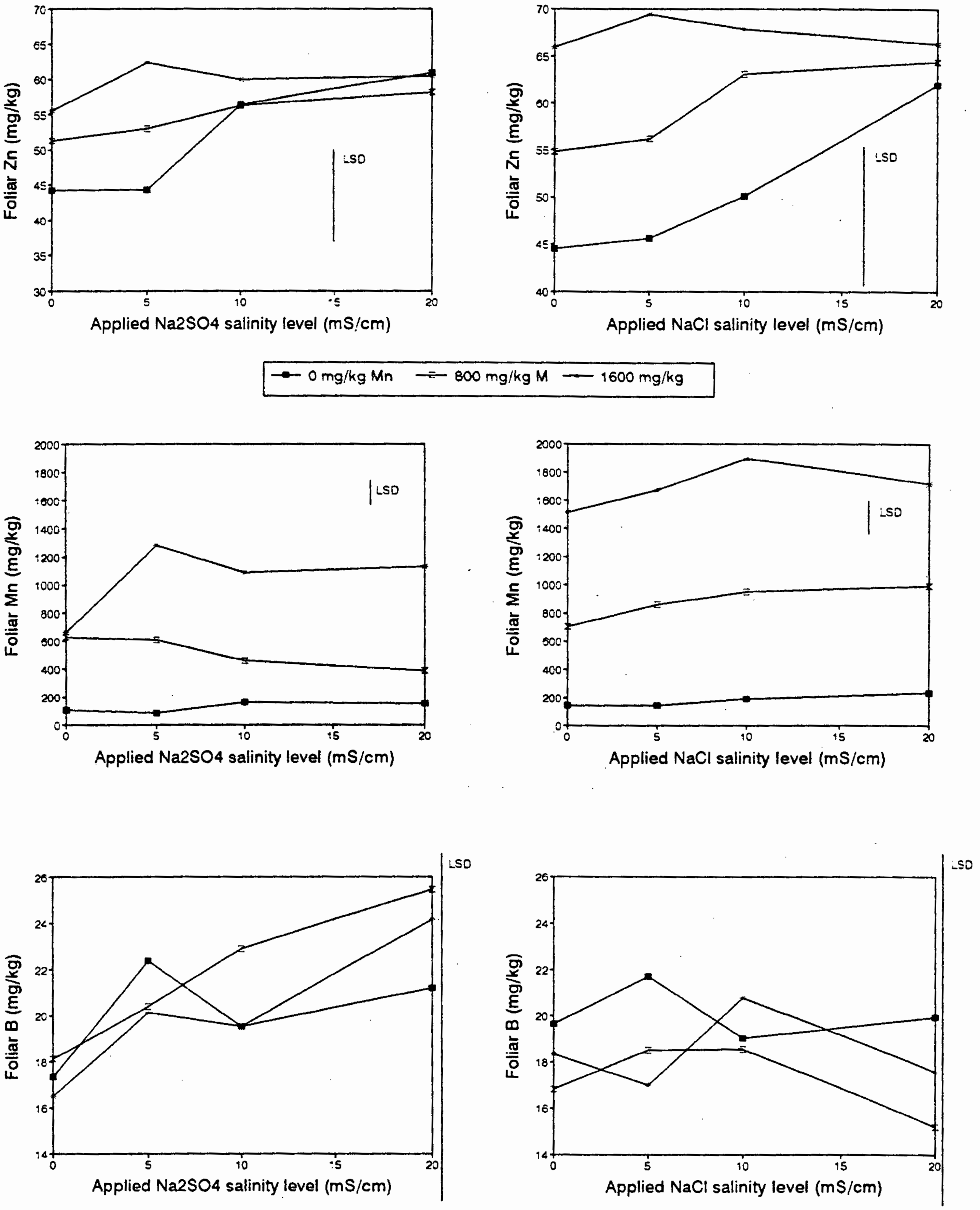


Fig. 2.10 The relationship between foliar Zn, Mn & B and Na_2SO_4/NaCl salinity at three levels of manganous sulphate.

2.3.4.1 *Salinity effects*

Foliar P, Na, Cu, Zn concentrations increased as salinity increased, with a significant difference being recorded between salinity treatments ($p<0.05$) (Figs. 2.8 - 2.10). Ca and Mg foliar concentrations decreased significantly ($p<0.05$) as salinity increased only in Na_2SO_4 treatments (Figs. 2.8 & 2.9). K increased significantly at the second salinity treatment, followed by a significant decrease at the third salinity treatment ($p<0.05$) (Fig. 2.8).

2.3.4.2 *Manganese effects*

The results of manganese effects have again been deferred for presentation and discussion in Chapter 3.

2.3.4.3 *Salt type effects*

K, Ca, Na, Cu, Zn and Mn concentrations were significantly lower in the Na_2SO_4 treatments ($p<0.05$) (Figs. 2.8 - 2.10). B concentrations were significantly lower in the NaCl treatments ($p<0.05$) (Fig. 2.10). Mean P concentrations were lower in the NaCl treatments but the differences were not significant (Fig. 2.8). Mean Mg concentrations were lower in the Na_2SO_4 treatments but the difference was not significant (Fig. 2.9).

2.3.4.4 *Discriminant analysis*

Discriminant analysis was performed on the plant data to determine the variables contributing most to variation between the various treatments.

Salinity effect

The first discriminant function accounted for 96.5% of the variation. The four variables contributing the most to the variation were as follows (highest contribution first):

Na, Mn, Mg and Ca

Salt type effect

The first discriminant function accounted for 100% of the variation. The three variables contributing the most to the variation were as follows (highest contribution first):

Ca, Mn and K

Manganese effect

The first discriminant function accounted for 98.0% of the variation. The three variables contributing the most to the variation were as follows (highest contribution first):

Mn, Na and Mg

2.3.4.5 *Foliar composition change over time*

Foliar Ca, Mg, Na, Cu and Zn concentrations were significantly higher ($p<0.05$) in yield 2 than in yield 1 (Fig. 2.11). P and B foliar concentrations were significantly lower ($p<0.05$) in yield 1.

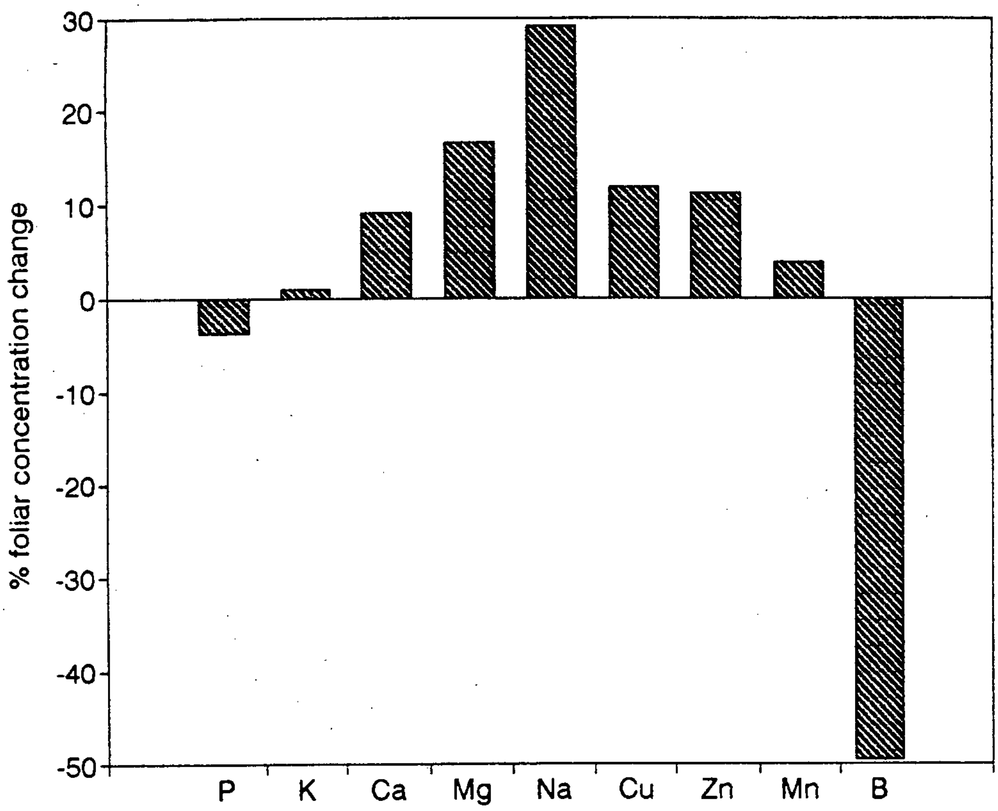


Fig. 2.11 The % foliar composition change from yield 1 to yield 2.

2.4 DISCUSSION

The linear decrease in yield with increasing salinity has been expressed in an equation developed by Maas & Hoffman (1977) as follows:

$$Y = 100 - b\ (EC_e - a)$$

where: Y = relative crop yield (percent)

EC_e = salinity of the soil saturation extract in mS/cm

a = salinity threshold value

b = yield loss per unit increase in salinity

This equation was used to categorise various agricultural crops according to their salinity tolerance. Figure 2.12, showing the Maas & Hoffman (1977) salinity categories, is overlain by kikuyu salinity tolerance equations from the following sources:

Experiment 1 Na_2SO_4 treatments: $y = 100 - 4.1\ (EC - 3.3)$

Experiment 1 NaCl treatments: $y = 100 - 2.7\ (EC - 3.4)$

Russell (1976): $y = 100 - 4.2\ (EC - 5.5)$

where y = relative yield (%). Saturation paste EC values (as opposed to applied salinity level EC) were used in the calculation of the above equations. An outlier yield value in the NaCl treatment of experiment 1 (EC = 7.3) was rejected.

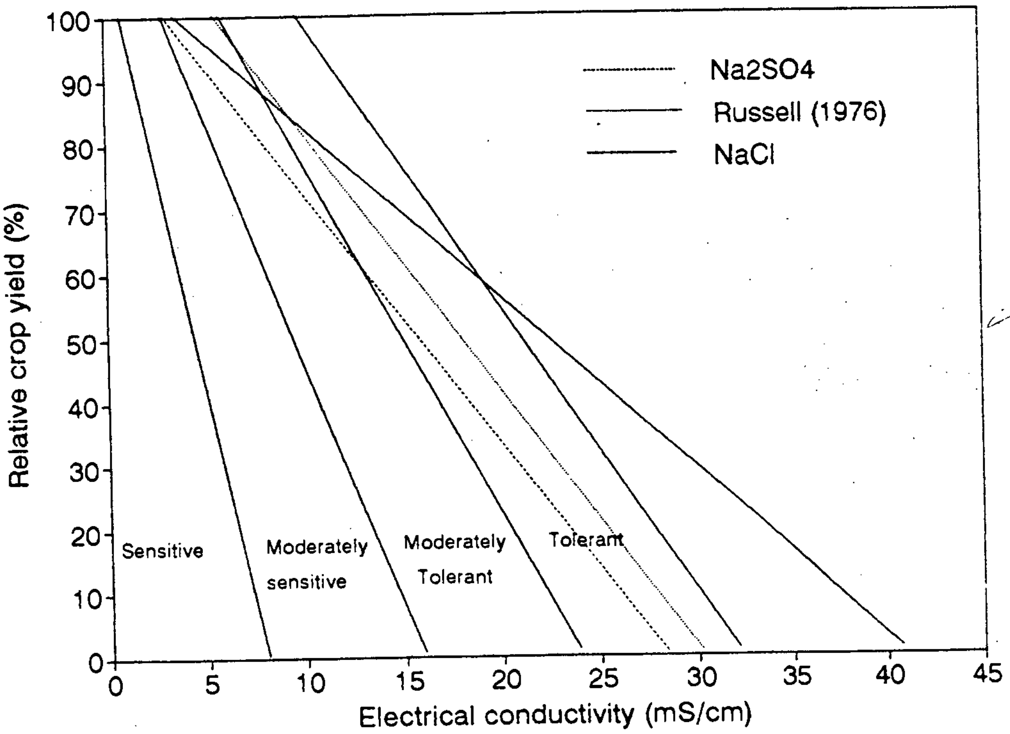


Fig. 2.12 Categories of crop salinity tolerance defined according to the relationship between relative yield and electrical conductivity of the soil solution, showing results for kikuyu (Russell, 1976, and this study) superimposed on the categories defined by Maas & Hoffman (1977).

The results from Na_2SO_4 and NaCl treatments in Experiment 1 confirm the relatively high salinity tolerance of kikuyu established by Russell (1976).

2.4.1 Soil saturation paste analyses

2.4.1.1 Sodium mass action and desorption: K, Mg, Mn and NH_4 responses

The increased concentration of K, Mg, Mn and NH_4 in the soil solution with an increase in salinity is probably due to a Na mass action competition for cation exchange sites giving rise to a desorption reaction. The moderate clay content (23%) and high organic matter content (3.8%) (Table 2.5) is indicative of a moderate cation exchange capacity (CEC). The desorption effects described may not have been as prevalent in soils with lower CEC.

Although Na is not particularly competitive in comparison to other ions such as K and Mg for exchange sites, at high concentrations it may dominate the cation exchange sites through a mass action swamping effect. The similar geochemical behaviour of K and Mg in the soil environment is evident in their significant correlation ($p<0.01$) (Appendix VII).

Mn also appears to play a role in desorption. At high salinity levels (20 mS/cm), Mn competition for cation exchange sites decreases Na adsorption, resulting in higher dissolved sodium levels in the $MnSO_4$ treated soil solutions (Fig. 2.4). The desorption effect described above probably explains an observation by Morris (1948) that gypsum can induce Mn toxicity by increasing water-soluble Mn concentrations in the soil.

2.4.1.2 $MnSO_4$ effects on K, Mg and NH_4

$MnSO_4$ appeared to induce greater desorption of K, Mg and NH_4, relative to EC, than either NaCl or Na_2SO_4. For example, treatment S20M0 had a lower K concentration (Fig. 2.5) but a higher EC value (Fig. 2.7) than treatment S10M2. This probably reflects a domination of exchange sites by Mn^{2+} in a more competitive manner than Na^+ ions.

2.4.1.3 Calcium trends and gypsum precipitation

Increased Ca concentrations with increasing salinity and $MnSO_4$ treatments (Fig. 2.5) are attributable to the same cation exchange processes described in the preceding section. Relatively decreased Ca concentrations are, however, evident at the highest $MnSO_4$ applications and the Na_2SO_4 treated soils have noticeably lower Ca levels than the NaCl treated soils (Fig.2.5). These observations can be explained by $CaSO_4$ (gypsum) precipitation. MINTEQA2 speciation calculated that 46.5% of Ca would precipitate as gypsum in sample S20M0.

2.4.1.4 Anion sorption

Decreases in Cl and NO_3 concentrations appeared to be a function of SO_4 concentration or activity (Fig. 2.13). Precipitation of an ettringite ($Ca_{12}Al_4(OH)_{24}(SO_4)_6 52H_2O$)-like mineral phase may possibly account for this apparent anion sorption. Such zeolite-like minerals may effectively "cage" anions within their structure and thus remove them from the soil solution.

Mn might well be present as a second dominant metal cation within such a mineral. The existence of such a mineral and associated Cl co-precipitation is undocumented and warrants XRD investigation.

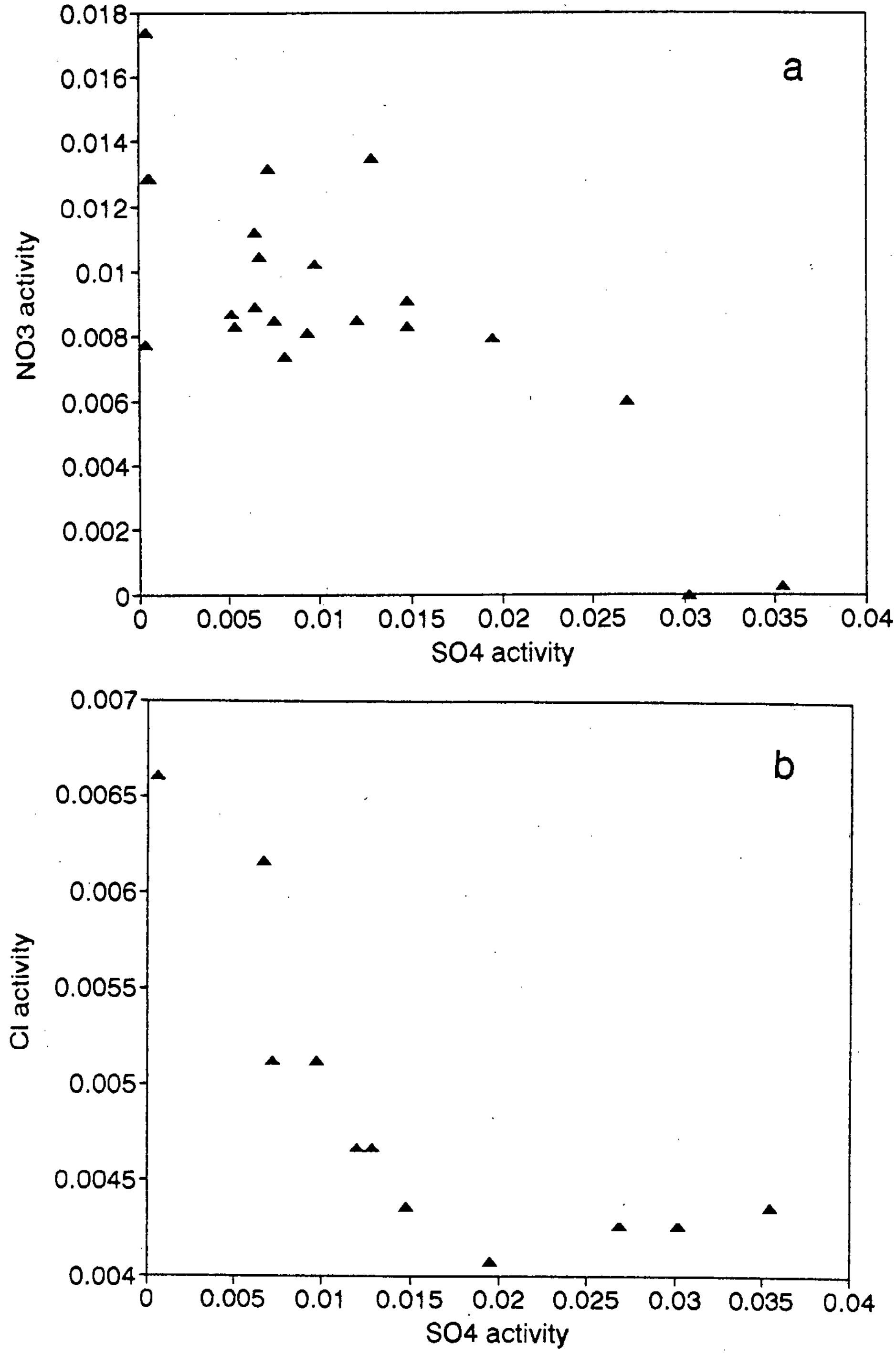


Fig. 2.13 The significantly correlated ($p<0.01$) relationships between (a) NO_3 (above) and (b) Cl (below) activity and SO_4 activity in the soil solution.

2.4.1.5 Nitrate reduction

NO_3 concentrations were generally lower in $MnSO_4$ treated soils than in soils without Mn application, in both Experiments 1 & 2 (Figs. 2.6 & 3.3). Possible reasons for this $MnSO_4$ effect are as follows:

- Addition of Mn^{2+} may decrease pe to the extent that reducing conditions more conducive to denitrification develop.
- The decreased pH of the soil solution (as a result of Mn^{2+} oxidation), evident at salinity levels 0-10 mS/cm, may inhibit nitrification (Tisdale *et al.*, 1985), thus allowing a bigger build-up of nitrate in the absence of Mn^{2+}. High salinity may have inhibited both microbial nitrification and Mn oxidation in the Na_2SO_4 20 mS/cm treatments, which would explain the anomaly of relatively high pH values and low NO_3 concentrations.

2.4.2 Foliar analyses

Mears (1970) reviewed kikuyu pasture management and compiled a table of the chemical composition of kikuyu leaves (Table 2.6). Kikuyu is recorded as having a foliar P content ranging from 0.2 to 0.42% of dry mass, while K deficiencies have been noted at levels of 0.64 to 1% (Mears, 1970).

P, K and Na foliar concentrations in Experiments 1, 2 & 3 were all higher than values in Table 2.6, which suggests that the kikuyu was not deficient in these nutrients. Ca and Mg concentrations did, however, reach lower values than those recorded in Table 2.6. The possible reasons for these deficiencies are discussed in section 2.4.2.1.

Table 2.6: Chemical composition of kikuyu leaves (% of dry matter) from various sources (adapted from Mears, 1970)

Province/ country	P	K	Ca	Mg	Na	Fertilizer applied
Natal	0.29	2.73	0.41		0.30	NPK
Natal	0.36	3.39	0.29			NPK
New South Wales	0.28	2.4	0.67	0.24	0.08	NPK
New South Wales	0.38	3.15	0.39	0.35		PK
Hawaii	0.28		0.26			NPK

The effects of micronutrients on kikuyu grass have not been studied in detail. Micronutrient concentrations of kikuyu grown in Kenya were Mn 48.5, Fe 117.0, Cu 8.0, Zn 33.8 and B 4.5 mg/kg. The micronutrient concentrations recorded in the pot experiments were generally greater than those reported from Kenya.

2.4.2.1 Salt type effects of NaCl and Na_2SO_4

Curtin *et al.* (1993) investigated Na_2SO_4 versus NaCl effects and pertinently noted that "...there are many possible interactions between salt concentration, salt type and plant nutrition." The same authors found Na_2SO_4 to be less inhibitory on growth than NaCl and concluded that, from a practical standpoint, response functions generated from NaCl salinization probably provide an acceptable measure of the tolerance of most crops to SO_4 salinity. Paek *et al.* (1988) found, however, that Na_2SO_4 was more than twice as inhibitory to growth as the same molar concentration of NaCl, while Warne *et al.* (1990) cautioned that it would be unwise to extrapolate results of Cl salinization studies to predict plant responses to SO_4 salts.

Results from Experiment 1 confirmed those of Paek *et al.* (1988) and Warne *et al.* (1990), in that kikuyu yields in SO_4 salinity treatments were significantly lower than in NaCl treatments (Fig. 2.1). The greater inhibitory effect of Na_2SO_4 on kikuyu growth was, however, only significant at the two highest salinity treatments. At the lowest salinity treatment yield reduction was similar in Na_2SO_4 and NaCl treatments.

Most plants respond to salinity as a function of the total osmotic potential of the soil solution without regard to the salt species present (Maas & Hoffman, 1977). Osmotic potential is thus the ideal measure for comparing the effects of different salt types on plant growth. This measurement was not made for the pot experiments, but can be approximated by a calculation of the total ion concentration of the solution (Fig. 2.14) since, in Na dominated systems, the salt is for the most part dissociated into its constituent ions. Yields in Na_2SO_4 treatments are noticeably lower than NaCl treatments for similar total ion concentrations (ie. osmotic potential) (Fig. 2.14). This suggests that an ion imbalance may be induced by Na_2SO_4 and which is not induced or is induced to a lesser degree in NaCl treatments.

The reason for the greater Na_2SO_4 inhibition is not, however, immediately apparent from the data and the following explanation draws on information obtained from an analysis of various aspects of the data as well as from the literature.

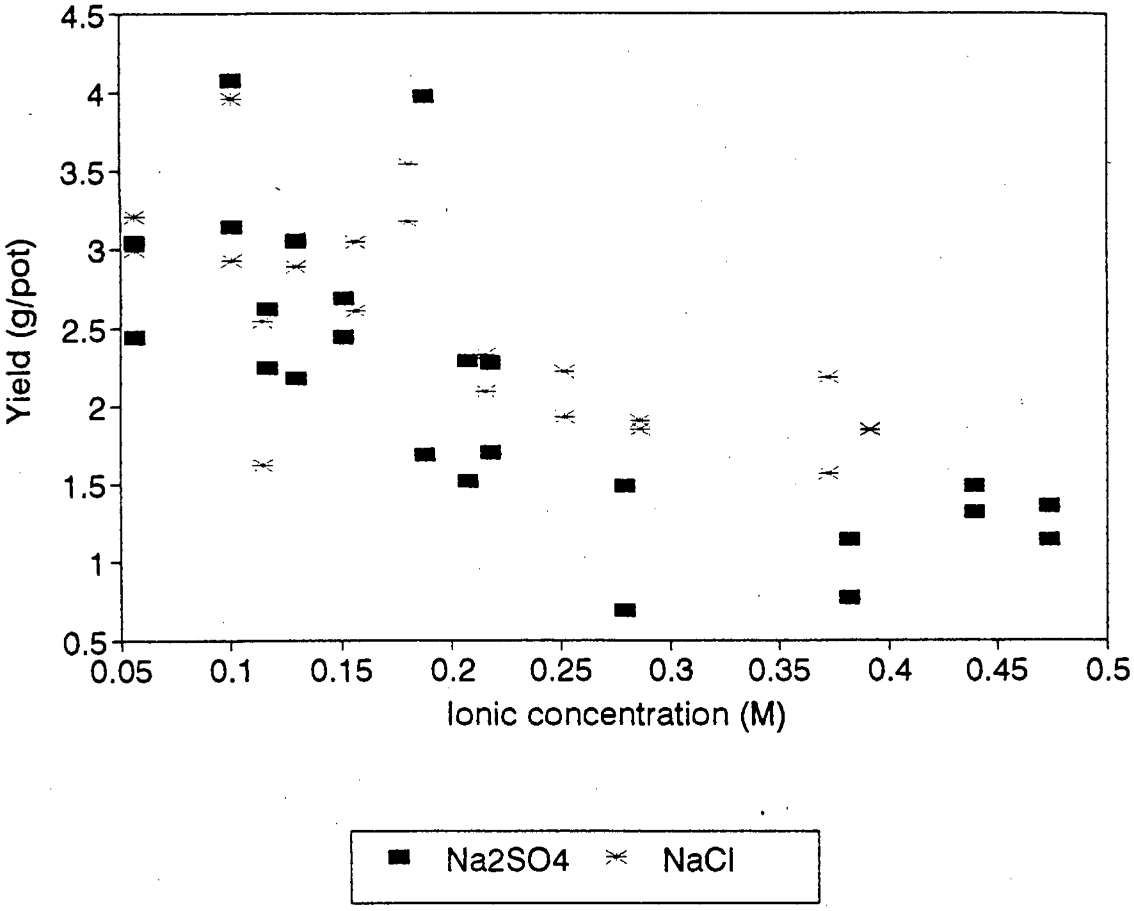


Fig. 2.14 Na_2SO_4 and NaCl effects on the relationship between kikuyu yield and total ionic concentration of the soil solution.

The apparent Na toxicity effect

Na toxicity or ion imbalances as a result of excess Na appear to be likely reasons for explaining the greater growth inhibition of Na_2SO_4 as opposed to NaCl for the following reasons:

- The Na concentrations in the soil solution of Na_2SO_4-treated soils are approximately twice those of NaCl-treated soils at the same applied salinity level (Fig. 2.4).

- Na in the soil solution and foliar Na were both negatively correlated with yield (significant at the 1% level with correlation coefficients of -0.85 and -0.68, respectively) (Appendix VII & IX; Fig. 2.15).

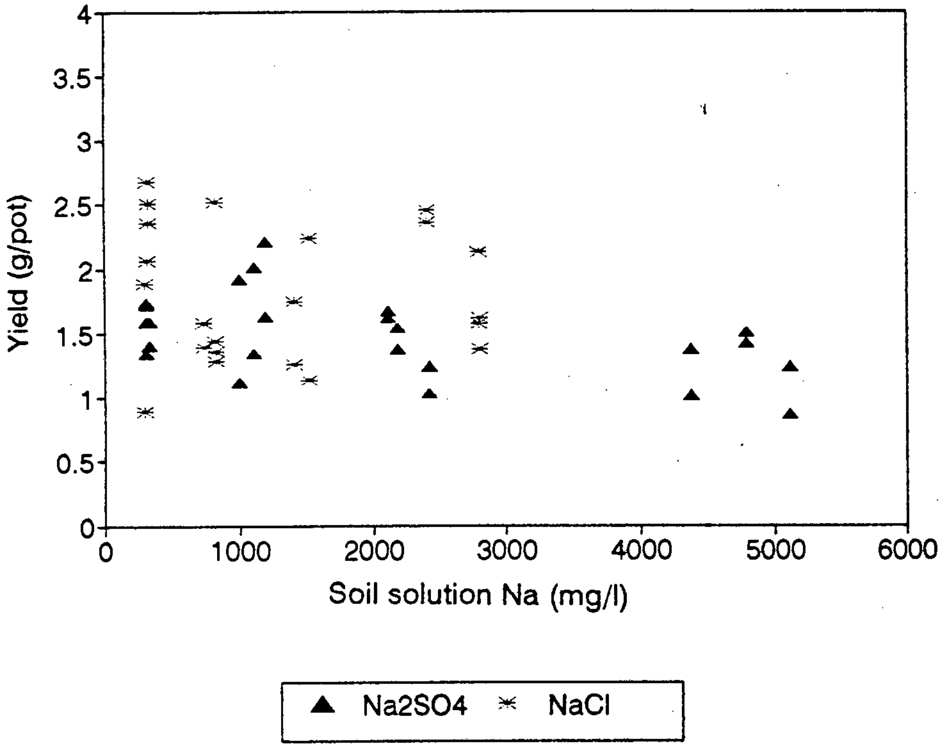


Fig. 2.15 The relationship between yield 1 and soil solution Na in response to addition of Na_2SO_4 or NaCl.

Refuting the Na toxicity effect

Na toxicity is an unlikely explanation for the differences of Na_2SO_4 and NaCl on kikuyu growth for the following reasons:

- Foliar Na was significantly lower in Na_2SO_4 treatments than in corresponding NaCl treatments ($p<0.01$) (Fig. 2.9).

- Discriminant analysis on the foliar composition data, showed that Ca, Mn and K uptake explained most of the variation between salt types.
- The negative correlation of Na with yield can be explained by an osmotic stress effect, rather than by Na toxicity. Osmotic stress and Na concentrations in the soil solution will increase as NaCl or Na_2SO_4 salinity increases. Yield may decrease due to the osmotic stress, yet yield will also be negatively correlated with Na concentrations. The correlation between Na and yield thus does not necessarily demonstrate a causal relationship.
- No visual evidence for Na toxicity such as leafburn and dead tissue along the outside edges of leaves (Ayers & Westcot, 1985) were evident in any of the treatments.
- Na excesses are not necessarily detrimental to plant growth. Eshel (1985) found that Na additions increased growth in a halophyte species (*Suaeda aegyptiaca*) by up to 900%, while transpiration and water use efficiency were shown to increase with Na salt additions.

The SO_4 factor

Sulphate in the soil solution appears to have an inhibitory effect on ion uptake and consequently the growth of kikuyu. The SO_4 factor can thus effectively explain the greater inhibitory effect of Na_2SO_4 in comparison to NaCl. The reasoning is as follows:

- SO_4 concentrations in the soil solution are approximately an order of magnitude greater in Na_2SO_4 treatments than in NaCl treatments (Fig. 2.6).

- A MINTEQA2 speciation on sample S20M0 revealed that 56% of Ca^{2+}, 53% of Mg^{2+}, 52% of Mn^{2+}, 25% of NH_4^+, 15% of K^+ and 11% of Na^+ are complexed with SO_4 as $CaSO_4^\circ$, $MgSO_4^\circ$, $MnSO_4^\circ$, $NH_4SO_4^-$, KSO_4^- and $NaSO_4^-$, respectively. It showed further that 46.5% of Ca would precipitate as gypsum ($CaSO_4$).
- It may be postulated that the SO_4 complexation lowers the bioavailability of various cationic nutrients, by reducing the activity of these ions. This is evident in the decreased trend of Mg uptake with an increase in SO_4 activity (Fig. 2.16).

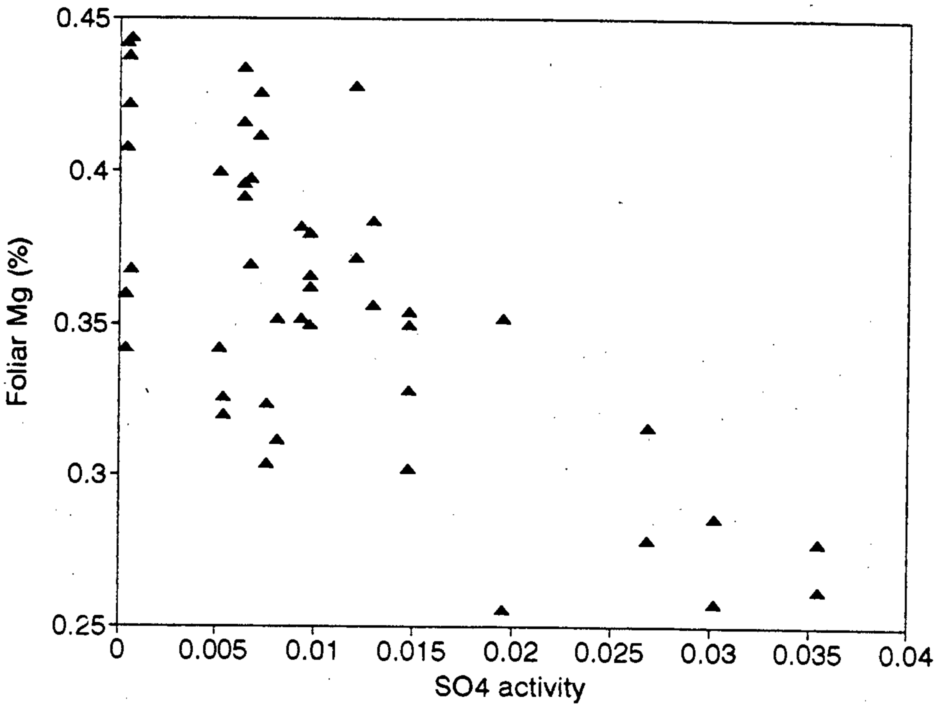


Fig. 2.16 The significantly correlated (p<0.01) relationship between foliar Mg accumulation and SO_4 activity in the soil solution.

- Sposito (1985) notes that nutrient uptake is often more closely related to the activity of the free, uncomplexed ion in solution than it is to the total concentration of the particular nutrient. The larger, uncharged or less charged ion pair is presumably absorbed less easily or not at all by plant roots. The uncharged or less charged nature of the complexed ions may prevent active root uptake often associated with the corresponding free cations. This is evident in the significantly lower accumulation of Ca, K, Na, Cu, Zn and Mn in Na_2SO_4 treatments. Magnesium also shows a trend of decreased uptake in Na_2SO_4 treatments, although the difference was not significant.

* Reduced uptake of Ca and K may have especially deleterious effects on salt stressed plants. Ca is an essential component of cell membranes and has been linked to maintenance of salinity tolerance (Hansen & Munns, 1988).

* K plays an important role in osmotic adjustment (Peacock *et al.*, 1993). Na_2SO_4 salinity may inhibit adequate accumulation of K in kikuyu and consequently reduces its salinity tolerance.

The role of Ca in salinity tolerance

Calcium is a structural component of the plasmalemma, playing a critical role in controlling cell membrane permeability and selectivity. It is thus involved in the salt economy of plants and may protect them against the deleterious effects of salinity (Hansen & Munns, 1988; Curtin *et al.*, 1993; Maas & Grieve, 1987; Suhayda *et al.*, 1992).

The literature reveals some debate on SO_4 effects on Ca uptake. Manchanda & Sharma (1989) showed that Ca tissue content in chickpea (*Cicer arietinum*) decreased considerably in SO_4 but not Cl-salinized soil. Yet, Curtin *et al.* (1993) remarked that salinity induced Ca deficiency is relatively uncommon, being limited to plants that are inefficient Ca absorbers. Janzen & Chang (1987) attributed Ca deficiencies induced by salinity stress in barley (*Hordeum vulgare*) to reduced activity of Ca in the soil solution due to precipitation with sulphate and high ionic strength. Gypsum precipitation in soils following irrigation with water high in sulphates has been considered beneficial because it minimises accumulation of SO_4 and Ca above the solubility of gypsum (Papadopoulos, 1986). The common ion effect, however, dictates that high SO_4 concentration will drive the reaction:

$CaSO_4 \rightarrow Ca^{2+}$ (aq) + SO_4 (aq) to the left, with a consequent decrease in Ca availability, as was evident in the soil solution data (see Figs 2.17 & 2.18).

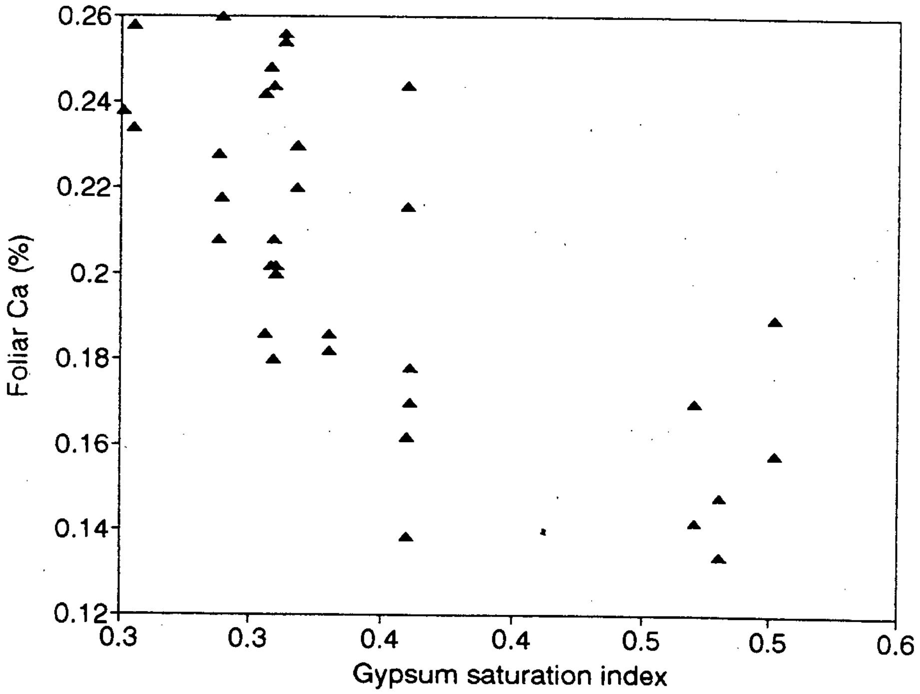


Fig. 2.17 **The significantly correlated ($p<0.01$) relationship between Ca foliar accumulation and the gypsum saturation index of the soil solution.**

Janzen & Chang (1987) do not, however, consider the effects of SO_4 neutral ion pair formation between nutrient cations and SO_4. This complexation may reduce the uptake of Ca and other nutrient cations, as is evident in Figs. 2.18 & 2.19. MINTEQA2 speciation calculations revealed that the divalent ions are complexed to a greater degree than monovalent ions, probably due to their greater charge affinity with the SO_4 anion.

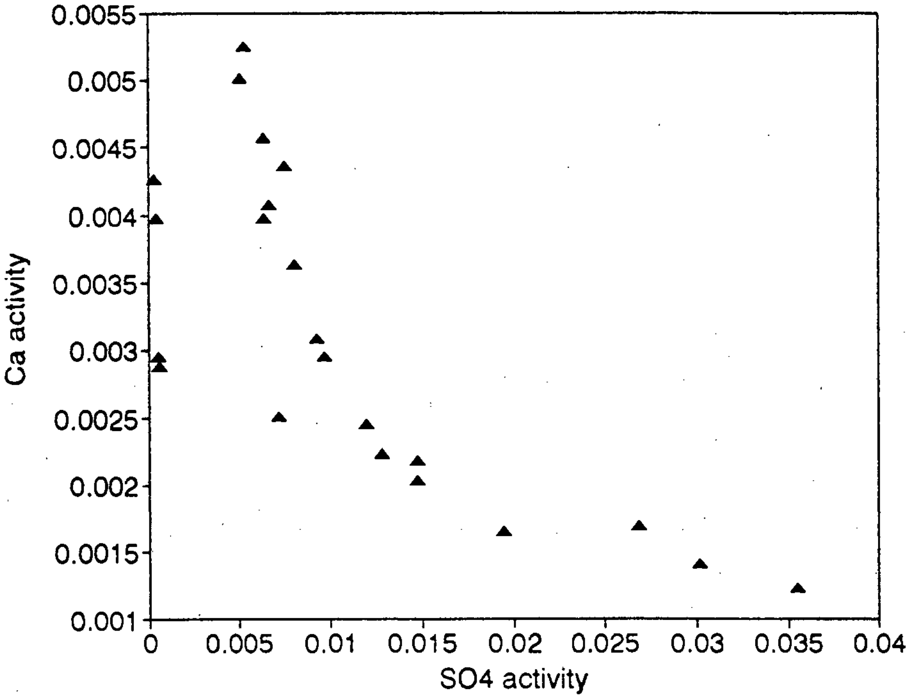


Fig. 2.18 The relationship between Ca activity and SO_4 activity in the soil solution.

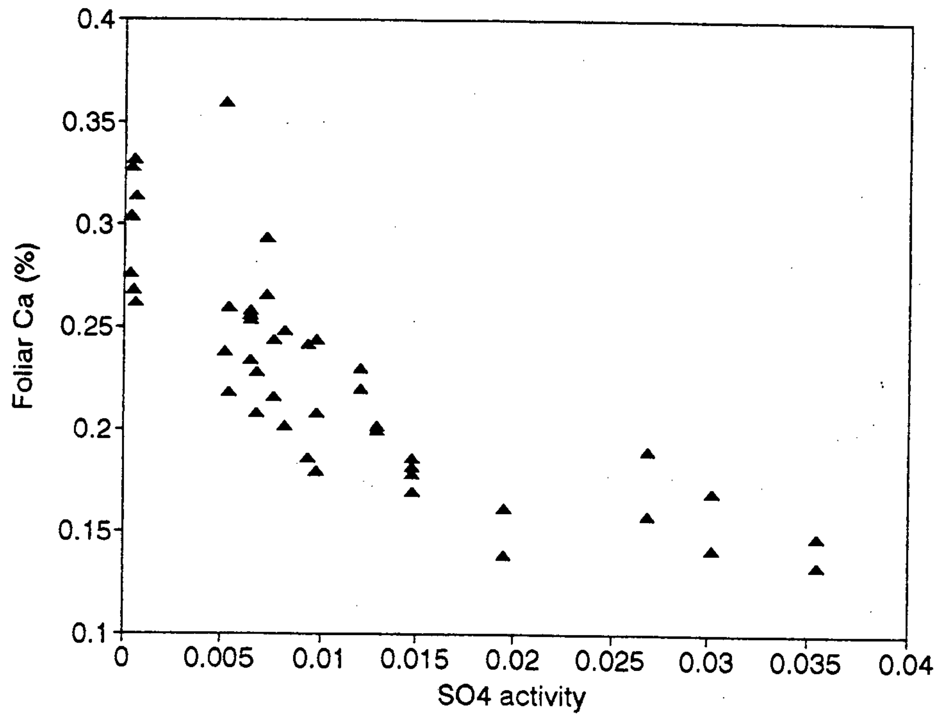


Fig. 2.19 The relationship between foliar Ca accumulation and SO_4 activity in the soil solution.

Na_2SO_4 induced nutrient deficiencies

The significantly lower accumulation of foliar Ca, K, Na, Cu, Zn and Mn in Na_2SO_4 treatments relative to those with NaCl (Figs. 2.8 - 2.10) suggests possible deficiencies of these nutrients. A SO_4-induced Ca deficiency in particular, appears to be evident in the kikuyu for the following reasons:

* Foliar Ca was significantly ($p<0.01$) and negatively correlated with soil solution SO_4 activity (Appendix XI).

- The mean Ca tissue concentration at the highest Na_2SO_4 salinity treatment was lower than Ca concentrations documented in the literature.

Altered nutrient sufficiency thresholds under saline conditions

Plant nutrient requirements are not fixed and are likely to change according to the conditions to which the plant is exposed. Under high salinity, kikuyu's nutrient requirements may be higher. Possible explanations for this are firstly, that additional Ca may be required for cell membrane selectivity functions and secondly, that K and Cl may be required in large quantities for osmotic adjustment. Na_2SO_4 salinity may thus lead to a relative nutrient deficiency given the enhanced nutrient requirements under saline conditions.

Osmotic stress in SO_4-dominated solutions

The use of electrical conductivity as an index of salinity stress to compare Na_2SO_4 and NaCl salinity effects is inaccurate. The neutral ion pairs that form in a SO_4 solution contribute to osmotic potential and thus osmotic stress to the plant. Yet these ion pairs do not contribute to measured EC. This is evident in Figure 2.20, which shows lower EC values in Na_2SO_4 treatments than NaCl treatments at the same equivalent ($mmol_c$) concentration. (The equivalent concentrations were calculated from 100 or 200X diluted solutions, where ion complexation is expected to be negligible.)

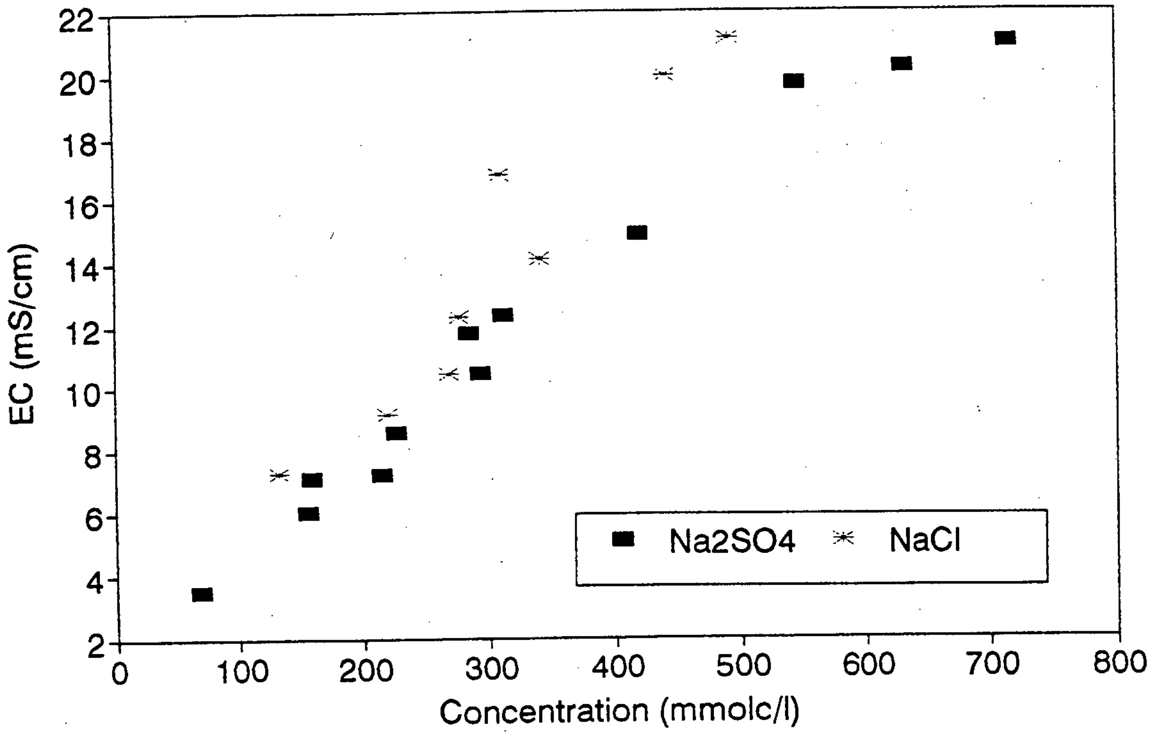


Fig. 2.20 The relationship between electrical conductivity of the soil solution and the equivalent concentrations of Na_2SO_4 and NaCl.

The lower kikuyu yield in response to SO_4 treatments compared with Cl treatments at the same EC levels, may thus be a function of higher osmotic stress in Na_2SO_4 treatments than in NaCl treatments. Thus higher EC levels are needed in Cl dominated solutions than in SO_4 dominated ones to induce an equivalent osmotic stress.

The chloride contribution

The anion in NaCl salinity is also a likely role player in the greater tolerance of kikuyu to NaCl salinity. Cl analyses were not performed on the plant material. Yet it is relatively safe to assume that some degree of Cl accumulation did occur, as reported in other studies on grass salinity tolerance (Dudeck *et al.*, 1983). Cl is reputedly a very effective ion for osmotic adjustment (Peacock *et al.*, 1993) and kikuyu is in all likelihood exploiting the raised Cl concentrations in NaCl treatments for this purpose. The lower tolerance of kikuyu for Na_2SO_4 salinity in comparison to NaCl salinity can thus be effectively explained by an anion "double blow" effect of:

SO_4 ions reducing the uptake of cations for osmotic adjustment, the uptake of Ca for membrane selectivity functioning and increasing osmotic stress relative to EC, while chloride ions increase the potential for osmotic adjustment.

In addition, nutrient uptake may depend to some extent on cation/anion balance, and if Cl is taken up more easily (or conversely SO_4 is excluded more readily) by the plant, then cations may be taken up in correspondingly different concentrations.

2.4.2.2 Salinity effects

Osmotic stress or ion imbalance?

Kikuyu can be categorised as a salt tolerant species according to Figure 2.12. This tolerance is either due to effective ion exclusion mechanisms or osmotic adjustment (Peacock *et al.*, 1993). It may be speculated that SO_4 exclusion in kikuyu takes place in SO_4 systems. An apparent exclusion may, however, be a function of reduced uptake due to ion pairing as discussed in section 2.4.2.1. The high accumulation of Na in kikuyu at high salinity of up to 7000 mg/kg suggests that osmotic adjustment is the most likely mechanism for salinity tolerance. Electroneutrality principles dictate that this cation uptake will be accompanied by an anion, whether Cl or SO_4.

Discriminant analysis showed that Na, Mn, Ca and Mg plant tissue concentrations accounted for most of the variability between salinity treatments. Foliar Na showed the greatest increase with salinity and thus raises a question of Na toxicity. Na toxicity was, however, deemed unlikely in section 2.4.2.1.

The proviso for effective osmotic adjustment is that none of the accumulated ions lead to severe ion imbalances or toxicities. Other than a reduction in growth, kikuyu did not exhibit any toxicity symptoms at high salinity. Salinity stress in kikuyu thus appears to be a function of nutrient deficiency (in SO_4 systems) and osmotic stress.

It may be argued by proponents of toxicity induced yield reduction that the salinity induced osmotic stress did not at any stage result in wilting - a characteristic symptom of severe osmotic stress (Ayers & Westcot, 1985). Wilting is, however, usually due to fluctuating water supply. The osmotic stress imposed by the salinity was a constant stress and thus the plant adjusted accordingly by slowing the growth rate to a level which the water supply could support.

Salinity effects on foliar composition

Ion concentrations in plant tissues vary in response to salinity from one species to another. Given the wide range of salinity tolerance and tolerance mechanisms this is not surprising. For example, Remison *et al.* (1988) noted a decrease in K with salinity in coconut while studies on Bermuda grass (*Cynodon dactylon*) have resulted in increases of K with increasing salinity (Peacock *et al.*, 1993).

The sum of all cations in kikuyu leaf tissue in Experiment 1 showed a significant increase with salinity. Garcia & Charbaji (1993) found the same trend in NaCl stressed grapevine.

Na, Mn, Zn, Cu, P and B foliar concentrations in Experiment 1 all showed significant increases with an increase in salinity (Figs. 2.8 - 2.10). The increased Na uptake is attributable to increased applications of NaCl and Na_2SO_4. The increased uptake of the other ions can be explained by soil desorption processes, synergistic ion effects or osmotic adjustment ion accumulation and are probably due to a combination of all three in some cases.

Soil desorption processes

These may involve the release of ions from exchange sites by the swamping mass action effect of the salinity inducing cation or anion. This results in a higher bioavailability of the released ion.

Synergistic ion effects

Cooper (1984) reported that Na may have a synergistic effect on the uptake of Mn. Mn was not significantly correlated with Na in Experiment 1, yet the correlation is confounded by effects of $MnSO_4$ application and is thus not an accurate portrayal of Na effects on Mn uptake.

Osmotic adjustment ion accumulation

Osmotic adjustment relies on the accumulation of ions in plant tissue so that the osmotic potential of the root tissue exceeds that of the soil solution. It is not clear whether kikuyu selects specific ions for accumulation or is non specific and accumulates any ions that are bioavailable. The latter appears more likely, given the number of ions that increase significantly with salinity.

Phosphate accumulation

P results in Experiment 1 (Fig. 2.8) were consistent with results obtained by Manson (1995). Manson (1995) observed an increase in P uptake with increasing salinity in Italian ryegrass (*Lolium multiflorum*) and suggested that P uptake was enhanced by Na through increased soil phosphate solubility.

P foliar concentrations were positively correlated with Na in the soil solution of Experiment 1 ($p<0.01$) which appears to confirm this relationship (Appendix X). The Na-induced enhanced P uptake would explain the higher P concentrations in Na_2SO_4 treatments in comparison to NaCl treatments, due to the relatively higher soil Na concentrations in Na_2SO_4 treatments.

An alternative explanation for enhanced P uptake may be found in soil desorption processes eg. Cl and SO_4 displacement of PO_4 from anion exchange sites. A greater displacement effect of SO_4 in comparison to Cl, would explain the higher P concentrations in Na_2SO_4 treatments (Fig. 2.8).

In addition, the lower P accumulation in NaCl treatments may be a function of Cl inhibition of PO_4 uptake as noted by Manchanda *et al.* (1982). Reduced P uptake with salinity has reportedly even resulted in severe P deficiencies (Peacock *et al.*, 1993).

Potassium uptake

K foliar concentrations usually decrease with an increase in salinity (Dudeck *et al.*, 1983; Janzen & Chang, 1987; Remison *et al.*, 1988). Kikuyu, however, exhibited a trend of increasing K at salinity treatment levels of 5 and 10 mS/cm. This may be a function of kikuyu's salt tolerance. Marcum & Murdoch (1990) found that in comparison to salinity intolerant species, salt tolerant grass accumulated greater K concentrations under salinity stress.

Manchanda & Sharma (1989) report that Cl salinity decreases K uptake more than SO_4 salinity. The exact opposite was observed in Experiment 1 (Fig. 2.8). Foliar K concentrations in Na_2SO_4 treatments were significantly lower than those in NaCl treatments, possibly due to SO_4 complexing effects.

Foliar magnesium and calcium

Ca and Mg decreases with salinity in grasses have been previously documented (Peacock *et al.*, 1993), while Na induced Ca, K and Mg deficiencies have been described in a number of plant species (Maas & Grieve, 1987; Garcia & Charbaji, 1993). Kikuyu did not, however, show any evidence of depressed Ca levels from NaCl treatment (Fig. 2.8).

Discriminant analysis revealed that Ca and Mg accounted for a large percent of the variation between salinity treatments. The decrease in Mg and Ca with salinity was, however, only significant in the Na_2SO_4 treatments (Figs. 2.8 & 2.9). Mg decreases only occurred at salinity treatments 10 and 20 in Na_2SO_4 treatments. Ca even showed a trend of increasing concentration with salinity in NaCl treatments. The decreased concentrations in Na_2SO_4 treatments can be explained by SO_4 complexation in the soil solution and reduced uptake as a result.

Foliar Zn, Cu and Mn

The Na_2SO_4 treatments produced significantly lower concentrations of Cu, Zn and Mn than NaCl treatments (Figs. 2.9 & 2.10). SO_4 complexation may be expected to reduce the uptake of Zn, Cu and Mn with an increase in salinity, as occurred with Mg and Ca (Figs. 2.8 & 2.9).

2.4.2.3 Foliar composition changes with time

Ca, Mg, Na, Cu, Zn, K and Mn foliar concentrations increased from the first to the second cut (yield 1 to yield 2) (Fig. 2.11). The increases are perhaps evidence of an adaption to salinity over time. The osmotic adjustment ion accumulation may take time to reach maximum efficiency which explains the higher ion accumulation in yield 2. The sum of all cations increased significantly from yield 1 to yield 2, further confirming this hypothesis. An initial period of root settling and establishment may also have played a part in relatively lower ion uptake in yield 1.

If osmotic adjustment was operating more effectively during growth after yield 1, the inhibitory effect of salinity should be less. This was indeed the case, as no significant difference was recorded between salinity treatments in yield 2. The decrease in foliar concentration of P, Fe and B from yield 1 to 2 may have been as a result of diminished supplies of these elements during the later stage of the experiment.

2.4.2.4 Concluding comment on salinity effects

Salinity induced reductions in yield in kikuyu are a function of both osmotic stress and ionic imbalances in the tissue. The relative contributions of these two factors are, however, difficult to determine. This study has found that besides osmotic stress as the most likely factor in salinity damage to kikuyu, when Na_2SO_4 is the dominant salt as opposed to NaCl, nutrient imbalances (and especially a significantly inhibited uptake of Ca) may also contribute to the apparently poorer performance of kikuyu in response to Na_2SO_4.

CHAPTER 3

EXPERIMENT 2: MANGANESE TOXICITY THRESHOLD IN KIKUYU

3.1 INTRODUCTION

The high manganese content of MMC waste constitutes a risk of manganese toxicity to the vegetation cover of a land disposal site. Kikuyu grass (*Pennisetum clandestinum*) is, however, manganese tolerant (Rayment & Verrall 1980) and is thus potentially a species tolerant to MMC waste. The critical Mn toxicity threshold and Mn tolerance of kikuyu was investigated to assess the risk of MMC waste disposal to kikuyu pasture sustainability.

3.2 MATERIALS AND METHODS

3.2.1 Experimental design

Manganous sulphate ($MnSO_4.H_2O$) treatment levels were as follows:
0, 800, 1600, 3200 and 8000 mgMn/kg soil

The materials and methods used were the same as in Chapter 2 (section 2.2). The three lower treatment levels were obtained from Experiment 1 salinity control treatments (ie. treatments with no Na_2SO_4 or NaCl applications).

3.3 RESULTS

3.3.1 Yield

Kikuyu yield response to increasing manganese applications is shown in Figure 3.1 and the plant appearance in Figure 3.2. Significant differences were recorded between Mn treatment levels in both yields 1 and 2 ($p<0.01$).

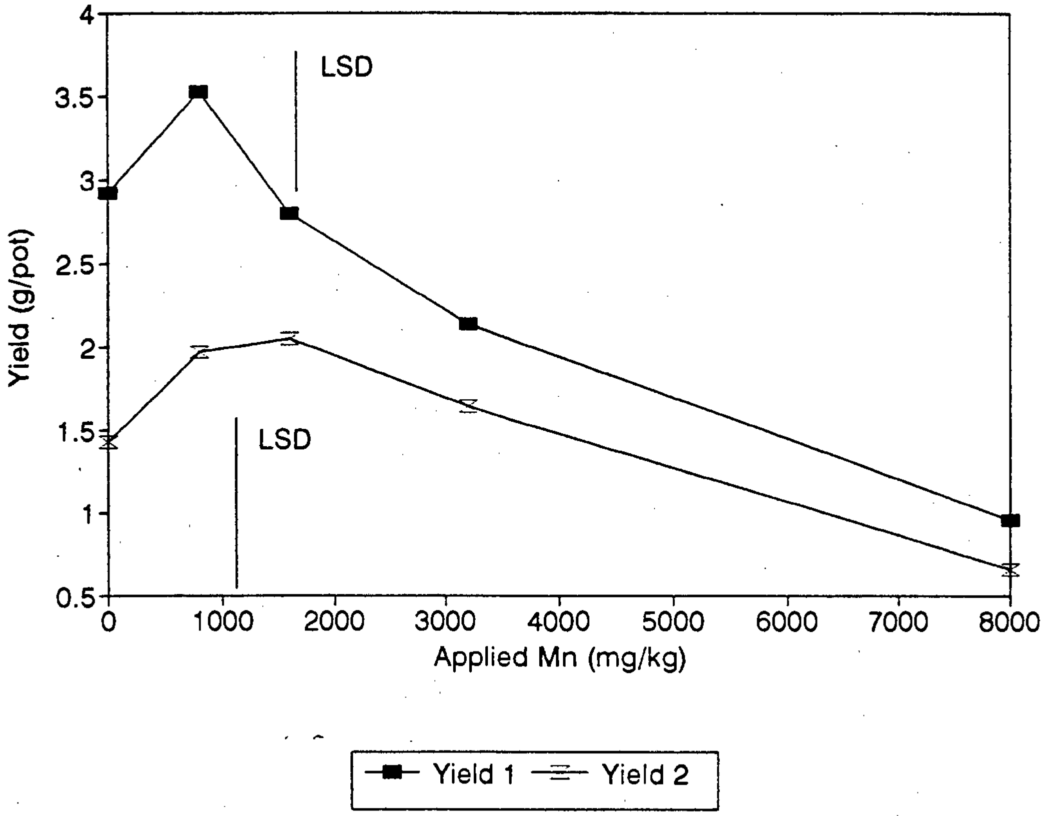
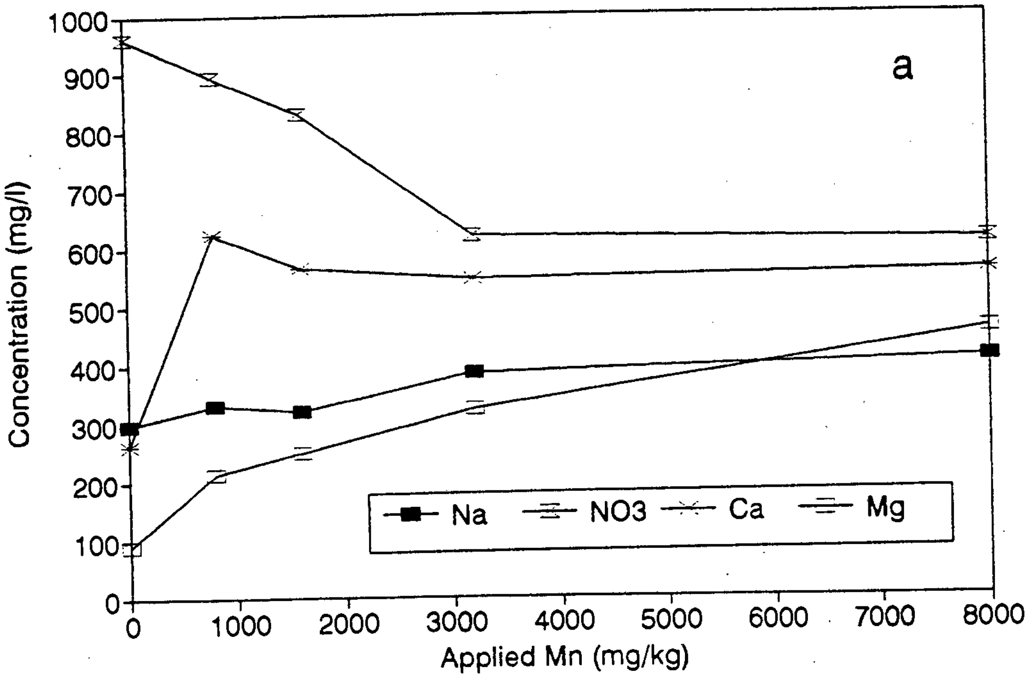


Fig. 3.1 The relationship between kikuyu yield and applied manganous sulphate for yields 1 & 2.

Fig. 3.2 Kikuyu response to manganous sulphate applications of (from left to right) 0, 800, 1600, 3200 and 8000 mgMn/kg.

3.3.2 Soil saturation paste extract

Mn, SO_4, Na, K, Mg and NH_4 increased with increasing $MnSO_4$ levels (Fig. 3.3 & 3.4). NO_3 decreased with increasing $MnSO_4$ levels (Fig. 3.3). Ca increased at the first $MnSO_4$ level and remained elevated at the same concentration through increasing $MnSO_4$ levels (Fig. 3.3). Cl decreased at the first $MnSO_4$ level and remained at the same decreased concentration through increasing $MnSO_4$ levels (Fig. 3.3). pH decreased and EC increased with increasing $MnSO_4$ application (Fig. 3.5).



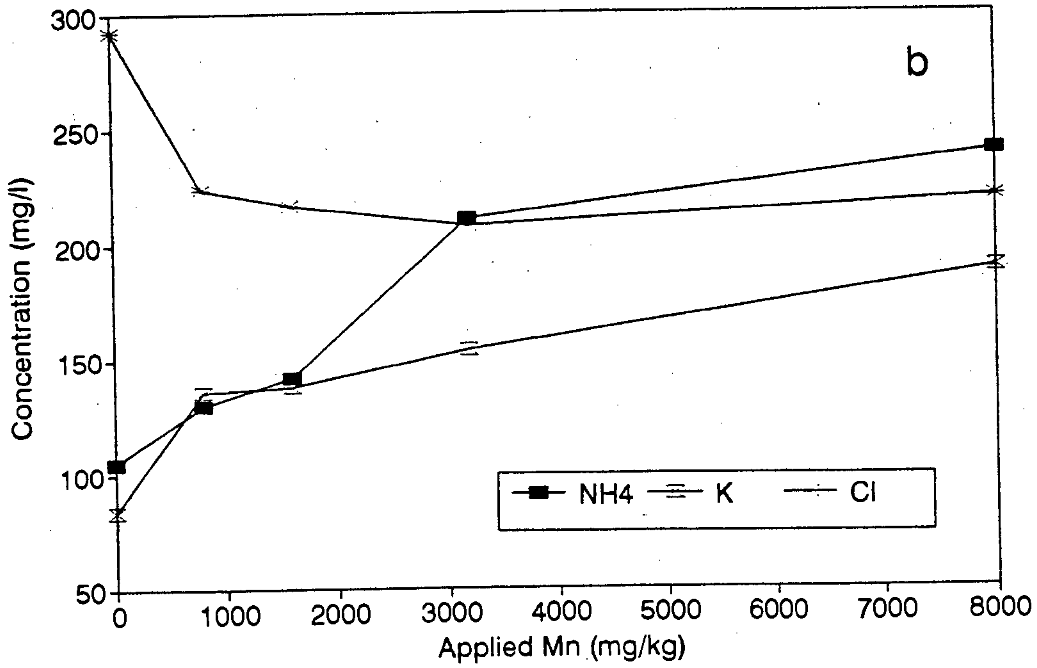


Fig. 3.3 The relationship between soil solution composition and applied Mn concentration: (a) Na, NO_3, Ca & Mg (b) NH_4, K & Cl.

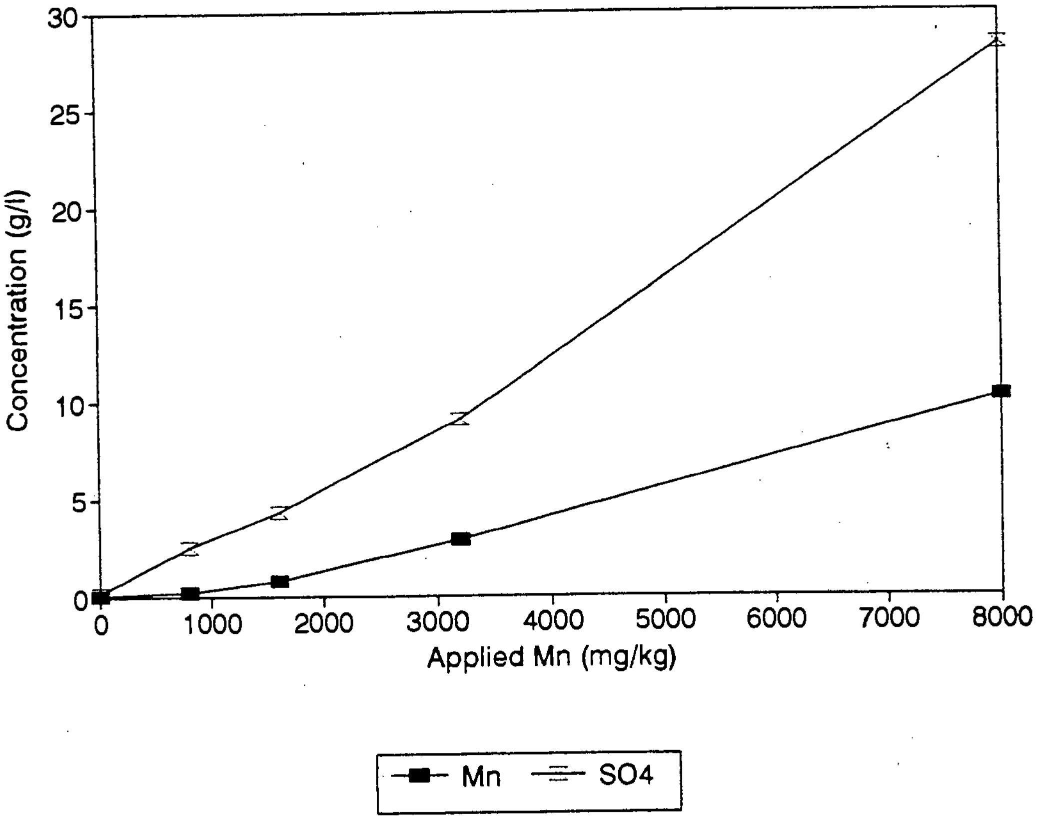


Fig. 3.4 The relationship between soil solution concentration of Mn and SO_4 and the concentration of applied Mn.

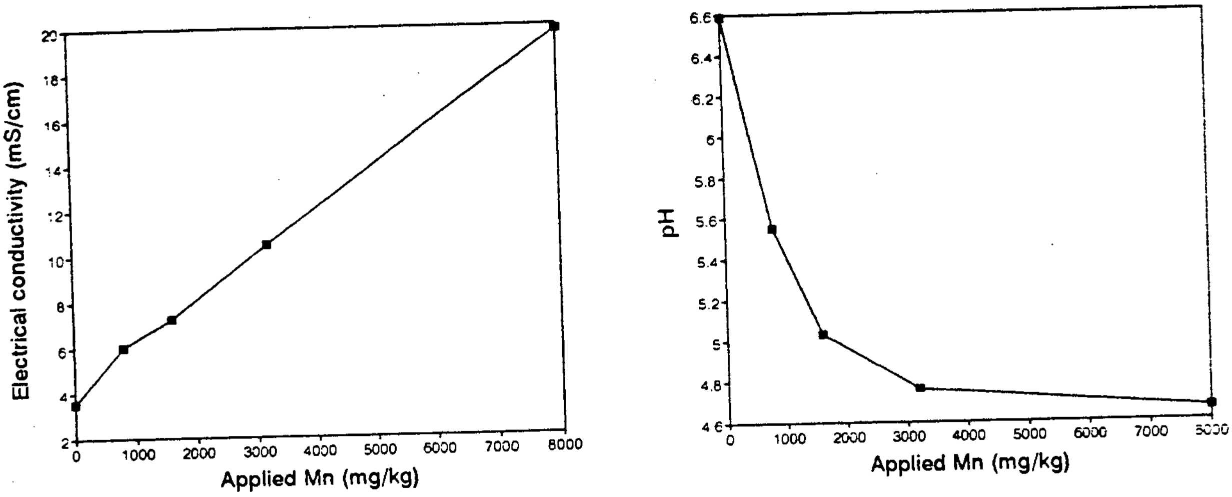


Fig. 3.5 The relationship between (a) EC, (b) pH in the soil solution and applied Mn concentration.

3.3.3 Foliar composition

Ca, Mg, Na, Fe and B foliar concentration decreased and Zn and Mn increased significantly with an increase in $MnSO_4$ application ($p<0.05$) (Fig. 3.6 & 3.7). P and K foliar concentrations showed an initial increase followed by a steady decrease to $MnSO_4$ applications (Fig. 3.7)

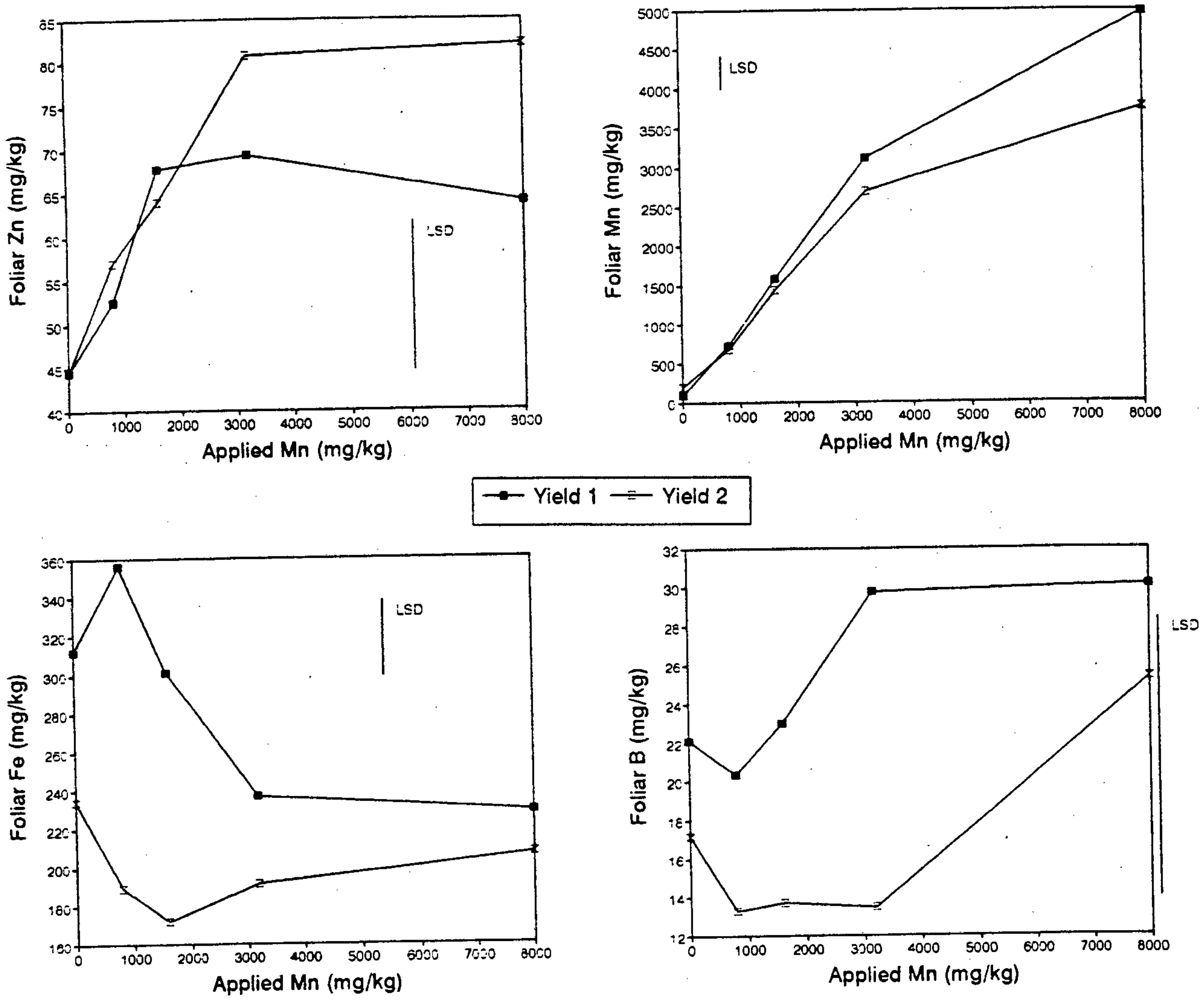


Fig. 3.6 The relationship between foliar Zn, Mn, Fe & B and applied manganous sulphate for yields 1 & 2.

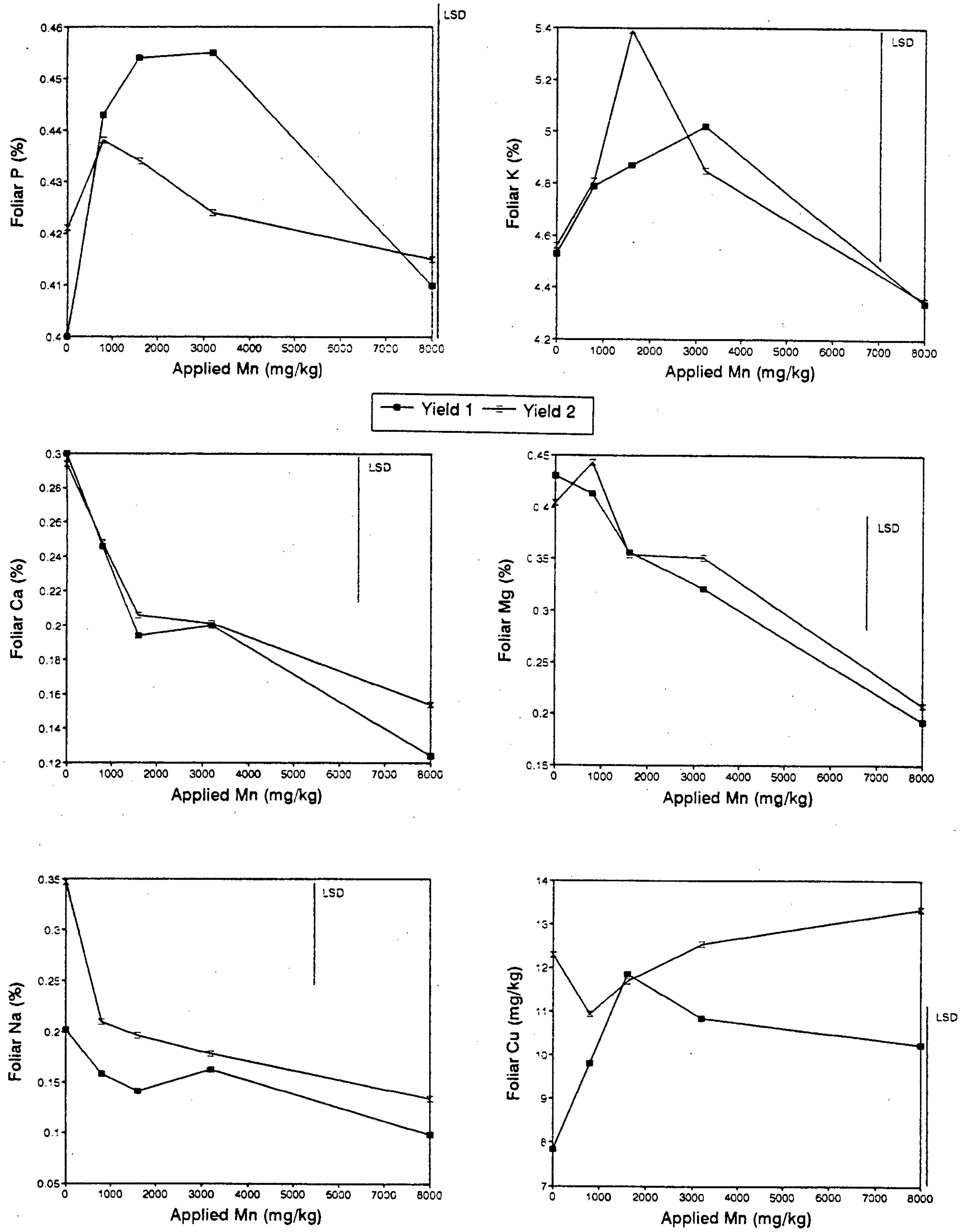


Fig. 3.7 The relationship between foliar P, K, Ca, Mg, Na & Cu and applied manganous sulphate for yields 1 & 2.

3.3.3.1 Foliar composition change over time

Na, Cu and Zn foliar concentrations were significantly higher in yield 2 ($p<0.05$) (Fig. 3.8). Mn, Fe and B foliar concentrations were significantly lower in yield 2 ($p<0.05$).

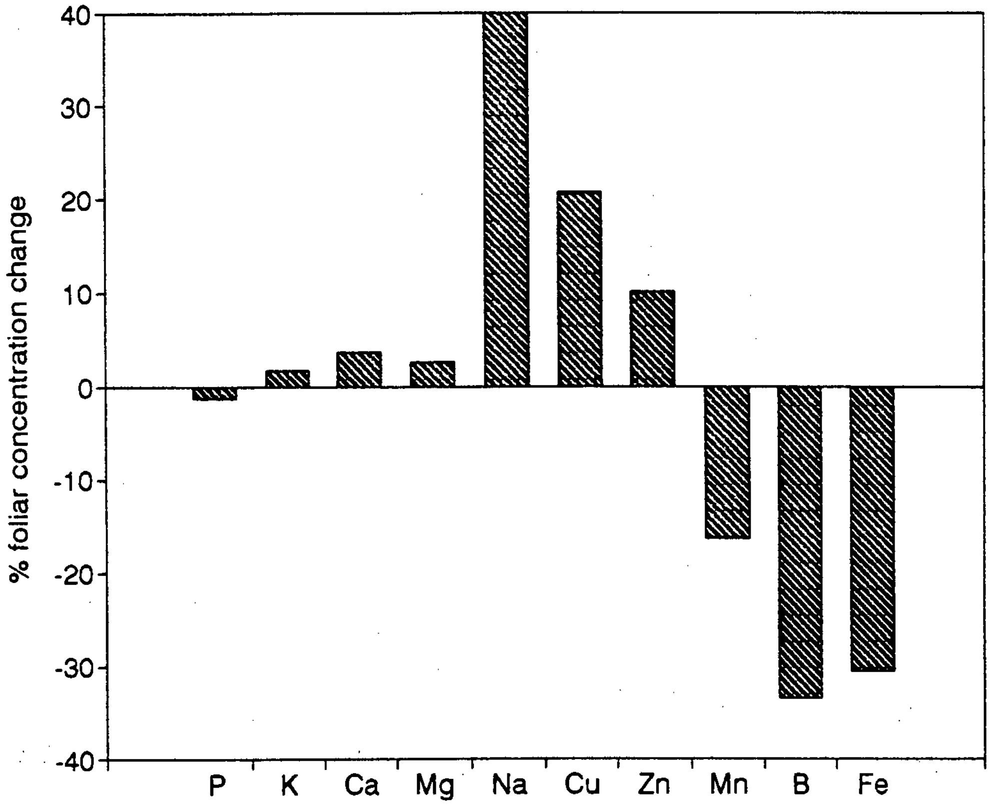


Fig. 3.8 The % foliar composition change from yield 1 to yield 2.

3.4 DISCUSSION

3.4.1 Kikuyu yield response as a function of soil chemical processes and nutrient uptake

The high kikuyu yields in yield 1 at 800 mgMn/kg and in yield 2 at 800 - 3200 mgMn/kg, although not significantly greater than the control treatments, suggest (due to the repeated trend in yield 1 & 2) a possible Mn stimulatory effect on kikuyu growth as documented by Rayment & Verrall (1980). A significant inhibitory effect on growth was, however, evident at 3200 & 8000 mgMn/kg in yield 1 and at 8000 mgMn/kg in yield 2.

3.4.1.1 Mn fertilization effect

Mn competition for cation exchange sites in the soil resulted in desorption and a release of ions such as K, NH_4, Mg and Ca into the soil solution (Fig. 3.3) (see section 2.4.1.1). This effect has a potentially positive feedback due to increased nutrient availability.

The initial increase in foliar K concentrations with $MnSO_4$ application ($p<0.05$ for pooled yield 1& 2 data) (Fig. 3.7) is probably due to this desorption process increasing K availability. Studies by Ohki (1984) which recorded a decrease in foliar K with Mn application were undertaken in nutrient solutions. This method did not enable the detection of the Mn desorption effect in enhancing the solubility of exchangeable K.

A reduction in foliar K ($p<0.05$) at the two highest $MnSO_4$ applications, may be due to increased Mn and SO_4 competition for root uptake sites. $MnSO_4$ thus appears to have both a positive and negative effect on K uptake, in the form of ion competition for soil ion exchange sites and root uptake sites respectively. At some point the (soil desorption benefit)/(ion antagonism) ratio declines to a level which negates the fertilization effect of $MnSO_4$.

The Mn fertilization effect may also be a function of direct benefit from Mn accumulation in the plant. Mn is an essential micronutrient used in photosynthetic enzymatic pathways. Cramer & Novak (1992) reported that supplemental Mn improved the relative growth, net assimilation and photosynthetic rates of salt stressed barley. An increase in Mn bioavailability may thus enhance kikuyu growth to some extent.

Rayment & Verrall (1980) observed an increase in kikuyu yield in all $MnCl_2$ applications, ranging from 200 - 1600 mgMn/kg soil (Fig. 3.9). They hypothesised that the increase was due to a reduction in pH of the soil solution, which in turn increased mineralisation of nitrogen resulting in a fertilization effect.

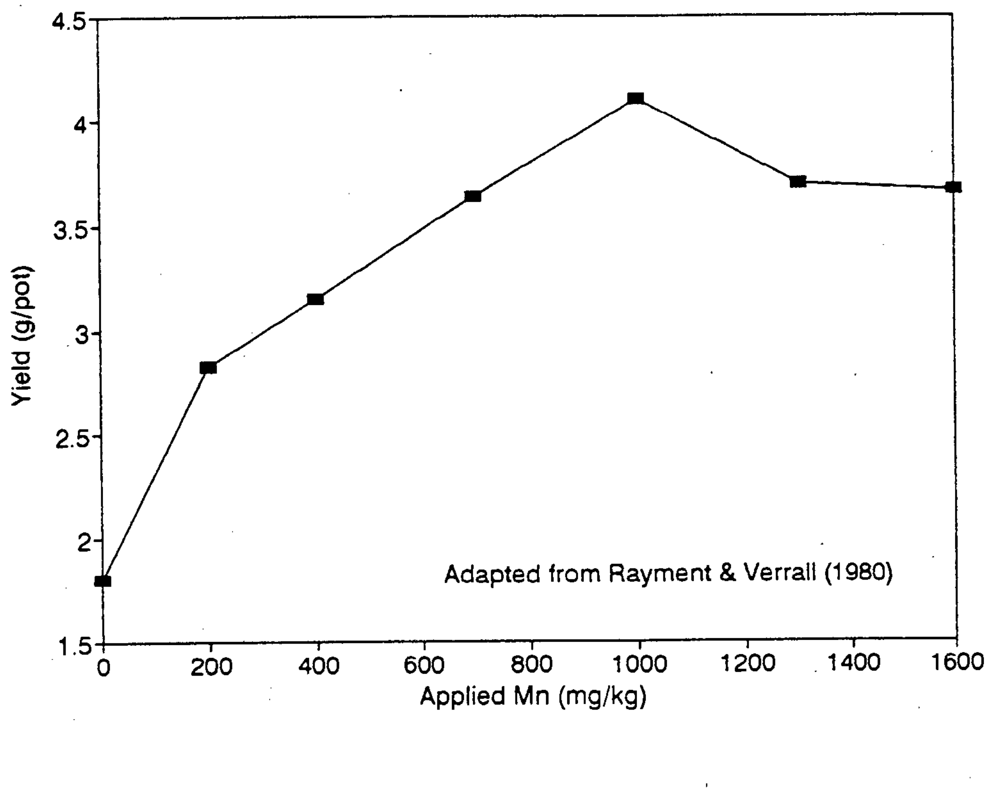


Fig. 3.9 The relationship between kikuyu yield and applied Mn as $MnCl_2$ (adapted from Rayment & Verrall, 1980).

The increase in NH_4 soil concentration with $MnSO_4$ application (Fig. 3.3) indicates that increased nitrogen mineralisation may indeed be taking place. The fertilization effect of Mn as documented by Rayment & Verrall (1980) and suggested by Experiment 2 data is thus most likely a function of both soil desorption processes and nitrogen mineralisation.

Salinity effects on the Mn fertilization effect

The Mn fertilization effect is only evident in the control and lowest salinity treatment in Experiment 1 (Fig. 2.2). The higher salinity treatments may impose too great an osmotic stress on the plant for a K or P fertilization response to take place.

3.4.1.2 Mn toxicity manifestation

Mn toxicity diagnosis is complicated by other potential toxicities and deficiencies that exhibit similar symptoms. Hence diagnosis by visual foliar symptoms is problematic (Hannam & Ohki, 1988). The most common symptoms of Mn toxicity are interveinal chlorosis, leaf puckering, necrotic brown spots and uneven chlorophyll distribution (Foy *et al.*, 1969).

Mn accumulated to a maximum level of 5148 mg/kg dry mass (Appendix VI) in Mn level 4, probably by means of passive absorption. This was described by Kabata-Pendias & Pendias (1985) as occurring at high Mn concentrations. Mn toxicity appeared to manifest itself as a yellow interveinal chlorosis (Fig. 3.10) at Mn levels 3 and 4 (and occasionally level 2). These symptoms were a probable Fe chlorosis induced by a Fe/Mn ratio < 0.1.

Fig. 3.10 **Manganese toxicity symptoms in kikuyu exposed to a Mn application of 8000 mg/kg.**

Osmotic stress effects

Mn toxicity is not necessarily a function of Mn induced Fe deficiency (Nable *et al.*, 1988; Morris & Pierre, 1949). Reduced yields at higher $MnSO_4$ applications are also attributable to osmotic stress imposed by the high salinity levels rather than a function of ion imbalances or toxicities. Electrical conductivities of 10.5 and 19.8 mS/cm were recorded for Mn levels 3 and 4, respectively (Fig. 3.5). The relative contributions of Mn toxicity and osmotic stress are difficult to determine. The correlation coefficients of yield with EC and soil Mn (Appendix VII) were -0.80 and -0.82, respectively, preventing any meaningful interpretation.

Root effects

The absence of Mn toxicity symptoms in kikuyu shoots at Mn levels 1, does not preclude the possibility of abnormal root growth. Burke *et al.* (1990) note, however, that Mn toxicity manifests itself predominantly in shoots and not roots. In addition, shoot growth is usually a function of root growth and abnormal root growth would be evident in reduced shoot growth. Root growth was not analysed in the pot experiments.

Critical threshold

Kikuyu's critical Mn toxicity threshold level, defined as a 10% reduction in growth, probably occurs between 800 and 1600 mg/kg soil (Fig. 3.1). This represents a Mn accumulation in yield 1 of approximately 700 & 1500 mg/kg, respectively. A possible physiological explanation for Mn tolerance in kikuyu is the ability to precipitate Mn oxides mainly within the epidermis, as documented for a number of plant species by Loneragan (1988).

The threshold estimation may appear misplaced as the kikuyu yield at Mn level 2 (1600 mg/kg soil) is greater than the control yield. The reasoning for the estimation is outlined below.

Control inadequacy

The fertilization effect of $MnSO_4$ as discussed in section 3.4.1.1 may raise soil nutrient availability. The control treatment is not effective for isolating Mn toxicity, as relative to Mn level 1 & 2, growth in the control may be limited by K and NH_4. Mn level 1 should thus for practical purposes be regarded as the control.

3.4.1.3 Kikuyu manganese tolerance reviewed

Rayment & Verrall (1980) concluded that kikuyu was not significantly affected by Mn applications (as $MnCl_2$) of up to 1600 mg/kg soil. Their supposition is perhaps incorrect in the light of the above discussion and the similar kikuyu growth response observed in their data (Fig. 3.9). SO_4 complexation with Mn^{2+} may reduce Mn toxicity effects to some extent, making a comparison between $MnSO_4$ and $MnCl_2$ difficult.

3.4.2 Mn effects on foliar composition

Discriminant analysis showed that Fe, Na and K tissue levels accounted for most of the variation between $MnSO_4$ treatments. The uptake of these elements and others are discussed below.

The effect of Mn on Ca and Mg uptake is inconsistent, with reports of both antagonistic and synergistic effects (Siman *et al.*, 1971). Ohki (1984) found that Mn toxicity in wheat (*Triticum aestivum*) reduced Ca, Mg and K foliar concentrations. Foliar Ca and Mg were both negatively correlated ($p<0.01$) with foliar Mn in Experiment 3, with correlation coefficients of -0.78 and -0.94 respectively. These correlations suggest an antagonistic effect of Mn on Ca and Mg uptake. The inhibitory effect may be explained by the similar metabolically controlled uptake of divalent cation species such as Mn^{2+}, Mg^{2+} and Ca^{2+} (Kabata-Pendias & Pendias, 1985), as well as an ion competition effect for root uptake sites.

The positive correlations between Zn, Cu and Mn (Appendix IX) suggests a synergistic uptake relationship between these elements. The increases may also be a function of soil desorption processes. These results are contrary to studies by Reisenauer (1988) who noted that Zn and Cu competed with Mn for plant uptake. Reddy *et al.* (1987) investigated the effect of Mn on concentrations of Zn, Fe, Cu and B in soybeans (*Glycine max*). Zn, Fe and B were not significantly affected by increasing Mn concentrations but Cu concentrations increased significantly with Mn application.

The antagonistic effect of Mn on Fe is well documented (Ohki, 1984; Reddy *et al.*, 1987) and was evident in the significant decrease in Fe concentrations with increasing $MnSO_4$ application (Fig. 3.6).

SO_4 is also probably implicated in the Ca, Mg and Na decrease with $MnSO_4$ application (Fig. 3.7). SO_4 complexation and resultant decrease in bioavailability of these ions is discussed in section 2.4.2.1. This effect was evident in the MINTEQA2 speciation of sample MN4 soil solution, where 64% of Ca, 60% of Mg and 16% of Na were calculated as being present as ion pairs with SO_4^{2-}. Mn antagonism probably accounted for much of the decreased Na levels, as only 16% of Na is complexed with SO_4.

3.4.2.1 Foliar composition change with time

The higher concentration of Na, Mg, Ca, K, Cu, and Zn (Fig. 3.8) in yield 2 may be attributable to the same reasons discussed in Chapter 2. The lower Mn, Fe, P and B uptake in yield 2 may be due to a diminished supply of these ions as a result of utilization during yield 1 growth.

3.4.3 **Concluding comment on kikuyu manganese** tolerance

Kikuyu exhibited both a fertilization effect and a Mn toxicity effect with Mn applications. An increase in yield occurred between Mn applications of 800 and 1600 mg/kg soil. This effect was attributed to increased P and K availability as a result of soil desorption processes. Mn applications of 3200 and 8000 mg/kg resulted in severe Mn toxicity symptoms and reductions in yield. The critical Mn toxicity threshold for kikuyu exceeds 800 mgMn/kg and is higher than that of any other plant species in the literature reviewed.

CHAPTER 4

EXPERIMENT 3: FERTILIZER EFFECTS ON KIKUYU YIELD: A COMPARISON OF MMC WASTE AND NH_4NO_3.

4.1 INTRODUCTION

The nitrogen content of MMC waste [$(NH_4)_2SO_4$] is a potential fertilizer resource. $(NH_4)_2SO_4$ is used as a commercial fertilizer in agriculture (Mengel & Kirkby, 1978) and has been shown to substantially increase yields of kikuyu pastures (Awad & Edwards, 1977). MMC waste disposal over kikuyu pastures may thus have a fertilization effect, provided that the other waste constituents do not have detrimental effects on yield. This potential fertilization effect of MMC waste was investigated and compared to a standard nitrogen fertilizer (NH_4NO_3).

4.2 MATERIALS AND METHODS

4.2.1 Experimental design

Treatment levels were designed to be equivalent to the following field application rates (assuming a 10 cm depth of incorporation):

NH_4NO_3:	0, 100, 200, 400, 800 kg N per hectare
MMC Waste:	0, 100, 200, 400, 800 kg N per hectare

Simulated MMC waste was made up in an untreated form as presented in Table 4.1.

Table 4.1: Manganese Metal Company waste effluent

pH	7.4
Mn, g/l	12.3
N, g/l	7.2
Ca, mg/l	588
Mg, g/l	2.45
SO_4 g/l	57.4

4.2.2 Soil treatment

Soil treatments are presented in Table 4.2 below. The materials and methods used were otherwise the same as in Chapter 2 (section 2.2).

Table 4.2: Soil treatments

Treatment	Solution	Level (kg N/ha)	Volume added (ml per kg soil)
NH_4NO_3	71 g/l	100	2
		200	4
		400	8
		800	16
MMC Waste	See Table 4.1	100	7
		200	14
		400	28
		800	56

4.3 RESULTS

4.3.1 Yield

Yield results are presented in Fig. 4.1 and the appearance of the plants in Fig. 4.2. The MMC waste mean yield was marginally higher than the NH_4NO_3 fertilizer mean yield, yet no significant difference was recorded.

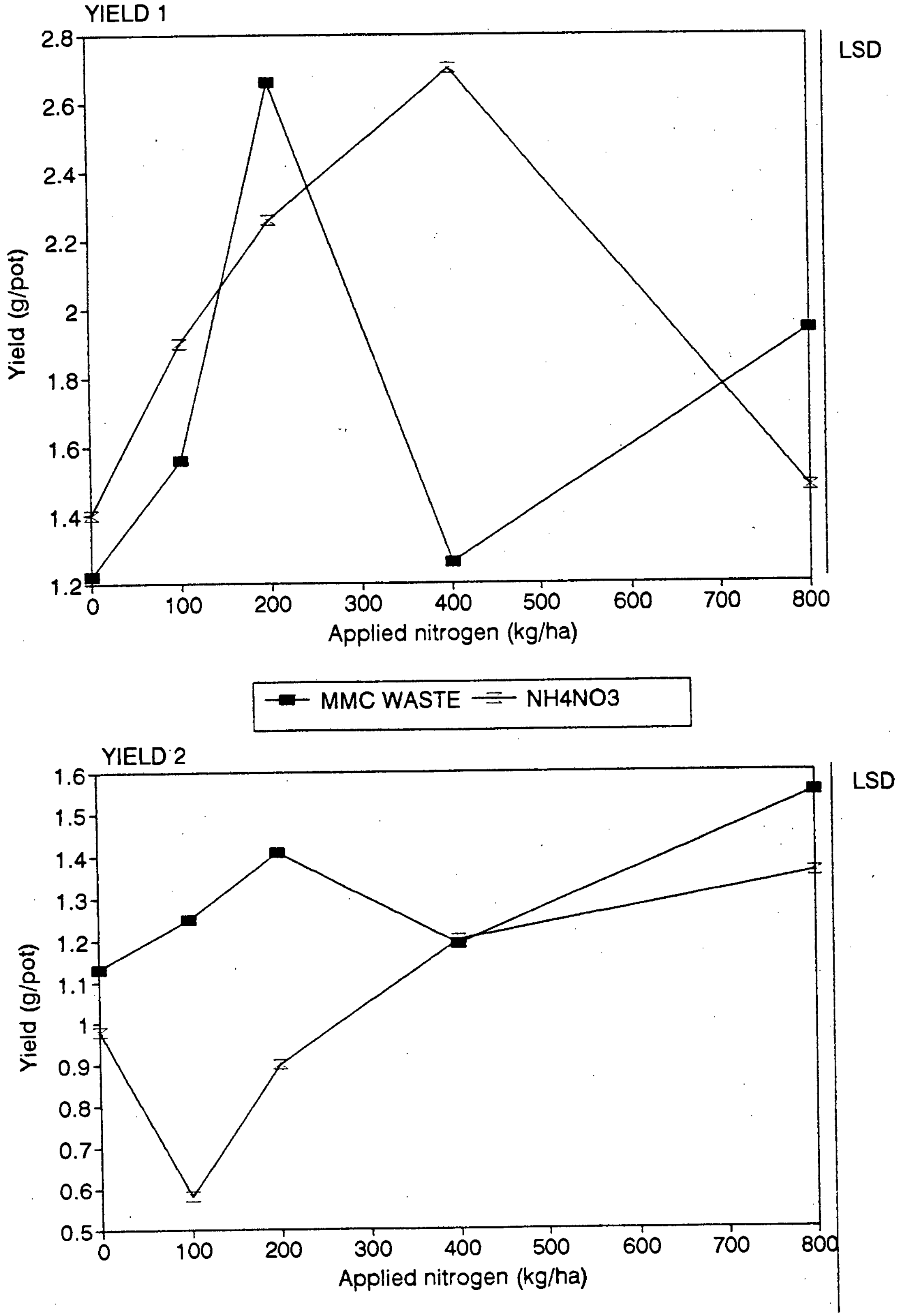


Fig. 4.1 The relationship between kikuyu yield and applied levels of nitrogen as MMC waste and NH_4NO_3.

Fig. 4.2 The response of kikuyu to five levels of MMC waste and NH_4NO_3 fertilization.

A nitrogen level equivalent to 200kg/ha and 400kg/ha produced the highest yields in the MMC waste and NH_4NO_3 treatment, respectively (Fig. 4.1). No significant difference between nitrogen levels or in the level/treatment interaction was calculated in the ANOVA. The low yield response at 400 kgN/ha of MMC waste in yield 1 is somewhat anomalous, as the yield subsequently increases at 800 kgN/ha.

4.3.2 Saturated paste extract analysis

Results of chemical analyses of the soil solution are presented in Figures 4.3, 4.4 & 4.5. Na, K, Mg, NH_4, Ca and EC increased with increasing fertilizer applications and were markedly higher in the MMC waste treated soils than in the NH_4NO_3 treated soils (Figs. 4.3 & 4.5). Mn and SO_4 concentrations increased with an increase in fertilizer application only in MMC waste treated soils (Figs. 4.3 & 4.4). NO_3 increased uniformly with an increase in fertilizer application only in NH_4NO_3 treated soils. Cl showed a relative decrease at high MMC waste application and a relative increase at high NH_4NO_3 application (Fig. 4.4).

4.3.3 Foliar composition

Results of chemical analyses of kikuyu foliage are presented in Figures 4.6 & 4.7. Foliar Ca and Na concentrations were significantly lower in MMC waste treatments ($p<0.05$) (Fig. 4.7). Foliar Mn, Fe, Al and B concentrations were significantly higher in MMC waste treatments ($p<0.05$) (Fig. 4.6 & 4.7). Foliar Mg concentrations were lower and P, K, Cu and Zn concentrations higher in MMC waste treatments, yet the differences were not significant.

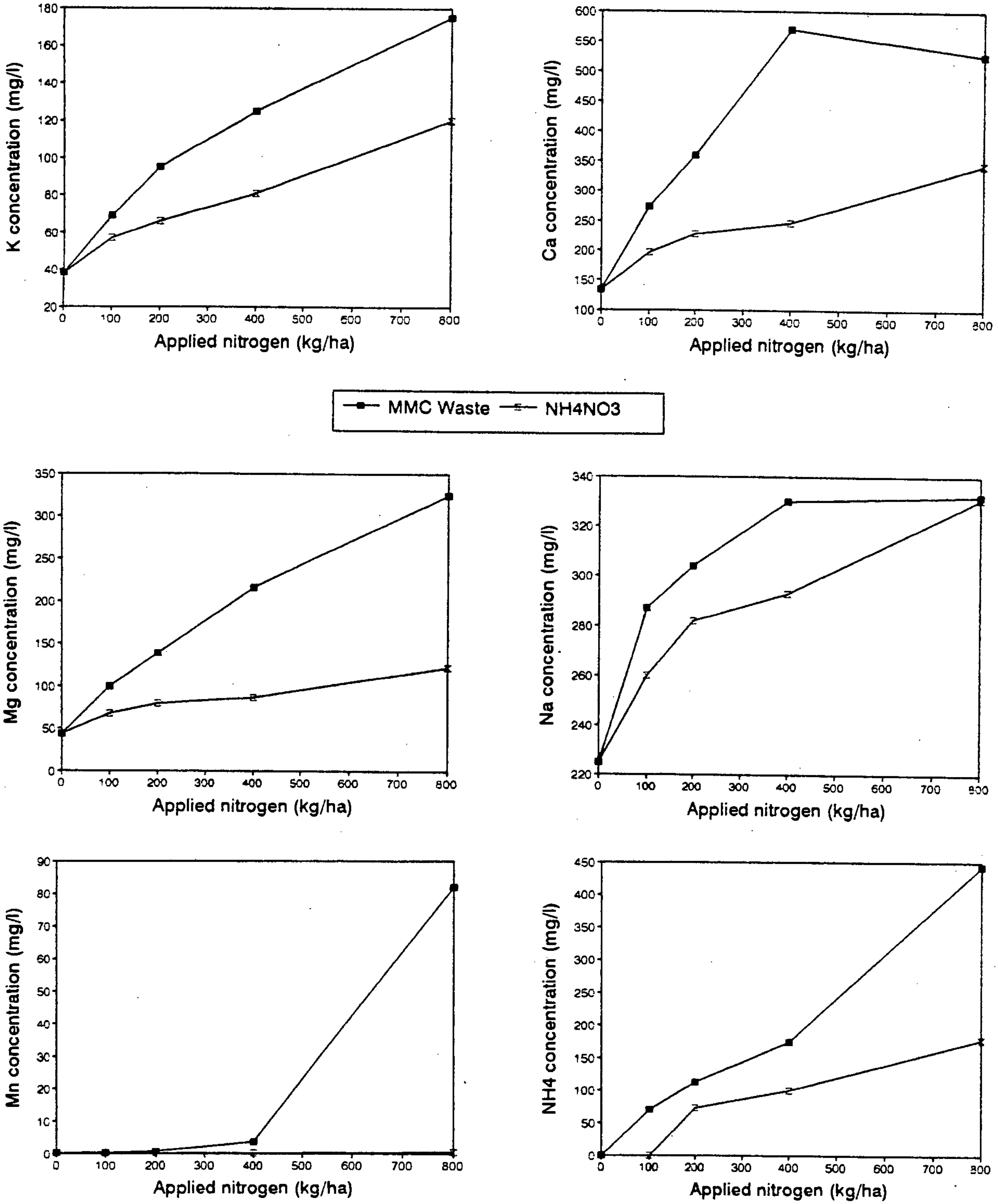


Fig. 4.3 The relationship between soil solution K, Ca, Mg, Na, Mn & NH_4 concentrations and levels of applied nitrogen as MMC waste and NH_4NO_3.

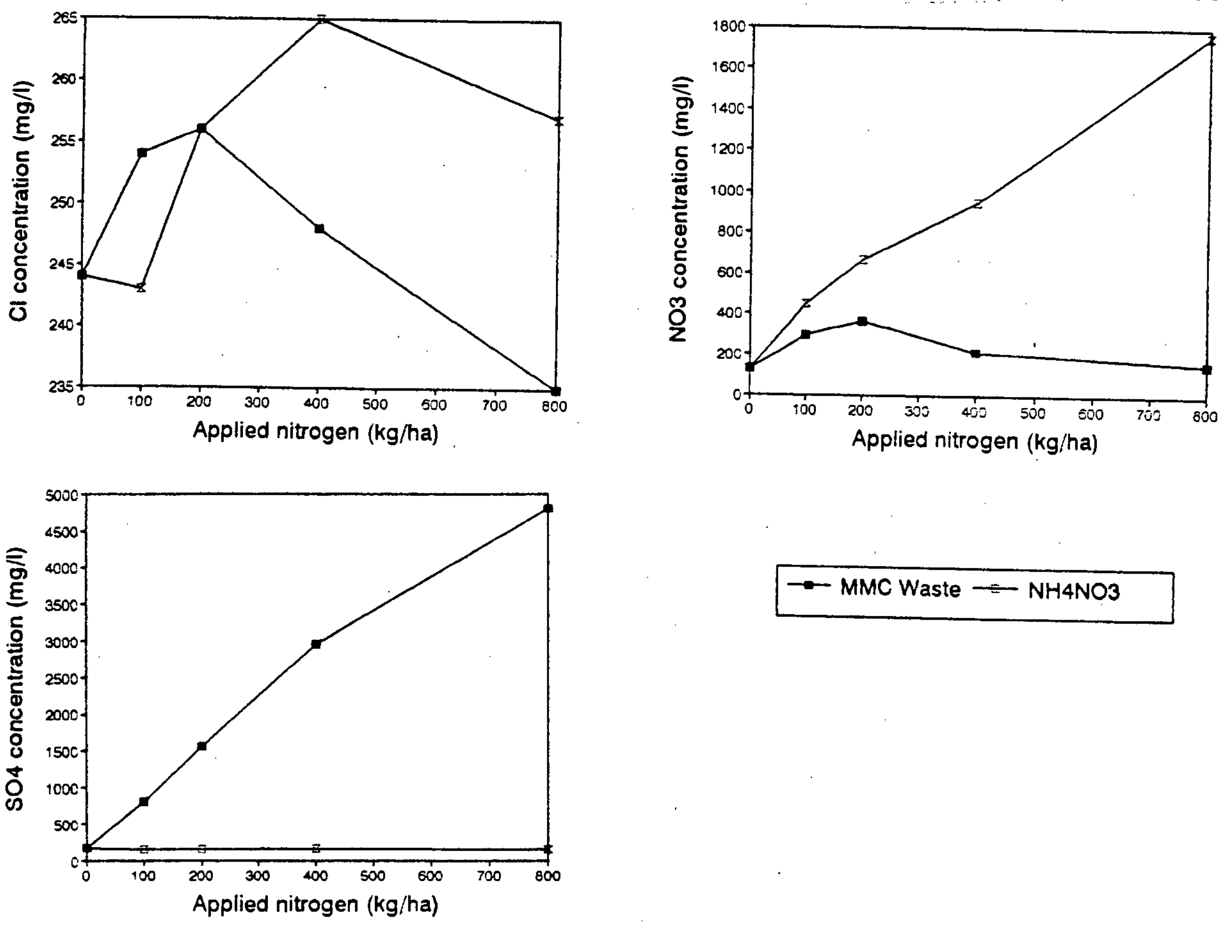


Fig. 4.4 The relationship between soil solution Cl, NO_3 & SO_4 concentrations and levels of applied nitrogen as MMC waste and NH_4NO_3.

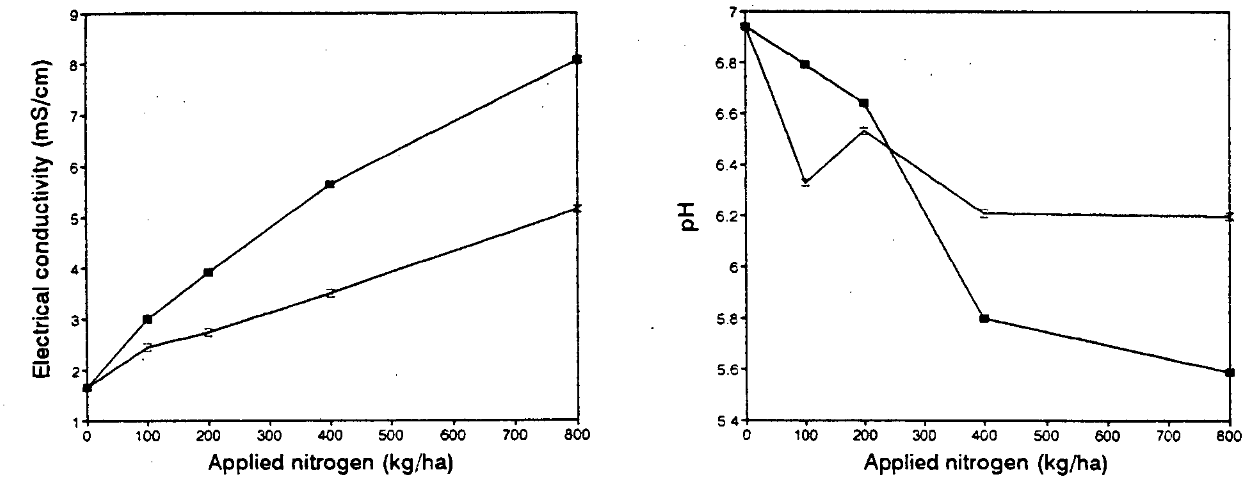


Fig. 4.5 The relationship between electrical conductivity; pH and levels of applied nitrogen as MMC waste and NH_4NO_3.

Foliar Ca and Na decreased and Zn and Mn increased with an increase in MMC waste application. NH_4NO_3 treatments showed a general increase in foliar Ca and Na with increasing application. Foliar P showed a general decrease and Mg a general increase with an increase in fertilizer application (Fig. 4.7).

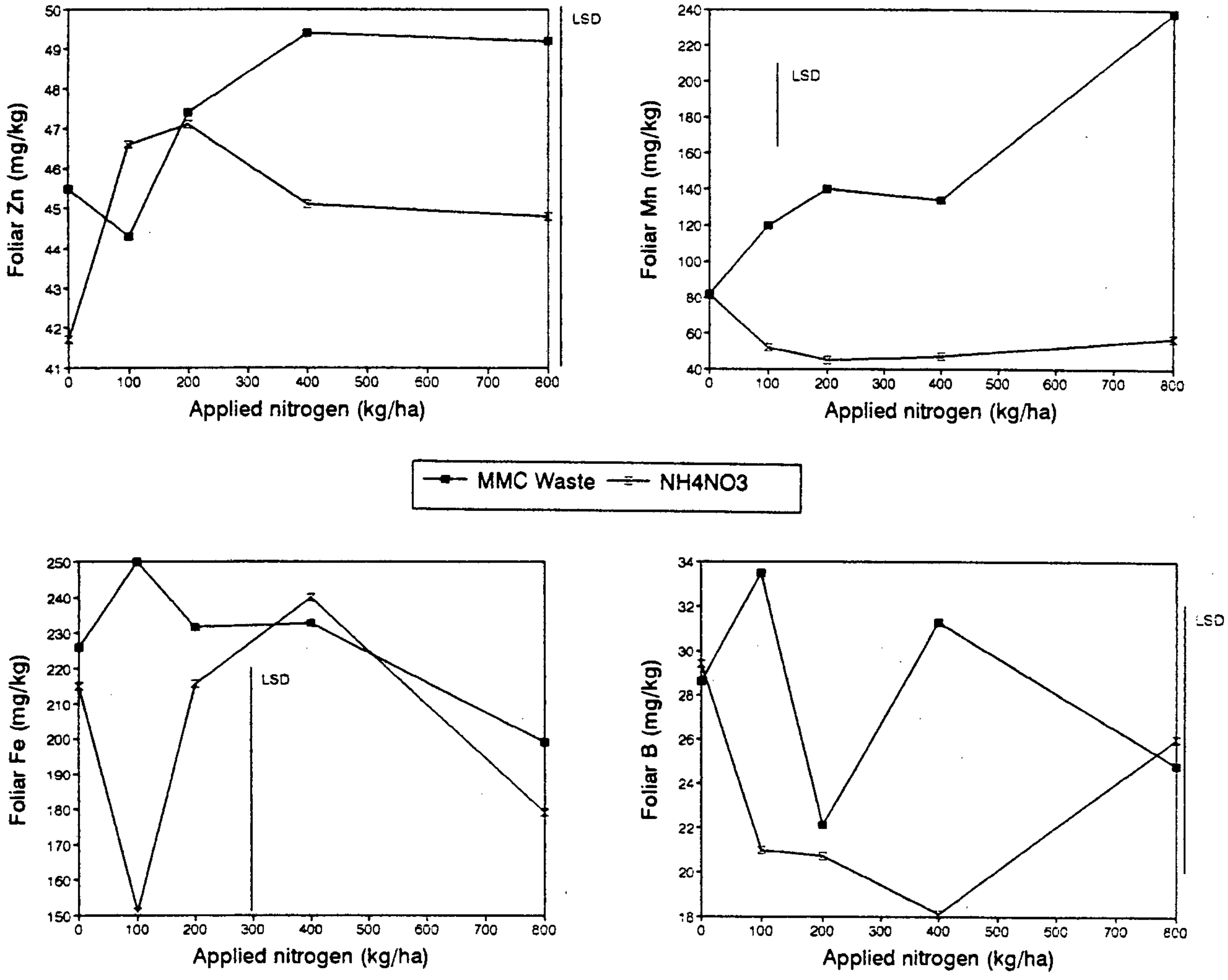


Fig. 4.6 The relationship between foliar Zn, Mn, Fe & B concentrations and levels of applied nitrogen as MMC waste and NH_4NO_3.

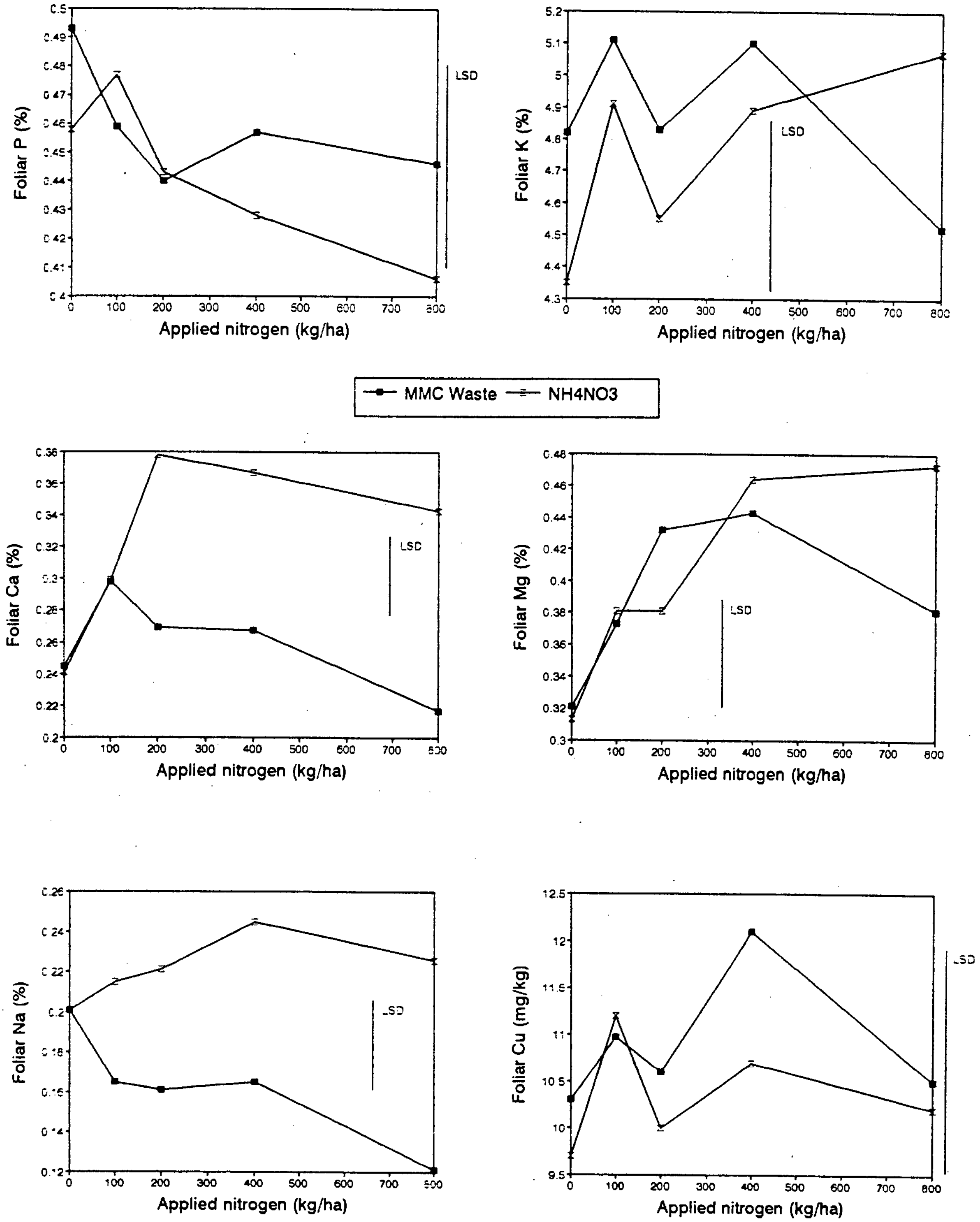


Fig. 4.7 The relationship between foliar P, K, Ca, Mg, Na & Cu concentrations and levels of applied nitrogen as MMC waste and NH_4NO_3.

4.3.3.1 Fertilizer type effects

Foliar Ca and Na concentrations were significantly lower in the MMC waste treatments ($p<0.05$) (Fig. 4.7). Mn, Fe and B levels were significantly higher in MMC waste treatments ($p<0.05$) (Fig. 4.6). Mg concentrations were lower in the MMC waste treatments, yet the difference was not significant (Fig. 4.7). P, K, Cu and Zn concentrations were higher in the MMC waste treatments, yet the difference was not significant (Figs. 4.6 & 4.7).

4.3.3.2 Fertilizer level

Foliar Ca and Mg concentrations showed a curved response to fertilizer application (Fig. 4.7). P concentrations decreased with an increase in nitrogen level, yet the differences between treatments were not significant (Fig. 4.7). Zn concentrations increased significantly with increasing fertilizer application ($p<0.05$) (Fig. 4.6). K and Cu concentrations were higher in all fertilizer treatments than the control although the differences were not significant (Fig. 4.7).

4.3.3.3 Foliar composition change over time

Foliar composition changes over time are presented in Figure 4.8. Mg, Na, Cu, Zn, Mn and B concentrations were significantly higher in yield 2 ($p<0.05$). K concentrations were significantly lower in yield 2 ($p<0.05$). P and Ca concentrations were higher in yield 2, yet the difference was not significant. Fe concentrations were lower in yield 2, yet the difference was not significant.

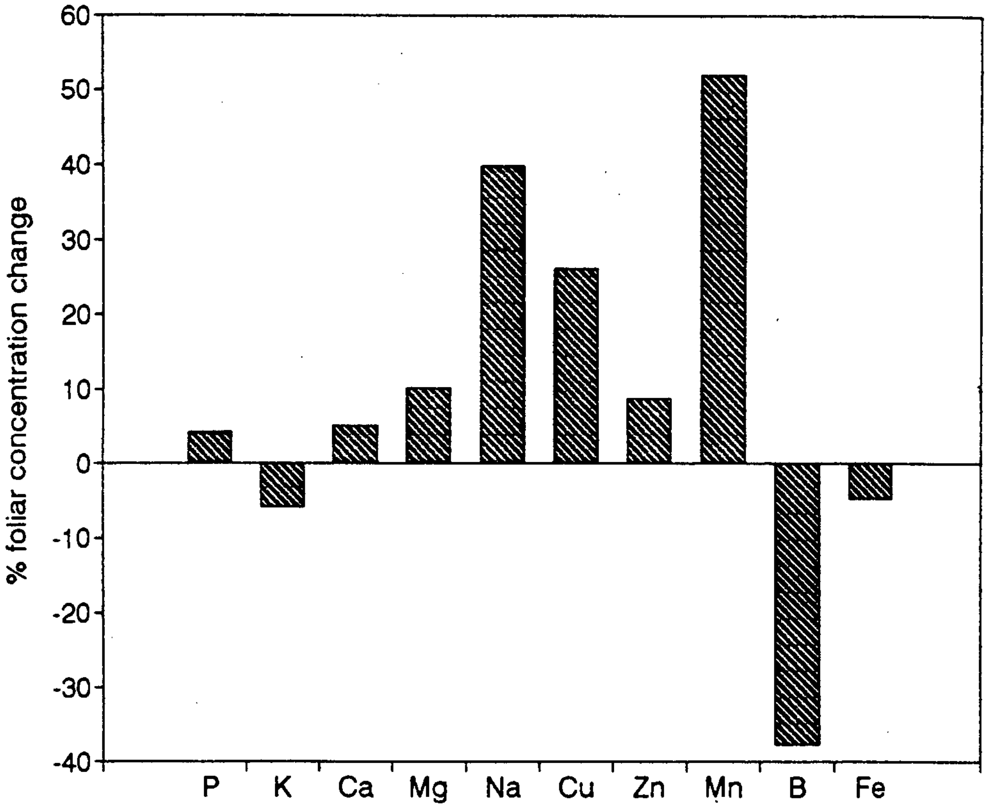


Fig. 4.8 % foliar composition change from yield 1 to yield 2.

4.4 DISCUSSION

4.4.1 Yield

The variation between replications as well as the limited number of replications and treatment levels probably resulted in no significant difference being detected between nitrogen treatments. A quadratic trend of increasing followed by decreasing yield in yield 1 is, however, clearly evident in Figure 4.1. This observation conforms to a standard fertilizer response (Mengel & Kirkby, 1978). This trend is not evident in yield 2 and possibly reflects diminished nitrogen availability due to plant utilization over time.

The lower yields of the controls in Experiment 3 in comparison to those in Experiment 1 are probably due to a N base fertilization of soil being implemented only in Experiment 1.

4.4.2 Soil saturated paste extract analysis

MMC waste constituents Mn, SO_4, NH_4, Ca & Mg (Table 4.1) increased in concentration with an increase in waste application (Figs. 4.3 & 4.4). The higher Na and K concentrations in MMC waste treated soils in comparison to the NH_4NO_3 treated soils are probably due to the higher salinity generated by the waste (Fig. 4.3). A cation exchange mass action effect by cations responsible for the high salinity (Mn, Mg & Ca) probably resulted in displacement of K and Na from cation exchange sites.

Gypsum precipitation at level 8 (800 kg N/ha) in the MMC waste treated soil is a likely explanation for the relatively decreased Ca concentration (Fig. 4.3). MINTEQA2 speciation calculated a gypsum saturation index of 0.322 in sample W8. Cl in the soil solution decreased with MMC application (Fig. 4.4), possibly due to an ettringite-like precipitate as discussed in section 2.4.1.4.

4.4.2.1 Nitrogen behaviour

The NO_3 concentrations are approximately an order of magnitude greater than the NH_4 concentrations in the NH_4NO_3 treated soils (Fig. 4.4). This suggests that nitrification of NH_4 into NO_3 occurs, although adsorption of NH_4^+ by cation exchange could also have contributed to the lower solution concentration relative to NO_3. Although NO_3 is not present within the MMC waste, NO_3 concentrations are increased relative to the control. It thus appears that the same nitrification reaction takes place in MMC treated soils. A relative NO_3 decrease occurred at levels 4 & 8, which suggests that the nitrification process is inhibited in some way. The oxidation of Mn^{2+} and NH_4 at these levels may decrease pH and pe to the point of retarding NH_4 oxidation to NO_3.

4.4.2.2 Manganese sorption

The vast increase of Mn in the soil solution from level 4 (4 mg/l) to level 8 (82 mg/l) is indicative of the Mn sorption capacity of the soil being exceeded (Fig 4.3).

4.4.2.3 pH decrease in MMC waste treatments

pH decreased with an increase in $MnSO_4$ application in all experiments (Fig. 4.5). Significant negative correlations were recorded between pH and soil Mn in Experiments 1 and 2 (Appendix VII). The decrease in pH is probably a result of two processes: the hydrolysis of the Mn^{2+} ion ($MnOH^+$), evident in the MINTEQA2 output for sample Mn4, and the oxidation of NH_4 and Mn^{2+}.

4.4.3 Foliar composition

4.4.3.1 MMC waste/NH_4NO_3 nutrient uptake effects

Discriminant analysis showed that K and Fe tissue levels accounted for most of the variation between fertilizer types. The higher salinity of the MMC waste treatments (Fig. 4.5) resulted in a desorption of ions from the soil into the soil solution. The higher concentrations of P, K, B, Cu and Zn in MMC treated plants are perhaps due to the greater bioavailability of these ions from the desorption process. The slightly higher mean yield of MMC waste treatments may be a result of greater K and P uptake (Fig.4.7). The difference was not, however, significant and thus the explanation is tentative and requires further investigation.

The lower foliar Ca and Mg concentrations in MMC waste treatments (Fig. 4.7) is unexpected, as the waste contains $CaSO_4$ and $MgSO_4$. Decreases in Ca, K and Mg at high MMC waste treatments may be due to the suppression of uptake of these ions by NH_4, as reported by Elamin & Wilcox (1986). The high SO_4 concentrations in the MMC waste may also have contributed to reduced uptake of Ca and Mg through complexation with SO_4 to form neutral ion pairs. SO_4 complexation is discussed in section 2.4.2.1. In addition, Mn may have an antagonistic effect on Ca and Mg uptake.

The higher Mn concentration in MMC waste treatments (Fig. 3.6) is due to the Mn present in the waste. The highest waste treatment resulted in an average accumulation of 240 mgMn/kg plant material in comparison to an average Mn accumulation of 55 mgMn/kg in NH_4NO_3 treatments.

Higher Fe concentrations in MMC waste treatments (Fig. 4.6) are explained by the lower average pH values of MMC waste treated soils. Fe concentrations are unexpectedly lower at the lower pH treatments, perhaps representing evidence for some ion antagonism effect of NH_4 at higher nitrogen levels.

The minimum pH value of 5.6 recorded in the highest nitrogen treatment of the MMC waste treatment (Fig. 4.5) is unlikely to cause an Al toxicity effect.

Vega *et al.* (1992) note that Al toxicity is usually eliminated at pH 5.2 - 5.5.

Interpretation of results

The comparison of nutrient uptakes of the two fertilizer types is somewhat limited by a lack of nitrogen analyses. The effects of NO_3 or NH_4 fertilization would result in different uptake rates and accumulation of various nitrogen forms. Interpretation of yield responses in relation to ion uptake is difficult without considering these nitrogen effects.

4.4.4 Foliar composition change over time

The trend of increased nutrient uptake in yield 2 can be attributed to the same reasons as discussed in Chapter 2 (section 2.4.2.3).

4.4.5 Fertilizer level effects

4.4.5.1 Nutrient uptake

Discriminant analysis showed that foliar P, K, Zn and Cu accounted for most of the variation between treatment levels. The decrease in Na and P (Fig. 4.7) with increasing fertilizer application may be a result of NO_3 or NH_4 antagonistic effects on uptake.

The increase in Ca, Mg and K (Fig. 4.7) can be attributed to the increased concentrations of these ions in the soil solution (see section 2.4.1.1). Cu and Zn foliar concentrations (Figs. 4.6 & 4.7) also increased with increasing fertilizer treatment, probably as a result of the desorption processes that were responsible for the increase in Ca, Mg and K.

4.4.6 Concluding comment on MMC waste fertilization and Mn toxicity

The overall fertilization effect of MMC waste is comparable to NH_4NO_3 and does not result in any unusual ion deficiencies or accumulations. The Mn accumulation of 286 mgMn/kg dry mass in sample W8 is not cause for concern in terms of Mn toxicity. Kikuyu accumulated 1537 mgMn/kg dry mass in experiments by Rayment & Verrall (1980) and 1690 mgMn/kg dry mass (sample MN2) in Experiment 2 without any obvious toxicity effects.

CHAPTER 5

GENERAL DISCUSSION: APPLICATION OF RESULTS TO POTENTIAL CO-DISPOSAL OF MMC AND PULP BLEACHING WASTE IN A LAND TREATMENT SYSTEM

Re-use of waste water as an irrigation source for turfgrass is becoming a more viable and appealing option, especially in arid environments where water resources are low (Devitt, 1989). In this chapter, various aspects relating to the feasibility of co-disposal of a saline waste and MMC waste over kikuyu pastures are discussed.

5.1 KIKUYU SALINITY TOLERANCE

Experiment 1 demonstrated the high salinity tolerance of kikuyu. Salt resistance in fodder plants should, however, express their ability to survive under saline conditions combined with their ability to rejuvenate after exposure to multiple clippings (Malkin & Waisel, 1986). The increase in salinity tolerance after harvesting (ie. yield 1 to 2) in Experiment 1 (Fig. 2.11) is evidence that kikuyu is a suitable salt tolerant fodder crop and confirms the findings of Russell (1976) concerning the high salt tolerance of kikuyu relative to a number of other grass species.

5.1.1 Salt type effects

Results from Experiment 1 showed that kikuyu growth is inhibited more by Na_2SO_4 salinity than NaCl salinity at the same EC value. The relative effects are evident in Figure 2.3 and the accompanying equations. These equations can be used to show that an 80% reduction in yield would occur at 8.1 mS/cm and

10.8 mS/cm for Na_2SO_4 and NaCl salinity, respectively. This finding could have significant implications for the management of a land disposal system of saline wastes over kikuyu pastures.

5.1.2 Salinity effects in a land disposal system

Devitt (1989) found that there is little relationship between soil salinity and osmotic stress in Bermuda grass (*Cynodon dactylon*) irrigated by saline waste water. The salinity of the irrigation water, rather than soil salinity, was more highly correlated with most of the parameters related to soil-plant-water relations.

The upper root zone, near the surface, usually has the lowest salinity (very close to the salinity of the applied water) since it is the zone most frequently replenished by irrigation and rainfall. The shallow-rooted nature of kikuyu may make it less susceptible to saline irrigation water, as it will mainly utilise soil water near the surface. The surface soil, however, dries out quickly due to an abundance of roots and exposure to surface heat, with a consequent increase in salinity. Frequent irrigation can prevent this effect (Ayers & Westcot, 1985). If irrigation is frequent, the salinity of the applied waste water can be used to estimate salinity-induced yield reductions. Careful consideration should, however, be given to potential water-logging problems and contamination of adjacent water resources.

5.2 KIKUYU TOLERANCE TO MMC WASTE

The major constituents of MMC waste are plant nutrients: NH_4, Mg, Ca, Mn and SO_4, all of which have potentially beneficial effects on plant growth. In the land treatment system proposed for MMC waste:

- NH_4 concentrations are anticipated to be controlled at an optimum fertilization level for growth.
- Ca and Mg may provide some fertilization effect and would help maintain soil structure.
- Mn and possibly SO_4 should be attenuated by the soil, depending on application rate.
- Mn loading at the anticipated N application levels may just be high enough to induce significant toxicity symptoms in the pasture.

5.2.1 Fertilizer effect

MMC waste had a similar fertilization effect to a standard N fertilizer (NH_4NO_3) on kikuyu growth (Fig 4.1). MMC waste application increased the kikuyu dry mass yield at all treatment levels. The highest yield response and thus optimal MMC waste application occurred between 200 & 400 kgN/ha. The optimal NH_4NO_3 application occurred at about 400 kgN/ha.

MMC waste irrigation does, however, require an assessment of the threat to kikuyu pasture sustainability for the following reasons:

- a possible increase in soil salinity
- changes in soil pH and redox potential
- changes in soil structure
- Mn toxicity

Each of these factors will be dealt with in the ensuing sections.

5.2.2 Salinity increases

It is anticipated that MMC waste could be used as a dilute liquid nitrogen fertilizer. The quantities involved would be negligible, however, in comparison to normal volumes of irrigation water. Due to this dilution effect an increased soil salinity effect is unlikely.

5.2.3 Soil pH and redox potential

Results from Experiment 3, predict a marked decrease in soil pH after MMC waste application (Fig 4.5). This decrease will depend on the soil's acid neutralising capacity and should be investigated thoroughly. Liming amendments may be necessary to prevent detrimental effects on the kikuyu pasture.

Ironically, if the pH of the soil drops to below 5.5, the greatest risk of MMC waste fertilization is perhaps not the Mn content of the waste, but a risk of Mn toxicity from Mn within the soil. This effect, however, represents little threat to pasture sustainability given the demonstrated degree of acidity and Mn tolerance of kikuyu.

5.2.4 Soil structure effects

$MnSO_4$ applications are likely to have a positive effect on soil structure. Mn in solution was found to induce flocculation of dispersed clay. Increased structural stability of the soil could therefore be anticipated and this would, if anything, promote more favourable drainage and aeration.

5.2.5 Mn toxicity and the critical threshold for MMC waste application

The use of untreated MMC waste as a nitrogen fertilizer will result in a Mn loading of the soil. The Mn content of the waste thus represents a potential threat of Mn toxicity. Mn is not a universally high risk pollutant but becomes problematic in terms of plant growth and water pollution if pH or pe decreases to the extent that soluble Mn concentrations increase as a result of reduction processes. Mn may then move through the soil profile into groundwater supplies or reach levels that are toxic to many plants. An inherent risk of Mn toxicity exists in most soils worldwide, since Mn makes up on average 650 mg/kg of the earths crust and 545 mg/kg of soils (Kabata-Pendias & Pendias, 1985; Gilkes & McKenzie, 1988). The low occurrence of Mn toxicity is testimony to the fact that most soils do not have pH or pe values in the range that allows for the continuous presence of high concentrations of soluble Mn.

The anticipated Mn loading relative to N fertilization is given in Table 5.1. The maximum MMC waste application (800 kgN/ha) produced a yield above the control (Fig. 4.1) in Experiment 3. A critical threshold level for MMC waste was therefore not established.

The Mn toxicity threshold determined in Experiment 2 suggests that, at a Mn loading of between 800 and 1600 mgMn/kg soil, kikuyu yield will decrease relative to a K and P fertilized control. This critical Mn level extrapolates into a MMC loading of 900 - 1800 kgN/ha which is far in excess of anticipated loading rates.

Table 5.1: MMC waste land disposal system: anticipated nitrogen fertilization and corresponding Mn loading.

Nitrogen (kg/ha)	Mn (kg/ha)	Mn (mg/kg soil)	Volume of waste (m^3/ha)
100	171	86	14
200	342	172	28
400	684	344	56
800	1368	688	110

5.2.6 Residual effects of Mn fertilization

The residual effects of Mn fertilization have not been extensively researched. Mascagni & Cox (1988) note that the rate of Mn applied in the field is seldom high enough to result in significant carry-over for succeeding crops.

Mascagni & Cox (1988) evaluated effects of Mn fertilization and time with an empirical model using extractable Mn measurements. Approximately 50 % of the Mn rate applied was predicted to be extractable immediately after application. Thereafter extractable Mn decreased exponentially with time. According to the model developed, if 14 kgMn/ha had been applied, it would take approximately 7 years to reduce the extractable Mn concentration to within 1 kgMn/ha of the original soil level.

Extractable Mn is not, however, a reliable indication of bioavailable Mn. The inclusion of water-extractable Mn measurements into the model would make it more useful for determining the residual effects of a Mn waste land disposal system in terms of plant toxicity and water pollution risks.

5.2.7 Mn sorption

The degree of Mn sorption/attenuation by the soil is important for determining the risk of groundwater or surface water contamination in a land treatment system for MMC waste. Soil pH plays a major role in Mn sorption as it affects the solubility, adsorption, desorption and oxidation of Mn^{2+} and the reduction of Mn oxides.

Mn sorption in the soil used for pot experimentation was calculated from soil solution data in Experiments 2 & 3, presented in Table 5.2. Kd values in Table 5.2 represent the distribution coefficient which describes the adsorption behaviour of Mn by the soil. The adsorption isotherm (Fig. 5.1) followed an L shape curve and fitted the von Bemmelen - Freundlich isotherm (Sposito 1989) as follows:

$$q_{mn} = 16\ c_{mn}^{(0.34)}$$

where q_{mn} = mmoles Mn adsorbed per kg dry soil

c_{mn} = equilibrium solution Mn concentration (mmol)

The linear regression of $\log q_{mn}$ as a function of $\log c_{mn}$ was significant at the 1% level (Fig. 5.2).

The Mn sorption capacity of the soil in Experiment 3 appeared to be exceeded (ie. where c_{mn} reached an environmentally unacceptable concentration) between 342 & 684 mgMn/kg soil (Table 5.2), where the c_{mn} value increased to 0.75 mmol Mn. This observation may, however, be misleading as field conditions of pH and pe will be different to those in an undrained container containing 400g of soil.

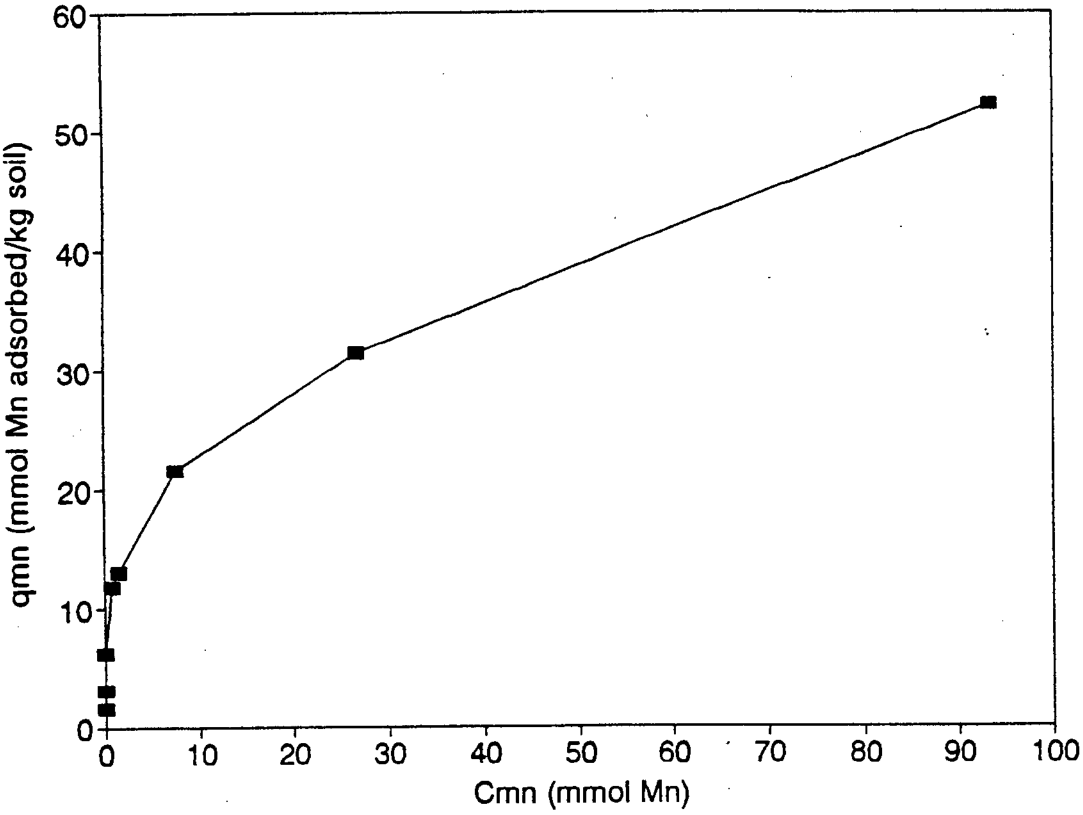


Fig. 5.1 The quadratic relationship between adsorped Mn (q_{mn}) and Mn in solution after equilibration (c_{mn}).

Table 5.2: Mn sorption in Experiments 2 & 3

Treatment Level (mg Mn/kg soil)	mmol Mn/kg soil	c_{mn} (mmol Mn)	q_{mn} (mmol Mn adsorbed per kg soil)	Kd (q_{mn}/c_{mn})
86	1.56	0.002	1.56	780
172	3.13	0.005	3.13	626
344	6.25	0.03	6.22	207
688	12.5	0.75	11.75	15.6
800	14.5	1.48	13.02	8.8
1600	29.1	7.5	21.6	2.9
3200	58.2	26.8	31.4	1.2
8000	145.5	93.3	52.2	0.56

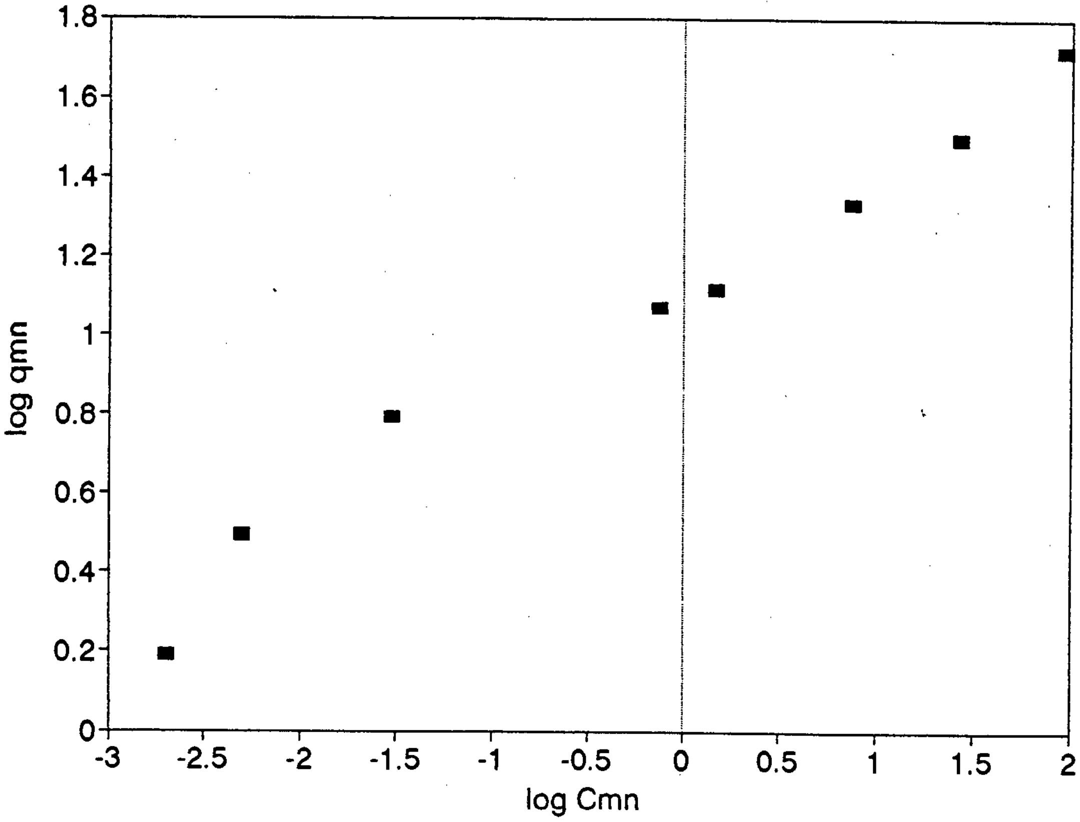


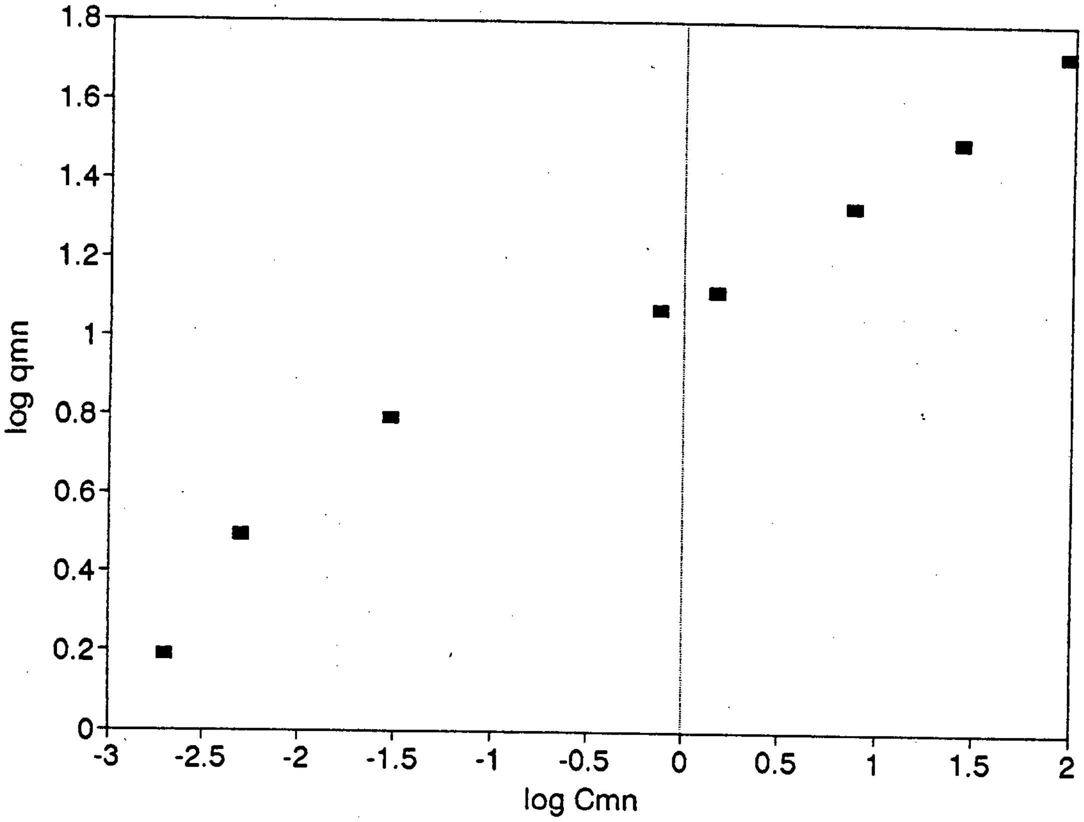
Fig. 5.2 **The relationship between adsorped Mn (q_{mn}) and Mn in solution after equilibration (c_{mn}).**

5.2.8 $MnSO_4$ behaviour in the soil environment

Mn mobility in the soil environment is predominantly to be controlled by the following processes:

- $MnCO_3$ precipitation
- Mn^{2+} oxidation
- Mn adsorption

These processes are discussed in the ensuing sections.



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- Mn adsorption

These processes are discussed in the ensuing sections.

MnCO$_3$ precipitation

Schwab and Lindsay (1983) found manganese solubility in soils to be controlled by Mn oxides at high pH and by MnCO$_3$ at redox values below pe + pH = 15. Most soil pe + pH values will fall below 15 and thus MnCO$_3$ commonly controls Mn^{2+} concentrations in soils. The mineral solubility diagram of Mn in soils, depicting the common oxide, hydroxide and carbonate phases is presented in Figure 5.2.

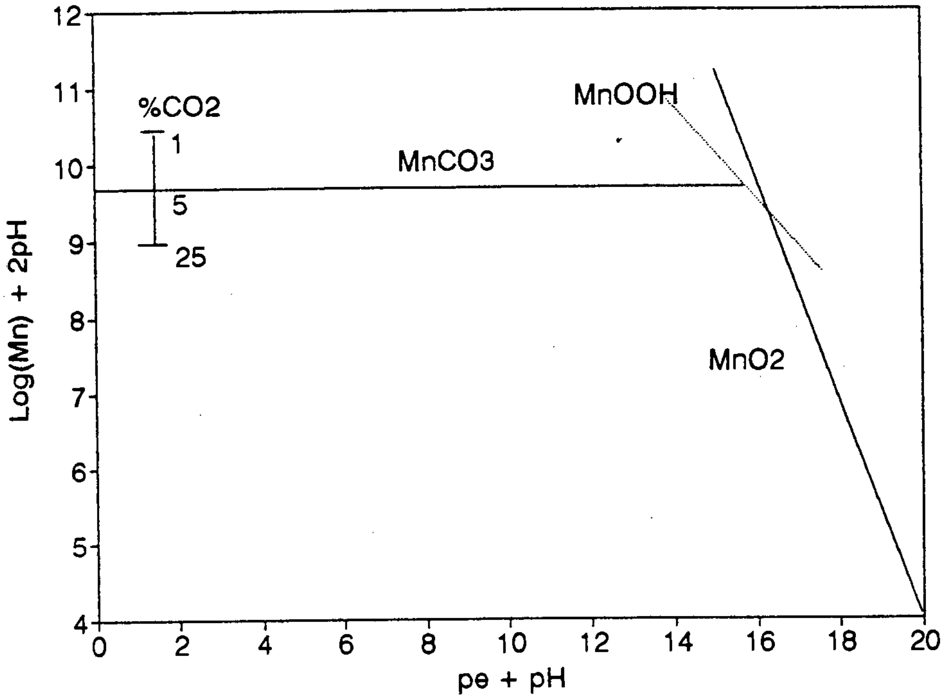

Fig. 5.2 Mn^{2+} activity plotted as a function of redox demonstrating which solid phases control the solubility of Mn in soils (adapted from Schwab & Lindsay, 1983).

Figure 5.3 shows the log(Mn) + 2pH values of soils in Experiment 1 plotted against pH.

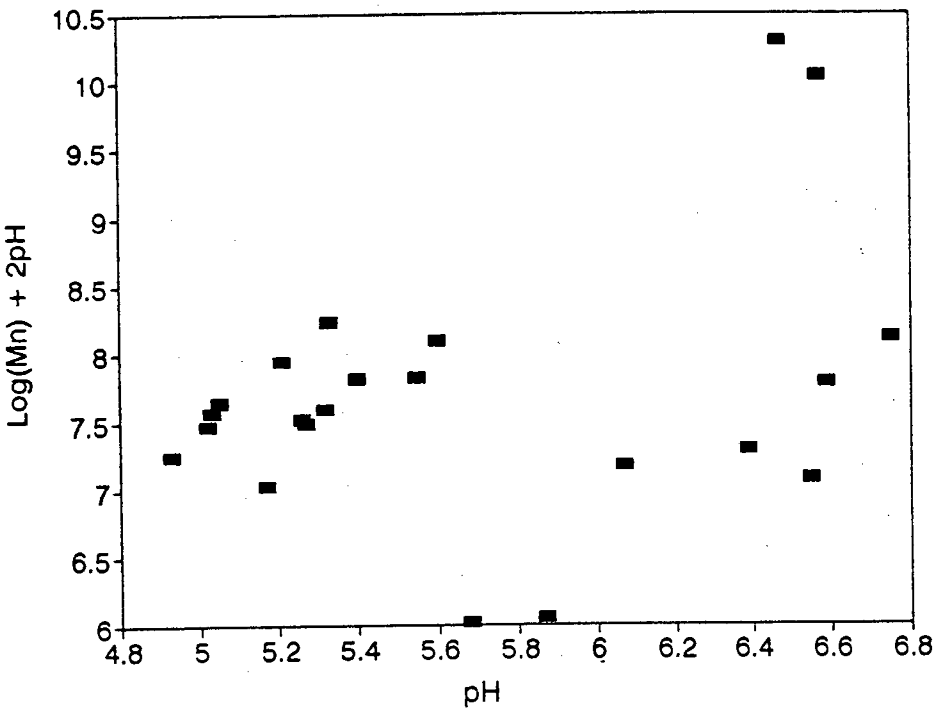

Fig. 5.3 **The relationship between Mn^{2+} activity and pH in Experiment 1.**

The values in figure 5.3 are somewhat lower than expected but follow a linear horizontal trend similar to the solubility of $MnCO_3$ depicted in Figure 5.2. The lower values suggests that a Mn oxide may be controlling Mn^{2+} solubility. Log(Mn) + 2pH does not, however, show a decrease with increasing pH, as would occur with a Mn oxide (Fig. 5.2) or Mn phosphate mineral (Reisenauer, 1988).

The increase in concentration of various soil solution cations and plant tissue cations with an increase in $MnSO_4$ application in Experiment 1 is a further clue to which mineral phase may control Mn solubility in this system.

Mn oxides have an extremely high cation exchange capacity (Gilkes & McKenzie, 1988) and their formation might be expected to result in decreased concentrations of cations in both the soil solution and foliage. Such an effect was not detected.

The chemical reaction likely to attenuate the Mn component of MMC waste could thus be $MnCO_3$ precipitation. This reaction depends on CO_2 partial pressure and thus CO_2 may largely control the attenuation of Mn^{2+}. Root and microorganism respiration in the soil could possibly maintain the elevated soil CO_2 partial pressures necessary to promote $MnCO_3$ precipitation.

Mn^{2+} oxidation

The application of $MnSO_4$ to a highly oxidising or high pH soil environment would result in the oxidation of Mn^{2+} to various forms of Mn oxides and hydroxides. The Mn oxides are reported to catalyse the oxidation of Mn^{2+} by providing a template for further oxidation (Reisenauer 1988). Mn attenuation may thus be a self perpetuating/stimulating process in a highly oxidising environment because Mn oxide formation further increases Mn precipitation/sorption. This process would be extremely favourable in the context of the proposed waste disposal system. If the pH and pe of soil are maintained at levels favouring oxidation, the Mn^{2+} attenuation capacity of a particular soil may be almost unlimited. Soil management should focus on maintenance of an oxidising environment to promote this process.

Mn adsorption

Mn adsorption in soils is associated with both organic and mineral fractions of soils and held by forces ranging from weak electrostatic forces to strong inner sphere bonds (Reisenauer, 1988). Mn is usually concentrated in top soils due to complexation with organic matter (Kabata-Pendias & Pendias, 1985). The clay and organic content of a soil will thus affect Mn sorption capacity. It is possible that the log Mn^{2+} + 2pH values shown in Figure 5.3 reflect equilibrium with adsorbed Mn, since undersaturation of the solutions with respect to $MnCO_3$ and other mineral phases is generally indicated.

5.2.9 Worst case scenario

Given the worst case scenario of Mn moving into groundwater and rivers in the area, the oxidising nature of most water bodies would result in the rapid oxidation and precipitation of Mn. A Mn oxide precipitate on the river bottom may be visible if the Mn concentration reached high enough levels. Unless the Mn attenuation capacity of the soil is exceeded (see section 5.2.7), it is unlikely that this scenario would occur.

5.2.9.1 Soil flooding and Mn toxicity

A decrease in redox potential such as occurs with flooding potentially increases the risk of Mn mobilization. Research into this phenomena has, however, produced conflicting results (Siman *et al.*, 1974). Precautions should nevertheless be taken to prevent flooding of the land disposal area. Lowered redox is unlikely to induce Mn toxicity in kikuyu, given the high tolerance evident in Experiment 1 & 2 and the results of Rayment & Verrall (1980). Prevention of flooding is more a precaution against the danger of groundwater contamination by the highly soluble reduced Mn^{2+}.

5.2.9.2 The tobacco concern

Crops grown downstream from the proposed land disposal area include tobacco (*Nicotiana tabacum*). Burley tobacco grown in solution cultures began showing Mn toxicity symptoms when tissue concentrations reached approximately 3000 mg/kg. This occurred at a Mn solution concentration of 30 mg/l (Hiaat & Ragland, 1969). If the Mn sorption capacity of the soil is not exceeded, Mn movement through soil profiles and into the river system is unlikely and thus a concentration of 30mg Mn/l in the river could effectively be ruled out. The Mn sorption capacity of the soil used in the experiments appeared to be exceeded between 342 & 684 mgMn/kg soil (Table 5.2), which corresponds to a MMC waste nitrogen loading of between 400 & 800 kgN/ha. Nitrogen loadings of MMC waste below 400 kgN/ha are thus unlikely to exceed the Mn sorption capacity of the soil used in the pot experiments. Determination of the field Mn sorption capacity of the disposal site soil is of the utmost importance for assessing the pollution risk of MMC waste disposal.

5.2.10 Possible amelioration of Mn toxicity/pollution

Liming of soil to a pH 5.8 - 6.2 is necessary for alleviating Mn toxicity (Vega *et al.*, 1992). Lime applications are, however, unlikely to affect Mn toxicity induced by a reduced soil redox potential (Siman *et al.*, 1974). Phosphate application may also be beneficial for reducing Mn solubility because relatively insoluble Mn phosphates are formed (Heintze, 1968; Boyle & Lindsay, 1986).

5.2.11 The need for field trials

The prediction of bioavailable Mn is extremely limited even though much is known about the nature and reactions of Mn in soils and its absorption and functioning in plants (Reisenauer, 1988). Due to this predictive limitation, field tests are imperative before decisions are taken on the feasibility of MMC waste disposal. In addition, plant responses to excess Mn are often dependent on genotype (Foy *et al.*,1969; Jones & Nelson, 1979; Burke *et al.*, 1990) and it is important to check that the kikuyu genotype concerned is not particularly sensitive to Mn toxicity. Three different ecotypes of kikuyu have been recognised in Kenya, but it would be difficult to recognise these ecotypes in existing kikuyu pastures as considerable clonal variation exists (Mears, 1970).

There also exists a need for establishing the longer term (2 to 3 years) effects of the sustained use of MMC waste as a nitrogen fertilizer. In addition, the applicability of MMC waste as fertilizer source may not be limited to kikuyu. Long term field trials with both kikuyu and other major crops in the Nelspruit area (eg. sugar cane) may thus be an appropriate step for further research.

5.2.12 Concluding comment on Mn toxicity effects of MMC waste

Amending an aerobic neutral soil with the addition of a dilute neutral $MnSO_4$ solution should not be regarded as a polluting process provided that soil Mn attenuation is sufficient to prevent any detrimental effects on agriculture, natural vegetation growth or water quality. The risk of detrimental Mn effects does however exist, if the $MnSO_4$ application results in a considerable decrease of pH or pe. The Mn attenuating capacity and susceptibility of a soil to pH and redox potential changes is a function of soil properties such as acid buffering capacity and degree of aeration. These effects should be thoroughly investigated before embarking on MMC waste disposal.

5.3 KIKUYU PASTURE MANAGEMENT: $(NH_4)_2SO_4$ FERTILIZATION

Kikuyu grass occurs naturally as a forest margin species on the highland plateaux of east and central Africa. Mean annual rainfall ranges from 1000 to 1600 mm. The soils where the grass is naturally distributed are often characterised by deep lateritic red loams with volcanic parent material. Successful kikuyu growth reportedly requires high soil fertility (Mears, 1970). Various aspects relating to fertility and pasture quality are discussed in the ensuing sections.

5.3.1 Optimal nitrogen loading

$(NH_4)_2SO_4$ fertilization of kikuyu has been shown to substantially increase yields (Awad & Edwards, 1977). Kikuyu responses to nitrogen fertilization vary from site to site. In northern New South Wales a maximum yield of 30 000 kg dry mass.$ha^{-1}yr^{-1}$ could be achieved by the application of 1 120 kgN/ha.

Awad & Edwards (1977) found that a $(NH_4)_2SO_4$ fertilization regime of 300 kgN/ha for kikuyu pastures was optimal. The fertilization, however, led to decreases in Ca, Mg and K uptake. The decreased uptake of Ca and Mg may be a function of NH_4 antagonism as reported by Cerda & Martinez (1988). MMC waste fertilization exhibited a similar type of response, with an optimum loading of 200 kgN/ha and reduced Ca and Mg uptake.

5.3.2 Acidifying effect

$(NH_4)_2SO_4$ applications decrease soil pH over time through nitrification and the loss of exchangeable bases (Ca, Mg and K). High yields can, however, be maintained at moderate nitrogen rates (eg. 140kg/ha) provided that lime is applied to alleviate a soil acidity build-up (Awad & Edwards, 1977).

5.3.3 Mn toxicity/nitrogen interactions

Elamin & Wilcox (1986) demonstrated the effect of N form on Mn toxicity in watermelons (*Citrullus lanatus*), whereby NO_3 stimulated rapid Mn absorption and consequent Mn toxicity, whereas NH_4 had a relative inhibitory effect on Mn uptake and no Mn toxicity developed. In a well aerated and not excessively acidic environment, rapid nitrification of NH_4 to NO_3 can be expected (Tisdale *et al.*, 1985).

The NH_4 content within the waste may thus serve a useful function of inhibiting Mn uptake if conversion to NO_3 is inhibited. There was some indication of such inhibition in the pot experiment (section 4.4.2.1) but field trials would be necessary to establish whether this will also occur in the pasture.

5.3.4 Possible animal disorders

Few animal disorders have been reported after kikuyu pastures have been grazed. Where rapid pasture growth follows a period of drought, however, cattle deaths have occurred in New Zealand and disorders in New South Wales (Awad & Edwards, 1977). The clinical symptoms of the disorders in both cases were abdominal distension, incoordination of hind legs, salivation, sunken eyes and death in extreme cases. In New South Wales, the disorder occurred on pastures which had previously received 336 kg N/ha as $(NH_4)_2SO_4$ over four years.

The animal disorders reported may affect the feasibility of cattle grazing after MMC waste disposal over kikuyu pastures. The disorders were not, however, adequately explained and the fertilizer type may have been inconsequential. Disorders occurring after drought may have been due to an increase in soil salinity, as salts generally rise to the soil surface during periods of drought (Maas & Hoffman, 1977). The kikuyu pastures are, however, presently under a saline waste irrigation scheme with no apparent side effects on the grazing livestock.

Mn accumulation within kikuyu also poses a potential risk of Mn toxicity in the cattle grazing on the pasture. The effects on cattle of kikuyu fertilized with $(NH_4)_2SO_4$, in combination with high salinity manganiferous irrigation, should be investigated before commencing with the land disposal system.

5.4 MMC WASTE TREATMENT AND AMMONIA TOXICITY

Due to ammonia volatilization the proposed liming treatment (see Introduction - page 1) of the waste to precipitate out Mn may make the waste unfeasible as a nitrogen fertilizer source. Ammonia volatilization from NH_4 within the waste would occur at the high pH levels required to remove Mn. Ammonia is toxic to plants even in concentrations as low as 6 mmol/l NH_3 (aq) (Mengel & Kirkby, 1978). Direct application to a pasture may therefore cause damage.

Results from a preliminary investigation into the potential ammonia toxicity of lime-treated MMC waste suggested that kikuyu may be relatively ammonia tolerant. Land disposal of lime-treated MMC waste over kikuyu pastures may thus be feasible for the following reasons: treated MMC waste may not have the anticipated ammonia toxicity effects on kikuyu pastures and dilution of the treated MMC waste in a co-disposal system with another neutral waste stream may eliminate the ammonia toxicity risk completely.

5.5 FEASIBILITY AND REQUIREMENTS OF MMC WASTE DISPOSAL

The disposal of MMC waste by a land treatment system is a feasible waste management strategy with potential fertilizing benefits for a pasture such as kikuyu. The unusually high Mn tolerance of kikuyu is particularly beneficial in light of the high Mn content of the untreated waste. Other crops may not be as amenable to MMC waste fertilization particularly if they are susceptible to Mn toxicity.

Further research necessary for making MMC waste land disposal decisions would include the following:

- detailed analyses of soil properties on the site to be used.
- Mn sorption capacity of the soil and consequent potential for groundwater contamination.
- Monitoring of the effects of possible redox potential and pH changes in the soil during field trials.
- Determination of likely foliar Mn accumulation in kikuyu and its potential effects on grazing stock.

CONCLUSIONS

The results from pot experimentation demonstrated that kikuyu grass is both salinity tolerant and Mn tolerant and thus suggests that kikuyu may be a suitable pasture grass for the co-disposal of sodic saline wastes and MMC wastes in a land treatment system.

Salinity tolerance

Kikuyu salinity tolerance, using electrical conductivity as a salinity index, was significantly greater for NaCl-induced than Na_2SO_4-induced salinity. This difference was attributed to the formation of SO_4 neutral ion pairs in Na_2SO_4 treatments which decreased cation uptake, increased osmotic stress relative to electrical conductivity and led to a possible SO_4-induced Ca deficiency. Gypsum precipitation may have exacerbated the latter effect. In addition, Cl tissue accumulation was a likely osmotic adjustment mechanism under NaCl salt stress, which could not be utilized in Na_2SO_4 salinity. Reduced Cl solubility in soils treated with $MnSO_4$ and Na_2SO_4 treated soils was speculatively attributed to the formation of an ettringite-like mineral phase which would have the capacity to co-precipitate chloride.

Mn tolerance

Kikuyu exhibited both a fertilization effect and a Mn toxicity effect with $MnSO_4$ applications. An increase in yield occurred for Mn applications of up to 1600 mg/kg soil. This effect was attributed to increased nutrient availability as a result of soil desorption processes and nitrogen mineralisation. Mn applications of 3200 and 8000 mg/kg resulted in severe Mn toxicity symptoms and reductions in yield.

MMC waste fertilization

Fertilization of kikuyu with NH_4NO_3 and MMC waste produced similar yield responses. Mn toxicity did not appear in MMC waste-treated kikuyu, even at nitrogen loadings of 800 kgN/ha. The decreased soil pH with MMC waste application is, however, cause for concern and further research is required. Mn attenuation in the soil is a function of $MnCO_3$ precipitation, oxidation of Mn^{2+} and/or Mn adsorption. These processes are expected to prevent excess Mn^{2+} accumulation which would pose a Mn toxicity and water pollution risk. Further research into the Mn attenuating capacity of the soil and the kikuyu pasture response to MMC waste application is, however, necessary. This could be effectively achieved with a trial fertilization of a limited area.

Concluding comment

The disposal of untreated MMC waste as a nitrogen fertilizer substitute for kikuyu pastures is in principle a feasible operation in terms of maintaining pasture sustainability and preventing pollution of water resources. Field trials are necessary to confirm the results of this phytotron study and to determine the longer term effects of sustained use of MMC waste as a nitrogen fertilizer. As discussed in the introduction, this research indicates that there is great potential for the beneficial utilization/disposal of MMC waste and that the exciting possibility exists of transforming a liability into an asset.

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APPENDIX I

SAMPLE CODES

Experiment 1

Codes are arranged in the order:
ABCD (eg. S0M2, C20M1)

where A = salt type (S = Na_2SO_4 , C = NaCl)
B = salinity level (0, 5, 10 or 20 mS/cm)
CD = manganese level (M0, M1 or M2 = 0, 800 or 1600 mg/kg soil respectively)

Experiment 2

Codes are as follows:

MN0 = 0 mg Mn/kg soil
MN1 = 800 mg Mn/kg soil
MN2 = 1600 mg Mn/kg soil
MN3 = 3200 mg Mn/kg soil
MN4 = 8000 mg Mn/kg soil

Experiment 3

Codes are arranged in the order:
AB (eg. W4, N8)

where A = fertilizer type (W = MMC waste, N = NH_4NO_3)
B = nitrogen loading X 100 kg/ha (eg. 2 = 200 kg N/ha)

APPENDIX II

Yield data for Experiments 1, 2 & 3

YIELD 1	REP1	REP2	YIELD 2	REP1	REP2
S0M0	1.59	1.34	SEOMO	1.59	1.34
S0M1	1.41	1.59	M1	1.41	1.59
S0M2	1.72	1.74	M2	1.72	1.74
S5M0	1.92	1.12	SE5MO	1.92	1.12
S5M1	1.34	2.01	M1	1.34	2.01
S5M2	2.21	1.63	M2	2.21	1.63
S10M0	1.54	1.37	SE10MO	1.54	1.37
S10M1	1.62	1.67	M1	1.62	1.67
S10M2	1.24	1.03	M2	1.24	1.03
S20M0	1.02	1.37	SE2OM0	1.02	1.37
S20M1	0.87	1.24	M1	0.87	1.24
S20M2	1.42	1.51	M2	1.42	1.51
C0M0	0.89	1.89	CE0M0	0.89	1.89
C0M1	2.51	2.36	M1	2.51	2.36
C0M2	2.06	2.68	M2	2.06	2.68
C5M0	1.39	1.58	CE5M0	1.39	1.58
C5M1	1.28	1.36	M1	1.28	1.36
C5M2	1.44	2.52	M2	1.44	2.52
C10M0	1.51	2.39	CE10M0	1.51	2.39
C10M1	1.75	1.26	M1	1.75	1.26
C10M2	1.13	2.24	M2	1.13	2.24
C20M0	2.45	2.36	CE20M0	2.45	2.36
C20M1	1.37	1.61	M1	1.37	1.61
C20M2	1.57	2.13	M2	1.57	2.13
W0	1.69	1.45	W0	1.69	1.45
W1	1.62	0.87	W1	1.62	0.87
W2	1.58	1.24	W2	1.58	1.24
W4	1.25	1.12	W4	1.25	1.12
W8	1.60	1.49	W8	1.60	1.49
N0	0.57	0.51	N0	0.57	0.51
N1	0.38	0.77	N1	0.38	0.77
N2	1.07	0.73	N2	1.07	0.73
N4	1.21	1.18	N4	1.21	1.18
N8	1.49	1.22	N8	1.49	1.22
Mn3	1.02	2.26	Mn3	1.02	2.26
Mn4	0.61	0.71	Mn4	0.61	0.71

APPENDIX III

XRF soil data

Major elements

	%
SiO2	63.26
TiO2	0.81
Al2O3	14.86
Fe2O3	6.92
MnO	0.07
MgO	1
CaO	0.22
Na2O	0.25
K2O	1.99
P2O5	0.1
Cr2O3	0
H2O	2.13
LOI	8.43

Minor elements

	ppm
Mo	1.2
Nb	17
Zr	268
Y	29
Sr	38
U	2.8
Rb	108
Th	15
Zn	100
Cu	23
Ni	29
Co	21
Mn	592
Cr	93
V	119

APPENDIX IV

Soil saturated paste data: Experiments 1,2 & 3

	pH	EC mS/cm	Mn mg/l	Na mg/l	NH4 mg/l	K mg/l
S0M0	6.59	3.53	0.5	314	101	83
S0M1	5.55	6.03	114	337	136	125
S0M2	5.03	7.23	145	319	134	125
S5M0	6.07	7.14	2.3	1005	82	94
S5M1	5.6	8.59	215	1109	134	123
S5M2	4.93	10.45	773	1199	146	142
S10M0	5.87	11.71	0.6	2183	156	118
S10M1	5.17	12.33	152	2118	207	134
S10M2	5.02	14.9	977	2426	215	154
S20M0	6.75	19.69	1.8	4371	200	139
S20M1	6.57	20.2	369	5115	245	166
S20M2	6.47	21	1133	4780	242	169
C0M0	6.39	3.53	0.4	298	105	84
C0M1	5.26	6.03	209	331	130	136
C0M2	5.03	7.23	825	322	142	138
C5M0	5.68	7.29	0.7	733	75	96
C5M1	5.27	9.14	207	833	144	143
C5M2	5.21	10.46	886	824	147	144
C10M1	5.32	12.28	211	1415	222	151
C10M2	5.05	14.08	952	1525	231	162
C20M0	6.55	16.81	0.2	2413	204	136
C20M1	5.4	19.93	285	2808	247	171
C20M2	5.33	21.1	1119	2803	248	188
W0	6.94	1.66	0.1	225	0	38
W1	6.79	3	0.2	287	71	69
W2	6.64	3.92	0.7	304	113	95
W4	5.8	5.63	3.56	330	175	125
W8	5.59	8.06	82	332	443	175
N0	6.94	1.66	0.1	225	0	38
N1	6.33	2.45	0.1	260	0	57
N2	6.53	2.74	0.1	282	73	66
N4	6.21	3.51	0.1	293	100	81
N8	6.2	5.15	0.4	331	178	120
Mn3	4.76	10.49	2944	386	211	154
Mn4	4.66	19.75	10250	410	240	189

	Mg mg/l	Ca mg/l	Cl mg/l	NO3 mg/l	SO4 mg/l
S0M0	88	258	286	960	186
S0M1	204	648	278	822	2663
S0M2	198	635	235	731	2682
S5M0	136	410	230	1056	2576
S5M1	196	522	219	684	4808
S5M2	246	491	209	757	6663
S10M0	185	506	218	1103	5444
S10M1	233	533	205	697	6557
S10M2	280	475	199	665	9625
S20M0	220	573	208	513	13395
S20M1	272	511	210	0	15622
S20M2	290	486	215	23	18909
C0M0	90	263	292	960	156
C0M1	214	625	224	894	2579
C0M2	253	566	217	830	4345
C5M0	139	418	1296	1358	149
C5M1	233	759	1250	728	2882
C5M2	254	603	1223	660	4409
C10M1	249	823	2339	708	2499
C10M2	279	696	2423	616	4218
C20M0	183	570	4700	642	162
C20M1	281	944	5287	694	2985
C20M2	361	867	4867	723	4485
W0	44	134	244	131	177
W1	100	274	254	294	805
W2	139	360	256	363	1555
W4	216	570	248	213	2953
W8	325	526	235	156	4796
N0	44	134	244	131	177
N1	68	196	243	448	155
N2	79	227	256	662	155
N4	87	246	265	949	164
N8	122	344	257	1764	156
Mn3	324	546	208	621	9095
Mn4	458	559	220	612	28251

APPENDIX V

Soil saturated paste activity data: Experiments 1,2 & 3

	Mn	Na	NH4	K	Mg
S0M0	3.98E-06	0.01122	0.004571	0.001738	0.001622
S0M1	0.000537	0.01122	0.00537	0.002399	0.002188
S0M2	0.003236	0.010233	0.00537	0.00257	0.002239
S5M0	1.07E-05	0.033113	0.003236	0.001778	0.001413
S5M1	0.000794	0.034674	0.004898	0.002239	0.001622
S5M2	0.002455	0.036308	0.005129	0.002512	0.001778
S10M0	2.04E-06	0.067608	0.005623	0.002089	0.001445
S10M1	0.00049	0.064565	0.007244	0.002344	0.001698
S10M2	0.002692	0.070795	0.007079	0.00257	0.001738
S20M0	4.07E-06	0.123027	0.006026	0.002188	0.001148
S20M1	0.000794	0.141254	0.007079	0.00257	0.001349
S20M2	0.002239	0.128825	0.006761	0.00257	0.001318
C0M0	3.24E-06	0.010715	0.004786	0.001778	0.00166
C0M1	0.001	0.010965	0.005248	0.00263	0.002344
C0M2	0.003236	0.010233	0.00537	0.00257	0.002239
C5M0	4.57E-06	0.025119	0.003311	0.00195	0.002188
C5M1	0.000891	0.026915	0.005623	0.002692	0.002399
C5M2	0.003388	0.026915	0.005495	0.00263	0.002291
C10M1	0.000891	0.045709	0.00871	0.002818	0.00257
C10M2	0.003548	0.047863	0.00871	0.002951	0.002455
C20M0	9.55E-07	0.079433	0.008511	0.00263	0.002291
C20M1	0.001047	0.087096	0.009333	0.00309	0.00263
C20M2	0.003802	0.087096	0.00912	0.003388	0.002754
W0	9.33E-07	0.008511	0	0.000832	0.000933
W1	1.38E-06	0.010233	0.003162	0.001445	0.001585
W2	3.98E-06	0.010471	0.004786	0.001905	0.00182
W4	1.62E-05	0.010965	0.006918	0.002399	0.002239
W8	0.000302	0.010471	0.016218	0.003162	0.002754
N0	9.33E-07	0.008511	0	0.000832	0.000933
N1	8.91E-07	0.00955	0	0.00123	0.00138
N2	8.51E-07	0.010233	0.003388	0.001413	0.001514
N4	8.13E-07	0.010471	0.004571	0.001698	0.001622
N8	3.02E-06	0.011749	0.007943	0.002455	0.002089
Mn3	0.008913	0.011482	0.007244	0.00263	0.002188
Mn4	0.019498	0.010965	0.006457	0.002818	0.00195

	Ca	Cl	NO3	SO4
S0M0	0.002884	0.006607	0.012882	0.000617
S0M1	0.004074	0.006166	0.010471	0.006761
S0M2	0.002951	0.005129	0.010233	0.009772
S5M0	0.002512	0.005129	0.013183	0.007244
S5M1	0.002455	0.004677	0.008511	0.012023
S5M2	0.002042	0.004365	0.00912	0.014791
S10M0	0.002239	0.004677	0.01349	0.012882
S10M1	0.002188	0.004365	0.008318	0.014791
S10M2	0.00166	0.004074	0.007943	0.019498
S20M0	0.001698	0.004266	0.006026	0.026915
S20M1	0.001413	0.004266	0	0.0302
S20M2	0.00123	0.004365	0.000269	0.035481
C0M0	0.002951	0.006918	0.012882	0.000513
C0M1	0.003981	0.004898	0.01122	0.006457
C0M2	0.002951	0.004677	0.010233	0.009772
C5M0	0.003981	0.02884	0.017378	0.000398
C5M1	0.004571	0.026915	0.008913	0.006457
C5M2	0.00309	0.025704	0.008128	0.009333
C10M1	0.005012	0.050119	0.00871	0.005129
C10M2	0.003631	0.050119	0.007413	0.008128
C20M0	0.004266	0.1	0.007762	0.000331
C20M1	0.005248	0.109648	0.008318	0.00537
C20M2	0.004365	0.1	0.008511	0.007586
W0	0.001738	0.006026	0.00182	0.000794
W1	0.00257	0.005888	0.00389	0.002754
W2	0.002754	0.005888	0.004786	0.004898
W4	0.003388	0.005495	0.002692	0.007943
W8	0.00257	0.005129	0.00195	0.011482
N0	0.001738	0.006026	0.00182	0.000794
N1	0.002399	0.004571	0.006166	0.000603
N2	0.00263	0.006026	0.008913	0.00055
N4	0.002754	0.006166	0.012589	0.000562
N8	0.003548	0.005888	0.022909	0.000457
Mn3	0.002138	0.004169	0.007413	0.016218
Mn4	0.001318	0.004266	0.007244	0.039811

APPENDIX VI

Foliar composition data for Experiments 1,2 & 3

	P %	K %	Ca %	Mg %	Na mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Fe mg/kg	B mg/kg
SOMO1 A	0.384	4.76	0.314	0.444	1998	9.52	48.60	51.0	114.0	25.60
SOMO2 A	0.352	4.08	0.262	0.368	1494	8.76	35.80	44.2	1886.0	16.58
SOM11 A	0.374	4.24	0.208	0.370	1090	9.42	47.40	688.0	1246.0	19.74
SOM12 A	0.376	4.16	0.228	0.398	1198	8.54	50.40	614.0	962.0	22.80
SOM21 A	0.402	4.62	0.244	0.380	1442	10.66	48.00	548.0	744.0	21.20
SOM22 A	0.398	4.26	0.244	0.366	1286	9.34	53.20	810.0	646.0	19.80
S5M01 A	0.406	4.52	0.294	0.426	3080	8.64	44.20	82.0	520.0	29.00
S5MO2 A	0.472	4.76	0.266	0.412	4720	8.68	44.80	54.0	512.0	29.00
S5M11 A	0.428	4.18	0.220	0.372	2326	10.38	52.20	712.0	450.0	25.80
S5M12 A	0.484	4.74	0.230	0.428	3310	10.30	57.00	604.0	416.0	27.00
S5M21 A	0.402	3.94	0.182	0.350	3070	11.88	55.60	1290.0	404.0	22.80
S5M22 A	0.434	4.52	0.186	0.354	2850	10.72	62.60	1270.0	418.0	29.60
S10M01 A	0.406	4.88	0.202	0.384	4020	8.70	50.20	155.8	344.0	24.40
S10M02 A	0.478	5.02	0.200	0.356	3830	9.42	51.00	66.4	370.0	25.60
S10M11 A	0.478	4.96	0.178	0.302	3670	9.48	53.00	448.0	336.0	35.80
S10M12 A	0.468	4.64	0.170	0.328	4260	10.64	52.80	466.0	348.0	30.00
S10M21 A	0.406	5.34	0.162	0.352	4130	10.54	57.40	1310.0	368.0	30.80
S10M22 A	0.446	4.55	0.138	0.255	3185	8.92	52.62	947.7	323.1	22.86
S20M01 A	0.517	4.37	0.158	0.279	5934	11.03	52.87	186.2	419.5	27.70
S20M02 A	0.464	4.46	0.190	0.316	7370	10.28	45.60	76.6	340.0	31.60
S20M11 A	0.456	4.64	0.170	0.286	4910	16.40	56.80	364.0	346.0	38.00
S20M12 A	0.480	4.68	0.142	0.258	5950	12.36	57.80	442.0	326.0	36.60
S20M21 A	0.474	4.72	0.148	0.262	5800	11.82	67.60	1160.0	354.0	31.00
S20M22 A	0.466	4.90	0.134	0.278	5510	11.64	54.60	1070.0	312.0	42.00
COMO1 A	0.410	4.64	0.268	0.422	2026	7.84	45.00	125.6	322.0	25.40
COM02 A	0.390	4.42	0.332	0.438	1984	7.84	44.00	47.8	302.0	18.84
COM11 A	0.404	4.56	0.234	0.392	1394	9.16	52.80	718.0	340.0	24.20
COM12 A	0.482	5.02	0.258	0.434	1762	10.44	52.40	744.0	372.0	16.50
COM21 A	0.462	5.08	0.180	0.362	1238	12.64	67.20	1480.0	290.0	25.60
COM22 A	0.446	4.66	0.208	0.350	1574	11.04	68.40	1690.0	312.0	20.40
C5M01 A	0.390	5.20	0.304	0.408	4100	10.28	44.40	154.6	280.0	23.60
C5M02 A	0.412	5.38	0.328	0.442	4230	10.38	43.80	65.4	328.0	36.20
C5M11 A	0.390	4.98	0.256	0.416	2980	9.10	58.20	873.0	314.0	26.40
C5M12 A	0.456	4.78	0.254	0.396	3270	10.24	56.40	964.0	306.0	26.20
C5M21 A	0.430	5.24	0.186	0.382	2700	10.34	71.20	1560.0	260.0	21.20
C5M22 A	0.450	5.14	0.242	0.352	2890	10.72	73.00	1730.0	268.0	20.20
C10M01 A	0.434	4.96	0.280	0.388	4700	9.76	51.00	228.0	264.0	30.80
C10M02 A	0.462	5.26	0.316	0.412	4620	10.24	45.20	84.6	248.0	21.00
C10M11 A	0.430	5.14	0.238	0.400	3710	10.96	56.60	916.0	240.0	20.80
C10M12 A	0.438	4.96	0.360	0.342	4900	10.44	53.00	972.0	264.0	25.60

A = cut 1
B = cut 2

	P %	K %	Ca %	Mg %	Na mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Fe mg/kg	B mg/kg
C10M21 A	0.462	4.86	0.202	0.312	4630	11.56	55.40	1942.0	278.0	29.60
C10M22 A	0.484	4.90	0.248	0.352	5370	11.94	68.20	1660.0	264.0	29.20
C20M01 A	0.530	4.60	0.304	0.360	7540	12.00	59.80	274.0	240.0	27.40
C20M02 A	0.492	5.38	0.276	0.342	5840	11.76	50.20	107.4	244.0	32.80
C20M11 A	0.482	5.08	0.260	0.326	6000	12.38	55.60	862.0	238.0	20.00
C20M12 A	0.494	4.88	0.218	0.320	6010	12.38	57.40	936.0	230.0	17.76
C20M21 A	0.512	5.24	0.216	0.324	5350	13.60	64.40	1660.0	244.0	23.00
C20M22 A	0.474	4.26	0.244	0.304	7770	11.70	53.40	1540.0	242.0	23.80
W0 1 A	0.456	5.02	0.250	0.314	3300	8.50	42.20	308.0	252.0	26.80
W0 2 A	0.538	5.50	0.236	0.298	2246	8.92	40.80	103.2	226.0	40.00
W1 1 A	0.466	5.38	0.320	0.394	1336	12.04	52.60	87.2	286.0	36.00
W1 2 A	0.400	5.32	0.282	0.374	1442	9.40	42.60	73.6	260.0	36.80
W2 1 A	0.458	5.08	0.270	0.430	1290	10.24	45.80	79.4	246.0	31.00
W2 2 A	0.386	4.44	0.246	0.392	1184	9.52	44.60	86.6	250.0	23.00
W4 1 A	0.484	5.14	0.223	0.398	1320	10.84	48.63	107.8	252.6	44.63
W4 2 A	0.534	5.36	0.268	0.426	1600	11.74	49.60	116.4	256.0	45.60
W8 1 A	0.444	4.40	0.218	0.358	978	9.86	53.00	286.0	232.0	30.40
W8 2 A	0.456	4.78	0.208	0.338	1114	9.32	45.00	242.0	218.0	35.00
N0 1 A	0.462	4.64	0.251	0.304	1571	8.76	39.78	63.1	226.7	42.22
N0 2 A	0.418	4.36	0.204	0.274	1550	6.82	32.80	46.0	244.0	32.80
N1 1 A	0.404	5.30	0.346	0.426	1850	12.24	49.40	39.0	107.0	22.40
N1 2 A	0.440	5.14	0.306	0.382	1822	8.64	45.60	27.8	95.2	22.60
N2 1 A	0.412	4.34	0.412	0.358	2062	8.86	51.40	40.8	282.0	25.60
N2 2 A	0.406	5.20	0.342	0.410	1760	7.80	39.00	27.4	104.8	26.40
N4 1 A	0.418	4.76	0.336	0.434	2136	8.42	39.60	43.0	270.0	19.96
N4 2 A	0.378	4.70	0.360	0.458	1870	8.22	41.80	30.8	240.0	18.70
N8 1 A	0.438	5.14	0.290	0.380	1748	8.76	41.80	31.8	99.0	37.40
N8 2 A	0.430	5.10	0.334	0.394	2276	9.28	38.20	40.4	232.0	33.00
MN3 1 A	0.466	5.28	0.214	0.328	1876	11.36	72.60	2970.0	232.0	30.00
MN3 2 A	0.444	4.76	0.186	0.314	1362	10.30	66.20	3260.0	242.0	29.60
MN4 1 A	0.376	4.20	0.126	0.198	882	8.84	63.40	4800.0	232.0	36.40
MN4 2 A	0.443	4.48	0.123	0.186	1086	11.61	64.55	5147.7	226.1	23.86
S0M01 B	0.382	4.48	0.324	0.452	2240	8.48	46.20	214.0	252.0	12.28
S0M02 B	0.400	4.76	0.280	0.404	2820	9.24	46.20	106.2	218.0	14.84
S0M11 B	0.434	4.86	0.284	0.472	1622	10.00	55.40	664.0	232.0	14.08
S0M12 B	0.450	4.80	0.268	0.514	1862	10.48	51.80	534.0	226.0	15.86
S0M21 B	0.412	5.28	0.314	0.476	1802	10.22	53.40	542.0	202.0	10.84
S0M22 B	0.474	4.84	0.326	0.424	1698	13.74	67.40	744.0	200.0	14.14
S5M01 B	0.390	4.44	0.270	0.426	4460	8.84	43.20	123.6	175.2	15.14
S5M02 B	0.390	4.36	0.316	0.444	6200	9.76	45.00	69.8	181.2	16.30
S5M11 B	0.472	4.92	0.278	0.436	4370	13.04	51.40	526.0	187.6	14.64
S5M12 B	0.456	4.56	0.244	0.460	3650	10.92	51.20	574.0	183.8	14.06
S5M21 B	0.486	4.32	0.202	0.446	4260	12.06	64.00	1310.0	218.0	15.18
S5M22 B	0.404	4.96	0.202	0.396	3050	11.06	67.40	1250.0	200.0	12.88
S10M01 B	0.480	4.84	0.234	0.462	5810	12.58	65.00	288.0	187.4	12.40
S10M02 B	0.454	4.70	0.246	0.458	6350	11.02	59.40	128.6	194.2	15.66

	P %	K %	Ca %	Mg %	Na mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Fe mg/kg	B mg/kg
S10M11 B	0.452	4.84	0.224	0.420	5170	10.58	56.60	446.0	188.8	11.90
S10M12 B	0.438	4.74	0.230	0.398	5100	13.96	62.60	478.0	183.0	13.88
S10M21 B	0.400	5.14	0.172	0.450	3980	12.10	69.00	1120.0	208.0	12.42
S10M22 B	0.404	4.16	0.165	0.372	4663	11.26	60.87	964.1	213.5	12.00
S20M01 B	0.486	4.56	0.220	0.402	8213	12.36	73.83	228.0	204.7	13.60
S20M02 B	0.494	4.58	0.236	0.452	8750	14.00	71.60	121.8	198.0	11.94
S20M11 B	0.517	4.39	0.171	0.385	7481	12.64	58.91	320.4	182.9	13.41
S20M12 B	0.448	4.58	0.174	0.348	7020	12.82	59.20	420.0	195.6	13.86
S20M21 B	0.414	4.60	0.142	0.304	6330	11.84	59.20	1036.0	204.0	11.24
S20M22 B	0.412	4.34	0.138	0.358	7130	12.02	60.40	1252.0	212.0	12.40
C0M01 B	0.439	4.61	0.258	0.398	3891	10.62	45.46	310.4	247.0	16.00
C0M02 B	0.402	4.50	0.330	0.410	3040	13.94	43.60	84.8	222.0	18.36
C0M11 B	0.408	4.48	0.230	0.378	1684	9.94	54.20	664.0	192.0	14.94
C0M12 B	0.468	5.14	0.266	0.508	2490	11.92	59.80	694.0	186.6	11.68
C0M21 B	0.430	5.50	0.206	0.340	1738	11.12	62.40	1330.0	171.4	10.48
C0M22 B	0.438	5.28	0.206	0.368	2186	12.24	65.60	1550.0	172.6	16.92
C5M01 B	0.340	4.90	0.302	0.392	5290	9.02	44.00	246.0	164.2	13.06
C5M02 B	0.414	5.80	0.288	0.400	4720	10.64	50.20	106.0	182.0	13.98
C5M11 B	0.388	5.60	0.252	0.380	3710	10.92	56.40	764.0	174.0	10.60
C5M12 B	0.394	4.86	0.250	0.382	5400	11.88	53.80	830.0	177.8	10.88
C5M21 B	0.386	5.62	0.194	0.330	3850	11.82	60.60	1590.0	175.8	11.58
C5M22 B	0.418	4.98	0.282	0.380	4210	15.46	72.80	1810.0	204.0	15.00
C10M01 B	0.366	4.80	0.276	0.378	6100	10.92	50.00	314.0	202.0	13.36
C10M02 B	0.378	4.56	0.334	0.500	5970	9.98	54.00	124.8	188.4	10.90
C10M11 B	0.418	4.94	0.272	0.502	5060	13.44	76.40	1052.0	218.0	14.60
C10M12 B	0.444	5.14	0.260	0.496	5970	12.98	66.40	852.0	220.0	13.20
C10M21 B	0.446	5.10	0.270	0.464	5510	13.32	72.20	1970.0	236.0	13.60
C10M22 B	0.434	4.82	0.262	0.400	5000	10.66	75.40	2020.0	195.8	10.68
C20M01 B	0.406	4.52	0.316	0.482	7530	11.38	73.80	376.0	204.0	10.26
C20M02 B	0.424	4.98	0.344	0.494	6470	11.64	64.20	181.8	197.0	9.26
C20M11 B	0.430	4.58	0.272	0.460	9120	13.88	73.00	1068.0	204.0	9.82
C20M12 B	0.394	4.90	0.284	0.418	7060	17.14	71.60	1092.0	189.8	13.12
C20M21 B	0.406	4.55	0.206	0.332	8633	13.00	65.44	1883.3	197.2	10.29
C20M22 B	0.434	4.80	0.260	0.406	7570	14.14	82.00	1780.0	220.0	13.16
W01 B	0.508	4.47	0.240	0.356	4901	12.93	57.27	831.4	216.2	17.55
W02 B	0.470	4.29	0.254	0.317	3209	10.87	41.81	263.4	209.1	30.10
W11 B	0.487	4.75	0.291	0.349	2437	11.69	43.30	173.9	229.9	42.45
W12 B	0.484	5.00	0.298	0.377	1372	10.79	38.52	144.8	223.8	18.63
W21 B	0.444	5.08	0.302	0.470	1962	10.74	45.40	165.0	200.0	19.14
W22 B	0.472	4.70	0.258	0.436	2000	11.98	53.80	228.0	230.0	15.12
W41 B	0.426	4.74	0.292	0.544	1584	11.94	53.40	156.0	208.0	16.48
W42 B	0.384	5.16	0.284	0.404	2090	13.72	45.80	154.6	214.0	18.64
W81 B	0.438	4.30	0.222	0.412	1280	11.14	49.80	208.0	168.0	17.72
W82 B	0.446	4.58	0.220	0.414	1476	11.54	49.00	216.0	178.2	16.02
N01 B	0.471	4.38	0.259	0.364	2380	11.68	49.16	109.8	191.2	22.42
N02 B	0.482	4.03	0.248	0.310	2522	11.73	45.13	106.6	197.3	20.18
N11 B	0.560	4.48	0.286	0.339	2595	12.68	48.15	78.0	189.3	18.04
N12 B	0.506	4.71	0.260	0.378	2331	11.41	43.23	61.6	212.6	20.90
N21 B	0.503	4.18	0.373	0.366	2536	11.71	50.73	64.6	239.1	15.17

	P %	K %	Ca %	Mg %	Na mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Fe mg/kg	B mg/kg
N22 B	0.453	4.50	0.385	0.390	2472	11.46	47.24	45.5	236.2	15.67
N41 B	0.490	5.18	0.358	0.476	2690	11.14	50.00	58.2	242.0	16.26
N42 B	0.424	4.90	0.414	0.488	3110	15.04	49.00	55.4	208.0	17.54
N81 B	0.378	4.82	0.358	0.556	2250	11.24	50.80	76.8	198.8	17.64
N82 B	0.378	5.22	0.388	0.560	2780	11.58	48.40	77.4	186.0	16.02
MN3 1 B	0.436	5.11	0.214	0.382	2105	13.29	79.19	2606.1	206.1	14.75
MN3 2 B	0.412	4.58	0.188	0.320	1448	11.80	82.40	2780.0	177.0	12.24
MN4 1 B	0.407	4.34	0.161	0.219	1224	12.34	83.42	3829.1	197.6	28.72
MN4 2 B	0.424	4.36	0.146	0.196	1455	14.33	80.69	3691.6	216.8	21.96

APPENDIX VII

Soil data correlation coefficients ($p<0.05$)

	Mn	Na	NH4	K	Mg
Mn		0.28	0.51	0.65	0.75
Na			0.72	0.56	0.53
NH4				0.92	0.85
K					0.96
Mg					
Ca					
Cl					
NO3					
SO4					

	Ca	Cl	NO3	SO4
Mn				
Na	0.3		-0.49	0.46
NH4			-0.74	0.84
K	0.64	0.33	-0.77	0.58
Mg	0.77	0.27	-0.73	0.52
Ca	0.74	0.23	-0.69	0.57
Cl		0.55	-0.32	
NO3				-0.32
SO4				-0.8

APPENDIX VIII

Soil solution activities correlation coefficients ($p<0.05$)

	Mn	Na	NH4	K	Mg
Mn			0.32	0.66	0.42
Na			0.54	0.3	-0.35
NH4	0.32	0.54		0.8	0.44
K	0.65	0.3	0.8		0.69
Mg	0.42	-0.36	0.44	0.69	
Ca		-0.36	0.33	0.43	0.88
Cl			0.72	0.64	0.68
NO3	-0.3	-0.75	-0.54	-0.48	
SO4		0.74			-0.61

	Ca	Cl	NO3
Cl	0.71		
NO3	0.36		
SO4	0.75	-0.39	-0.77

APPENDIX IX

Foliar composition correlation coefficients ($p<0.05$)

	Yield1	P	K	Ca	Mg	Na
P	-0.54			-0.28	-0.24	0.32
K						
Ca	0.33				0.64	
Mg	0.62					
Na	-0.68					
Cu	-0.36					
Zn						
Mn						
B	-0.56					

	Cu	Zn	Mn	B
P	0.34	0.28		0.31
K				
Ca		-0.22	-0.36	-0.26
Mg			-0.27	-0.53
Na	0.49	0.34		
Cu		0.64	0.38	
Zn			0.66	-0.31
Mn				
B				

APPENDIX X

Soil and foliar data correlation coefficients ($p<0.05$)

		Foliar composition			
Soil data	Yield 1	P	K	Ca	Mg
Mn				-0.57	-0.45
Na	-0.85	0.48		-0.56	-0.46
NH4	-0.59	0.44		-0.5	-0.38
K	-0.38	0.38		-0.53	-0.38
Mg	-0.36	0.39		-0.62	-0.42
Ca		0.27			
Cl				0.32	
NO3	0.45	-0.39		0.61	0.45
SO4	-0.63	0.36	-0.21	-0.79	-0.5
EC	-0.72	0.7		-0.48	-0.82
pH	-0.31				

		Foliar composition			
Soil data	Na	Cu	Zn	Mn	B
Mn		0.34	0.55	0.88	
Na	0.73	0.45	0.3		
NH4	0.48	0.54	0.56	0.47	
K	0.32	0.53	0.61	0.66	
Mg	0.29	0.53	0.66	0.76	
Ca	0.26	0.45	0.53	0.56	
Cl	0.54	0.36	0.32	0.26	
NO3	-0.31	-0.45	-0.41	-0.34	
SO4	0.36	0.31	0.28		
EC	0.86	0.69	0.36	-0.37	0.43
pH				-0.67	

APPENDIX XI

Soil solution activities and foliar data correlation coefficients ($p<0.05$)

Soil solution			Foliar composition		
activities	Yield 1	P	K	Ca	Mg
Mn				-0.36	-0.34
Na	-0.77	0.62		-0.52	-0.79
NH4	-0.41	0.57			-0.6
K		0.47			-0.48
Mg	0.32		0.32		
Ca	0.33				0.36
Cl		0.46	0.33	0.32	
NO3	0.43	-0.49		0.63	0.77
SO4	-0.53	0.31		-0.81	-0.71

Soil solution			Foliar composition		
activities	Na	Cu	Zn	Mn	B
Mn		0.37	0.67	0.9	
Na	0.82	0.59			0.58
NH4	0.61	0.57	0.38	0.43	
K	0.37	0.62		0.75	
Mg			0.31	0.53	-0.47
Ca					-0.48
Cl	0.58	0.43			
NO3	-0.46	-0.62	-0.49	-0.38	-0.47
SO4	0.33	0.37			0.56