INTERACTIVE EFFECTS OF A CALCIUM AND MAGNESIUM SULPHATE ENRICHED WASTE WATER ON CROP GROWTH AND NUTRITION

by

Petronella Hermina Elizabeth Ströhmenger

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University of Pretoria
Pretoria

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Supervisor: Prof A S Claassens
Co-Supervisor: Prof JG Annandale

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Declaration

I, the undersigned, hereby declare that the work contained in this thesis is entirely my own original research, except where acknowledged, and that it has not at any time, either partly or fully, been submitted to any University for the purposes of obtaining a degree.

Signed: ....Strohmenger..........   Date: ....2001/02/14.......

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ABSTRACT

The coal industry of Mpumalanga Province is faced with the problem of developing cost effective ways of using large volumes of calcium and magnesium sulphate enriched waste waters. Use of the waste waters for agricultural production may contribute as a stabilising factor with regard to yields in this high potential agricultural area. The objectives of this study were to determine the effect of such waste waters on yield and to compare crop response to calcium and magnesium sulphate salinity at different nutrient levels. Two separate glasshouse experiments were conducted. Wheat (*Triticum aestivum* L. cv. SST 825) was grown in calcium and magnesium sulphate salinised nutrient solutions (Ca:Mg 2:1) with differential levels of NO_3, NH_4, P and K. A soil pot experiment was subsequently conducted with maize (*Zea mays,* cv. PAN 6256), three gypsum and magnesium sulphate salinity levels and a 6 x 2 x 3 factorial combination of N, P and K. Calcium and magnesium sulphate salinity decreased the biomass production of both crops. This was mainly due to interactions of Mg with the uptake of essential nutrients in wheat and a Mg toxicity and/or Ca deficiency induced by high levels of Mg and/or SO_4 in maize. The application of NO_3, NH_4, and K at rates different from the level considered beneficial for non-saline conditions improved wheat growth under sulphate saline conditions. Strongly inhibitory salinity levels controlled the maize yield of the highest salinity treatment regardless of the level of fertiliser application. A beneficial effect of higher NH_4 supply was observed in both experiments. This can be ascribed to the antagonistic effect that NH_4 exerted on Mg concentrations in plants (both experiments) and SO_4 (soil pot experiment) and/or to a higher N-utilization efficiency where N was supplied as NH_4 compared to NO_3. Differential application levels of P had no effect on the yield of wheat. Phosphorus concentrations in maize were marginal to low, even at extremely high soil Bray I-P levels. This was probably caused by the precipitation of P as insoluble calcium phosphate complexes in the soil and/or between the free space of the cortex cells of plant roots. These results could also indicate that the Bray I extraction method does not give a true reflection of plant available P in sulphate saline soil. Further experimentation is needed to verify these results under field conditions and determine the optimal rate, method and timing of especially NH_4 and PO_4 fertilisers when irrigating crops with these calcium and magnesium sulphate enriched waste waters.

UITTREKSEL

Een van die knellendste probleme wat die steenkool-industrie van Mpumalanga Provinsie ondervind, is om koste-effektiewe maniere te vind vir die gebruik van groot hoeveelhede kalsium- en magnesiumsulfaat verrykte afloopwater. Gebruik van dié afloopwater vir die produksie van landboukundige gewasse in hierdie hoë-potensiaal landboukundige gebied kan daartoe bydra dat opbrengste meer betroubaar en minder wisselvallig sal wees. Die doelwitte van hierdie studie was om die effek van hierdie afloopwater op opbrengs te bepaal en om die invloed van differensiële voedingselementvlakke onder hoë kalsium- en magnesiumsulfaatvoorsiening op gewasreaksie te vergelyk. Twee verskillende glashuis eksperimente is uitgevoer. Koring (*Triticum aestivum* L. cv. SST 825) is in verrykte kalsium- en magnesiumsulfaat (Ca:Mg 2:1) waterkultuur mediums gegroei met differensiële NO_3, NH_4, P en K vlakke. 'n Potproef in grond met mielies (*Zea mays,* cv. PAN 6256) is daarna uitgevoer. Die behandelings het uit drie gips en magnesiumsulfaat vlakke bestaan waarby N, P en K toegedien is in 'n 6 x 2 x 3 faktoriaal kombinasie. Die biomassa opbrengste van beide gewasse is verlaag deur hoë kalsium- en magnesiumsulfaatvlakke. Dit was hoofsaaklik toe te skryf aan die interaksie van Mg met die opname van essensiële voedingselemente in koring en 'n Mg toksisiteit en/of Ca-tekort wat geïnduseer is deur Mg en/of SO_4 by mielies. Die toediening van NO_3, NH_4, en K teen tempo's wat verskil van die vlakke wat as voldoende beskou word onder normale toestande, het die opbrengs van koring verhoog onder toestande van hoë kalsium- en magnesiumsulfaat voorsiening. Uitermatige hoë gips en magnesiumsulfaat voorsiening het egter die groei van mielies gestrem, nieteenstaande die toevoeging van voedingselemente. Die toediening van verhoogde NH_4-vlakke het 'n voordelige invloed gehad op die opbrengste van beide gewasse. Dit kan toegeskryf word aan die antagonistiese effek wat NH_4 uitgeoefen het op Mg (waterkultuur en grond-potproef) en SO_4 konsentrasies in plante (grond-potproef). Die effektiwiteit waarmee N deur plante benut is, was ook hoer waar N as NH_4 toegedien is in vergelyking met NO_3. Differensiële toedieningsvlakke van P het geen effek op die opbrengs van koring gehad nie. Die presipitasie van P as onoplosbare kalsiumfosfaatkomplekse in die grond en/of tussen die vry spasie van die korteksselle van plantwortels het waarskynlik veroorsaak dat die P konsentrasie in plante baie laag was, selfs by uitermatige hoë Bray I-P vlakke in die grond. Die resultate kan ook aandui dat die Bray I-ekstraksiemetode nie 'n goeie aanduiding gee van die hoeveelheid plantbeskikbare P in gronde wat hoë konsentrasies sulfaatsoute bevat nie.

Verdere navorsing is nodig om die verkreë resultate te verivieer onder veldtoestande en om die optimale toedieningstempo, metode en tyd van toediening van veral NH_4 en PO_4 bemesting te bepaal tydens die besproeiing van gewasse met die verrykte kalsium- en magnesiumsulfaat afloopwater.

CHAPTER 1
INTRODUCTION

The South African mining industry experiences many water management problems in terms of both quality and quantity. One of the most compelling water management problems that coal mines of Mpumalanga Province are faced with is the disposal of saline water that comes from underground pillared workings where opencast mining cannot proceed if the water is not removed. This 'naturally' occurring aquifer water becomes saline when it comes into contact with the oxidation products of the coal and coal overburden material exposed during mining. Most South African coal deposits contain pyritic formations. When pyrite is oxidised in the presence of oxygen, water and the catalytic action of *Thiobacillus ferrooxidans* bacteria, iron (Fe^{2+}), hydrogen (H^+) and sulphate (SO_4^{2-}) ions are released into the water. Hydrogen ions are largely inactivated by ion exchange and weathering reactions; ferrous Fe is oxidised to ferric Fe; and most of the sulphate remains in solution and undergoes further reactions with products from mineral weathering (Sobek *et al.*, 1987). In addition to large concentrations of soluble sulphate and soluble sulphate complexes in the water, several types of sulphate salts are also formed, the most predominant being gypsum ($CaSO_4.2H_2O$) and magnesium sulphate. The water is unsuitable for direct uncontrolled discharge to water courses. Current measures to prevent pollution of the environment include pumping this water into previously excavated areas or into dams from where water is released only during periods of high rainfall.

The environmental constraints that are associated with the discharge of this water into water courses include salinisation of rivers, dams and catchment areas. Increasing salinity renders water less suitable for urban and industrial application and can have a devastating effect on food crops. High levels of sulphate in drinking water are associated with human and livestock health hazards like diarrhoea and reduced copper absorption (Alberta Agriculture, Food and Rural Development, 1993; Rendig, 1986). Winter and Kickuth (1989a) also reported interference of sulphate with the limnic metabolic cycle.

Water treatment is extremely expensive and mostly involves precipitation of sulphur (S), but this is just a shift to the solid phase, which will itself lead to the problem of sludge contamination and the need for space for sludge deposition. Gas stripping of hydrogen sulphide and sulphur dioxide could also cause new kinds of pollution, as these gases are not only odorous, but also highly toxic. Winter and Kickuth (1989b) investigated the significance of sulphur removal in an eight-year-old 'Root Zone' works. This consisted of an artificial wetland biotope planted with helophytes. From mass balance calculations they indicated that 82% of the sulphur in waste water could be eliminated with this method. Water is, however, an extremely scarce resource in South Africa and the increasing demand for food and water by a growing population will necessitate careful use of all water resources. Disposal of water without any returns thus becomes less of an option.

Another important aspect to consider is that the coalfields on the Highveld of Mpumalanga underlie one of the most important high potential agricultural areas in the country. Using the waste water to irrigate crops in this region may prove to be a stabilising factor with regard to yields and has therefore been proposed as an economically attractive alternative. The mines generate sufficient waste water to sustain large areas of irrigation.

Several questions arise about the viability and sustainability of using this waste water for irrigation when considering that the soil, on which plant growth has to be sustained, will serve as the 'filter' for these sulphate salts. Questions like: "How will gypsum precipitation influence the hydraulic conductivity of the soil?", "What type of crops can be grown successfully with the sulphate saline water?", "What type of management practices need to be followed to keep the system productive?" need to be addressed for both short- and long-term use of this saline water.

The execution of long-term experiments monitoring slow environmental processes can, however, be prohibitively expensive and it is not always possible to wait for their outcome. It is for this reason that a computer model was developed to serve as a tool for predicting long-term consequences of irrigating crops with mine waste water (Annandale *et al.*, 1999). The Soil Water Balance (SWB) model was initially developed for the management of irrigation with acid mine drainage water and proved a useful tool for crop growth simulations and irrigation scheduling. The SWB model was further developed for use as a tool to assess the long-term impact of irrigation with gypsiferous mine water on soil and water resources (Annandale *et al.*, 1999). This study was initiated as a result of the need that was identified to optimize the model to predict soil and crop nutritional problems that are likely to result from use of this mine water, and to propose management plans to prevent or solve these problems in a more effective and timely manner.

In order to be able to make a contribution to the model, it was considered important to get an understanding of the effect of calcium and magnesium sulphate salinity on soil solution properties, crop growth and nutrient interactions.

Applying gypsiferous irrigation water to soil has generally been considered beneficial, because gypsum that precipitates in soil after the application of water high in sulphates is not sufficiently soluble to cause salt damage to a growing plant (Doneen & Henderson, 1960; Olsen & Rehm, 1986; Stroehlein and Pennington, 1986). The composition and concentration of ions in the applied water and soil exchange characteristics can, however, alter the soil solution concentration and composition, which can change the amount of gypsum precipitation or dissolution (Rhoades *et al.*, 1973). As a result, an inevitable salt build-up was reported to occur in soil irrigated with sulphate water (Suarez & van Genuchten, 1981; Russo, 1983) and the soil solution electrical conductivity (EC) could exceed that of the sulphate water used for irrigation (Papadopoulos, 1988). It is anticipated that soil salinity that results from irrigation with the sulphate mine water will be characterized by low nutrient ion activities and extreme ratios of Ca^{2+}:Mg^{2+}, Ca^{2+}:K^{+}, Mg^{2+}:K^{+}, SO_4^{2-}:NO_3^{-} and SO_4^{2-}:PO_4^{3-}. Being a moderately soluble salt, Ca is also likely to replace other cations on the soil exchange complex and render them prone to leaching (Shainberg *et al.*, 1989).

Accumulation of salts in the root zone can adversely affect plant growth due to a lowered water potential, caused by the high concentration of soluble ions, or due to specific ion effects (Grattan & Grieve, 1994). Specific ion effects include toxicity, unfavourable ratios of ions and also a lowered activity of nutrient ions that will lead to a disturbance in the inorganic nutrition of plants. When reviewing the literature on how sulphate salinity affects plant growth, there seem to be contradicting views. Some studies advocate that high sulphate concentrations in the growth medium have no effect on plant growth (Rennenberg, 1984; Olsen & Rehm, 1986; Barnard *et al.*, 1998) or ion uptake (Grobler, 1976). Other investigations have shown that excess sulphur can reduce yield (Rennenberg, 1984; Manchanda *et al.*, 1991; Curtin *et al.*, 1993; Soltanpour *et al.*, 1999), delay flowering (Papadopoulos, 1984) and often suppress growth more than chloride at iso-osmotic concentrations (Mengel & Kirkby, 1987; Bilski *et al.*, 1988; Subbarao & Johansen, 1994; Datta *et al.*, 1995; Soltanpour *et al.*, 1999). Besides the different response of crops to sulphate salinity compared to Cl systems, results from literature studies also clearly indicate that nutrient relations and the mechanism whereby plants adjust osmotically in SO_4-dominated salinity vary greatly from that in Cl salt systems. Results obtained from studies conducted with Cl-dominated salts can thus not be extrapolated to situations where SO_4 is the predominant salt.

Nutrient imbalance may result from the effect of salinity on nutrient availability, uptake, or partitioning within the plant or may be caused by physiological inactivation of a given nutrient, resulting in an increase in the plant's internal requirement for that essential nutrient (Grattan & Grieve, 1994). Most crop plants have evolved under conditions of low soil salinity and consequently have developed mechanisms for absorbing nutrients in non-saline soil. The utilization of saline soil raises the problem of providing growing conditions that will support reasonable plant productivity. If salinity causes certain nutritional deficiencies or imbalances, the possibility exists that application of this specific nutrient can alleviate the inhibition of growth by salinity. Several studies have shown that crop growth under NaCl saline conditions can be sustained and even improved with specific fertiliser application (Papadopoulos & Rendig, 1983; Cordovilla *et al.*, 1995; Khan *et al.*, 1994; Gómez *et al.*, 1996). Salinity-fertility relationships are of great economic importance. An attempt at alleviating the effects of calcium and magnesium sulphate salinity on agricultural crops, by changing the fertilisation regime from that considered appropriate for non-saline conditions, would therefore be valuable.

As a result of this, and the apparent contradictions in the literature concerning the effects of high sulphate levels on plant growth, it was considered necessary to achieve the following objectives:

- Determine the effect of calcium and magnesium sulphate salinity on crop growth;
- Investigate the possibility of alleviating the effects of calcium and magnesium sulphate salinity on agricultural crops by changing the N, P and K fertilisation regime from that considered appropriate for non-saline conditions; and
- Investigate the nutritional composition of two test crops at varied growth medium concentrations of NO_3, NH_4, P and K under sulphate saline conditions.

The thesis consists of five chapters. Chapters 3 and 4 are to be condensed and submitted for publication in the *South African Journal of Plant and Soil*. In addition to these two chapters, this general introduction, a literature review, general conclusions and recommendations and a comprehensive list of references are included.

CHAPTER 2
LITERATURE REVIEW

This chapter deals with the literature mainly on calcium and magnesium sulphate salinity. The term 'calcium and magnesium sulphate salinity' used here, refer to salinity caused by high concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-}, $CaSO_4^0$, $MgSO_4^0$ and gypsum. The first section of this literature review gives a brief overview of the chemical composition of the waste water under consideration. The interaction of the water with the soil and the consequential effect on soil nutritional properties are reviewed in the second section. The effects of sulphate, calcium, magnesium sulphate and gypsum on the growth and quality of agricultural crops are presented in section three. The final two parts of this review take stock of the available information on nutrient interactions that result from sulphate salinity, the types of salinity-fertility responses of crops and how fertilisation or fertigation could be used to sustain or improve crop growth under saline conditions. The chapter ends with concluding remarks on the available literature.

2.1 CHEMICAL COMPOSITION OF THE IRRIGATION WATER

The water that is under investigation in this study comes from Kleinkopje Colliery situated near Witbank, Mpumalanga Province. Kleinkopje Colliery currently generates approximately 14 megalitres of sulphate-rich water per day. Furthermore, underground workings still to be mined contain 12000 megalitres of sulphate-rich water (P.D.Tanner, Amcoal Environmental Services, personal communication, 1999). The water is predominantly high in calcium sulphate, with significant amounts of magnesium. The chemical composition of the Kleinkopje mine water over a period of two years is compared to literature target norms in Table 2.1. Differences between the mean and maximum pH, electrical conductivity (EC) and concentration of some elements in the waste water indicate the variability in the quality of the water, which is mostly attributed to variations in rainfall.

Table 2.1 Chemical composition of the Kleinkopje mine waste water assessed over a two-year period compared to target water quality guidelines

Attribute	Mean value	Maximum value	Crop yield, quality and soil sustainability	Target water quality range	Reference
pH	6.5	7.3	No problems with either unavailability of plant nutrients or toxic levels of elements	6.5-8.4	Department of Water Affairs and Forestry, 1996
EC	272 mS m^{-1}	306 mS m^{-1}	An 80% relative yield of moderately salt-tolerant crops can be maintained provided that a high-frequency irrigation system is used. A leaching fraction of up to 0.2 may be required	≤40 mS m^{-1}	Department of Water Affairs and Forestry, 1996
Na	49 mg ℓ^{-1}	88 mg ℓ^{-1}	The mean Na value should prevent accumulation of Cl to toxic levels in all but the most sensitive plants, even when foliage is wetted. Foliar injury and yield decrease may occur when the Na concentration in the water exceeds 70 mg ℓ^{-1}	≤70 mg ℓ^{-1}	Department of Water Affairs and Forestry, 1996
Cl	18 mg ℓ^{-1}	84 mg ℓ^{-1}	No accumulation of Cl to toxic levels in all but the most sensitive plants, even when foliage is wetted	≤100 mg ℓ^{-1}	Department of Water Affairs and Forestry, 1996
HCO_3	86 mg ℓ^{-1}	104 mg ℓ^{-1}	The tendency for calcium carbonate to precipitate from high-bicarbonate waters is defined as: $RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+})$ The RSC value for this water is much lower than 1.25 and is considered safe	RSC<1.25	Bohn *et al.*, 1985
F	1.10 mg ℓ^{-1}	2.30 mg ℓ^{-1}	Acceptable for fine textured neutral to alkaline soils	≤2.00 mg ℓ^{-1}	Department of Water Affairs and Forestry, 1996
Mn	5.58 mg ℓ^{-1}	52.73 mg ℓ^{-1}	Acceptable for irrigation only over a short term on a site-specific basis	≤0.20 mg ℓ^{-1}	Department of Water Affairs and Forestry, 1996
Mo	0.03 mg ℓ^{-1}	1.76 mg ℓ^{-1}	Acceptable for irrigation only over the short term on a site-specific basis	≤0.01 mg ℓ^{-1}	Department of Water Affairs and Forestry, 1996

According to the chemical analysis, the waste water is neutral and the mean EC varies between 235 and 306 mS m^{-1}. The criterion used for salinity hazard of irrigation water in South Africa denotes an EC_{iw} of 90 to 270 mS m^{-1} as "high" and from 270 to 540 mS m^{-1} as "very high" (Department of Water Affairs and Forestry, 1993). Although this criterion already classifies the EC of this particular water as high, a high proportion of ions can be in the form of ion pairs not accounted for in the EC value (Papadapoulos, 1987). Jurinak *et al.* (1987) stated that since about one-third of the total Ca^{2+} and SO_4^{2-} in solution exist as a neutral ion pair in a saturated gypsum solution, the measured EC is about one-third less than expected. The expected EC of the water is thus rather in the order of 300 to 400 mS m^{-1}.

The SO_4 concentration in the water ranges from 2040 to 2197 mg ℓ^{-1}. Sulphur is an essential element for crop growth and applying this irrigation water to soil will thus serve an effective nutrient replacement role supplying the S removed by crops. Although a critical level of S in irrigation water cannot be established, Olsen and Rehm (1986) reported that it is suggested that broadcast application of S be eliminated for maize production when the SO_4-S content of the irrigation water is greater than 6 mg ℓ^{-1}.

Calcium and magnesium are also macronutrients and thus essential for crop growth. The mean Ca concentration in the water is in the order of 467 mg ℓ^{-1} with a maximum concentration of 716 mg ℓ^{-1}, while the mean Mg concentration is approximately 210 mg ℓ^{-1} with a maximum concentration of 393 mg ℓ^{-1}. The mean mol ratio of Ca:Mg in the water is 1.4:1, while the mean Ca:K and Mg:K ratios are 45:1 and 33:1 respectively.

Sodium and manganese concentrations as high as the maximum concentrations reported in Table 2.1 could cause salinity and toxicity problems. Crops that are sensitive to foliar absorption can accumulate toxic levels of sodium when foliage is wetted with water containing Na concentrations greater than 70 mg ℓ^{-1}. Although some crops show Mn toxicity at a small fraction in the nutrient solution, Pratt and Suarez (1990) stated that typical soil pH and oxidation-reduction potentials control Mn in soil solution so that the Mn concentration in the irrigation water is relatively unimportant.

2.2 CALCIUM AND MAGNESIUM SULPHATE SALINITY IN SOIL

2.2.1 THE DYNAMICS OF CALCIUM AND MAGNESIUM SULPHATE SALINITY IN SOIL

The interaction of the irrigation water with the soil on which it is used will determine the salinity of the soil solution and, therefore, crop yield. The complex chemical interactions that take place in the soil between the solid exchanger, soil solution and gas phases are illustrated in Figure 2.1 (Tanji, 1990). It can be seen that the concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-} in the soil solution, and therefore soil salinity and fertility, are controlled by the solid, gas and exchange phases and by ion association. A dynamic equilibrium exists between these phases.

Salinity is the occurrence of a high concentration of soluble salts in the soil solution in which plants grow (Munns & Termaat, 1986). A common definition of a saline soil is one having an electrical conductivity of the saturated soil extract (EC_e) of 400 mS m^{-1}, but for practical purposes EC_e values as low as 200 mS m^{-1} may cause problems for the germination of salt-sensitive plants.

During a laboratory study, Papadopoulos (1985a) distinguished and investigated two salinisation stages when irrigating soils with sulphate saline water, namely a transient- and a steady-state salinisation stage. During the transient-state period of salinisation the soil solution concentration is changing and chemical reactions are occurring at enhanced rates. For cropped soils irrigated for the first time with water high in sulphates, an initial period of salinisation characterized by a sharp build-up occurs. At this stage no precipitation of gypsum occurs and salts of both high and low solubility contribute to salinisation (Papadapoulos, 1984). Evaporation and water extraction by plants lead to an inevitable salt build-up that raises the soil solution EC value higher than the EC of the irrigation water. Shainberg and Oster (1978) stated that the salt concentration of the soil solution in the root zone could increase to between two and five times that in the irrigation water as water is removed from the soil by transpiration or by evaporation from the soil surface.

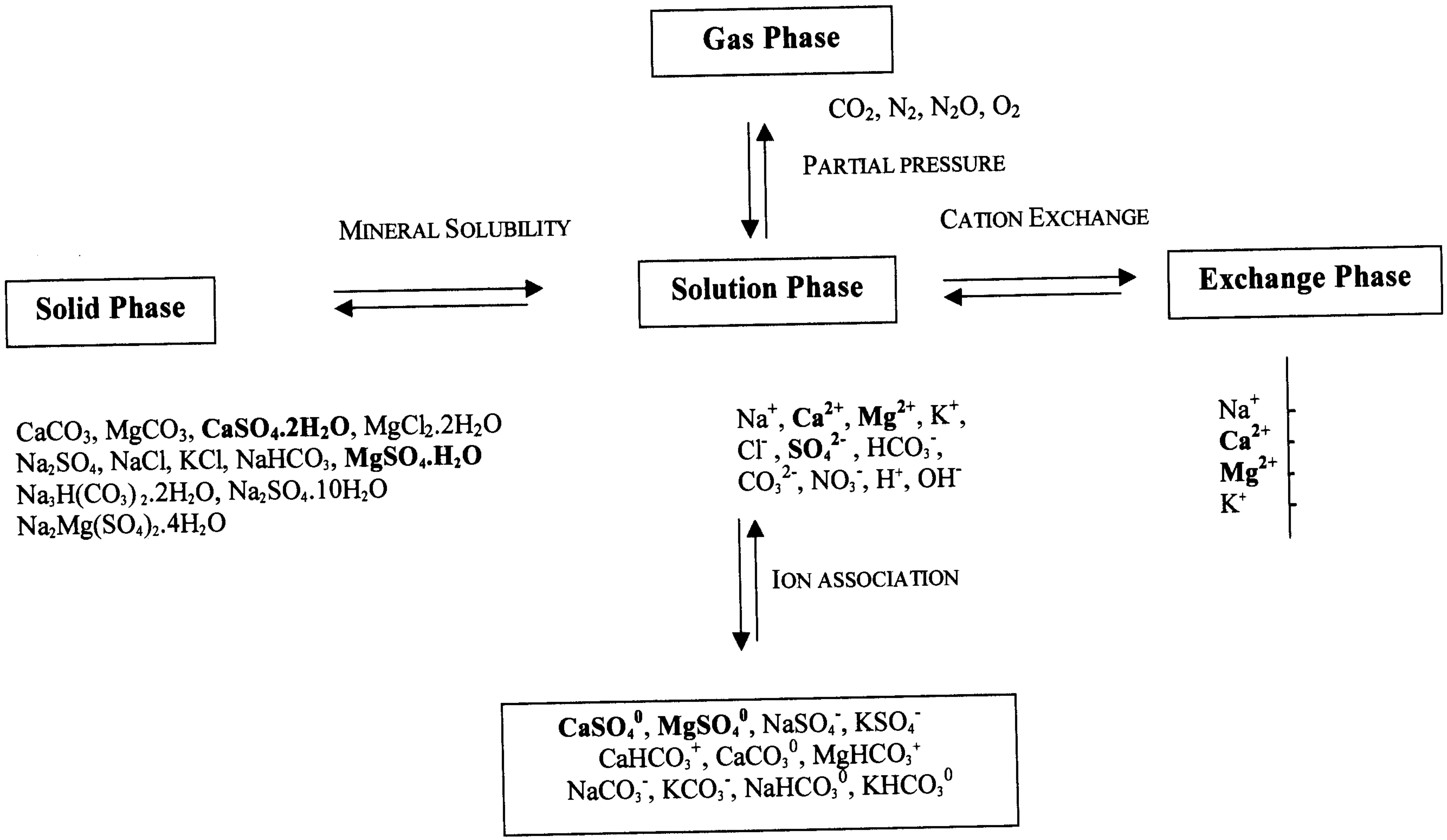


Figure 2.1 Interactive chemical reactions in soil-water systems (Tanji, 1990).

In his laboratory study, Papadopoulos (1985a) further indicated that until saturation with gypsum, the EC of the soil solution was equal to the sum of the EC of all ions (in dS m^{-1}). After saturation of the soil solution with gypsum the EC of the soil solution was equal to the EC at saturation with gypsum plus the concentration of soluble ions (in mmol ℓ^{-1}) multiplied by a factor of 0.10. The higher the concentration of soluble ions, the higher the salt build-up will be. The restricted solubility of gypsum limits the EC_e to about 280 mS m^{-1} (Prasad & Power, 1997), but Papadopoulos (1987) stated that the salt build-up in soil due to gypsum precipitation or dissolution will rather be in the order of 350 mS m^{-1} in addition to the contribution from highly soluble salts. In a soil solution, a situation of supersaturation with respect to gypsum can easily arise. It is to be expected, however, that such a supersaturation will last for only a short time, since nuclei needed for rapid crystallization are always abundantly present in soil (van den Ende, 1991).

Papadopoulos (1985a) indicated that the decrease in soil solution EC was very gradual and strongly dependent on gypsum dissolution after a steady-state stage was reached. The solubility of gypsum is 2600 mg ℓ^{-1} in pure water at 25°C and 0.1 MPa pressure and varies as a function of temperature (maximum solubility at 30-35°C), particle size and the presence of other salts in the system (Verheye & Boyadgiev, 1997). The main factors controlling gypsum solubility are Ca and SO_4 concentrations, common ion effects, ionic strength, soil moisture content, surface area of gypsum particles, thickness of the diffusional layer around gypsum particles, flow velocity, exchangeable Na and the Mg:Ca ratio of the solution (Singh & Bajwa, 1990; Mayland & Robbins, 1994). The solubility of gypsum is not pH-dependent (Jurinak, 1990). Salts that have common ions like calcium bicarbonate and sodium sulphate decrease the solubility of gypsum in solution, whereas the presence of other ions would increase it (Figure 2.2). Gypsum solubility is significantly enhanced through complex formation (Shainberg *et al.*, 1989), ion-pair formation and electrolyte effects (Gupta *et al.*, 1985). Because the formation of the $CaSO_4^0$ ion pair requires both Ca^{2+} and SO_4^{2-} ions, gypsum solubility increases as ion association occurs (Jurinak, 1990). Magnesium also forms a moderately strong ion pair with SO_4^{2-}, and thus also increases the solubility of gypsum (MacAdam *et al.*, 1997. Dissolution of gypsum increases with increases in exchangeable Na and Mg:Ca ratio of the soil solution (Gupta *et al.*, 1985).

Overall dissolution of gypsum is promoted by exchange of Ca for other exchangeable ions, which may have a limited effect on raising equilibrium Ca levels by releasing diverse ions into the soil solution (Russo, 1983; Shainberg *et al.*, 1989).

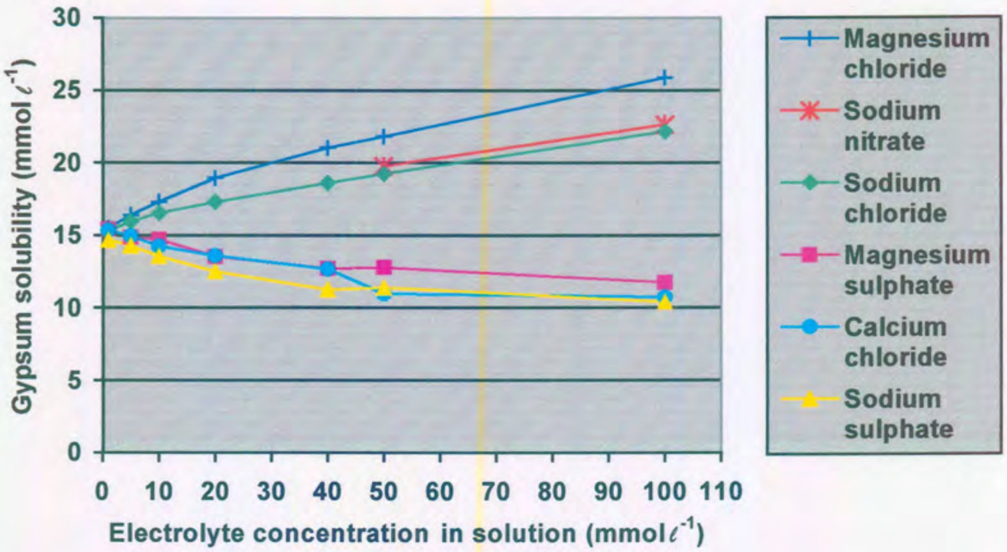


Figure 2.2 Average experimental solubility of gypsum in different electrolytes (data from Arslan & Dutt, 1993).

Precipitation of gypsum, on the other hand, is a function of the nature and composition of the soil solution and of the effect of alternating wet and dry soil conditions. Gypsum is easily redistributed in the soil (Verheye & Boyadgiev, 1997). Usually, gypsum precipitates near the maximum depth of wetting in the soil. It dissolves in the wet season and precipitates when the soil dries out. Gypsum may crystallize in a great variety of forms in the soil environment. Under saturated conditions gypsum may impregnate most of the soil matrix, but when less calcium sulphate is present in the system it precipitates in localized spots. Simulations done with the SWB model and a weather data generator predicted that 30 years of irrigation with the gypsiferous waste water from Kleinkopje Colliery will lead to between 340 and 404 Mg ha^{-1} of calcium sulphate being precipitated (Annandale *et al.*, 1999). Gypsum will, however, not be precipitated uniformly within the soil profile because of differences in root distribution and water uptake. Depending on the type of crops that are grown and the irrigation management practices that are employed, the model predicted that most gypsum would probably precipitate in the 200 to 300 mm soil zone.

Magnesium sulphate has a very high solubility (dissociation log $K°$ of 8.15) and mobility (Lindsay, 1979) and it is therefore not expected that it will form in soils irrigated with the sulphate saline mine water. The $MgSO_4°$ ion pair may contribute significantly to total magnesium in solution as SO_4^{2-} increases above 1 mmol ℓ^{-1}. This ion pair increases 10-fold for each 10-fold increase in SO_4^{2-} (Lindsay, 1979).

From the foregoing discussion it is clear that the concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-}, $CaSO_4^0$, $MgSO_4^0$ and gypsum in the soil will depend on many factors, especially local soil and climatic conditions. The relative magnitudes of and interactions among, these factors will determine the fate of these ions and salts added through irrigation to the soil.

2.2.2 THE EFFECT OF CALCIUM AND MAGNESIUM SULPHATE SALINITY ON SOIL NUTRITIONAL PROPERTIES

The presence of excessive Ca^{2+}, Mg^{2+}, SO_4^{2-} and gypsum, in the active root zone can affect soil nutrient contents and availability to plants in several ways.

Excess Ca^{2+}, Mg^{2+} and SO_4^{2-} in the soil solution can have nutritional implications due to a decrease of activity of nutrient ions or reduced uptake and disrupted translocation through competition. The presence of Ca^{2+} and SO_4^{2-} in high concentrations in the soil solution could decrease the plant uptake of nutrients such as K, Mg, Mn, Fe, Cu, Zn, phosphate and nitrate through ion competition and complementary ion effects on nutrient uptake (Mashali, 1996).

Large amounts of gypsum in the active root zone, on the other hand, can change the form in which nutrients is present in the soil. The precipitation of phosphate ions and fixation of micronutrients in an unavailable form seem to be the most compelling problems associated with excessive gypsum in the soil.

The presence of gypsum in soil appears to decrease the availability of phosphate, and plant growth in these soils may be restricted by shortages of phosphate (Panahi & Rowell, 1996). Phosphate availability is reduced in saline soils not only because of ionic strength effects that reduce the activity of phosphate but also because P concentrations in the soil solution are tightly controlled by sorption processes and by low solubility of Ca-P minerals (Grattan & Grieve, 1994). In contradiction to this, Curtin *et al.* (1993) stated that calcium sulphate salinised plants enjoyed better P nutrition from the fact that the solutions contained less Ca, so that less of the added P was precipitated as insoluble calcium phosphates. Manchanda *et al.*(1982) also stated that the Ca activity in SO_4 systems seems to be low enough to prevent complexation of P as insoluble Ca-P compounds. Differences in the results obtained on the effect of P availability in the presence of calcium sulphate may be ascribed to differences in the experimental procedures and concentration of salts used. The studies that indicated that the availability of P was enhanced in the presence of calcium sulphate was conducted in the glasshouse with sand and soil cultures which was irrigated with solutions made up from mixed sulphate and chloride salts. The Ca^{2+} concentration was limited by the solubility of gypsum in these solutions and was much lower than that in soils containing excessive gypsum. High concentrations of gypsum in soils will, on the other hand, decrease the availability of P because sufficient Ca^{2+} will be available to cause the precipitation of insoluble Ca-P compounds.

There is also conflicting statements on the effect of gypsum application on micronutrient availability and contents in the literature (Martin & Walker, 1966; Olsen & Watanabe, 1979; Shainberg *et al.*, 1989; Oyonarte *et al.*, 1996; Mashali, 1996). The diversity of the results obtained on this subject may be due to the fact that the acid reaction of gypsum may differ in severity in different soils and even in different horizons within the same soil. The acid reaction of gypsum results from the replacement and release of exchangeable acidity (H^+ and Al^{3+}) by Ca^{2+} ions on the soil exchange complex. The extent and severity of this process seems to depend on the initial level of exchangeable acidity present in the soil. The acidification of especially calcareous soils from gypsum increments can be beneficial within limits for increasing the solubility and availability of P and various micronutrients (Olsen &

Rehm, 1986). In other instances, gypsum was also reported to have a neutral or even alkali reaction (Szabolcs, 1989), which could decrease the availability of P and micronutrients.

Excessive gypsum in the active root zone may cause loss of nutrients through cation and anion interaction effects (Mashali, 1996). High concentrations of Ca^{2+} and Mg^{2+} in the soil solution will lead to a substantial release of K^+ from the adsorption complex with a possible loss through deep percolation under leaching. Fey *et al.* (1997) reported that gypsum enhanced the soluble concentrations of all cations, presumably as a result of Ca exchange for other cations held on soil surfaces. Gypsum reduced the soluble concentrations of NO_3, PO_4 and Cl at low levels of application (1.7 Mg ha^{-1}) but enhanced them at the highest level of application (13.7 Mg ha^{-1}) (Fey *et al.*, 1997). These authors proposed two possible explanations for this phenomenon. Firstly, at lower levels of gypsum application, a decrease in pH due to Ca displacement of exchangeable acidity enhances anion sorption, which is reversed at higher levels of gypsum application as a result of displacement by the SO_4 ligand. Alternatively, an hydroxy-Al precipitate or Al-phosphate phase could possibly have been formed, during which process some incorporation of other ligands (PO_4, NO_3, Cl) might occur.

Mashali (1996) further stated that there exists an inverse relationship between the gypsum content and exchange capacity of the soil (as gypsum does not absorb or release nutrient ions). The fertility of the soil and its capability to absorb ions in available form is thereby lowered.

Since large amounts of gypsum in soil reduces the availability and uptake of water and causes irregularities in the moisture distribution in the soil (Poch & Verplancke, 1997), it can also be expected that nutrient uptake by plants will be reduced. Furthermore, a major disadvantage of gypsiferous soils is that gypsum is soluble and can recrystallize around roots (Minashina *et al.*, 1983), reducing water and nutrient extraction by plants, especially perennial crops or fruit trees. The nature and distribution of this precipitation has a major impact on both the physiochemical properties of the solum and on plant behaviour.

2.3 THE EFFECT OF SALINITY ON THE GROWTH, QUALITY AND NUTRITION OF AGRICULTURAL CROPS

Salt stress inhibits plant growth as a result of osmotic effects on water availability or specific ion effects (Figure 2.3). Osmotic effects can increase plant growth and quality under certain circumstances. Under low to moderate salinity, plants can adjust osmotically by using a portion of their photosynthates to increase internal solute concentrations and thus do not show dehydration symptoms (Subbarao & Johansen, 1994). Excess salts reduce plant growth, primarily because a low soil water potential results in equilibration of the water potential inside the plant by cell water loss and a accompanying decrease in the cell osmotic potential and turgor. The osmotic effects are associated with lack of cell wall extension and cellular expansion leading to cessation of growth (Greenway & Munns, 1980).

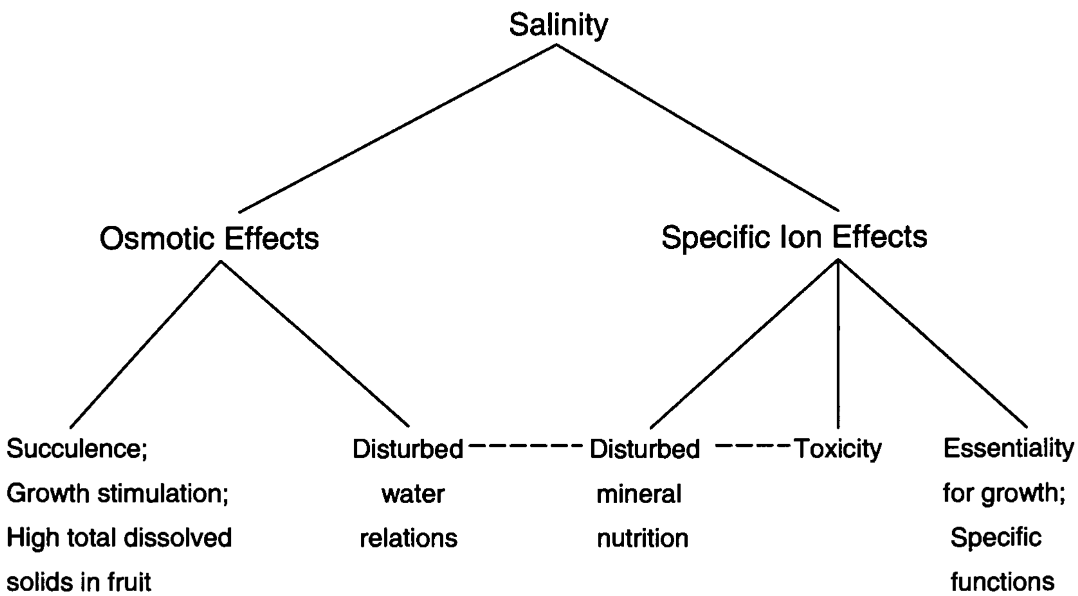


Figure 2.3 Effects of salinity on plants (modified from Läuchli & Epstein, 1990).

As suggested by Läuchli and Epstein (1990), specific ion effects may be categorized under three headings. First, high concentrations of a given ion may cause nutritional disorders. Second, certain ions may have toxic effects, which may not always be clearly distinguishable from deficiencies. Third, there may be specific ion effects that promote the growth or qualitative features of the plant. It is generally recognized that both osmotic and specific ion effects could simultaneously be responsible for growth reduction, but the relative contribution of osmotic potential or specific ion effects is difficult to assess (Barnard *et al.*, 1998).

2.3.1 SULPHATE SALINITY

2.3.1.1 Effect on Crop Growth

There are generally three views held on the effect of sulphate salinity on plant growth: firstly that plant growth can be improved by moderate sulphate salinity; secondly that high sulphate concentrations in the growth medium have no effect on plant growth; and thirdly that growth is depressed by high sulphate concentrations.

Hassan *et al.* (1970) reported that growth and grain yield of barley were stimulated by moderate salinity (EC_e of 400 to 600 mS m^{-1}) when SO_4^{2-} salts were used. Alfalfa yield was also improved when it was irrigated with a moderate SO_4^{2-} saline (6.7 mmol ℓ^{-1} SO_4^{2-}) water (MacAdam *et al.*, 1997). Manchanda *et al.* (1982) indicated that the grain yield of barley grown in SO_4-dominated salinity ($Cl:SO_4$ 1:11 and 60 mmol ℓ^{-1} total salts) was higher than that of the lower SO_4-salt treatment ($Cl:SO_4$ 1:7 and 40 mmol ℓ^{-1} total salts) and of the non-saline control. The yield was thus higher when grown with the 50 mmol ℓ^{-1} SO_4 treatment than with the 35 mmol ℓ^{-1} SO_4 treatment or the control. Manchanda *et al.* (1991) also reported that the grain yield of broad bean increased by 13% relative to the control (EC_e 80 mS m^{-1}) even at an EC_e as high as 800 mS m^{-1} with SO_4-dominated salinity.

Duke and Reisenauer (1986) stated that most crops, with the exception of citrus, are quite insensitive to high concentrations of SO_4^{2-} when grown in nutrient solutions. Grobler (1976) evaluated the influence of differential levels of nitrate, phosphate and sulphate on the growth and ion uptake of wheat grown in water culture. He found that high concentrations of sulphate in the growth medium, in direct contrast to nitrate and phosphate, had no effect on growth or ion uptake. The sulphate concentrations in the nutrient solutions used in this trial ranged between 1 and 14 mmol ℓ^{-1}. He concluded that as long as this element was available in amounts that ensured sufficient uptake, the actual amount of available sulphate could vary considerably without having any noticeable effects. MacAdam *et al.* (1997) demonstrated that the yield of tall fescue grown in a calcareous soil and irrigated with increasing levels of high SO_4 water was not significantly affected. The SO_4 concentration in the irrigation water ranged from 2 to 18 mmol ℓ^{-1}. Barnard *et al.* (1998) also stated that plants are comparatively insensitive to high sulphate concentrations in the nutrient medium. Manchanda *et al.* (1981) did not observe a reduction in seed yield of chickpea under continuous irrigation with SO_4-dominated (SO_4 = 80%) saline water (EC = 500 mS m^{-1}) on a sandy loam soil.

Some investigations have shown, however, that excess sulphur by itself can reduce dry weight, yield and delay flowering (Papadopoulos, 1984; Rennenberg, 1984; Curtin *et al.*, 1993). Mengel and Kirkby (1979) stated that plants are usually only affected when SO_4 is in the order of 50 mmol ℓ^{-1} and higher. The symptoms, a reduction in growth rate and a dark green colour of the leaves, are not specific for excess S and are more typical of salt- affected plants. Duke and Reisenauer (1986) stated that growth reductions from high SO_4^{2-} levels can be attributed to toxic reactions from excesses of the cation associated with the SO_4^{2-} or from disturbed Ca^{2+} nutrition and root membrane functioning.

Papadopoulos (1984) found that tomato fresh fruit weights decreased by 40 and 53% when irrigated with water having a SO_4 concentration of 8 and 16 mmol ℓ^{-1} respectively. When a 0.3 leaching fraction was allowed, the respective decreases in fruit fresh weight were 12 and 32% for the two levels of sulphate. Tops were less affected than fruits. Linear correlation analysis of various components on salt build-up indicated that the growth decrease in plants could have been ascribed to an increase in Na and the sodium adsorption ratio of the soil solution that resulted from gypsum precipitation. Rennenberg (1984) reported that decreases in yield caused by excess sulphur were accompanied by a decreased uptake of Mo and an increased uptake of Cu, Mn and Fe. Manchanda *et al.* (1981) reported that seed yield of chickpea was decreased by 40% when it was irrigated with SO_4-dominated (EC of 1000 mS m^{-1}) saline water. Manchanda *et al.* (1991) also reported that straw yield of chickpea decreased significantly at an EC_e of 500 mS m^{-1} in SO_4-dominated salinity, while grain yield decreased only at an EC_e of 700 mS m^{-1}. Yields of barley and kochia were significantly reduced by SO_4 salinity at salt solution electrical EC levels of 1750 and 2750 mS m^{-1} (Curtin *et al.*, 1993). These authors ascribed the yield decrease to a sulphate salinity-induced Ca deficiency. Soltanpour *et al.* (1999) indicated that the yield of two alfalfa species decreased gradually with increasing SO_4 concentrations from 0.6 mmol ℓ^{-1}

(EC of 70 mS m^{-1}) to 38.4 mmol ℓ^{-1} (EC of 770 mS m^{-1}) in the nutrient solution. They attributed this decrease in yield to a possible SO_4 toxicity, a SO_4-induced P deficiency and/or an organic anion (cation – anion concentration) deficiency.

Barnard *et al.* (1998) investigated the effect of increasing sulphate concentrations of a simulated sulphate mine water on germination and seedling growth of several crops. Their results indicated that the sulphate saline water did not significantly influence germination of most cultivars of both subtropical and temperate crops. There was a general tendency for seedling growth to be increasingly suppressed to a point usually in the vicinity of 21 to 31 mmol ℓ^{-1} SO_4 in the solution culture. Seedling growth did not decrease in a linear fashion with an increase in SO_4 concentrations in the medium. There were gradual but not significant decreases of relative seedling growth from 16 to 24 mmol ℓ^{-1} total SO_4 in the growth medium. Above this value the general trend was that the depression stayed between 86 and 100% relative growth up to 63 mmol ℓ^{-1} total SO_4 in the growth medium. Where the SO_4 concentration was increased with Na_2SO_4 in addition to a saturated gypsum solution, in order to obtain solutions with soluble SO_4 levels higher than those obtained through solubilization of gypsum, the growth decrease of wheat seemed to be linear with increasing EC, decreasing very gradually up to 52 mmol ℓ^{-1} SO_4.

From the foregoing discussion it can be concluded that the contradicting views and findings with regard to the effect of SO_4 salinity on plant growth can firstly be ascribed to the range of tolerances to SO_4 that is displayed by crop plants. This may be the result of different mechanisms whereby plants cope with excess sulphate (section 2.3.1.3). It was also evident that excess SO_4 *per* se was seldom reported to cause a decrease in yield. Yield decreases were usually ascribed to excesses of the accompanying cation, nutrient imbalances or organic anion deficiencies.

2.3.1.2 Effect on Crop Quality and Animal Production

Apart from reports of growth reductions due to high SO_4 levels in the growth medium, high SO_4 concentrations in plants can also influence crop quality negatively and cause health problems in animals. Because of its function in protein structures, S affects properties of cereal grains that are important in their use as flour in baking (Rendig, 1986). Zhao *et al.*

(1997) reported that high SO_4 in wheat grain decreased the elastic strength of the dough, which means that grain with a large concentration of SO_4 is less suitable for bread-making. An excessive S supply can also lower the quality of rapeseed meal as animal feed by increasing the glucosinolate concentration (Zhao *et al.*, 1997). Mayland and Robbins (1994) reported that herbage containing large amounts of SO_4 is associated with health problems in ruminants. Ruminant intake of large amounts of SO_4 in feed and water may cause clinical abnormalities including polioencephalomalacia characterized by depression, incoordination, and blindness (Mayland & Robbins, 1994). Ample evidence also implicates S as a factor influencing Cu utilization in animal nutrition (Rendig, 1986).

2.3.1.3 Sulphate Accumulation by Plants in Response to Sulphate Salinity

Sulphur accumulates in higher plants when applied to the soil in amounts exceeding those optimal for growth. Once it has been taken up by the plant, SO_4^{2-} is activated and can thus be used in its oxidised form; e.g., as a component of SO_4^{2-} esters in cell membranes. Activated SO_4^{2-} can also be reduced and metabolized by plants to the essential amino acid cysteine, and then to many other S-containing organic compounds (Marschner, 1995).

Both the uptake and requirements for S differ greatly amongst species, amongst cultivars within species, and with stage of development of the crop. Concentrations of S in plants usually range from 0.1% to 0.3% tissue dry weight (MacAdam *et al.*, 1997). Duke and Reisenauer (1986) reported that crops that commonly contain the largest amounts of S include the halophytes (salt-tolerant species) and most species of the *Cruciferae* and *Liliacae* families, whereas cotton, the legumes and tobacco are intermediate, while the small grains and maize contain least.

Sulphur taken up in excess is stored as SO_4-S (Mengel & Kirkby, 1979). Plants are known to vary in the degree to which they accumulate SO_4^{2-} or S-containing compounds in their tissues (Marscher, 1995). Duke and Reisenauer (1986) reported that leaf S levels greater than 0.5% in citrus are associated with retarded growth and an interveinal chlorosis extending along leaf margins. Sulphate levels as high as 5.8% were reported for alfalfa plants grown in 52.4 mmol ℓ^{-1} SO_4 solutions (Soltanpour *et al.*, 1999). Besides accumulation of sulphate, a two- to three-fold increase in soluble organic sulphur has been observed (Rennenberg, 1984).

Glutathione (a low molecular weight thiol) may also function in cells of higher plants as a reservoir of reduced sulphur (Rennenberg, 1984).

Most glycophytes (salt-sensitive species) are ion excluders, but they can regulate their ion content to some extent by limiting ion transfer to the shoot, by re-export of ions to the growth medium via roots, or redistribution of ions in different organs and in different cellular components (Huang & Redmann, 1995). Rennenberg (1984) reported that an immediate injury by excess sulphur taken up seems to be prevented by a series of metabolic processes in the plant, rather than by avoidance of sulphur intake. The metabolic processes that seem to be of importance are the following:

i. Storage of excess sulphur in a metabolically inactive compartment, i.e. the vacuole appears to occur in most plants (Rennenberg, 1984).
ii. Sulphate can be translocated in both xylem and phloem, and can thus be stored in plant parts not directly exposed to the excess. Salisbury & Ross (1985) stated that transport of both free SO_4^{2-} and organic sulphur compounds back to roots and to other parts of the plant can occur through the phloem. Retranslocation of sulphate to the roots via phloem transport may be a mechanism to prevent the leaves being supplied with excess sulphur, even if an excess of this sulphur is taken up by the roots.
iii. Sulphate can also be decreased in plants by emission of volatile sulphur compounds (Rennenberg, 1984).
iv. Rennenberg (1984) reported that with increasing accumulation of sulphate its reduction and storage as glutathione also increases. Glutathione is the predominant long-distance transport form of reduced sulphur in higher plants. This suggests that this compound may be removed from the leaves when in the presence of excess inorganic sulphur.

Colmer *et al.* (1996) reported that a 1000-fold increase in the external sulphate concentration, from 0.1 mmol ℓ^{-1} to 100 mmol ℓ^{-1} in the growth medium, only resulted in a four-fold increase in the leaf concentration of SO_4 in *Spartina alterniflora* plants. The mechanism whereby this halophyte prevents injury by excess SO_4 seems to be ion exclusion or avoidance of sulphur intake.

The ionic composition of the nutrient-salt solution may also affect the balance between the total concentration of cations and anions in plant tissues. Normally plant cells must remain electronically neutral to perform their physiological activities by antiport or symport. A positive relationship between biomass accumulation and the excess of cations over anion concentration was found in different plant species (Sagi *et al.* 1997). According to Mengel & Kirkby (1979) the difference between the sum of cations and that of anions is balanced by the production of organic anions. A normal organic acid anion concentration, which is affected by salinity and other factors, is one of the conditions for good plant growth (Soltanpour *et al.*, 1999). Abd El-Samad and Shaddad (1996) found that pea plants accumulated soluble saccharides, proteins, and shoot prolines in case of Na_2SO_4 stress in order to adjust osmotically. Huang and Redmann (1995) found, however, that proline appeared to have minor importance in contributing to leaf osmolality in case of SO_4 stress induced on barley plants. Colmer *et al.* (1996) also reported that a 1000-fold increase in external sulphate concentration had no effect on the leaf blade levels of proline, glycinebetaine, aspergine or dimethylsulphoniopropionate. Curtin *et al.* (1993) reported that kochia and barley plants stressed with SO_4 salts produced oxalate to maintain charge balance. Plants that produce oxalate under conditions of stress may, however, suffer from self-inflicted Ca deficiency due to Ca-oxalate precipitation.

Biddulph *et al.* (1956) found that SO_4 is strongly absorbed at low concentrations and that intake approaches saturation at low levels, about 10 µmol ℓ^{-1}. Biddulph *et al.* (1956) attributed this to uptake inhibition from intracellular SO_4 and reduced S compounds. This apparent saturation relationship was not obtained in experiments in which the S was supplied as Na_2SO_4 (Duke & Reisenauer, 1986). Sulphur intake continued to increase with the SO_4 level of the media and unusually high plant tissue levels of the element were obtained. The effect seemed to be specific to sodium.

2.3.2 CALCIUM SALINITY

2.3.2.1 Effect on Crop Growth and Quality

The Ca requirement of a plant is generally low, i.e., 0.7 mmol ℓ^{-1} to 1.5 mmol ℓ^{-1} (Pratt & Suarez, 1990), with no toxicity to plants from higher accumulation (MacAdam *et al.*, 1997).

The Ca requirement appears to depend on the presence of other ions. It may be related to ion competition and, thus, is better expressed in terms of ion ratios. Claassens (1973) stated that the macronutrients, Ca, K and Mg, can vary widely with respect to each other without any significant effect on plant growth provided that the Mg-supply would not greatly exceed the Ca supply on an equivalent base. Guidelines for specific ratios cannot be established because cultivars respond in widely varied ways to cation composition (Pratt & Suarez, 1990).

When external calcium concentrations are high, they may mitigate the effects of salinity (Läuchli & Epstein, 1990). Calcium plays a crucial role in controlling cell membrane permeability and selectivity (Marschner, 1986). It is thus important in regulating the salt economy of plants and may protect them against the deleterious effects of salinity (Curtin *et al.*, 1993).

2.3.3 MAGNESIUM AND MAGNESIUM SULPHATE SALINITY

2.3.3.1 Effect on Crop Growth

Excess Mg in nutrient solutions and soils has long been known to result in reduced plant growth (Franklin *et al.*, 1991). Szabolcs (1989) stated that a solution with a high concentration of magnesium ions is one of the most toxic and harmful agents for plants. This could either be due to a "toxic effect" of Mg, an induced Ca-deficiency by partial exclusion of Ca by Mg from plants or a "general plant nutrient imbalance" brought about by excess Mg and, in part, a high pH effect (Franklin *et al.*, 1991).

Magnesium toxicity symptoms in green beans (*Phaseolus vulgaris*) have been described by Claassens (1973). Symptoms of Mg deficiency compared to Mg toxicity are illustrated in Plate 2.1. Deficiency symptoms developed where the Ca:Mg ratio in the nutrient solutions was 20:1 (Ca 2.9 mmol ℓ^{-1} and 0.1 mmol ℓ^{-1} Mg), while Mg toxicity symptoms developed where the Ca:Mg ratio was 1:20 (0.3 mmol ℓ^{-1} Ca and 5.7 mmol ℓ^{-1} Mg). Magnesium toxicity symptoms developed at the same position where Mg deficiency symptoms were noted, i.e. at the base of the leaf where it is attached to the leaf stem. The toxicity symptoms consisted of areas on the leaf blade that turned yellow and appeared bulged. The chlorosis spread progressively from the base to the leaf margins.

a)

b)

Plate 2.1 a) Magnesium deficiency symptoms in green beans at a nutrient solution Ca:Mg ratio of 20:1. Potassium was supplied at a rate of 12 mmol K ℓ^{-1}.
b) Magnesium toxicity symptoms in green beans at a nutrient solution Ca:Mg ratio of 1:20. Potassium was supplied at a rate of 6 mmol K ℓ^{-1}.

Franklin *et al.* (1991) evaluated the effect of high $MgSO_4$ in combination with different EC levels in the irrigation water (EC_{iw}) on the growth of maize. The maize plants were grown in a soil equilibrated and irrigated with $MgSO_4$ solutions of EC_{iw} 100, 300 and 600 mS m^{-1}. The dry matter production of maize was reduced by 35% with the EC_{iw} of 100 mS m^{-1} treatment (electrical conductivity of soil solution (EC_{sw}) of 200 mS m^{-1}), by 55% with the EC_{iw} of 300 mS m^{-1} treatment (EC_{sw} of 430 mS m^{-1}) and by 82% by the 600 mS m^{-1} treatment (EC_{sw} of 800 mS m^{-1}), relative to the control. The yield data of the $MgSO_4$ treatment was compared to that of a mixed salt treatment of the same EC_{iw} to differentiate "salinity effects" from "Mg-effects". The data indicated that salinity effects were minor compared to specific ion effects since maize yield was only slightly reduced by the mixed salt treatment at comparable ECs of the soil solution. Very pronounced Ca-deficiency symptoms occurred on plants irrigated with the highest $MgSO_4$ treatment.

Magnesium sulphate soil salinity was reported to reduce the yield of barley when Ca:total cation ratios were less than 0.15 or when ion activity ratios (*a*Ca:*a*Total cations) were less than 0.09 (Suhayada *et al.,* 1992). Subbarao and Johansen (1994) reported that mung bean and red kidney bean are more affected by $MgSO_4$ than by Na_2SO_4 and K_2SO_4 salts, while the reverse is the case with alfalfa.

2.3.4 EFFECT OF GYPSUM ON CROP GROWTH AND QUALITY

Crops vary widely in their tolerance to gypsum (Table 2.2). In soils with less than 2% gypsum by volume, all crops, including many of the most gypsum-sensitive crops, can be grown without yield reductions (Verheye & Boyadgiev, 1997).

Verheye and Boyadgiev (1997) reported that crops could also be grown in soil layers with 2 to 10% gypsum by volume without any significant yield reductions or deterioration of soil structure, consistency and water-holding capacity. Observations in Iraq, the former USSR, Algeria, Syria and Jordan indicate, however, that beyond the critical limit of 10% by volume, root growth becomes inhibited and gypsum precipitation increasingly tends to break the continuity of the soil mass and disperse into voids so as to reduce and ultimately prevent water and air penetration and root functions (Smith & Robertson, 1962; Verheye &

Boyadgiev, 1997). Keren (1990) also stated that large amounts of gypsum might temporarily reduce the soil hydraulic conductivity, since small gypsum particles lodge in the soil pores.

Table 2.2 A tentative scale of crop tolerance to gypsum (Verheye & Boyadgiev, 1997)

Sensitive crops (tolerance 2-3% gypsum vol. basis)	**Semi-sensitive crops** (tolerance 3-10% gypsum vol. basis)	**Semi-tolerant crops** (tolerance 10-25% gypsum vol. basis)	**Tolerant crops** (tolerance >25% gypsum vol. basis)
Potatoes	Groundnut	Sugarbeet	Alfalfa
Tobacco	Sunflower	Maize	Clover
Pistachio		Wheat	Oats
Sugarcane		Cotton	Onion
Soybean		Broad beans	Lentil
Rice		Sorghum	Barley
Field bean		Pearl millet	Apricot
		Olives	Date
		Pomegranates	
		Figs	

Dramatic crop yield reductions take place if the gypsum content in soils exceeds 20-25% by volume. The physical characteristics of these soils are often unfavourable as a result of limited water retention, slaking of (loamy) topsoils, lack of plasticity and cohesion, and structural deterioration (Mashali, 1996). Verheye and Boyadgiev (1997) stated that satisfactory yields with gypsum-tolerant crops could only be obtained on these soils with irrigation, drainage and heavy fertilisation.

The effect of gypsum in the soil on cotton quality and yield was studied in a field experiment by Minashina *et al.* (1983). They indicated that in the presence of fine-grained gypsum in soils that consist of more than 10% gypsum, the yield of cotton was reduced by 1.6% with an increase of 1% gypsum in the root zone. With a gypsum content in excess of 25%, the movement of the upper boundary of the gypsic horizon from the lower part of the root zone (700 mm) towards the soil surface, reduced the yield first by 0.5% per 100 mm, then by 1% and then by 2% in the ploughed horizon. The quality of the cotton fibre deteriorated as the gypsum content of soils increased. These authors suggested that the yield reduction was caused by a decreased water-retention capacity of the soil.

2.4 INTERACTIVE EFFECTS OF SALINITY AND FERTILITY ON THE CHEMICAL COMPOSITION OF PLANTS

When the effect of one factor is influenced by the effect of another factor, the two factors are said to interact. The simultaneous presence of salts and nutrient elements in the root zone can influence ion uptake by plants and affect plant chemical composition. The concentration of elements in a plant is influenced by different types of nutrient interactions.

There is firstly an interaction, in a generic sense, between an element concentration in the solution (supply) and that element's concentration in the plant. Plants that are, for example, not sufficiently supplied with K, have greater Ca and Mg concentrations in their leaves (Fontes *et al.*, 1996).

Secondly, the absorption process of cations and anions influences the uptake of other cations or anions. An increase in the uptake of one of the cations frequently leads to a decrease in the uptake of others. This phenomenon is known as antagonism and the opposite effect is called synergism (Mengel & Kirkby, 1979). When the combined effect of two factors is more than their additive effects, the interaction is said to be positive (or synergistic). If the combined application of two nutrients results in the highest response, it does not automatically mean that the interaction is positive. The effect is positive only when the combined response to nutrients A + B exceeds the response to A and response to B (Tandon, 1992). When their combined effect is less than their additive effects, the interaction is said to be negative (antagonistic) (Prasad & Power, 1997).

Thirdly, interactions within the plant occur between ions either because they are able to form chemical links or because they have similar abilities to compete for sites of adsorption, absorption, transport or function. Calcium and magnesium, for example, have a high affinity for phosphate-O ligands and carboxilate (Sanchez de la Puente & Belda, 1994).

2.4.1 Salinity-fertility interactions as a result of a high sulphate concentration in the growth medium

2.4.1.1 Nitrogen

Nitrogen and S enhance the efficiency of one another. The interaction between N and S is generally positive (Ceccotti, 1996; Rasmussen, 1996; Prasad & Power, 1997) and occasionally additive (no interaction) (Tandon, 1992). Manchanda *et al.* (1991) reported that the N content of plants increased significantly with increased SO_4 content of the soil, particularly at an EC_e of 400 mS m^{-1} and higher. Plants grown in SO_4 salinity also contained significantly more N than those in Cl-dominated salinity at comparable EC levels (Manchanda & Sharma, 1989; Curtin *et al.*, 1993; Datta *et al.*, 1995).

2.4.1.2 Phosphorus

Both positive and negative interactions have been reported between S and P but recent research has shown that the nature of the P-S interaction depends on their rate of application (Tandon, 1992). Several workers have reported that the P-S interaction is synergistic at low to medium levels of P and antagonistic only at higher levels (Tandon, 1992).

A synergistic relation between S and P with respect to their absorption was observed in wheat (Manchanda *et al.*, 1982; Rasmussen, 1996). Curtin *et al.* (1993) also reported that the P concentration in barley and kochia plants increased with increasing SO_4 salinity (from EC_{sw} 760 to 2760 mS m^{-1}). Sulphate and phosphate do not compete for the same carrier, as the uptake of sulphate is enhanced in the presence of phosphate or 3-phosphoglycerate. From this observation it has been concluded that phosphate or 3-phosphoglycerate increases the affinity of the phosphate translocator for sulphate (Rennenberg, 1984).

Manchanda *et al.* (1991) reported that the P content in broad bean and chickpea grown in a sandy soil was unaffected by excess SO_4.

An antagonistic effect of increasing SO_4 concentration in the growth medium on P uptake was found with barley and sunflower (Zhukovskaya, 1973), tomato grown in nutrient solution (Terabayashi *et al.*, 1995) and in alfalfa (Soltanpour *et al.*, 1999). Datta *et al.* (1995) found that the P content in four wheat cultivars decreased significantly in both Cl- and SO_4-dominated salinity. The SO_4 concentration in the growth medium of these trials ranged from 0.6 to 52.4 mmol ℓ^{-1} SO_4.

2.4.1.3 Potassium

Increasing SO_4 concentrations in the nutrient medium decreased the K content in tomato (Terabayashi *et al.*, 1995), chickpea, broad bean and pea plants (Manchanda *et al.*, 1991) and in barley and kochia plants (Curtin *et al.*, 1993). Increased levels of sulphate did, however, increase the K content in plants simultaneously exposed to NaCl salinity (Huang *et al.*, 1994).

2.4.1.4 Calcium

Sulphate salinity can reduce plant-available Ca by precipitation of gypsum. A tendency of decreasing Ca contents with increasing SO_4 concentrations in the nutrient medium was reported in tomato, wheat, chickpea, broad bean, pea plants and alfalfa (Manchanda & Sharma, 1989; Manchanda *et al.*, 1991; Terabayashi *et al.*, 1995; Datta *et al.*, 1995; Soltanpour *et al.*, 1999). Calcium was reported to be reduced in plants by high concentrations of SO_4 even under high Ca salt treatment when turgor was well maintained (Datta *et al.*, 1995; Huang & Redmann, 1995). Controversially, MacAdam *et al.* (1997) reported that alfalfa accumulated Ca in preference to Mg and was approximately four times greater than that of tall fescue when irrigated with SO_4 saline water.

2.4.1.5 Magnesium

Both synergistic and antagonistic effects have been reported for the S and Mg interaction. Tandon (1992) reported that the antagonism between S and Mg was greater when potash was also applied. A tendency of decreasing Mg concentration in barley and kochia, tomato and wheat plants grown with increasing SO_4 concentrations in the nutrient medium was found by Curtin *et al.* (1993), Terabayashi *et al.* (1995) and Datta *et al.* (1995) respectively. These results are not commensurate with Manchanda and Sharma (1989) and Manchanda *et al.*

(1991) who advocated a decreased Ca absorption in SO_4-dominated salinity, which enhanced Mg absorption in chickpea, broad bean and pea. Manchanda and Sharma (1989) reported that the Mg concentration increased significantly in SO_4-dominated salinity (40-80% more Mg than in control plants). MacAdam *et al.* (1997) also reported that the Mg content increased in tall fescue and alfalfa grown in a calcareous soil with increasing SO_4 salinity.

2.4.1.6 Sodium

The Na concentrations of plant shoot tissues of alfalfa and tall fescue grown in a calcareous soil increased with increasing SO_4 concentration in the irrigation water (MacAdam *et al.*, 1997). Results from Manchanda and Sharma (1989), Manchanda *et al.* (1991) and Curtin *et al.* (1993) also showed that plants grown in SO_4-dominated salinity accumulated significantly more Na than in Cl-dominated salinity at comparable EC levels. They attributed the greater Na content in SO_4-dominated salinity to decreased Ca absorption in SO_4-dominated salinity, because of lower activity of Ca in the former. Duke and Reisenauer (1986) reported that plant S intake continued to increase with increasing Na_2SO_4 levels of the medium. They reported that this effect appears to be specific to sodium.

2.4.1.7 Manganese

Increased SO_4 salinity was reported to reduce Mn and cause growth reductions in barley even under high Ca salt treatment when turgor was well-maintained (Huang & Redmann, 1995). Soltanpour *et al.* (1999) also reported that the Mn concentration decreased in alfalfa with an increasing SO_4 concentration of the nutrient medium.

2.4.1.8 Boron

A synergistic relationship between sulphur and boron was reported in groundnut (Prasad & Power, 1997). The boron concentrations in tomato (Terabayashi *et al.*, 1995) and in alfalfa and tall fescue (MacAdam *et al.*, 1997) increased with increasing SO_4 in the nutrient solution and irrigation water.

2.4.1.9 Zinc

MacAdam *et al.* (1997) reported that the zinc concentration in plant shoot tissue increased in tall fescue and alfalfa grown in a calcareous soil with increasing SO_4^{2-} concentration in the irrigation water. Soltanpour *et al.* (1999) also reported that the zinc concentration increased in alfalfa with increasing SO_4 in the nutrient medium.

2.4.1.10 Molybdenum

High sulphate levels induce molybdenum deficiency in plants (Albasal & Pratt, 1989), since the SO_4^{2-} anion competes with the molybdenum anion for uptake (Marschner, 1995). Decreasing molybdenum uptake with increasing supply of sulphates to crop plants, sometimes with the occurrence of molybdenum deficiency, has been reported by several authors (Martin & Walker, 1966; Albasal & Pratt, 1989; Soltanpour *et al.*, 1999).

2.4.1.11 Selenium

Although not essential to plants, selenium is essential to animals. Sulphate was reported to interact with the absorption of selenium (Murphy & Quirke, 1997). A strong antagonism exists between divalent selenate (SeO_4^{2-}) and sulphate because of many chemical and physical similarities between them and the fact that Se is present in minute quantities in soils (usually less than 10 mg kg^{-1}) (Salisbury & Ross, 1992, Higgins & Fey, 1993; Murphy & Quirke, 1997).

2.4.2 SALINITY-FERTILITY INTERACTIONS AS A RESULT OF A HIGH CALCIUM CONCENTRATION IN THE GROWTH MEDIUM

2.4.2.1 Potassium

Excessive addition of calcium to soil often decreases the absorption of K by plants. However, optimum amounts of calcium result in an increase in the availability of exchangeable and water-soluble potassium (Ananthanarayana & Hanumantharaju, 1992). Iyengar and Reddy (1994) also reported that a high Ca^{2+} content in the growth medium decreased K^+ and Mg^{2+} levels, while a mixed solution (Ca + K + Mg + Na) corrected the imbalance.

2.4.2.2 Magnesium

The calcium-magnesium antagonism was observed as early as 1892. Calcium is strongly competitive with Mg, and the binding sites on the root plasma membrane appear to have less affinity for the highly hydrated Mg^{2+} than for Ca^{2+} (Marschner, 1986). Calcium is also frequently reported as an inhibitor of enzymes that require magnesium and that a high activity of calcium counteracts the function of magnesium (Clarkson & Hanson, 1980). Calcium and magnesium compete for active sites in puruvate-kinase, for instance. Grattan and Grieve (1994) also reported that excessive leaf Ca concentrations may interfere with CO_2 fixation by inhibition of stroma enzymes, particularly those that are Mg^{2+} activated.

Ananthanarayana and Hanumantharaju (1992) reported, however, that Mg exerts a more depressing effect on Ca uptake than Ca levels did on the uptake of Mg. The antagonistic effect of Ca or Mg on the uptake of the other seems to be more pronounced on applied cations than on these cations under natural soil conditions. Increasing levels of Mg had little effect on Ca uptake (no Ca added) and the effect of increasing levels of Ca on Mg (no Mg added) was similar.

2.4.2.3 Micronutrients

The interaction between Ca and micronutrients is generally antagonistic, with the exception of molybdenum.

Huang and Redmann (1995) found that tissue manganese concentration in barley was substantially lower under high Ca salt (10 mmol ℓ^{-1} $CaCl_2$) treatment than under low Ca salt (5 mmol ℓ^{-1} $CaCl_2$) treatment, indicating a possible Ca-Mn antagonism. This is in contradiction to Suhayda *et al.*'s (1994) statement that saline solutions rich in divalent cations may enhance the accumulation of Mn in plant tissue.

An antagonistic interaction between boron and calcium has been reported in several crops (Prasad & Power, 1997).

Low Ca salinity was reported to increase the iron content in roots of certain barley species (Grattan & Grieve, 1994). Ananthanarayana and Hanumantharaju (1992) reported that calcium salts in the growth medium lowered the availability of iron and copper to plants.

2.4.3 SALINITY-FERTILITY INTERACTIONS AS A RESULT OF A HIGH MAGNESIUM CONCENTRATION IN THE GROWTH MEDIUM

2.4.3.1 Nitrogen

Sanchez de la Puente and Belda (1994) stated that magnesium is the most liable nutrient-element to interact. Magnesium exerts a synergistic effect on N uptake by crops (Ananthanarayana & Hanumantharaju, 1992).

2.4.3.2 Phosphorus

The correlation between phosphorus content and magnesium content suggests that magnesium is relevant to the absorption of P and responsible for the transport of P (Sanchez de la Puente & Belda, 1994). This is probably due to the requirement for magnesium in all the enzymatic systems related to phosphorus metabolism. Among the functions of Mg are the formation of the complex Mg-substrate-enzyme, which activates P transfer, and the depression of excessive Mn absorption (Sanchez de la Puente & Belda, 1994).

2.4.3.3 Calcium

Magnesium exerts a depressing effect on Ca uptake (Ananthanarayana & Hanumantharaju, 1992). Calcium was reported to be reduced in plants by high concentrations of Mg even under high Ca salt treatment when turgor was well maintained (Huang & Redmann, 1995).

2.4.3.4 Potassium

The antagonistic effect of K on Mg is widely reported in the literature, but reports of the antagonistic effect of Mg on K are few. An antagonistic effect of increasing Mg levels on K uptake has been reported and could be attributed to the differences in their ionic mobility, i.e.

ion competition for sorption sites (Ananthanarayana & Hanumantharaju, 1992). The antagonism between Mg and K seems, however, to be confined to the deficiency range of nutrient availability.

2.4.3.5 Micronutrients

Increased Mg concentrations reduced the manganese concentration in barley and caused growth reductions even under high Ca salt treatment when turgor was well maintained (Huang & Redmann, 1995). The interaction between zinc and Mg seems to be synergistic at lower levels of Mg and antagonistic at high levels of Mg. Zinc and Mg ions can substitute each other in the soil and within the plant (Ananthanarayana & Hanumantharaju, 1992). This is due to their similarity in charge and size. A synergistic interaction between molybdenum and Mg was also reported (Ananthanarayana & Hanumantharaju, 1992). Since the geometry of the molybdate and phosphate ion is similar, it is possible for Mg to act as a carrier for molybdenum. Magnesium is a carrier for phosphate in plants.

2.5 INTERACTIVE EFFECTS OF SALINITY AND FERTILITY ON THE YIELD OF AGRICULTURAL CROPS

2.5.1 TYPES OF SALINITY-FERTILITY RESPONSES OF CROPS

Crops grown on infertile soil may seem more salt-tolerant than those grown with adequate fertility. This is because inadequate nutrition depresses yields more under non-saline conditions than under saline conditions (Rhoades, 1990). When fertility is low, proper fertiliser application increases yields regardless of the soil salinity, but proportionally more if the soil is non-saline. When both salinity and fertility limit yields, decreasing salinity or increasing fertility is beneficial (Francois & Maas, 1994).

Grattan and Grieve (1994) preferred to define Bernstein *et al.*'s (1974) interactions based on plant performance at optimal fertility relative to the performance at suboptimal fertility (Figure 2.4). The graphs given in this figure are idealized, showing only the range of yield that is linearly responsive to salinity. Actual salinity response graphs usually follow a sigmoidal relationship (Maas, 1990). The solid line of each part of Figure 2.4 represents a theoretical yield response to salinity under conditions of optimum nutrition. Figure 2.4a illustrates that if yield is severely limited by suboptimal nutrition, a crop may appear relatively more tolerant than if it were grown with adequate fertility, because the effects of salinity on absolute yield cannot be as great as when fertility is adequate (increased salt tolerance). In Figure 2.4b, the lower graph represents independent responses to salinity and a limiting fertility condition; i.e. response to salinity is the same when nutrition is limiting as when it is adequate (no effect on salt tolerance). However, if salinity decreases yields by the same absolute amounts for adequate and limiting nutritional conditions, a crop may appear relatively less tolerant under the suboptimal condition (decreased salt tolerance) (Figure 2.4c). Generally, plant growth is thus promoted more if the most limiting factor is relieved rather than the least limiting factor.

Bernstein *et al.* (1974) presented data supporting the validity of the proposed types of salinity-fertility interactions. Feigin (1985) reported that other published data on interactive effects of salinity and fertility on the yield of crops fit well into this scheme. Bernstein's salinity and fertility interaction model was also supported in work conducted with two halophytes (salt-tolerance species) and a glycophyte (salt-sensitive species) (Grattan & Grieve, 1994). In this study, nutrient applications increased the growth of the halophytes under saline conditions, presumably because salinity was moderately growth- limiting. On the other hand, nutrient applications did not improve the growth of the glycophyte under saline conditions, presumably because salinity was severely growth- limiting.

Salinity and fertility interactions need to be examined under low, moderate and high salinity levels (Grattan & Grieve, 1994). This is illustrated in Figure 2.5. Under low salinity stress, nutrient deficiency limits plant growth more than salinity and a positive (+) interaction or increased salt tolerance response occurs. Under moderate salinity, nutrient deficiency and salinity may equally limit plant growth and no interaction (0) occurs. Under high salinity conditions, salinity limits growth more than nutrient deficiency and a negative (-) response to nutrient application will be obtained. Excessive application of fertiliser, particularly N and K because of their high solubility, may result in a salinity build-up in the soil. This is typically reflected in a decline in yield when fertiliser exceeds the optimum level (Iyengar & Reddy, 1994).

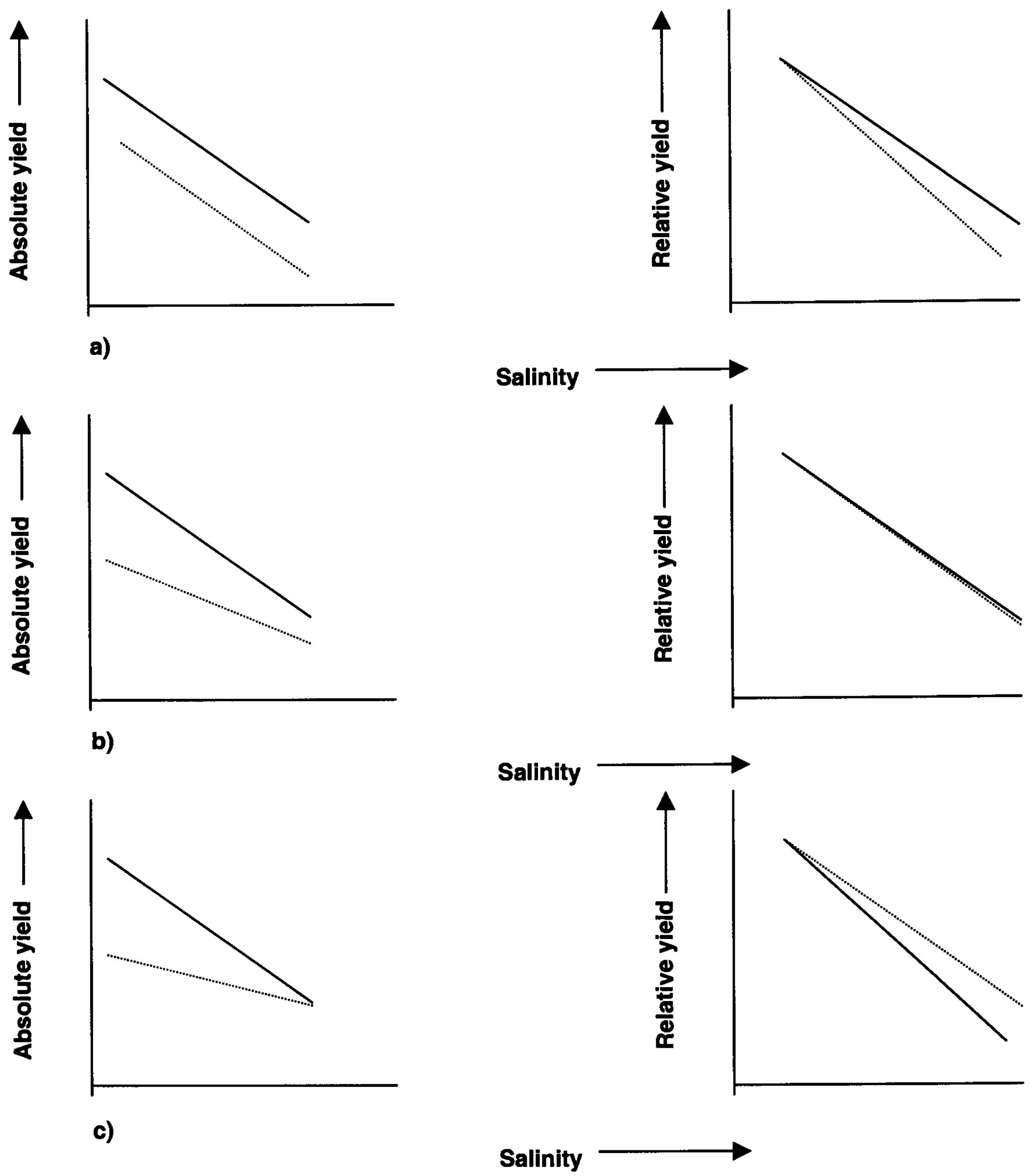


Figure 2.4 Types of growth responses a plant can exhibit under variable salinity as the nutrient status within the substrate increases from suboptimal (dashed line) to optimum level (solid line). a) Salt tolerance increased by optimizing plant nutrient status. b) Salt tolerance unaffected by optimizing plant nutrient status. c) Salt tolerance decreased by optimizing plant nutrient status (Grattan & Grieve, 1994).

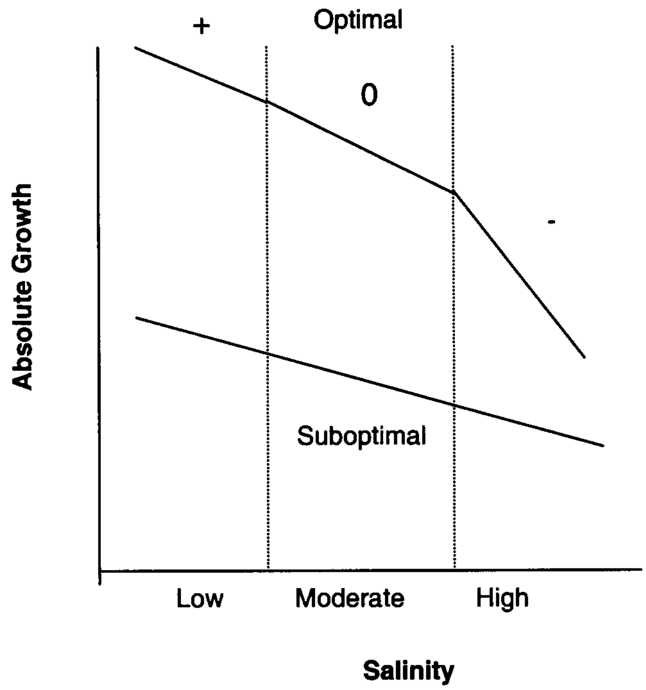


Figure 2.5 Influence of low, moderate and high salinity levels at optimal and suboptimal levels of nutrient supply on plant growth (Grattan & Grieve, 1994).

2.5.2 CORRECTIVE FERTILISATION STUDIES

There are a large number of studies that demonstrate that salinity reduces nutrient uptake and accumulation or affects nutrient partitioning within the plant (Grattan & Grieve, 1994). Salinity and fertility, because of their economic implications, have been the subjects of many greenhouse and field studies. These studies were conducted to evaluate improved fertilisation management as a means of alleviating growth inhibition by salinity. Work on corrective fertilisation under saline conditions has invariably been confined to Cl-dominated salinity and there is very little systematic information with respect to SO_4-dominated salinity.

The interactive effect of different N levels under SO_4 salinity on the ion composition, accumulation of organic solutes and growth of *Spartina alterniflora* grown in salt marshes on the coast of North America was investigated by Colmer *et al.* (1996). Treatments consisted of a factorial combination of two SO_4 levels (0.1 mmol ℓ^{-1} and 100 mmol ℓ^{-1} SO_4) and two

N levels (0.5 mmol ℓ^{-1} and 10 mmol ℓ^{-1} N supplied in a NO_3:NH_4 ratio of 7:1). Leaf growth of the plants was increased by the high nitrogen treatment under both low and high sulphate levels.

Results from a glasshouse crop screening trial with sulphate saline water, indicated that growth of wheat seedlings was less sensitive to a high sulphate water when N was partly supplied as NH_4 (Barnard *et al.*, 1998). These authors ascribed the beneficial effects of an enhanced NH_4 nutrition under SO_4 salinity to NH_4 being a supplementary N source when large SO_4 concentrations suppress NO_3 uptake.

Manchanda *et al.* (1982) conducted a greenhouse and field study to compare the effect of differential phosphorus application levels on the yield of barley and wheat grown under non-saline and SO_4-dominated saline conditions. Results from the greenhouse study indicated that increasing P additions from 0 to 50 mg kg^{-1} increased the straw and grain yield of barley of the control, low SO_4 treatment (Cl:SO_4 1:7 and 40 mmol ℓ^{-1} total salts) and the high SO_4 treatment (Cl: SO_4 1:11 and 60 mmol ℓ^{-1} total salts) significantly. The mean straw and grain yield of barley of the highest SO_4 treatment was higher than that of the lower SO_4-salt treatment and the non-saline control. The field study of Manchanda *et al.* (1982) indicated that the grain yield of wheat under SO_4-dominated salinity was approximately 1%, 3% and 15% higher with P application rates of 25, 50 and 75 kg ha^{-1} respectively, relative to the treatment that received no phosphorus. This increase was, however, not statistically significant.

There is not much information on the fertilisation or chemical amendment of soils containing high amounts of gypsum. This is probably because rates of fertiliser application vary and are always based on farming, local conditions, crop species and varieties and on gypsiferous soil characteristics. Mashali (1996) reported that nitrogen, phosphorus and microelements are virtually always needed to optimize crop production on gypsiferous soils. Because the phenomena which govern N, P and K uptake in gypsiferous soils are not yet fully understood, fertiliser applications are usually made on an empirical basis.

As a rule of thumb it is suggested that N be supplied at rates of 20 to 50% above the anticipated removal by the crop (Verheye & Boyadgiev, 1997). Mashali (1996) stated, however, that there is no significant difference in the N requirement of crops grown in gypsiferous soils compared to that in non-gypsiferous soils under irrigated agriculture. Larger P applications are needed in gypsiferous soils because of greater phosphorus immobilization (Mashali, 1996; Panahi & Rowell, 1996; Verheye & Boyadgiev, 1997). Applications as high as 98 kg P per ha for irrigated alfalfa have been reported. Mashali (1996) stated that potassium can generally be applied at rates of 13 to 21 kg per ha to various crops such as wheat, maize, alfalfa and cotton on irrigated land with gypsiferous soils.

2.5.3 FERTILISATION AND FERTIGATION UNDER SALINE CONDITIONS

Several factors need to be taken into account when fertilisers are applied to a saline soil or saline irrigation water.

In addition to the nutritional effect, fertilisers may increase the osmotic pressure of the soil solution and thus add to the salinity effect. Therefore, such fertilisers should be chosen which would minimize the increase of osmotic pressure in the soil solution. Fertilisers with large amounts of water-soluble ballast ions are undesirable. Among the common N fertilisers, urea produces the lowest osmotic pressure in solution and this permits its application at concentrations up to 15% (Hagin & Tucker, 1982). Interactions between nutrient elements that result from the application of fertilisers should also be considered. Finck (1982) stated that increased application of potassium fertilisers to salt affected soils, beyond the usual amounts, reduces sodium intake through antagonistic effects. An increase in the concentration of K^+, Na^+ and PO_4^{3-} in the soil solution by fertilisation, will on the other hand, lead to complete desorption of adsorbed SO_4^{2-} (Chao *et al.*, 1963; Bohn *et al.*, 1986) with consequential nutrient interactions.

Application of fertilisers with irrigation water - fertigation - has several advantages over broadcast fertilisation (Bar-Yosef, 1991), but is usually more advantageous on coarse-textured, sandy soils than on finer-textured soils (Hagin & Tucker, 1982). The possibility of applying fertilisers with irrigation water depends to a large extent on the quality of the irrigation water. Where the EC of the irrigation water is greater than 100 mS m^{-1}, care should be taken to minimize the amount of accompanying ions added with N, P and K. The solubility characteristics of the fertiliser and the critical ratio of the fertiliser to irrigation water should be determined in order to prevent precipitation problems. The injection of ammonia directly into water high in dissolved calcium and magnesium salts causes, for example, precipitation because of an increased water-pH and lowered solubility of dissolved materials (Hagin & Tucker, 1982). The presence of salts in water also enhances dissociation of NH_4OH and thus increases volatilization losses (Hagin & Tucker, 1982). Lowering the pH of the water may reduce losses of ammonia by volatilization and at the same time reduces precipitation of calcium and magnesium carbonates.

In any case of injecting P-containing ferilisers into irrigation water, a test should be run to establish the critical ratio of the phosphate fertiliser to irrigation water in order to prevent precipitation problems. Orthophosphoric acid (H_3PO_4) solutions can be induced into the irrigation water. The dosage of soluble salts of orthophosphoric acid, such as ammonium orthophosphate in irrigation water should be controlled because of the precipitation of calcium and magnesium salts. Injection of large quantities of ammonium polyphosphate into the irrigation water can also be used because of the sequestering ability of this polyphosphate (Hagin & Tucker, 1982). The presence of polyphosphates in fluid fertilisers enhances the quality of the solution by diminishing precipitation problems and allows higher concentrations of micronutrients to be included (Murphy, 1991). There has also been interest in the production and use of very acid fertilisers, like urea phosphates, that could be injected into high-calcium irrigation water without the formation of insoluble calcium and magnesium phosphates (Murphy, 1991).

Potassium application in irrigation water is relatively problem-free due to the high solubility of most potassium salts. Potassium nitrate or potassium pyrophosphate may be more advantageous than potassium chloride or potassium sulphate when applied to saline soils, since the accompanying ion in the latter case would aggravate soil salinity effects. Micronutrients can also be added by fertigation but solubility principles must be adhered to.

2.6 CONCLUDING REMARKS

Salinity-fertility interactions in soils that result from irrigating crops with sulphate saline water can be distinguished similarly to the salinisation stages that Papadopoulos (1985a) investigated, namely, those that occur during the transient-state stage and those that occur during the steady-state stage of salinisation. Since high concentrations of soluble salts will decrease the availability of water to plants during the transient-state of salinisation, it is expected that the nutrient activity in the soil solution and nutrient extraction by plants will be decreased. Gypsum precipitation during the steady-state salinisation stage will most probably cause changes in the forms of nutrient elements, loss of nutrients through cation and anion interaction effects and a lowered cation exchange capacity of the soil (Mashali, 1996). The amount of gypsum precipitated in the soil during irrigation with the sulphate saline water will determine the intensity and severity of these salinity-nutrient interactions.

Simulations done with the SWB model predicted that 30 years of irrigation with the gypsiferous waste water from Kleinkopje Colliery will lead to between 340 and 404 Mg ha^{-1} of calcium sulphate being precipitated (Annandale *et al.*, 1999). These amounts of gypsum can be compared to those in naturally occurring gypsiferous soils by calculating the volume of gypsum precipitated in a soil to a depth of 1100 mm. Gypsum quantities of 340 and 404 Mg ha^{-1} would amount to between 1.35% and 1.59% of gypsum being precipitated on a volume basis over 30 years of irrigation with the sulphate saline water. These predicted values are below 2% gypsum by volume, the norm given in the literature where most crops can be grown without yield reductions (Verheye & Boyadgiev, 1997). Simulations done with SWB indicated, however, that the gypsum will not be precipitated uniformly within the soil profile because of differences in root distribution and water uptake in the soil profile. It can be expected that most gypsum will precipitate and recrystallize around roots in the soil zone of water extraction. This can result in reduced water and nutrient extraction by plants, since small gypsum particles may lodge in the soil pores, preventing water and air penetration and root functions (Smith & Robertson, 1962; Keren, 1990; Verheye & Boyadgiev, 1997).

The diversity of results obtained from studies that investigated the effect of sulphate salinity on crop growth can partly be ascribed to the range of tolerances to SO_4 that is displayed by crop plants. This may be the result of different mechanisms whereby plants cope with excess sulphate. Although no clear answer can yet be provided on the mechanism or the critical sulphate concentration in the growth medium whereby plant growth is reduced, most studies on the effect of sulphate salinity on crop growth had indicated that excess SO_4 *per se* seldom cause a decrease in yield. Yield decreases are usually attributed to excesses of the accompanying cation, nutrient imbalances or organic anion deficiencies.

On the other hand, it is important to take into consideration that even if high sulphate levels in the growth medium or in plants do not cause yield reductions, that high SO_4 levels in plants can influence the quality of especially forage and grain crops negatively (Rendig, 1986; Zhao *et al.*, 1997) or cause health problems in animals (Mayland & Robbins, 1994).

An attempt has further been made to summarize the literature on salinity and nutrition of crops and reconcile results from experiments conducted in a variety of conditions such as soil and solution cultures, those using mixed and single-salt compositions and those conducted over short and long periods of time. In general it was reported that positive interactions occur between high concentrations of sulphate and N, Na, B and Zn in the growth medium, while negative interactions were reported between sulphate and P, K, Ca, Mn, Mo and Se. High concentrations of calcium were reported to reduce the uptake of K, Mg and micronutrients, while high magnesium concentrations exerted a negative effect on Ca, K, Mn and Zn uptake. Negative interactions between gypsum and P, K, Mg and micronutrients have been reported. It was not always possible to clearly distinguish between nutrient interactions that occurred under low and moderate salinity conditions or even deficient to adequate fertility levels from those that occurred under severely saline conditions. Care should thus be taken when using these general interactions to make fertilser recommendations under calcium and magnesium sulphate saline conditions. An important observation from the literature is that most interactions between nutrients seem to be confined to the deficiency range of nutrient availability. This implies that application of a given nutrient will only result in an increase in crop yield when it exerts a synergistic effect on the uptake of a nutrient that is present in the soil at marginal to low concentrations. Similarly, application of a given nutrient will result in a decrease in yield when it exerts an antagonistic effect on the uptake of a nutrient that is already present in the soil at marginal to low concentrations.

Although little research was done on fertilisation management under sulphate saline conditions, the available information suggests that an increased N and P nutrition may improve crop yield under these conditions (Manchanda *et al.*, 1982; Colmer *et al.*, 1996; Barnard *et al.*, 1998).

From the available literature on fertilisation management of gypsiferous soils (Mashali, 1996; Panahi & Rowell, 1996; Verheye & Boyadgiev, 1997), it can be recommended that N and K must be supplied at rates similar to those used on non-gypsiferous soils under irrigated agriculture, but that larger P and micronutrient applications will be needed. It seems that the rate of P and micronutrient application will primarily depend on the reaction of gypsum with soil components – an acid reaction will cause P and micronutrients (excluding B and Mo) to be more available to plants, while a neutral or alkali reaction will require a higher application rate of these nutrients.

Although critical levels for micronutrients in soil are not readily available, it is suggested that soil testing, together with plant analysis, should be performed whenever a micronutrient deficiency is suspected. Indiscriminate application of micronutrients can lead to pollution of soil and water systems, while excessive application of fertiliser, particularly N and K because of their high solubility, may result in greater salinity build-up in the soil with subsequent yield reductions. Care must be exercised when making a decision on the type of fertiliser, since the accompanying cation or anion could aggravate salinity effects. Nitrogen fertilisers that were reported to cause the smallest increase in the osmotic pressure of the soil solution are non-ionic forms of N, like urea or a slow release form like urea formaldehyde (Hagin & Tucker, 1982). Fertigation offers a suitable way to accurately and uniformly apply nutrients, since small amounts of liquid fertiliser solutions can be injected through center pivot irrigation systems. Solubilities and compatibilities of liquid fertilisers with the calcium and magnesium sulphate enriched irrigation water must, however, be considered. Although Hagin and Tucker (1982) stated that the injection of ammonia into water high in dissolved calcium and magnesium salts could cause precipitation problems because of an increased water-pH, this may not be problematic in the case of the calcium sulphate enriched waste water, since the solubility of gypsum is not pH-dependent (Jurinak, 1990). Orthophosphoric acid, polyphosphates or urea phosphates may serve as possible P sources, while K can be applied as potassium nitrate or potassium pyrophosphate when fertigation is considered.

CHAPTER 3

IMPLICATIONS OF NO_3, NH_4, P AND K NUTRITION ON THE RESPONSE OF *Triticum aestivum* L. TO SULPHATE SALINITY: SOLUTION CULTURE EXPERIMENT

3.1 INTRODUCTION

Saline waste waters will become increasingly important as an alternative source of irrigation water, as effective management strategies for their use are developed. The negative effects of salinity can be overcome to some extent and in some cases by applying suitable water management strategies and by growing crops that are relatively tolerant to high soil salinity. Since salt damage to crops involves not only an osmotic effect but also specific ion effects, the possibility also exists to improve crop growth through fertiliser application. Considerable research has been conducted evaluating improved nutritional management as a means of alleviating growth inhibition by salinity (Papadopoulos & Rendig, 1983; Tshivhandekano & Lewis, 1993; Cachorro *et al.*, 1994; Khan *et al.*, 1994; Soliman *et al.*, 1994; Cordovilla *et al.*, 1995; Gómez *et al.*, 1996). These studies have invariably been confined to chloride-dominated salinity, due to its widespread effect on crop production.

The South African coal industry is, however, faced with the problem of developing cost effective ways of using large volumes of sulphate-dominated saline waste waters. The high concentration of sulphate in the waste waters originates from pyrite that is oxidized and mobilized during the mining process. The coal overburden material also influences the chemical composition of the water. Coal mines on the Highveld of Mpumalanga generate, for example, large quantities of waste water enriched with calcium and magnesium in addition to sulphate. The chemical composition of the water is of course, not only a local problem, but is found worldwide where similar coal and overburden deposits are found.

Using such waters to irrigate crops has been proposed as an environmentally acceptable and economically attractive alternative to other desalinisation options (P.D.Tanner, Amcoal

Environmental Services, personal communication, 1999). It can, however, be expected that the soil solution will become saline following continuous irrigation with the sulphate-enriched water (Papadopoulos, 1988). The literature on sulphate salinity reveals that there are divergent opinions concerning the effect of high sulphate concentrations in the growth medium on plant growth. Some studies have shown that plant growth can be improved by sulphate salinity (Hassan *et al.*, 1970; Manchanda *et al.*, 1982; Manchanda *et al.*, 1991; MacAdam *et al.,* 1997), while others have indicated that growth is depressed by high sulphate concentrations in the growth medium (Papadopoulos, 1984; Rennenberg, 1984; Curtin *et al.*, 1993; Manchanda & Sharma, 1989; Soltanpour *et al.*, 1999). Growth reductions from high sulphate levels have been attributed to possible sulphate toxicity, to toxic reactions from excesses of the cation associated with sulphate and/or to disturbances in soil and plant nutrition.

Sulphate was reported to interact *inter alia* with the absorption of N, P and K. The interaction between N and S is generally positive (Ceccotti, 1996; Rasmussen, 1996; Prasad & Power, 1997) and occasionally additive (Tandon, 1992). Both positive and negative interactions have been reported between S and P, but the nature of the interaction seems to depend on their rate of application (Tandon, 1992). Increasing sulphate concentrations in the nutrient medium was reported to decrease the K content in tomato (Terabayashi *et al.*, 1995), chickpea, broad bean and pea plants (Manchanda *et al.*, 1991) and in barley and kochia plants (Curtin *et al.*, 1993). Excess Ca and Mg in nutrient solutions or soils are also known to interact with various nutrients. Excessive addition of Ca or Mg to soil often decreases the absorption of K by plants (Ananthanarayana & Hanumantharaju, 1992). If excessive Ca, Mg or SO_4 concentrations cause certain nutritional deficiencies or imbalances, the possibility exists that application of specific nutrients can alleviate any possible inhibition of growth by salinity resulting from use of this mine waste water.

There is very little systematic information in respect of nutritional management under sulphate-dominated salinity. A small number of reports indicate that yield under sulphate salinity can be improved by specific nutrient application. Colmer *et al.* (1996) indicated that leaf growth of *Spartina alterniflora* plants was increased by a high nitrogen treatment under both low and high sulphate levels. Results from a glasshouse crop screening trial with sulphate saline water, indicated that growth of wheat seedlings was less sensitive to a high sulphate water when N was partly supplied as NH_4 (Barnard *et al.*, 1998). Other investigations have shown that additions of NH_4 appreciably enhanced the uptake of sulphate by plants (Cox & Reisenauer, 1973; Kirkby, 1968; Haynes & Goh, 1978). Results from Manchanda *et al.* (1982) indicated that the yield of barley and wheat grown under sulphate-dominated salinity conditions was improved by increased P application. An attempt to alleviate the effects of salinity on agricultural crops by changing the nutritional regime from that considered appropriate for non-saline conditions would be of great economic importance.

The objectives of this study were to determine the effect of calcium and magnesium sulphate salinity on wheat growth and to compare crop response to sulphate salinity at differential levels of NO_3, NH_4, P and K in order to give guidelines for the management of crops irrigated with such waters. Sulphate salinity in this chapter refers to salinity caused by calcium sulphate and magnesium sulphate enriched waste water that is characteristic of waste water from certain Mpumalanga coal mines.

3.2 MATERIALS AND METHODS

3.2.1 EXPERIMENTAL PROCEDURE

The investigation was conducted in solution culture under controlled glasshouse conditions. Wheat (*Triticum aestivum* L.) cv. SST 825 was used as test crop. Seed were germinated in vermiculite and after 10 days, four sets of five uniform seedlings were transplanted to 11ℓ of the treatment solutions. The seedlings were supported with foam rubber strips through holes in the lids of the containers. The pots were placed on rotating tables and aerated continuously to ensure uniform radiation on crops.

The treatments consisted of a control (full strength modified Hoagland solution no. 2, P supplied at half-strength) (Hoagland & Arnon, 1950), one calcium and magnesium sulphate salinised control (NO_3, NH_4 and K supplied as full strength Hoagland solution no. 2, P supplied at half strength) and nine calcium and magnesium sulphate salinised treatments with differential levels of NO_3, NH_4, P and K. The Ca:Mg ratio of the salinised treatments was 2:1. The nutrient solutions of the salinised treatments had a mean EC of 354 mS m^{-1} and a pH of 5.8 over the experimental period while the mean EC and pH of the control was 173 mS m^{-1} and 4.5, respectively. The different application rates of NO_3, NH_4, P and K to the salinised solutions are given in Table 3.1. The salinised control treatment (shaded) is given as four seperate treatments in Table 3.1 for the sake of comparison.

Table 3.1 Chemical composition of the different nutrient treatments

Treatments (mmol ℓ^{-1})	Nutrient (mmol ℓ^{-1})						
	NO_3	NH_4	P	K	Ca	Mg	SO_4
Control	14	1	0.50	6	4	2	2.25
7 NO_3	**7**	1	0.50	6	14.5	7.3	21.5
14 NO_3	**14**	1	0.50	6	16.8	8.5	21.5
20 NO_3	**20**	1	0.50	6	18.8	9.45	21.5
1 NH_4	14	**1**	0.50	6	16.8	8.5	21.5
7 NH_4	14	**7**	0.50	6	14.8	7.45	21.5
9 NH_4	14	**9**	0.50	6	14.3	7.2	22.0
0.25 P	14	1	**0.25**	6	16.7	8.4	21.5
0.5 P	14	1	**0.50**	6	16.8	8.5	21.5
0.75 P	14	1	**0.75**	6	16.9	8.5	21.5
3 K	14	1	0.50	**3**	17.8	9.0	21.5
6 K	14	1	0.50	**6**	16.8	8.5	21.5
8 K	14	1	0.50	**8**	16.1	8.2	21.5
10 K	14	1	0.50	**10**	15.5	7.8	21.5

Other than the nutrient under study, all other nutrients were approximately balanced to give a full strength Hoagland solution (APPENDIX A). Micronutrients were added as a full Hoagland solution to provide 0.5 mg ℓ^{-1} B (as H_3BO_3), 0.5 mg ℓ^{-1} Mn (as $MnSO_4.4H_2O$), 0.05 mg ℓ^{-1} Zn (as $ZnSO_4.7H_2O$), 0.02 mg ℓ^{-1} Cu (as $CuSO_4.5H_2O$), 0.01 mg ℓ^{-1} Mo (as $NaMoO_4.2H_2O$) and 1 mg ℓ^{-1} Fe (as ferric sodium EDTA). The nutrient solutions were replaced once a week.

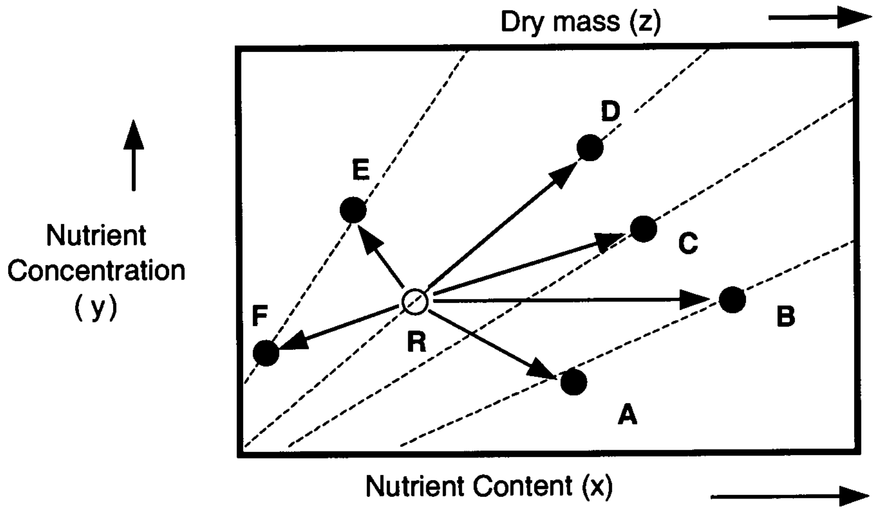
3.2.2 GROWTH AND NUTRIENT CONCENTRATION MEASUREMENTS

Roots and tops were harvested separately, 28 days after transplanting the seedlings. The plant parts were washed with dionized water, dried at 65°C and weighed until constant mass. The top dry matter of the replicates for each treatment was then composited, milled and chemically analysed according to the standard procedures as prescribed by ALASA (1998). Nitrogen and P were determined with an auto-analyser after an H_2SO_4 digestion was performed. For determination of Ca, Mg, K, SO_4, Zn, Cu, Fe and Mn, samples were wet-digested using nitric acid and perchloric acid in a digestion block. These nutrients were analysed by atomic absorption spectroscopy.

3.2.3 STATISTICAL ANALYSIS AND DATA INTERPRETATION

Dry matter production and leaf nutrient composition data were evaluated statistically by analysis of variance (ANOVA) (Genstat 5 Committee of the Statistics Department, 1993). The Bonferroni multiple comparison test was used to compare treatments when the ANOVA showed significant differences among means at the 5% probability level. Data of the top dry matter yield and chemical composition were interpreted using a graphical vector nutrient diagnostic technique (Timmer & Stone, 1978; Teng & Timmer, 1990; Timmer & Teng, 1999). Its application recognizes and applies the biological principle that growth of plants is dependent on nutrient uptake (or content). The nutrient content in the plant is estimated as the product of the plant nutrient concentration and biomass accumulation. A brief discussion of the method follows.

The relationship between nutrient content and biomass accumulation is examined by comparing growth and nutrient status of plants, differing in productivity and/or health with the aid of a nomogram. Biomass (z) is plotted on the upper horizontal axis, plant nutrient content (x) on the lower horizontal axis, and corresponding plant nutrient concentration (y) on the vertical axis (Figure 3.1). The dashed diagonals are isopleths representing change of y on x where z remains unchanged. When normalized to a specified reference sample (R), which is usually the control set to 100%, differences are depicted as vectors because of shifts in both direction and magnitude.



Vector shift	Change in relative			Nutritional effect	Nutrient status	Possible diagnosis
	z	*x*	*y*			
A	+	+	-	Dilution	Non-limiting	Growth dilution
B	+	+	o	Accumulation	Non-limiting	Sufficiency, steady-state
C	+	+	+	Accumulation	Limiting	Deficiency response
D	o	+	+	Accumulation	Non-limiting	Luxury consumption
E	-	-, +	+	Concentration	Excess	Toxic accumulation
F	-	-	-	Antagonism	Limiting	Induced deficiency by E

Figure 3.1 Nutrient vector analysis. Interpretation of directional changes in relative dry mass and nutrients status of plants differing in productivity (modified from Timmer & Teng, 1999).

Analysis of any set of data is based on vector direction of individual nutrients, identifying occurrence of dilution (A), sufficiency (B), deficiency (C), luxury consumption (D), toxicity (E) and antagonism (F) as illustrated in Figure 3.1. Each configuration corresponds to a specific phase in dose response curves relating changes [increasing (+), decreasing (-), or no change (0)] in plant growth, nutrient content and nutrient concentration to increasing nutrient supply in the growth medium. Vector magnitude reflects the extent or severity of specific diagnoses, and facilitates relative ranking and prioritizing.

3.3 RESULTS AND DISCUSSION

3.3.1 PLANT GROWTH AND YIELD

High concentrations of sulphate salts were reported to cause disorder symptoms typical to that of salt affected plants i.e. a reduction in growth rate and a dark green colour of the leaves (Mengel & Kirkby, 1987). The plants of this experiment grown with high concentrations of calcium and magnesium sulphate were, however, chlorotic when compared to the control plants. The mean root and top dry matter yields of the control and sulphate-treated plants with differential levels of K, P, NO_3 and NH_4 are presented in Table 3.2 and illustrated in Figures 3.2 to 3.6. There were no significant differences between treatments at the 5% significance level using the Bonferroni multiple comparison test. This comparison test is, however, very stringent for use in interpreting data from nutrient solution trials. The F-probability value of the analysis of variance indicated that differences between the largest and smallest mean top dry matter yields were significant at the 5% probability level. There were, however, no significant differences between dry matter yields of the roots. The top growth of the SO_4 salinised treatment plants was relatively more depressed than the root growth when compared to the top and root growth of the non-salinised control.

Table 3.2 Mean root and top dry matter yields of wheat plants

Mean dry mass per pot (g)	Treatments (mmol ℓ^{-1})										
	Control	Salinised control	7 NO_3	20 NO_3	7 NH_4	9 NH_4	0.25 P	0.75 P	3 K	8 K	10 K
Roots	1.38	1.23	1.26	1.08	1.46	1.22	1.01	1.04	1.40	1.52	1.30
Tops	6.12	3.85	4.86	4.09	6.01	4.19	3.79	3.86	4.28	5.69	4.29

Root growth p = 0.167, c.v. 21.7%; Top growth p = 0.029, c.v. 24.8%

The root and top dry matter yields of the NO_3 and NH_4 treatments are presented in Figures 3.2 and 3.3.

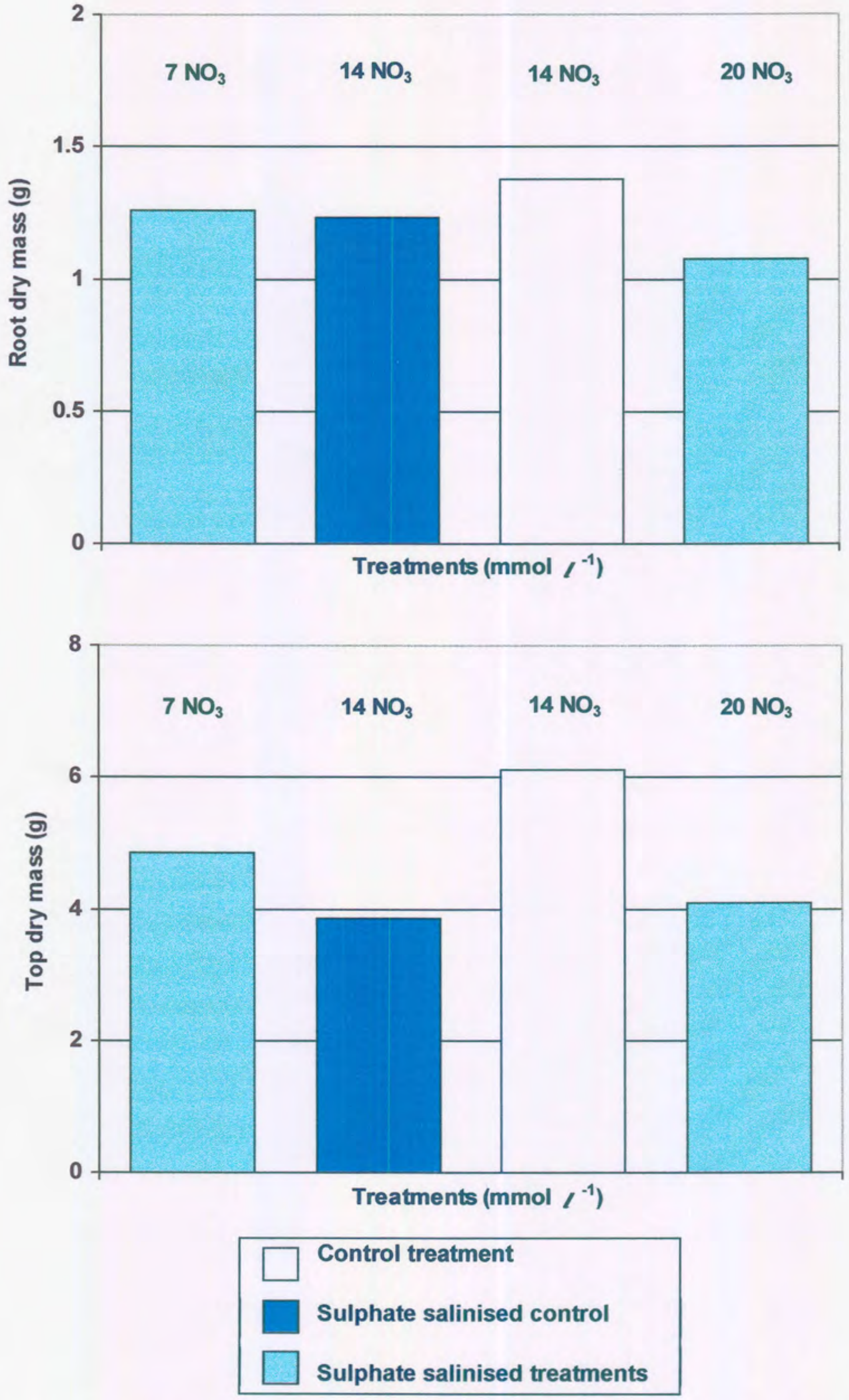


Figure 3.2 Mean root and top dry matter yield of wheat grown under different control and sulphate salinised treatments with differential levels of NO_3.

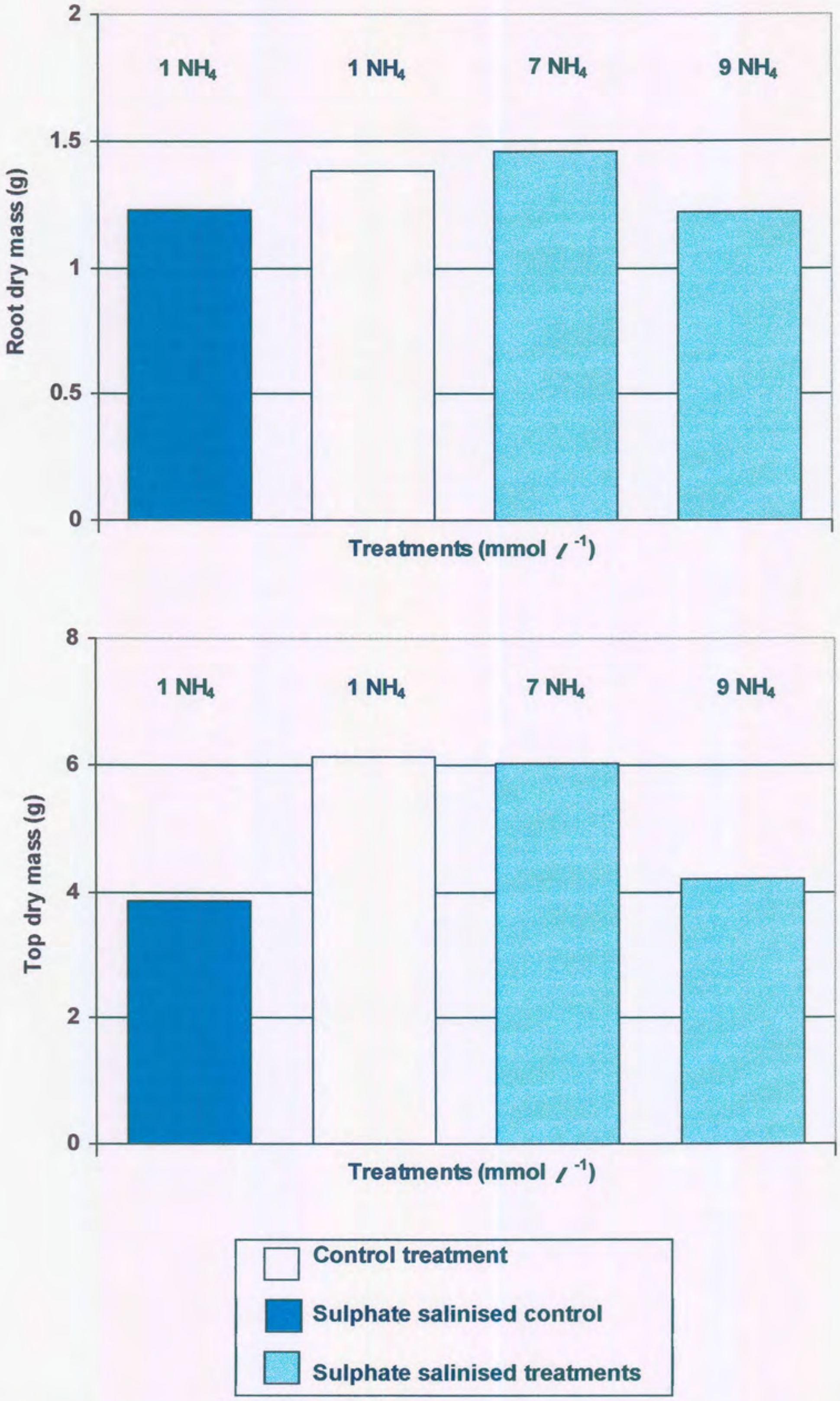


Figure 3.3 Mean root and top dry matter yield of wheat grown under different control and sulphate salinised treatments with differential levels of NH_4.

Root growth of the SO_4 salinised treatments was reduced with increasing NO_3 concentrations in the medium. Top dry matter production of the SO_4 salinised treatments that received 7, 14 and 20 mmol ℓ^{-1} NO_3 was reduced by 21, 37 and 33% respectively, relative to the non-salinised control.

Root and top dry matter production of the 7 mmol ℓ^{-1} NH_4 treatment was the highest of the SO_4 salinised treatments that received different levels of NH_4. Root growth of the 7 mmol ℓ^{-1} NH_4 treatment was increased by 6% relative to the non-salinised control, while the top dry matter production was only slightly (1.8%) lower than the control. This is of great significance, since NH_4 concentrations greater than 5 mmol ℓ^{-1} in the growth medium are generally reported to be toxic to crops (Magalhães & Wilcox, 1984; Magalhães *et al.*, 1995). No symptoms of NH_4 toxicity were observed in this experiment. In addition to this, results obtained by Barnard *et al.* (1998) and from a pilot test study conducted prior to this experiment explicitly indicated that a NO_3:NH_4 of 2:1, even at low NH_4 concentrations in the growth medium, suppressed the growth of wheat under non-saline conditions while the growth of SO_4 salinised plants was normal. A plot of the dry matter yield on a linear scale against the NH_4 concentration in the growth medium is given in Figure 3.4. The fitted regression line indicates that the highest root and top dry matter yields would probably be attained at a NH_4 concentration of 5 mmol ℓ^{-1} in the growth medium.

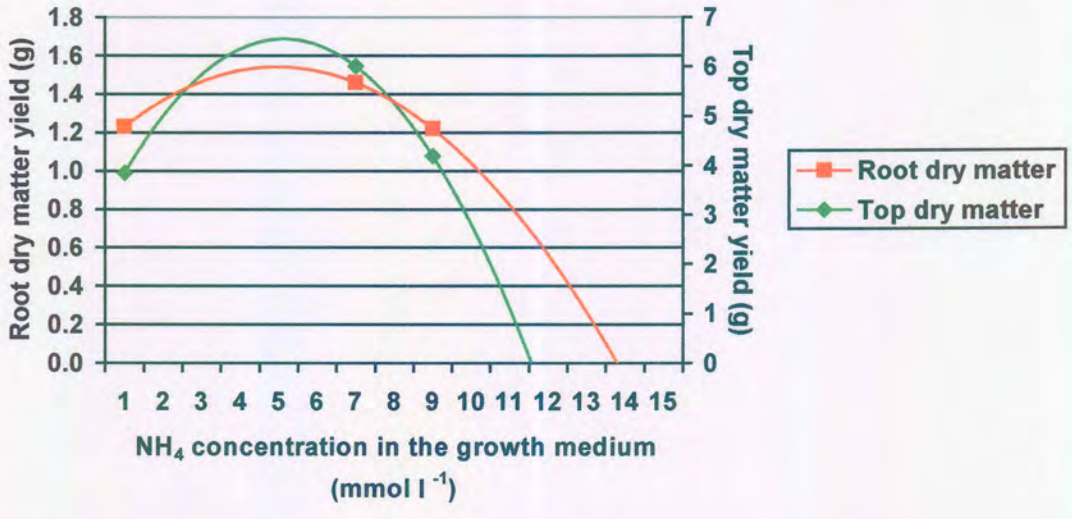


Figure 3.4 Root and top growth dry matter yield as a function of the NH_4 concentration in the medium.

The 0.5 mmol ℓ^{-1} P treatment produced the highest root dry matter yield of the SO_4 salinised treatments that received different levels of P (Figure 3.5). Increasing levels of P in the growth medium had no effect on top dry matter production under sulphate salinity.

Root and top dry matter production of the 8 mmol ℓ^{-1} K treatment was the highest of the SO_4 salinised treatments that received different levels of K, while that of the SO_4 salinised control was the lowest (Figure 3.6). Root dry matter production of the 3 and 8 mmol ℓ^{-1} K salinised treatments was increased by 1.5% and 10% respectively, relative to the non-salinised control, while it was reduced by 11% and 6% by the 6 and 10 mmol ℓ^{-1} K treatments respectively. Top dry matter production was reduced by 30, 37, 7 and 30% respectively by the 3, 6, 8 and 10 mmol ℓ^{-1} K salinised treatments relative to the control.

3.3.2 PLANT NUTRIENT STATUS

The nutrient concentrations in the top growth are given in Table 3.3. Pre-established "critical" concentration ranges of nutrients obtained from Reuter (1986) were used as indicators of nutrient sufficiency or toxicity in plants. The nutrient levels in plants of all treatments were greater than the lower critical literature concentration except for the N concentration of the 10 mmol ℓ^{-1} K treatment and the Fe concentration of the 0.75 mmol ℓ^{-1} P treatment. All nutrient concentrations in plants of the salinised control were higher than the non-salinised control, except for K and Fe.

The plants of the SO_4 salinised treatments accumulated large concentrations of SO_4 relative to the control plants. Root and top dry matter yields decreased with increasing concentrations of SO_4 in plants ($r = -0.563$ and -0.746).

The N concentration in plants decreased with increasing K supply, while it tended to increase with an increased NH_4 concentration in the medium but not with NO_3. Also, at comparable solution N concentrations of 7 mmol ℓ^{-1} (as NH_4-N) and 7 mmol ℓ^{-1} (as NO_3-N), tissue N concentrations were higher with NH_4 than with NO_3, suggesting that N utilization efficiency was higher with NH_4 than with NO_3. Although the N concentration of the plants was adequate to high, the N:S ratio in plants of all treatments was below the optimal ratio of 15:1.

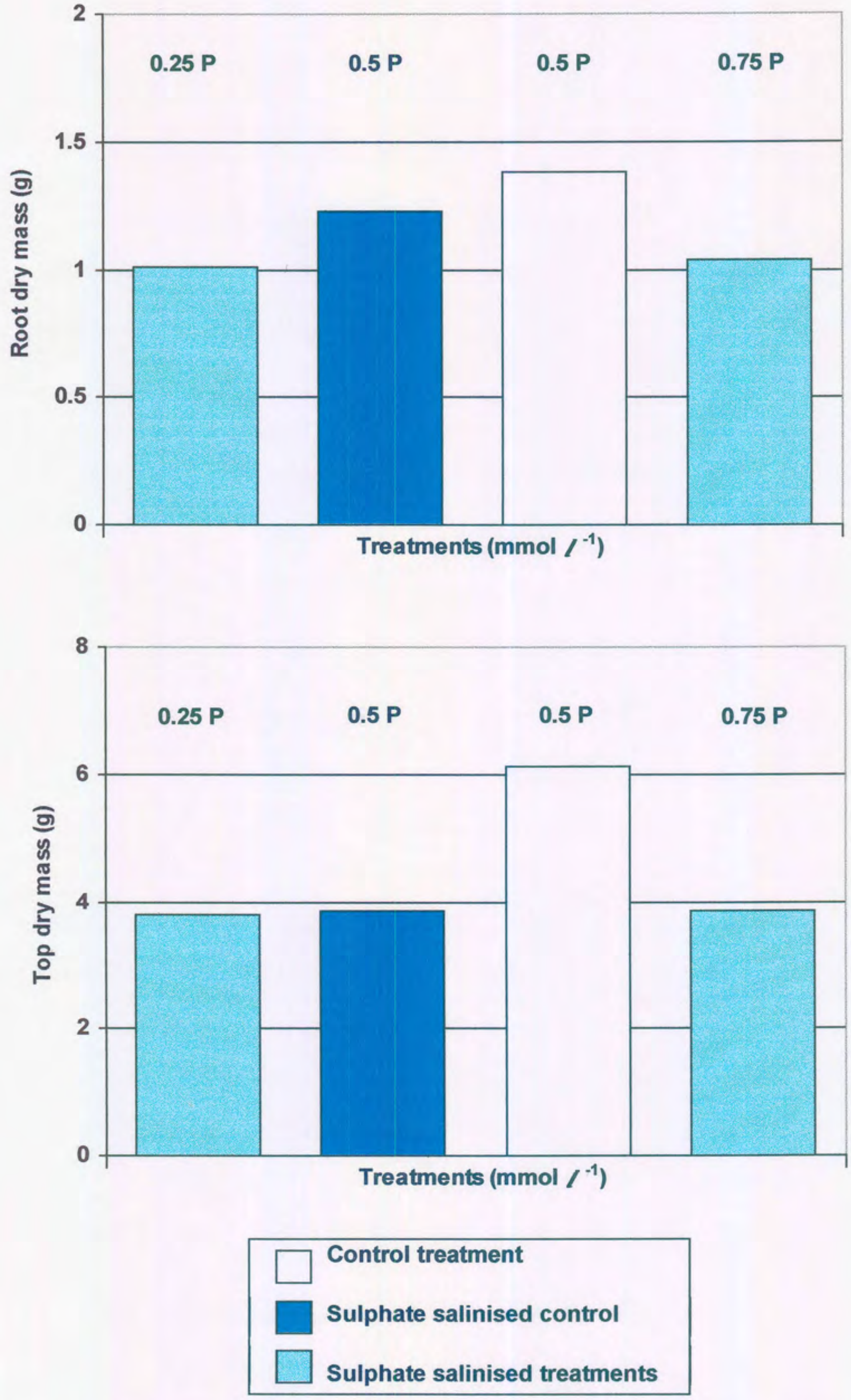


Figure 3.5 Mean root and top dry matter yield of wheat grown under different control and sulphate salinised treatments with differential levels of P.

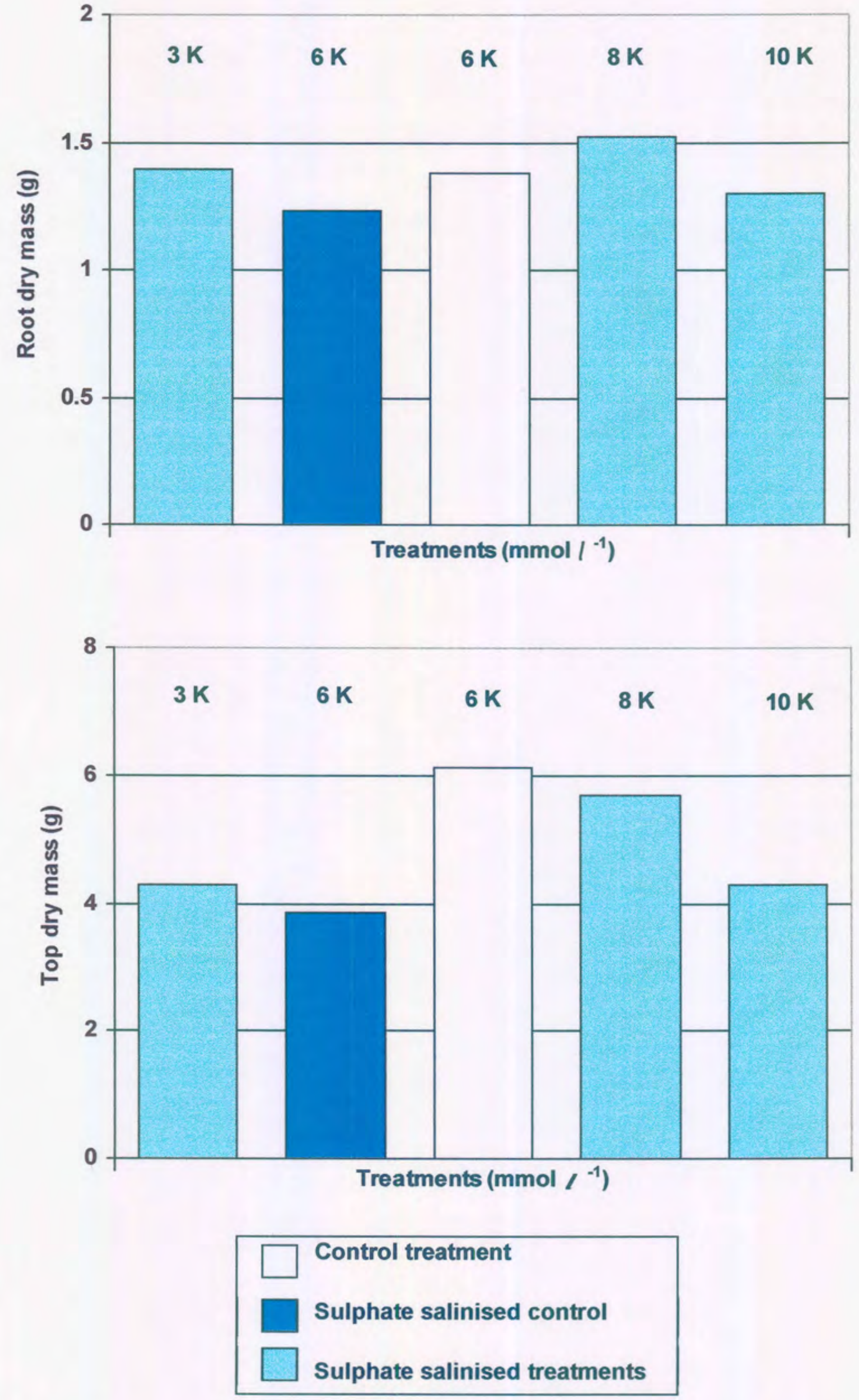


Figure 3.6 Mean root and top dry matter yield of wheat grown under different control and sulphate salinised treatments with differential levels of K.

This ratio is given for attaining maximum dry matter production of wheat (Zhao *et al.*, 1997). The N:S ratio decreased with increasing K supply and increased with an increasing NH_4 concentration in the nutrient medium.

One of the effects of SO_4 salinity is the reduction of plant-available Ca (Manchanda & Sharma, 1989; Manchanda *et al.*, 1991; Terabayashi *et al.*, 1995; Soltanpour *et al.*, 1999). Huang and Redmann (1995) reported that Ca was reduced in plants by high concentrations of SO_4 even under high Ca salt treatment when turgor was well maintained. The concentration of Ca in plants of this experiment was, however, within the reported sufficiency range for wheat. Calcium and Mg concentrations decreased with increasing NH_4 supply, while an opposite trend was observed with increasing NO_3 supply. These effects of N forms on Ca and Mg concentrations were consistent with that of Cao and Tibbits (1998). Top dry matter yield decreased with an increasing Mg concentration in plants (r = -0.719). The Mg concentration in plants of all the salinised treatments was lower than 0.5%, which is the concentration above which Mg is reported to be high in wheat (Reuter, 1986).

The K concentration in plants increased with an increasing NH_4 concentration in the nutrient medium. Although a strong positive interaction was reported to exist between N and K uptake (Singh, 1992) and Mengel (1976) stated that it was unlikely that NH_4^+ and K^+ compete for selective binding sites in the absorption process, the K concentration in the plants of the NH_4 treatments was still low in comparison to the control and most of the other salinised treatments. The K concentration in plants was poorly related with dry matter yield, but the K content increased with increasing top dry matter yield (Figure 3.7).

Further analysis of nutrient concentrations in plants of the salinised treatments relative to nutrient supply revealed that the Cu and Zn concentrations increased while the Mn concentration decreased in plants with increasing NH_4 supply. With the exception of the Mn concentration in plants of the control treatment, the plants of the 7 and 9 mmol ℓ^{-1} NH_4 treatments had the lowest Mn status. The Mn concentration in plants further increased with increasing plant Mg concentration (r = 0.971). In contradiction to this, several reports have shown that the Mn concentration in plants was decreased with an increasing Mg supply and concentration in plants (Mengel & Kirkby, 1987; Huang & Redmann, 1995).

The P concentration in plants decreased with an increasing K supply and was the lowest for the 10 mmol ℓ^{-1} K treatment. This value was, however, still higher than the upper critical literature norm.

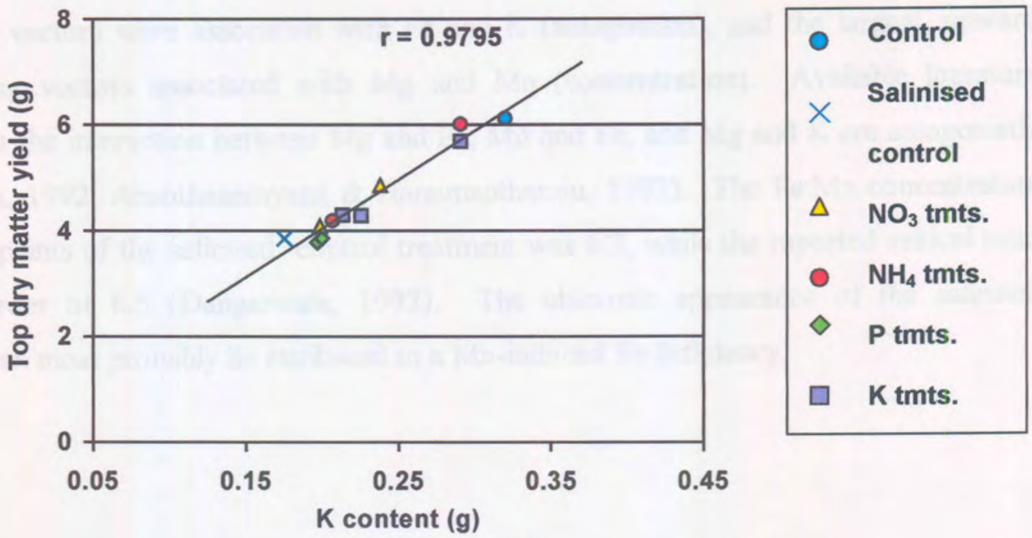


Figure 3.7 Correlation between dry matter yield and K content in top growth.

3.3.3 NUTRIENT VECTOR ANALYSIS

Representation of changes in plant nutrient concentration, content and dry mass in a single graph simplifies interpretation and reduces subjective judgement. Vector nutrient diagnosis is independent on pre-established critical levels and nutrient ratios and proved to be particularly useful where plant concentration and content are poorly correlated (Timmer & Stone, 1978).

The approach is demonstrated in Figures 3.8 to 3.12 for the different treatments. The nomograms indicate the vector analysis for the specific treatment relative to the non-salinised control treatment, which status was normalized to 100% to allow comparison on a common base.

Since the nomograms tend to become cluttered and difficult to interpret when too many treatments are plotted on the same graph, the vector analysis for only the salinised control treatment relative to the non-salinised control is given in Figure 3.8. The largest downward, left-pointing vectors were associated with Fe and K (antagonism), and the largest, upward right pointing vectors associated with Mg and Mn (concentration). Available literature suggests that the interaction between Mg and Fe, Mn and Fe, and Mg and K are antagonistic (Dangarwala, 1992; Ananthanarayana & Hanumantharaju, 1992). The Fe:Mn concentration ratio of the plants of the salinised control treatment was 0.2, while the reported critical ratio is in the order of 6.5 (Dangarwala, 1992). The chlorotic appearance of the salinised treatments can most probably be attributed to a Mn-induced Fe deficiency.

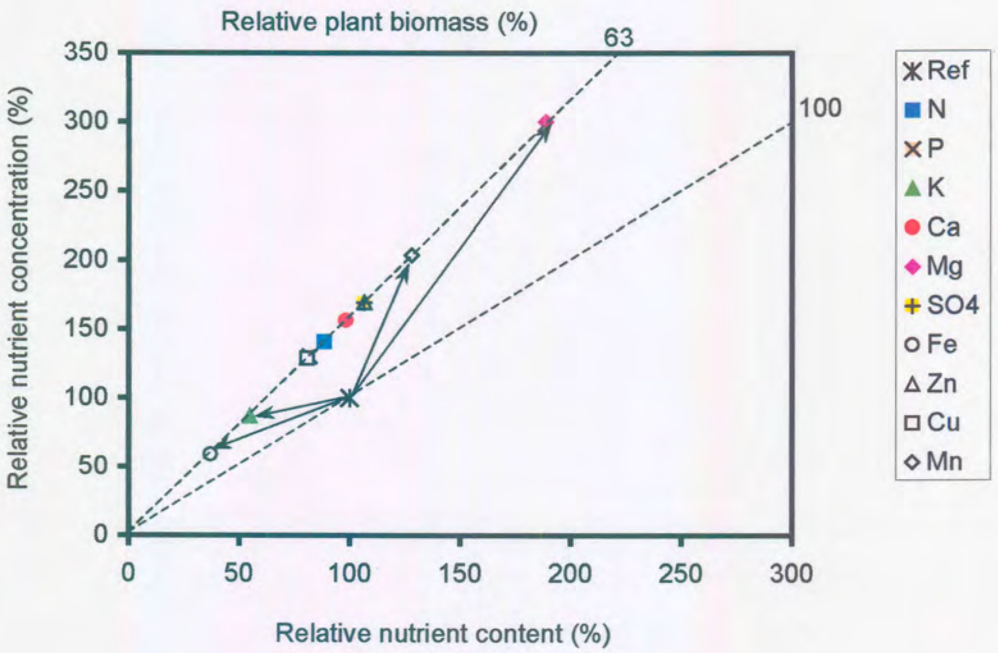
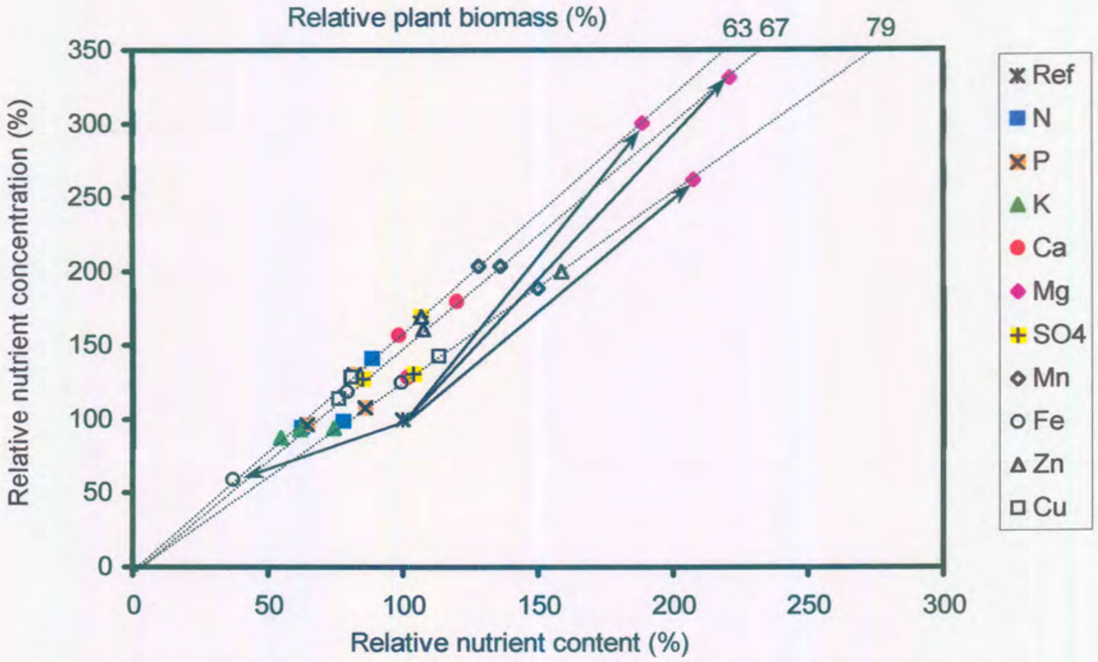


Figure 3.8 Relative response in nutrient concentration, content and dry mass of the sulphate salinised control treatment

Figure 3.9 illustrates the vector analysis for the NO_3 treatments. Only the N concentration of the 14 mmol ℓ^{-1} NO_3 treatment was higher than that of the control. Nitrogen uptake was 22, 11 and 37% lower than the control for the 7, 14 and 20 mmol ℓ^{-1} NO_3 treatments respectively.

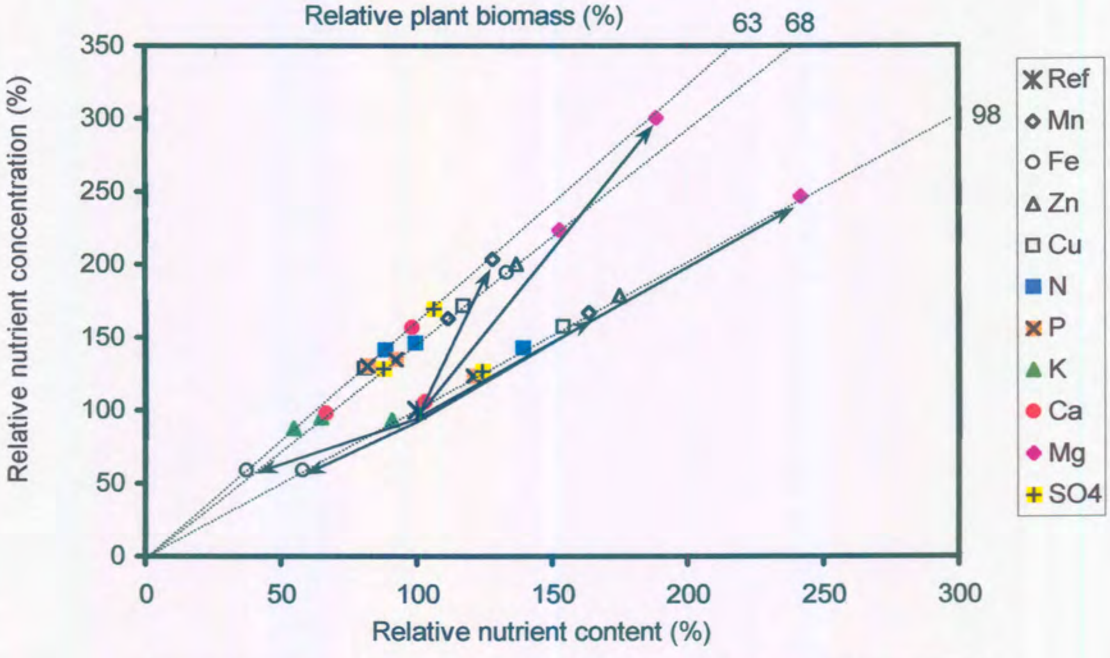
Interpretations based on matching vector direction with those in Figure 3.1 suggest that Mg uptake in excess of 100% relative to the control antagonistically decreased Fe uptake of only the 14 mmol ℓ^{-1} NO_3 treatment and K uptake of all treatments. Interpretation of the vector nomogram suggests that increased growth of the SO_4 salinised treatments occurred with increased uptake of K, Fe and Mn. Poorer growth of the salinised treatments was accompanied by relatively higher concentrations of SO_4 and N and the nutrient concentration and uptake patterns with biomass accumulation of these nutrients were the same.

The vector analysis for the NH_4 treatments is illustrated in Figure 3.10. The N concentration in plants of the 1, 7 and 9 mmol ℓ^{-1} NH_4 treatments was 41, 42 and 46% higher than the control, respectively. Nitrogen uptake was 11% lower for the 1 mmol ℓ^{-1} NH_4 treatment, 40% higher for the 7 mmol ℓ^{-1} NH_4 treatment and the same for the 9 mmol ℓ^{-1} NH_4 treatment. Interpretations based on matching vector direction with those in Figure 3.1 suggest that Mg uptake in excess of 100% relative to the control antagonistically decreased uptake of Fe (1 and 7 mmol ℓ^{-1} NH_4 treatment) and K (1 and 9 mmol ℓ^{-1} NH_4 treatment). Although the vector magnitude indicated that the highest level of NH_4 application (9 mmol ℓ^{-1} NH_4) caused less Mg to be taken up and that no Mg-induced Fe deficiency occurred, yield of this treament was still lower than that of the 7 mmol ℓ^{-1} NH_4 treatment. Calcium uptake of this treatment was 33% lower than that of the other treatments and the control and this could probably have caused comparatively poorer growth. Increasing additions of NH_4 did not enhance the uptake of sulphate by plants, contradictory to what was stated by other investigators (Cox & Reisenauer, 1973; Kirkby, 1968; Haynes & Goh, 1978). Interpretation of the vector nomogram suggests that increased growth of the SO_4 salinised treatments occurred with increased uptake of N, P, K, Cu and Zn. Poorer growth of the salinised treatments was accompanied by relatively higher concentrations of Mg, Mn, SO_4 and Ca in the top growth.



Treatment (mmol ℓ^{-1})	Control	7 NO_3	14 NO_3	20 NO_3
Normalized biomass (%)	100	79	63	67

Figure 3.9 Relative response in nutrient concentration, content and dry mass of wheat plants grown at differential NO_3 levels in the sulphate saline medium.



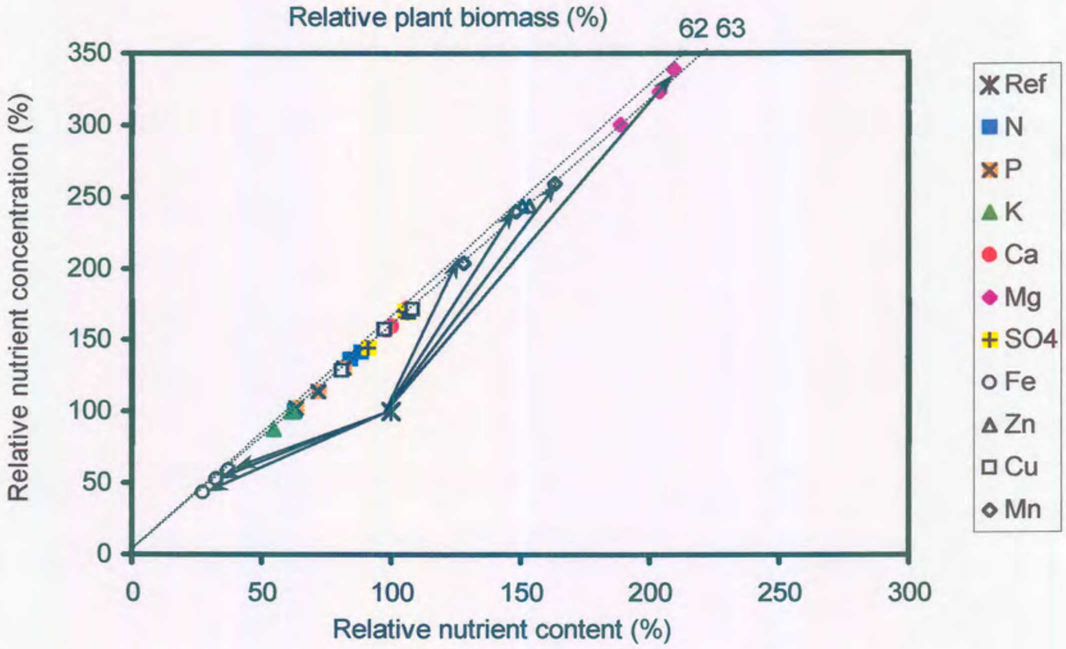
Treatment (mmol ℓ^{-1})	Control	1 NH_4	7 NH_4	9 NH_4
Normalized biomass (%)	100	63	98	68

Figure 3.10 Relative response in nutrient concentration, content and dry mass of wheat plants grown at differential NH_4 levels in the sulphate saline medium.

The vector analysis for the P treatments is illustrated in Figure 3.11. Although the P concentration in plants of the 0.25, 0.5 and 0.75 mmol ℓ^{-1} P treatments was respectively 2, 30 and 14% higher than the control, P uptake was 37, 18 and 28% lower than the control for these treatments respectively. Interpretations based on matching vector direction with those in Figure 3.1 suggest that Mg or Mn uptake in excess of 100% relative to the control antagonistically decreased uptake of Fe of all treatments. Iron deficiency was likely induced by Mn accumulation, as can be seen by comparing relative vector length for Mn and Fe of the same P treatments in the nomogram.

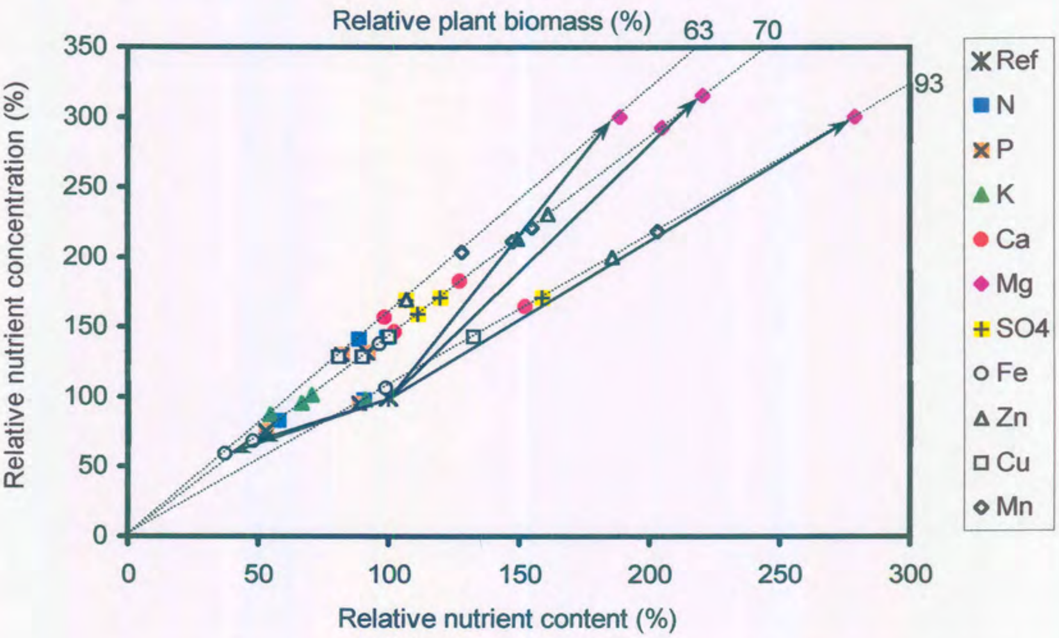
The vector analysis for the K treatments is illustrated in Figure 3.12. Potassium uptake was not proportional to the amount of K supplied in the external medium. The potassium content in plants was the lowest for the 6 mmol ℓ^{-1} K treatment and the highest for the 8 mmol ℓ^{-1} K treatment, besides the control. Although the K concentration of all salinised treatments was comparable to that of the control, a definitive pattern with regards to K uptake and biomass production could be seen. Biomass production increased as the K uptake increased. This trend was also observed when all treatments were considered (Figure 3.7).

The nomogram shows that the largest upward, right-pointing vectors were associated with Mg. This vector shift indicates concentration and a possible diagnosis of Mg toxicity. Vector length associated with Mg increased, however, with improved biomass production. The largest downward, left-pointing vectors were associated with Fe of the 6 and 10 mmol ℓ^{-1} K treatments. This shift indicates antagonism and a possible Fe-induced deficiency by Mg. Further interpretation of the vector nomogram suggests that increased growth of the salinised treatments occurred with increased uptake of Ca, SO_4, Mn, Zn and Cu.



Treatment (mmol ℓ^{-1})	Control	0.25 P	0.5 P	0.75 P
Normalized biomass (%)	100	62	63	63

Figure 3.11 Relative response in nutrient concentration, content and dry mass of wheat plants grown at differential P levels in the sulphate saline medium.



Treatment (mmol ℓ^{-1})	Control	3 K	6 K	8 K	10 K
Normalized biomass (%)	100	70	63	93	70

Figure 3.12 Relative response in nutrient concentration, content and dry mass of wheat plants grown at differential K levels in the sulphate saline medium.

3.4 SUMMARY AND CONCLUSIONS

High concentrations of calcium and magnesium sulphate in the nutrient solution suppressed the top dry matter yield of wheat plants. The plants did not exhibit signs of salinity stress, but appeared chlorotic in comparison to the control plants. High concentrations and contents of Mg and Mn in plants and low Fe and K concentrations and contents caused the comparative lower top dry matter yield of the salinised treatment plants. Dry matter yield was also decreased by increasing SO_4 concentrations in plants.

Root growth of the 3 and 8 mmol ℓ^{-1} K and 7 mmol ℓ^{-1} NH_4 salinised treatments was better than that of the non-salinised control. Although the top growth yield of the salinised treatment plants supplied with differential levels of NO_3, NH_4, P and K was lower than that of the control plants, top dry matter yield of the NO_3, NH_4 and K salinised treatments was improved relative to the salinised control treatment. The application of NO_3 at a level 7 mmol ℓ^{-1} lower, and NH_4 and K at respective levels of 6 mmol ℓ^{-1} and 2 mmol ℓ^{-1} higher than the level considered beneficial for non-saline conditions, improved top growth of wheat under sulphate saline conditions. The highest dry matter yield was obtained when N was supplied in a NO_3:NH_4 ratio of 2:1. Differential levels of P under calcium and magnesium sulphate saline conditions had no effect on top dry matter production.

The results of this experiment further suggest that the beneficial effects of an enhanced NH_4 nutrition under SO_4 salinity can be ascribed to the antagonistic effect of NH_4 on the plant Mg concentration and/or to NH_4 being a supplementary N source when large SO_4 concentrations suppressed NO_3 uptake. Nitrogen utilization efficiency was higher with NH_4 than with NO_3 at similar solution concentrations of N. This is presumably due to the lower energy cost of NH_4 uptake, which is a result of active and passive uptake of this cation, and that NH_4 as a cation can follow its electrochemical gradient in wheat seedlings (Botella *et al.*, 1994). Ammonium, with respect to NO_3, Cl and SO_4, was further reported to restore the electrical equilibrium that is disturbed by high anion levels (Víllora *et al.*, 1998). Although an increasing NH_4 supply had a synergistic effect on the K concentration in plants, the NH_4 treatment plants still had a lower K concentration than that of the other salinised treatments. The results obtained may possibly be strictly valid for wheat only and the beneficial effect of an enhanced NH_4 nutrition under high SO_4 concentrations in the growth medium on the growth response of other species need to be tested.

The highest NH_4 and K treatment levels (9 mmol ℓ^{-1} NH_4 and 10 mmol ℓ^{-1} K) produced comparatively lower yields than the 7 mmol ℓ^{-1} NH_4 and 8 mmol ℓ^{-1} K treatments, probably because of inhibited Ca uptake. The poorer Ca status of these treatments can possibly be ascribed to decreasing root-medium pH due to H^+ excretion by roots in exchange for K^+ and NH_4^+ absorption, which in return decreased the availability of Ca.

Although the growth of plants in nutrient solutions is an invaluable tool for plant nutritional studies because the growth medium can be carefully defined and controlled, a major disadvantage of this technique is that the system is artificial compared to field conditions. The results obtained from the solution culture trial must therefore be interpreted with caution, since the effect of sulphate salinity on nutrient availability and uptake may differ in the field, particularly for P and K, since their concentrations are controlled by the solid phase and are difficult to measure or predict. Confirmation of the results obtained should thus be sought in field trials.

CHAPTER 4

EFFECT OF CALCIUM AND MAGNESIUM SULPHATE SALINITY ON GROWTH AND NUTRITION OF *Zea mays* L.: SOIL POT EXPERIMENT

4.1 INTRODUCTION

Although gypsiferous water is generally considered beneficial for irrigation of crops (Doneen & Henderson, 1960), several studies have indicated that continuous irrigation with water containing high concentrations of sulphate, may lead to a build-up of salts in the root zone (Suarez & van Genuchten, 1981; Russo, 1983; Papadopoulos, 1985a and b). Excess salts reduce plant growth, primarily because a low soil water potential results in equilibration of the water potential inside the plant by cell water loss and an accompanying decrease in the cell osmotic turgor and potential. The osmotic effects are associated with lack of cell wall extension and cellular expansion leading to cessation of growth (Greenway & Munns, 1980). Excess salts may also reduce plant growth because of specific ion toxicities, which may not always be clearly distinguishable from deficiencies. Besides osmotic reduction of water availability and specific ion toxicities, salinity *per* se may also induce nutritional imbalances (Bernstein *et al.*, 1974).

The simultaneous presence of excessive amounts of Ca, Mg and SO_4 and other nutrient elements in the root zone can influence nutrient uptake by plants and affect their chemical composition. Synergistic and antagonistic effects can increase or decrease the intensity of this uptake process. Excessive concentrations of sulphate in the growth medium are known to reduce *inter alia* the uptake of P (Datta *et al.*, 1995; Terabayashi *et al.*, 1995; Soltanpour *et al.*, 1999) and K (Manchanda *et al.*, 1991; Curtin *et al.*, 1993) by crops, while excessive addition of Ca and Mg to soil also decreases the absorption of K by plants (Ananthanarayana & Hanumantharaju, 1992). An antagonistic relationship is further known to exist between calcium and magnesium. Marschner (1986) stated that the binding sites on the root plasma membrane appear to have less affinity for the highly hydrated Mg^{2+} than for Ca^{2+}, while Ananthanarayana and Hanumantharaju (1992) reported that Mg exerts a more depressing effect on Ca uptake than Ca levels did on the uptake of Mg. There also seems to be little general agreement on the effect of sulphate salinity on calcium and magnesium uptake (Manchanda & Sharma, 1989, Curtin *et al.*, 1993; MacAdam *et al.*, 1997)

Besides high root zone concentrations of Ca, Mg and SO_4, gypsum will precipitate in the soil as water is removed by transpiration or by evaporation from the soil surface. Gypsum may cause loss of nutrients through cation and anion interaction effects (Mashali, 1996; Fey *et al.*, 1997). Gypsum is likely to replace other cations on the soil exchange complex and render them prone to leaching (Shainberg *et al.*, 1989). Szabolcs (1989) stated that the ion exchange equilibrium shifts in favour of cations with two valences during leaching. It can thus be expected that K^+ will be displaced from the ion exchange complex and lost from the soil profile during leaching. Excessive amounts of gypsum in the active root zone may also affect nutrient availability and uptake by plants (Mashali, 1996). The precipitation of phosphate ions and fixation of micronutrients in an unavailable form seems to be the most important problems associated with excess gypsum in soil (Panahi & Rowell, 1996; Mashali, 1996; Oyonarte *et al.*, 1996).

The utilization of soils that contain excessive amounts of salts raises the problem of providing growing conditions, which will support reasonable plant productivity. One aspect that requires clarification is the effect of specific fertiliser application under SO_4 saline conditions on crop growth and quality. The present study was undertaken to determine the effect of calcium and magnesium sulphate salinity on maize growth and yield and compare crop response to SO_4 salinity at different levels of NO_3, NH_4, P and K.

4.2 MATERIALS AND METHODS

4.2.1 EXPERIMENTAL PROCEDURE

A glasshouse trial was conducted with maize (*Zea mays* L., cv. PAN 6256) as test crop. Use was made of a sandy clay loam top-soil which had been collected from a maize-growing area at the University of Pretoria's experimental farm in Hatfield, Pretoria. The principal soil properties are presented in Tables 4.1 and 4.2.

Table 4.1 Physical and chemical properties of the Hatfield experimental farm soil

Particle size distribution %			pH (H_2O)	Resistance (ohm)	EC_e mS m^{-1}	Organic C %
Clay 1	Silt 1	Sand 2				3
25.0	26.2	48.8	6.6	700	63	1.9

1) Hydrometer 2) Sieve 3) Walkley Black

Table 4.2 Nutrient status of the Hatfield experimental farm soil

P 1	Ammonium acetate extractable cations				Fe 2	Mn 2	Zn 2	Cu 2	Mo 2	B 3
	Ca	Mg	K	Na						
mg kg^{-1}										
15.5	1118	411	226	6	132.78	570.00	5.83	7.76	0.06	1.32

1) Bray 1 2) Amm. EDTA 3) Warm water extraction

The experiment consisted of three salinity treatments namely the control (S0), 80 Mg ha^{-1} gypsum ($CaSO_4.2H_2O$) and magnesium sulphate ($MgSO_4.7H_2O$) (S1) and 160 Mg ha^{-1} gypsum and magnesium sulphate (S2). The gypsum and magnesium sulphate were applied in a Ca:Mg ratio of 60:40 on a mass basis resulting in 48 Mg ha^{-1} gypsum and 32 Mg ha^{-1} magnesium sulphate (S1) and 96 Mg ha^{-1} gypsum and 64 Mg ha^{-1} magnesium sulphate (S2).

A 6 x 2 x 3 factorial combination of the following were imposed on the three salinity treatments:

(a) Nitrogen: NO_3:NH_4 4:1 ⇒ 80 kg ha^{-1} (N1) and 160 kg ha^{-1} (N2);
NO_3:NH_4 2:1 ⇒ 80 kg ha^{-1} (N3) and 160 kg ha^{-1} (N4);
NO_3:NH_4 1:1 ⇒ 80 kg ha^{-1} (N5) and 160 kg ha^{-1} (N6)

(b) Phosphorus: 40 kg ha^{-1} (P1) and 60 kg ha^{-1} (P2)

(c) Potassium: 30 kg ha^{-1} (K1); 60 kg ha^{-1} (K2) and 120 kg ha^{-1} (K3)

These treatments were replicated four times, resulting in a total of 432 pots. The gypsum and magnesium sulphate were applied to 3 kg air-dried, sieved soil as a powder and thoroughly mixed in the dry soil. The chemical analysis of the gypsum is given in Table 4.3.

Table 4.3 Chemical composition of the gypsum saturation extract

EC_e	pH	Ca	P	Al	Mg	K	Na	Fe	Mn	Zn	Cu	B
mS m^{-1}		%										
424	4.3	27	0.48	0.53	<0.10	<0.05	<0.02	<0.05	<0.02	<0.02	<0.01	<0.01

The nutrients were applied as solutions to each replicate. The nutrient solutions were separately mixed with the soil and placed in 185 mm diameter x 220 mm tall pots. The calculation of the respective amounts of salts and nutrients added to the soil were made using the assumption that 1 ha soil to a depth of 150 mm has a mass of 2 x 10^6 kg at a bulk density of 1333 kg m^{-3} (Soil Classification Working Group, 1991). Seed of the maize cultivar Pan 6256 were sown in the treated soil and placed on rotating tables in the glasshouse. Plants were thinned to three per pot after seedling emergence. Water was added frequently, but did not exceed container capacity. Container capacity was approximated by determining the amount of water held by the 3 kg of soil against gravity, without leaching. The experiment was conducted from January to March 1999 at mean day/night temperatures of 30.5 °C and 13.8 °C in the glasshouse.

4.2.2 PLANT AND SOIL ANALYSIS

After seven weeks plant tops were cut at the soil surface, washed with deionized water and dried to constant mass at 65°C. Thereafter, representative soil samples were taken from all pots to determine electrical conductivity (EC_e), pH and chemical composition of the saturation extracts. Dry matter yield of plants was determined. The dry matter of the replicates for each treatment was then composited, milled and chemically analysed according to the standard procedures employed by the Analytical Division of the Soil Science Department of the University of Pretoria (ALASA, 1998). In short these procedures were as follows: Nitrogen and P were determined with an auto-analyser after an H_2SO_4 digestion was performed. For determination of Ca, Mg, K, SO_4, Zn, Cu, Fe and Mn, samples were wet-digested using nitric acid and perchloric acid in a digestion block. These nutrients were analysed by atomic absorption spectroscopy.

The soil samples were air dried and passed through a 2-mm screen. They were then analysed for electrical conductivity of the saturation extract, pH(H_2O), Bray-I extractable P, ammonium acetate extractable Ca, Mg, K and Na, soluble Ca, Mg, K and Na, exchangeable Ca, Mg, K and Na and soluble SO_4 according to standard methods (Non-Affiliated Soil Analysis Work Committee, 1990).

4.2.3 STATISTICAL ANALYSIS AND DATA INTERPRETATION

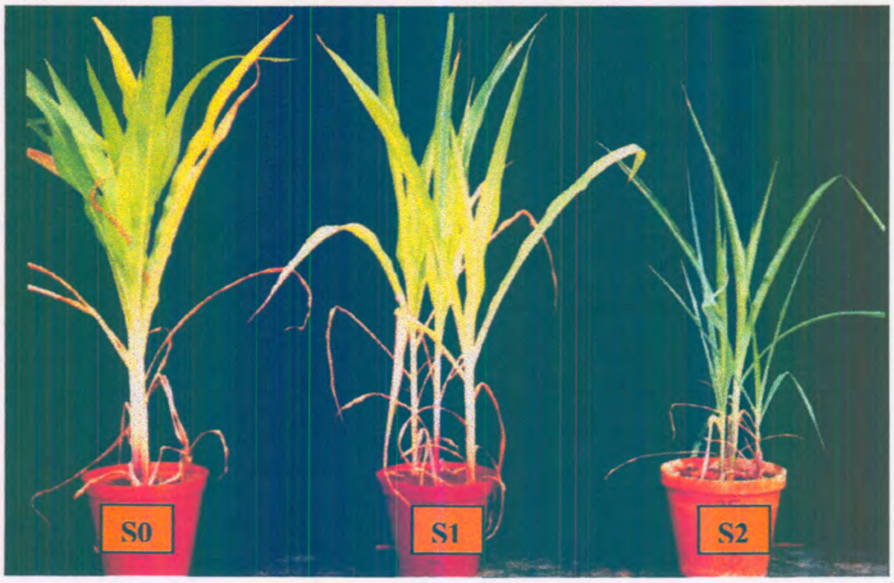
Dry matter production data of the salinity treatments was evaluated statistically by analysis of variance (ANOVA) (Genstat 5 Committee of the Statistics Department, 1993). Selection of the fertiliser treatments within a salinity treatment group that yielded significantly higher dry matter than the rest was done according to the Multiple t-distribution test procedure of Gupta and Panchapakesan (1979) and with the Additive Main effects and Multiplicative Interaction, or AMMI model (Gauch, 1992). Data of the top dry matter yield and chemical composition were interpreted using a graphical vector nutrient diagnostic technique (Timmer & Stone, 1978; Teng & Timmer, 1990; Timmer & Teng, 1999). A discussion of the nutrient vector analysis method was given in section 3.2.3.

4.3 RESULTS AND DISCUSSION

4.3.1 VISUAL SYMPTOMS

The initial growth response of the maize to the salinity treatments was that the leaves were generally smaller, narrower and a darker green than that of the control plants (Plate 4.1a). Growth of the S2 treatment plants was stunted but considerable variation in growth was present (Table 4.4). The maize foliage of the S2 treatment plants exhibited a high incidence of both necrophily (wilting and dying-back of tips) and malformation (Plate 4.1b). These symptoms are similar to those described by Mengel and Kirkby (1987) for a Ca deficiency.

a)



b)

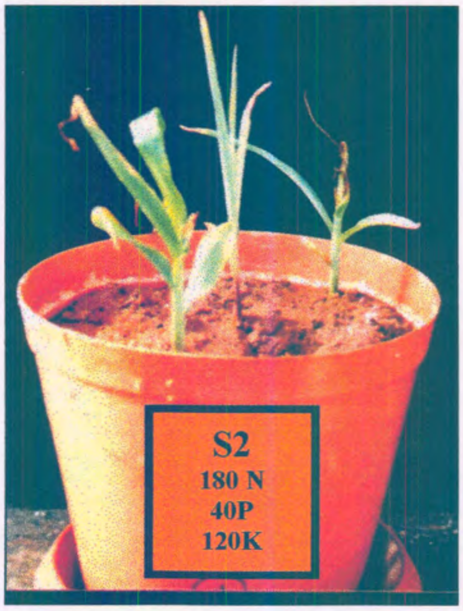


Plate 4.1 a) Comparative growth of the S0, S1 and S2 salinity treatments. These treatments received 80 kg N ha^{-1} in a NO_3:NH_4 ratio of 1:1, 60 kg P ha^{-1} and 120 kg K ha^{-1}.

b) Stunted growth of the S2 treatment that received 180 kg N ha^{-1} in a NO_3:NH_4 ratio of 2:1, 40 kg P ha^{-1} and 120 kg K ha^{-1}.

4.3.2 DRY MATTER YIELD IN RELATION TO TREATMENTS

4.3.2.1 Salinity treatments

The mean dry matter yields of the three salinity treatments are presented in Table 4.4 and Figure 4.1. There were significant differences between the salinity treatments at the 1% probability level.

Table 4.4 Results of the analysis of variance performed on yield data of the salinity treatments

Salinity Treatments	Mean dry matter yield per pot (g)	Standard error of the mean (e.s.e.)	Coefficient of variation (%)
S0	26.45	1.06	8.00
S1	19.85	1.15	11.60
S2	4.85	0.95	39.00

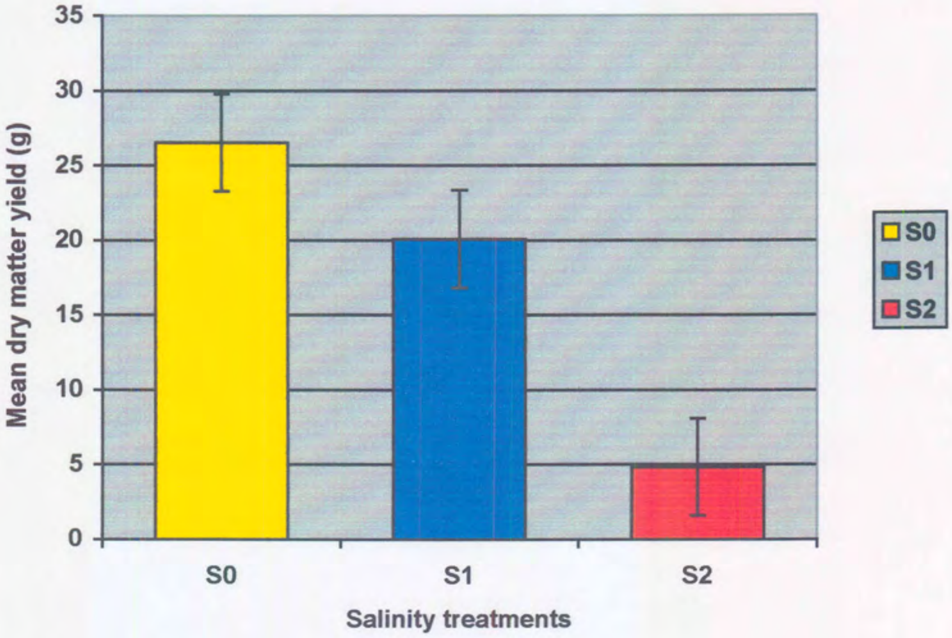


Figure 4.1 Mean dry matter yield per pot of the three salinity treatments. Bars on graphs indicate the standard deviation from mean.

4.3.2.2 Fertilisation treatments

The response of the three salinity treatments to the different fertiliser treatments differed widely from each other, with treatment S0 being the most insensitive (stable) to the fertiliser treatments, while S2 was the most sensitive. Gupta's Shortfall test and an AMMI-estimates model were used to evaluate which fertiliser treatments within each salinity treatment group gave the best yields. The ranking of treatments according to the Gupta Shortfall test is given in APPENDIX B. The results of the two tests indicated that the highest N application level led to higher dry mass production for all three salinity levels. Both tests also indicate that the fertiliser treatments of the S1 salinity treatment where N was supplied in a NO_3:NH_4 ratio of 1:1 produced higher dry matter yields than the other S1 fertiliser treatments. The fertiliser treatments of the S2 treatment that received K at an application rate of 120 kg ha^{-1} produced the highest dry matter yields within this salinity treatment.

It is important to not only consider individual application rates of N, P and K, but also the combined effect of N, P and K fertiliser application amounts and ratios on the yield of maize plants subjected to SO_4 salinity. The fertiliser treatment that gave the highest dry matter yield overall, regardless of salinity treatment, was the treatment that received 160 kg N ha^{-1} in a NO_3:NH_4 ratio of 1:1, 60 kg P and 30 kg K ha^{-1} (N6P2K1). This treatment was, however, sensitive to the highest salinity treatment level. The dry matter yields of the 12 main fertiliser treatments (sum of the dry matter yields of treatments with the same rates of N, P and K regardless of NO_3:NH_4 ratios) for each salinity treatment group are presented in Figure 4.2. The fertiliser treatment that received 160 kg N, 40 kg P and 120 kg K ha^{-1} produced the highest dry matter yield within the S0 and S2 treatments, while the treatment that received 160 kg N, 60 kg P and 30 kg K ha^{-1} produced the highest dry matter yield within the S1 salinity treatment. Differences between dry matter yields of the S0 and S1 fertiliser treatments were not significant at the 5% probability level. Significant differences between dry matter yields of the S2 fertiliser treatments are indicated on the graphs of Figure 4.2.

The effect of different NO_3:NH_4 ratios within each fertiliser and salinity treatment group is considered in Table 4.5. The application of N in different NO_3:NH_4 ratios had no notable effect on the dry matter yield of the control treatment, while an equal NO_3:NH_4 supply led to higher dry matter production for the S1 and S2 salinised treatments.

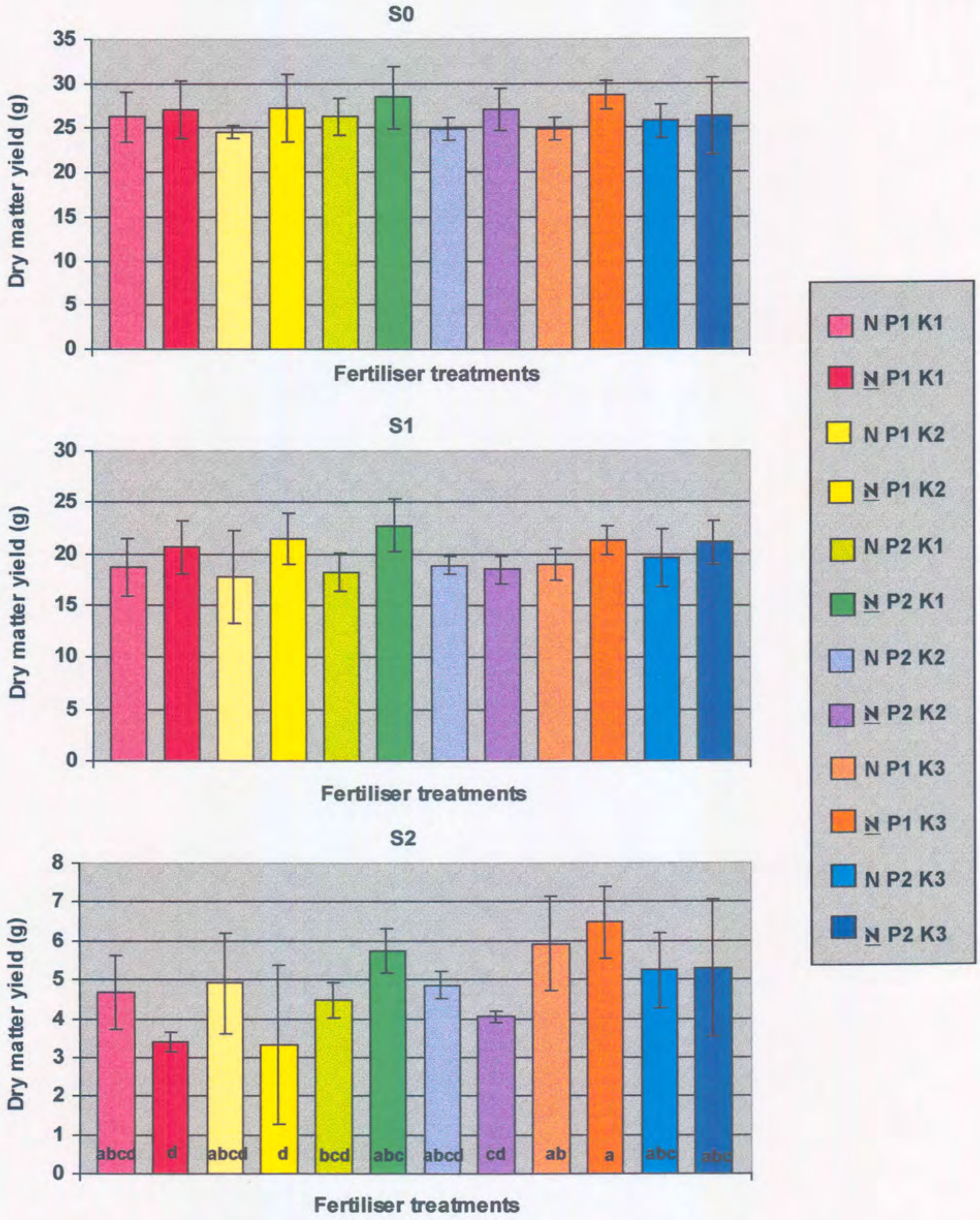


Figure 4.2 Dry matter yields of the main fertiliser treatments for each salinity group (regardless of NO_3:NH_4 ratio). Standard deviations from mean and significant differences between S2 fertiliser treatments are indicated on graphs (LSD 1.81g). **N** = 80 kg N ha^{-1}; **N** = 160 kg N ha^{-1}.

These results are commensurate with the findings of the water culture experiment and those of Barnard *et al.* (1998) who indicated that wheat plants were less sensitive to SO_4 salinity when grown with elevated levels of NH_4.

Table 4.5 The fraction of treatments with the highest dry matter yields when the NO_3:NH_4 ratio treatments within each of the 12 main fertiliser treatment groups were compared

Salinity treatments	NO_3:NH_4		
	4:1	2:1	1:1
S0	4	3	5
S1	3	0	9
S2	0	3	9

4.3.3 SOIL CHEMICAL PROPERTIES

The MINTEQA2 (version 3.10) chemical speciation model (Allison *et al.*, 1991) was used to calculate the equilibrated mass distribution of the principal dissolved and precipitated species in the S1 and S2 treatment soils that resulted from the gypsum and magnesium sulphate application. These results are given in APPENDIX C. The concentration data for PO_4 and Al (Table 4.3) was also included in the speciation calculations, since the gypsum contained substantial amounts of these elements.

According to the equilibrated mass distribution data for the S1 salinity treatment, 56.3% of the applied SO_4, 95.9% of the applied Ca, 98.8% PO_4 and 100% Al would precipitate, while all the Mg would dissolve. The speciation data for the S2 treatment indicated that 57.9% of the applied SO_4, 98.2% of the applied Ca, 98.5% PO_4 and 100% Al would precipitate, while all of the applied Mg would dissolve. The ion and ion-pair activities of the principal species in the soil solutions of the S1 and S2 treatment soils (expressed as a percentage of the total activity) are presented in Figure 4.3. The model predicted that the activity of the $MgSO_4^0$ ion-pair would be the highest, while the $CaSO_4^0$ ion-pair activity and the Ca^{2+} ion activity would be the lowest for both treatments.

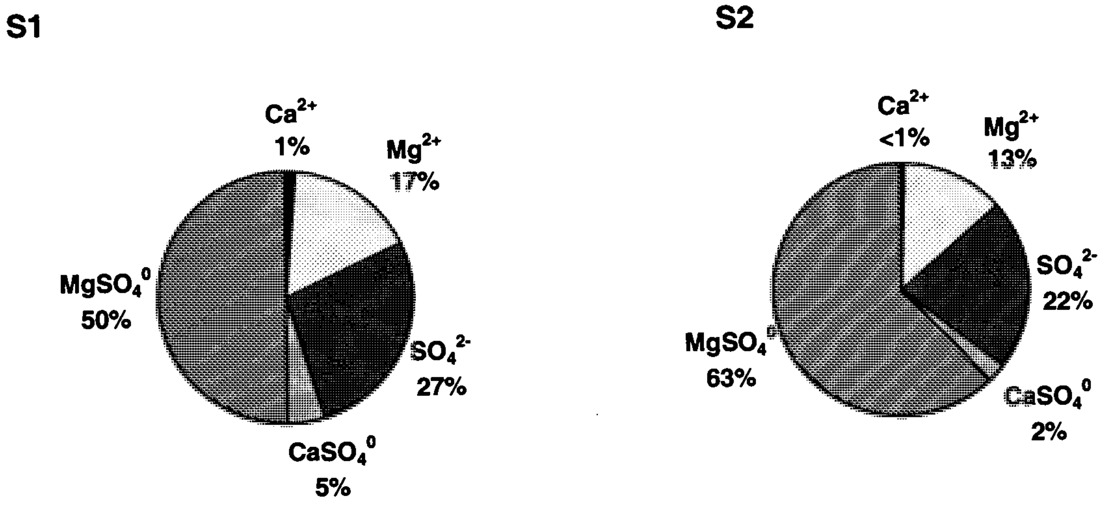


Figure 4.3 Relative ion and ion-pair activities of the principal species in the S1 and S2 treatment soil solutions expressed as percentage of the total ion activity calculated using the MINTEQA2 chemical equilibrium model.

MINTEQA2 predicted a Ca^{2+}:Mg^{2+} activity ratio of 1:12 for the S1 treatment soils and a ratio of 1:29 for the S2 treatment soils. The principal precipitated species and their sequence of precipitation in the S1 and S2 treatment soils were diaspore (AlO(OH)), hydrapatite ($Ca_5(PO_4)_3(OH)$) and gypsum. Both diaspore and hydrapatite are insoluble in water and only slightly soluble in citrate. Phosphate and the more soluble monocalcium phosphate species, $CaHPO_4$, $CaPO_4^-$ and $CaH_2PO_4^+$, were predicted to be present in minute concentrations at equilibrium.

The analysis data of the soil that were sampled at the end of the experimental period are presented in APPENDICES D and E. The mean soil pH, EC_e and concentrations of nutrients in the soil of the salinity treatments are given in Table 4.6.

Increasing levels of gypsum and magnesium sulphate had no effect on the pH of the soil solution. In general, gypsum application to soils has been reported to cause a decrease in soil pH (Olsen & Rehm, 1986; Szabolcs, 1989). The reported decrease in pH seems mainly to be caused by displacement of H^+ and Al^{3+} by Ca^{2+}. The initial pH of the experimental soil indicated that exchangeable acidity was insignificant. Speciation calculations indicated that H^+ and Al^{3+} concentrations were present in minute quantities at equilibrium.

Table 4.6 Mean soil pH, EC_e and concentrations of nutrients of the salinity treatments

Treatment	$pH(H_2O)$	EC_e	Bray I P	Ammonium acetate extractable cations				SO_4
				Ca	Mg	K	Na	
		$mS\ m^{-1}$	$mg\ kg^{-1}$					
S0	6.2	98	17.9	717	515	65	7.9	548
S1	6.1	713	52.3	6321	2009	71	11.9	21989
S2	6.1	1475	73.1	10419	3492	159	17.1	45844

The EC value of the saturated gypsum solution was 424 mS m^{-1} (Table 4.3), but since a high proportion of ions can be in the form of ion pairs not accounted for in the EC value (Papadapoulos, 1987), it can be expected that the EC_e values of the gypsum and soil would be higher (about one-third more than the measured EC_e values according to Jurinak *et al.* (1987)). Increases in the EC_e of the S1 treatment soils were positively correlated with increasing soluble soil-Mg and -Na concentrations. Although the dry matter yield of maize decreased with increasing EC_e when all salinity treatments were considered, there was no correlation between EC_e and dry matter yield within a salinity treatment group (Figure 4.4).

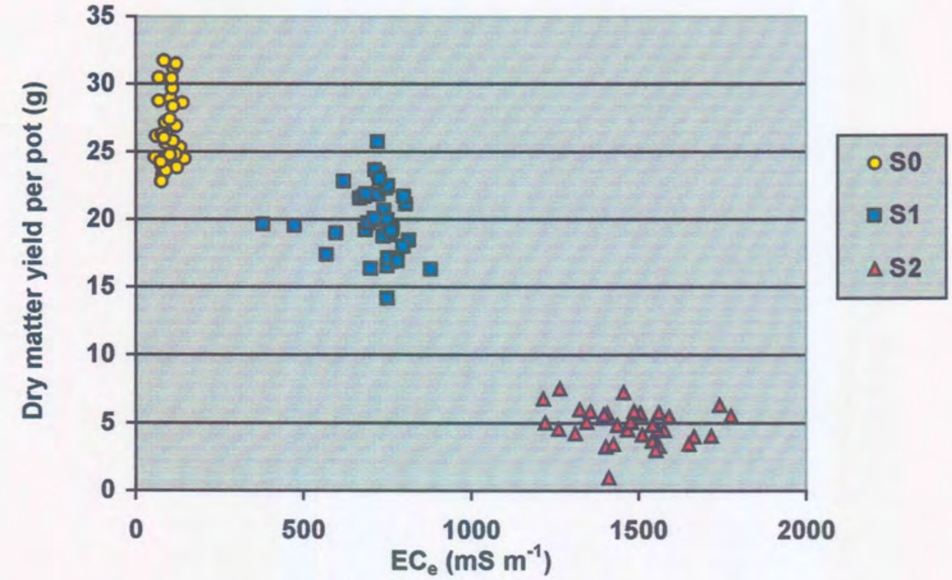


Figure 4.4 Dry matter yields of salinity treatments in relation to the EC of the soil saturation extract at the end of the experimental period.

The dry matter yields of several S1 treatment plants grown with an EC_e seven times higher than that of the S0 treatment soils were in fact higher or similar to some S0 treatment plants. These results led one to conclude that inadequate nutrition depressed yields more under non-saline conditions than under moderate saline conditions, which is in accordance with statements made by Rhoades (1990) and Grattan and Grieve (1994). When the dry matter yield of the same fertiliser treatments of the S0 and S1 treatments were compared, however, only the mean dry matter yield of the N6P2K3 S1 treatment was slightly higher than that of the same non-saline fertiliser treatment.

The mean soluble and exchangeable base cation fractions encountered in the soils at the end of the experimental period are presented in Table 4.7 and Figures 4.5 and 4.6.

Table 4.7 Mean soluble and exchangeable cations in soil solution extract

Treatment	Soluble cations				Exchangeable cations			
	Ca	Mg	K	Na	Ca	Mg	K	Na
	$cmol_c\ kg^{-1}$				$cmol_c\ kg^{-1}$			
S0	0.307	0.337	0.003	0.008	6.864	3.896	0.164	0.055
S1	0.830	6.812	0.010	0.015	30.710	9.723	0.171	0.039
S2	0.798	19.350	0.040	0.046	51.190	9.392	0.368	0.057

The water-soluble and exchangeable cations give an indication of the 'plant-available' nutrient pool. The 'plant-available' Ca fraction increased from approximately 7 $cmol_c\ kg^{-1}$ in the S0 soil to over 30 $cmol_c\ kg^{-1}$ in the S1 treatment soil and more than 50 $cmol_c\ kg^{-1}$ in the S2 treatment soil (Figure 4.5). The soluble Ca fraction was only slightly increased by gypsum application and constituted only a small fraction of the total soil-Ca.

Soil-Mg concentrations increased from less than 5 $cmol_c\ kg^{-1}$ soil for the S0 treatment to over 15 $cmol_c\ kg^{-1}$ soil for the S1 treatment and approximately 29 $cmol_c\ kg^{-1}$ soil for the S2 treatment. The soluble Mg fraction increased with increasing salinity, while the exchangeable Mg increased from S0 to S1 but decreased slightly from S1 to S2.

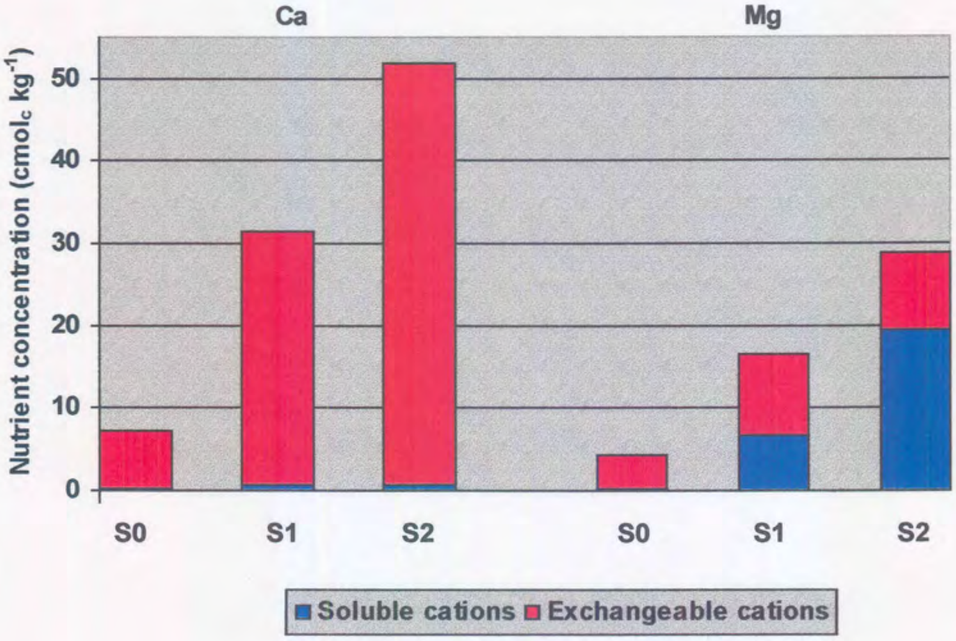


Figure 4.5 Mean soil-Ca and -Mg concentration fractions of the salinity treatment:

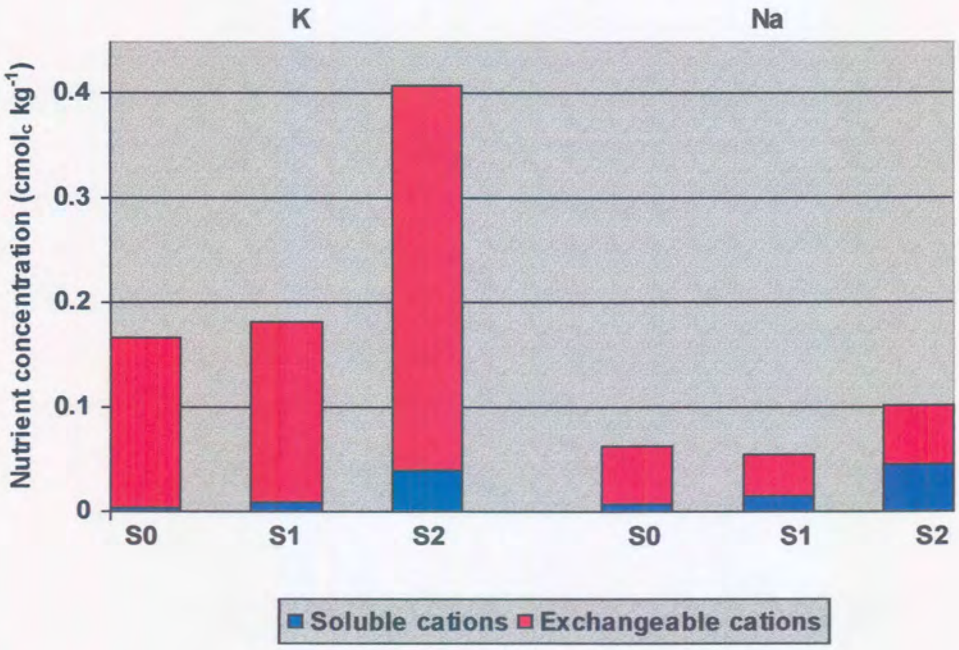


Figure 4.6 Mean soil-K and -Na concentration fractions of the salinity treatments.

When considering the ammonium acetate and exchangeable Ca and Mg fractions, the S0 treatment had a mean Ca:Mg ratio of between 1:1 and 2:1, while the mean Ca:Mg ratio of the S1 and S2 treatments was greater than 2:1. The soluble fractions revealed, however, that the Ca:Mg ratio of the S0 treatment was approximately 1:1, while that of the S1 treatment was 1:8 and 1:24 for the S2 treatment respectively. These ratios are almost similar to those predicted with the MINTEQA2 model. It has been known for over 30 years that solutions with a Ca:Mg ratio less than 1 reduce the growth of maize plants (Grattan & Grieve, 1994). A low ratio of Ca^{2+} to other cations is unfavourable to Ca^{2+} uptake and membrane stability (Epstein, 1972). The maize yield decreased with increasing soil-Ca and -Mg concentrations when all salinity treatments were considered.

The extractable K concentrations in the S0 and S1 treatment soils were considerably lower at the end of the trial compared to the K level at the onset of the trial (Table 4.2). This indicates that the soil K was depleted and that the K supplied at onset of the trial was not sufficient for the duration of the seven-week growing period. All soil-K fractions increased with increasing salinity (Figure 4.6). This could be due to the retarded growth of the salinised treatment plants and a subsequent lower level of K uptake or to a lowered soil-K activity caused by the high level of soluble salts, whereby K extraction was inhibited. The dry matter yield of the maize decreased with increasing soil K (all fractions) when all salinity treatments were considered.

Increasing salinity levels increased the soluble Na levels in the soil solution, while the exchangeable Na of the S1 treatment was slightly reduced relative to the control (Figure 4.6). This is probably due to displacement of Na^+ by Mg^{2+} and Ca^{2+} on the soil exchange complex.

The mean SO_4 concentration in the soil solution of the S1 treatment was 40 times higher than that of the control, while it was more than 80 times higher for the S2 treatment. Dry matter yield decreased with increasing SO_4 concentrations in the soil when all salinity treatments were considered.

4.3.4 PLANT NUTRIENT CONCENTRATIONS AND CONTENTS

The plant nutrient analysis data are presented in APPENDIX F. The mean concentrations of nutrients for the salinity treatments are given in Table 4.8, while the nutrient vector analysis is given in Figure 4.7. The nutrient concentration ranges considered 'adequate' for maize (Reuter, 1986) are included in Table 4.8.

Table 4.8 Mean nutrient concentration in maize plants of the three salinity treatments

Salinity treatments	N	K	P	Ca	Mg	SO_4	Cu	Fe	Mn	Zn
	%						mg kg^{-1}			
'Adequate' range	3.0 - 3.5	2.0 - 2.5	0.25 - 0.45	0.25 – 0.50	0.13 - 0.30	0.24 - 0.72	3.0 - 15	30 - 200	20 - 300	15 - 60
S0	0.79	1.91	0.16	0.31	0.31	0.22	4.46	47.83	31.08	26.88
S1	0.92	2.24	0.18	0.13	0.64	1.26	2.50	41.21	29.50	24.96
S2	2.29	3.12	0.19	0.18	1.38	2.37	5.00	50.83	46.08	27.04

The N concentration in all plants of the S0 and S1 treatments was deficient, while that in the S2 treatment plants was marginal. The N:S ratio of the S0 plants was, however, within the normal range (Reuter, 1986), but that of the S1 and S2 plants was far below the given norm. The average plant-N concentration increased with increasing salinity. Dry matter yields of the S2 treatment plants were, however, negatively correlated to increasing N concentrations in plants.

The K concentration in plants of the S0 treatment was marginal, while that of the S1 and S2 treatments was adequate. Increases in plant-K concentrations occurred under calcium and magnesium sulphate salt stress. The mean plant-K content of the S0 treatment was, however, higher than that of the S1 and S2 treatments. Dry matter yield was increased with increasing plant-K contents for all salinity treatments.

Plant analysis showed that fertiliser application at the onset of the trial supplied insufficient N and K. If the amount of N and K which may have come from the soil or gypsum application is disregarded, it is shown by the data in Table 4.9 that N uptake by the S0 and S1 treatment plants was higher than that supplied by the lowest N application rate and N supplied at 160 kg N ha^{-1} (NO_3:NH_4 ratio of 1:1) for the S0 treatment, while the K uptake of plants of all treatments was higher than that supplied by fertiliser application. Although the concentration and forms of N in the soil was not determined at the end of the experimental period, it can be expected that some of the applied N was rendered unavailable for plant uptake by microbial fixation. Thus, even where N uptake by plants did not exceed the level of applied N, this does not indicate that plants were sufficiently supplied with N. Calculations show that N utilization efficiency was higher for all salinity treatments when N was supplied in a NO_3:NH_4 ratio of 1:1 compared to a ratio of 4:1 or 2:1. Dry matter yield increased as the N content in plants increased for all salinity treatments. The plant available K concentration in the S2 treatment soils was more than two times higher at the end of the experimental period than that of the S0 and S1 soils and it is therefore unlikely that higher application rates of K to the soils of the extremely saline S2 soils at the onset of the trial would have caused higher dry matter yields.

Table 4.9 Mean N and K uptake by salinised treatments in comparison to the N and K supplied by fertiliser application

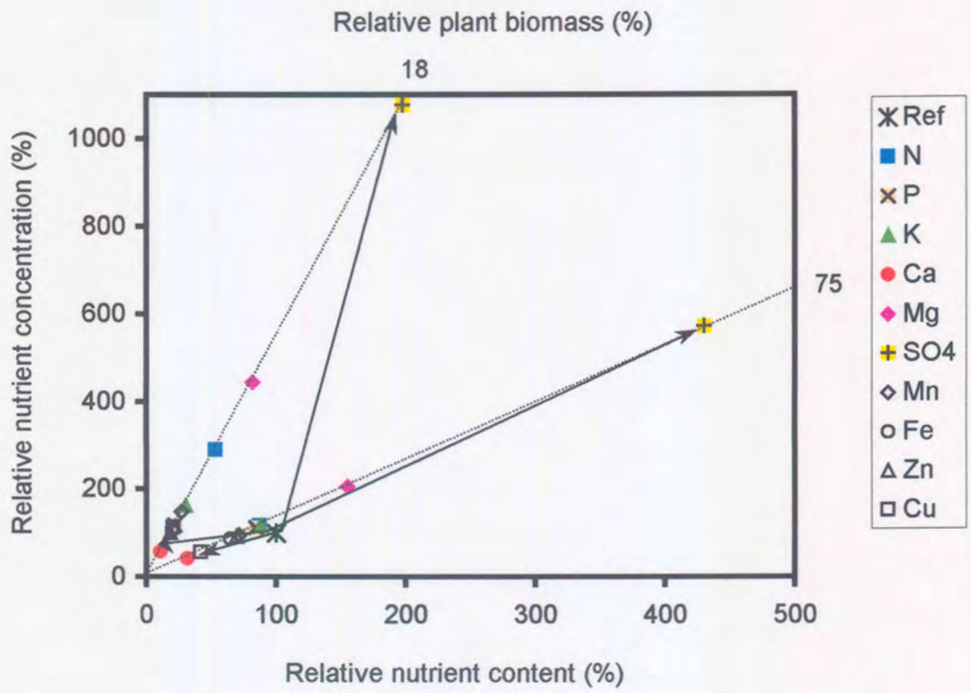
Mean N uptake (g per pot)	**N applied (g per pot)**					
	0.12 (80 kg N ha^{-1})			**0.24** (160 kg N ha^{-1})		
	NO_3:NH_4 ratio applied					
	4:1	**2:1**	**1:1**	**4:1**	**2:1**	**1:1**
S0	0.17	0.18	0.22	0.20	0.21	0.28
S1	0.15	0.15	0.19	0.21	0.18	0.21
S2	0.10	0.10	0.11	0.09	0.11	0.13

Mean K uptake (g per pot)	**K applied (g per pot)**		
	0.045 (30 kg K ha^{-1})	**0.09** (60 kg K ha^{-1})	**0.18** (120 kg K ha^{-1})
S0	5.8	5.8	6.6
S1	5.2	5.0	5.8
S2	1.6	1.6	2.2

The P concentration in plants of all treatments was marginal to deficient, although the Bray I-P concentrations were very high for the S1 and S2 treatment soils. The plant-P content was the lowest for the S2 and S1 treatments, although soil-P was the highest for these treatments. This phenomenon can possibly be ascribed to the precipitation of P as insoluble Ca-P compounds so that P absorption or its availability was adversely affected. This was confirmed by the speciation data calculated by the MINTEQA2 program for the phosphate species: most of the PO_4 had precipitated as hydrapatite, while minute quantities of PO_4^{3-}, $CaHPO_4$, $CaPO_4^-$ and $CaH_2PO_4^+$ were present in the soil solution. Although hydrapatite is soluble in citrate, it seems that the Bray I extraction, which is a very weak acid, did not give a good indication of plant-available P in the calcium and magnesium sulphate enriched soils. Another possible explanation for the low P concentration in the top growth of maize, despite high soil P levels, can be that calcium phosphates had precipitated in the free space between cortical cells of the roots and consequently restricted P translocation to the top growth. Claassens and Fölscher (1988) postulated this hypothesis after they had observed that Ca and P had accumulated in the roots of wheat and that the content of the tops had stayed much lower.

The Ca concentrations in plants of the S0 treatment were adequate, while the Ca concentration of the S1 and S2 treatments was marginal to deficient despite the high application rate of gypsum. The largest, downward left-pointing vectors in Figure 4.7 are associated with Ca. This shift indicates antagonism and a possible Ca deficiency induced by SO_4 and/or Mg. The mean ratio of Ca to Mg in the maize plants of the S0 treatment was similar to the total 'plant-available' Ca and Mg ratios in the soil, while that of the S1 treatment was closely related to the average Ca:Mg ratios in the soil solution. The ratio of Ca to Mg in plants of the S2 treatment was double (1:12) that of the ratio in the soil solution (1:24). The antagonistic effect of high concentrations of SO_4 and Mg on Ca uptake is well-documented (Ananthanarayana & Hanumantharaju, 1992; Datta *et al.*, 1995; Huang & Redmann, 1995). Besides uptake inhibition by high concentrations of Mg and SO_4, calcium also has a low uptake potential because only young root tips in which the cell walls of the endodermis are still unsuberized, can absorb it. The Ca content of plants is to a large extent genetically controlled and is little affected by the Ca supply in the root medium, provided that the Ca availability is adequate for normal plant growth (Mengel & Kirkby, 1987).

The mean Mg concentration in the plants of the S1 and S2 treatments was toxic according to literature norms given for Mg in maize (Jones, 1967). Plant-Mg concentration and dry matter yield of the S1 treatment was negatively correlated.



Treatment	S0	S1	S2
Normalized biomass (%)	100	75	18

Figure 4.7 Relative response in the mean nutrient concentration, content and dry mass of the salinity treatments. The status of the S0 treatment was normalized to 100% to allow comparison on a common base.

The largest upward, right-pointing vectors in Figure 4.7 were associated with sulphate and indicate concentration and a possible SO_4-toxicity. Although plants of the S2 treatment accumulated high levels of SO_4 (up to 3.23%), there was no reduction in dry matter yield with increasing plant SO_4 concentrations or contents. Dry matter yield of the S2 treatment was in fact strongly positively correlated with plant-SO_4 content. The sulphate content in plants of the S2 treatment was lower than that of the S1 treatment. The average SO_4 concentration in plants of the S0 treatment increased as the NO_3:NH_4 ratio changed from 4:1 to 2:1 to 1:1 (Table 4.10). This effect of N forms on SO_4 concentration in plants was consistent with other reports (Cox & Reisenauer, 1973; Kirkby, 1968; Haynes & Goh, 1978; Cao & Tibbits, 1998). The opposite trend was, however, observed for the two salinity treatments. The average SO_4 concentration in plants of these treatments decreased as the NO_3:NH_4 ratio changed from 4:1 to 2:1 to 1:1. A clear trend was further observed between the fraction of fertiliser treatments with a specific NO_3:NH_4 ratio that produced the highest dry matter yields within the S1 and S2 salinity treatment groups (Table 4.5) and the Mg concentration in plants grown with different NO_3:NH_4 ratios (Table 4.10). The fraction of fertiliser treatments that produced the highest dry matter yields was the greatest for the treatments that had the lowest plant-Mg concentrations. These were the S1 and S2 treatments that received N in a NO_3:NH_4 ratio of 1:1. The fraction of fertiliser treatments that produced the highest dry matter yields was the lowest for the treatments that had the highest plant-Mg concentrations. These were the S1 treatments that received N in a NO_3:NH_4 ratio of 2:1 and the S2 treatments with a NO_3:NH_4 ratio of 4:1.

Table 4.10 Mean nutrient concentration in maize plants of the salinity treatments grown with different NO_3:NH_4 ratios

Salinity treatments	NO_3:NH_4 ratio applied	N	P	K	Ca	Mg	SO_4
		%					
S0	4:1	0.71	0.14	2.05	0.31	0.29	0.17
	2:1	0.75	0.17	1.93	0.26	0.31	0.19
	1:1	0.93	0.17	1.76	0.36	0.33	0.30
S1	4:1	0.94	0.18	2.25	0.13	0.64	1.30
	2:1	0.88	0.18	2.19	0.13	0.70	1.25
	1:1	0.93	0.19	2.29	0.13	0.59	1.23
S2	4:1	2.26	0.19	3.24	0.19	1.42	2.58
	2:1	2.29	0.17	3.00	0.18	1.39	2.32
	1:1	2.33	0.21	3.12	0.18	1.34	2.22

Concentrations of Cu, Fe, Mn and Zn were largely unaffected by sulphate salinity. The mean micronutrient concentrations, with the exception of Cu in plants of the S1 salinity treatment, were adequate according to literature norms for micronutrients in maize.

4.3.5 NUTRIENT INTERACTIONS IN SOIL AND PLANTS

The main interactions between nutrients in the soil were those between Ca and Mg, Ca and K, Mg and SO_4, and Mg and Na. Increasing exchangeable and extractable Mg concentrations in the soil solution of the S1 treatment decreased the soluble soil-Ca concentrations. The exchangeable soil-K fraction increased with increasing soluble Ca for the S0 treatment, while the soluble soil-K fraction increased with increasing soluble Ca for the S1 treatment. Ananthanarayana and Hanumantharaju (1992) stated that optimum amounts of Ca result in an increase in the availability of exchangeable and water-soluble K, while results from other studies indicated that excessive addition of calcium to soil often decreases K levels (Iyengar & Reddy, 1994). Soluble soil-Mg concentrations of the S1 treatment were positively correlated with soil-SO_4 levels. A positive relationship was further found between the soluble Mg and Na concentrations in the soil of both the S1 and S2 treatments.

The most prominent interactions between nutrients in plants of the different salinity treatments were analysed in Figure 4.7 and discussed in section 4.3.3. Other significant interactions are discussed below.

An antagonistic effect of K in soil and plants with the Mg in plants of all treatments, was observed. The literature on plant nutrition contains many references of antagonism between magnesium and potassium (Epstein, 1972; Mengel & Kirkby, 1987). Ananthanarayana and Hanumantharaju (1992) stated that the antagonism between Mg and K seem to be confined to the deficiency range of nutrient availability, but in this experiment, K suppressed Mg uptake even under extremely high soil-Mg concentrations (S2 treatment soils had Mg:K ratios in the order of 35:1). The Mg concentration in plants of the S0, S1 and S2 treatments decreased with increasing extractable and exchangeable soil-K and increasing concentrations of K in plants. Magnesium uptake was also suppressed with increasing concentrations of soluble, extractable and exchangeable K in the soil solution of the S2 treatments. The Mg concentration in plants of the S1 and S2 treatments was, however, still toxic, notwithstanding this antagonism. Further experimentation with less saline soils and higher levels of applied K may prove valuable to elucidate the extent to which the antagonistic effect of K on Mg uptake could be harnessed.

The Mg concentration in plants of the S2 treatment increased with increasing plant-SO_4. This finding is consistent with those of Manchanda and Sharma (1989) and MacAdam *et al.* (1997) who reported an enhanced Mg absorption by plants grown with increasing sulphate salinity.

The plant-Mn concentration increased with increasing plant-Mg for the S1 treatment, while it increased with increasing soil-Mg for the S2 treatment. These results are commensurate with those obtained in the nutrient solution trial with wheat, where plant-Mn concentrations were strongly correlated with the plant-Mg concentrations. Suhayda *et al.* (1994) hypothesized that a saline medium, rich in divalent cations, might enhance the accumulation of Mn in plant tissue.

4.3 SUMMARY AND CONCLUSIONS

Calcium and magnesium sulphate salinity significantly reduced the dry matter yield of maize plants. The most limiting factor with regards to dry matter production of the S1 treatment plants seemed to be specific ion effects rather than osmotic stress, since several fertiliser treatments of the S1 treatment group, grown with an average EC_e of 700 mS m^{-1}, out-performed some of the S0 fertiliser treatments (EC_e of 100 mS m^{-1}). Specific ion effects that caused the growth decline in S1 salinised plants include a deficiency of Ca induced by Mg and SO_4 and/or a Mg toxicity.

The S2 treatment plants exhibited disorder symptoms typical of salt-affected plants. Severe yield reductions were probably caused by a combination of osmotic stress and specific ion deficiencies and toxicities.

Although there was no absolute proof that specific fertiliser application did improve crop growth under sulphate saline conditions, certain trends could be observed in the obtained results. There was an indication that the dry matter yield of salinised plants supplied with the highest N level (160 kg ha^{-1}) in a NO_3:NH_4 ratio of 1:1 (N6) was somewhat higher than the rest. This was possibly the result of a higher N utilization efficiency and a decreased SO_4

and Mg concentration in plants. It is, however, questionable whether these beneficial effects on plant growth and nutrient uptake was directly caused by an enhanced NH_4 supply, since NH_4 was only applied once at the onset of the experiment and could have been nitrified, immobilized or volatilized. The possibility exists that these beneficial effects may have resulted from some other secondary effects resulting from supplying NO_3 and NH_4 in equal ratios to the saline soil. Further investigation is needed to clarify this matter.

The fact that the obtained results does not prove that specific fertiliser application could improve crop growth under sulphate saline conditions can be ascribed to too low application rates of N and K and no significant differences in the amount of P applied within a salinity treatment group that resulted from the erroneous use of phosphogypsum. The chlorotic appearance of the maize foliage of all fertiliser treatments within the control treatment group and the fact that N and K uptake by plants was higher than the N and K supplied through fertiliser application confirmed that the once-off fertiliser application was insufficient for the seven-week duration of the trial. Besides this, there was an indication that the fertiliser treatments that received the highest N application level (160 kg ha^{-1}) produced higher dry matter yields overall. Higher, split dosages of especially N and K supplied throughout the growing season and/or foliar application of nutrients to prevent further salinity build-up in soils, may enlighten if the effects of moderate sulphate salinity could be corrected by fertilisation.

The erroneous use of phosphogypsum instead of a more preferable pure gypsum source, cancelled the P fertilisation treatment effects to a great extent and resulted in large amounts of P being added to the S1 and S2 treatment soils. An important observation with practical implications, however, resulted from this. Even with a phosphorus application rate of 560 kg ha^{-1} (P2, S2 treatment soils), the P concentrations in plants was still marginal to low. The precipitation of P as insoluble calcium phosphates in the soil or between the free space of the cortex cells of plant roots, could possibly explain this phenomenon. It is also questionable whether the Bray I-P extraction method gives an accurate indication of the amount of plant available P in calcium and magnesium sulphate salinised soils. Further experimentation is needed to put sensible guidelines in place for application methods, rates and timing of P-containing fertilisers.

Although there were significant differences between the dry matter yields of the main S2 fertiliser treatment groups, the extremely low yields confirmed Bernstein *et al.*'s (1974) finding about fertiliser application under saline conditions. They stated that the effects of salinity and fertility on grains and several vegetables tended to be independent and additive, when either nutrient deficiency or salinity was moderate and yields were only moderately depressed. Strongly inhibitory salinity levels controlled the yield of S2 treatment plants regardless of the level of soil nutritional status.

The application rates of gypsum and magnesium sulphate selected for this study did not result in the desired activities and concentrations of Ca, Mg and SO_4 in the soil solutions of the salinised treatments. The practice of maintaining the glasshouse soils at field capacity also resulted in an extremely unfavourable Ca^{2+}:Mg^{2+} ratio in the salinised soils, which caused the high incidence of necrophily and die-back of the youngest leaf blades of the S2 treatment plants. It is not anticipated that $MgSO_4$ will accumulate to such an extent in the soils that will be irrigated with the mine water, since $MgSO_4$ is mobile and must be leached from the soil profile. These results, however, clearly indicate that Ca can become limiting for plant growth, even in a gypsiferous soil, if the soluble Mg and SO_4 concentrations are in excess. The management of the soluble ion concentrations in the root medium will thus be of extreme importance when irrigating crops with sulphate saline water.

Finally it is important to note that the application of the results obtained in this glasshouse experiment to field problems and growth processes must be made with caution. The unnatural situation created by growing plants in pots in the glasshouse (size of pots, plant density, temperature, humidity etc.) caused that no correspondence between nutrient concentration and fertiliser rate per hectare is possible. The uptake and distribution of nutrients may also show different relationships in plants grown in soil cultures and in the field. Inconclusive results on the interactive effects of salinity on crop growth and nutrition obtained from this glasshouse experiment emphasize the need for field investigations.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Calcium and magnesium sulphate salinity decreased the biomass production of wheat and maize grown under glasshouse conditions. The yield decline of wheat grown in solution culture with moderate salinity levels was mainly due to high concentrations of SO_4 and Mg in plants. The N:S ratio of salinised plants indicated that excess SO_4 was taken up by plants. Symptoms of excess SO_4 given by Mengel and Kirkby (1979) do, however, not coincide with the chlorotic appearance of sulphate salinised plants in this experiment and it can therefore be concluded that growth reductions were rather due to high concentrations and contents of Mg in wheat, which antagonistically decreased the uptake of K and Fe. Growth reductions in maize grown under high soil salinity levels were mainly due to a Mg toxicity and/or Ca deficiency induced by excess SO_4 and/or Mg. Maize grown under very high salinity levels exhibited symptoms typical of salt stressed plants and growth reductions were probably caused by a combination of osmotic effects and specific ion toxicities. Although plants of the highest salinity treatment accumulated high levels of SO_4, no direct correlation was found between reductions in dry matter yield with increasing plant-SO_4 concentration or content.

The application of NO_3, NH_4 and K at quantities other than the level considered beneficial for non-saline conditions, improved top dry matter yield of wheat under sulphate saline conditions. Root and top dry matter production of wheat increased up to a NH_4 concentration of 5 mmol ℓ^{-1} in the growth medium, from where it decreased gradually. Dry matter yield did not follow a specific trend with increasing NO_3 and K concentrations in the growth medium. Differential phosphorus levels under calcium and magnesium sulphate saline conditions had no effect on top dry matter production of wheat.

No absolute indication, besides that of an enhanced NH_4 application, was obtained that specific fertiliser application other than that considered beneficial for non-saline conditions, did improve maize growth under sulphate saline conditions. Strongly inhibitory salinity levels controlled the yield of the highest salinity treatment regardless of the level of fertiliser application.

The application of NH_4 in a NO_3:NH_4 ratio of 2:1 and at a level 6 mmol ℓ^{-1} higher than the NH_4 level considered beneficial for non-saline conditions, improved top growth of wheat under sulphate saline conditions the most. This finding is of great significance, since nutrient solutions containing such an unfavourable NO_3:NH_4 ratio and such high concentrations of NH_4, are known to impair plant growth under non-saline conditions (Magalhães & Wilcox, 1984; Magalhães *et al.*, 1995; Barnard *et al.*, 1998). A beneficial effect of an enhanced ammonium nutrition (NO_3:NH_4 ratio of 1:1) was also observed for maize grown in the calcium and magnesium sulphate salinised soil. The beneficial effect of an enhanced NH_4 nutrition under calcium and magnesium sulphate salinity can be ascribed to the following nutrient interactions:

(i) Increasing NH_4 concentrations in the growth medium resulted in a decrease in the Mg concentration in wheat. Although the Mg concentrations in maize did not consistently decrease with increasing NH_4 applications to the salinised soil, they were the lowest in plants supplied with N in a NO_3:NH_4 ratio of 1:1. The biomass production pattern coincided with the Mg concentrations in plants, which was related to the NO_3:NH_4 ratio applied to the soil.

(ii) The SO_4 concentration in maize of the salinity treatments decreased as the NO_3:NH_4 ratio changed from 4:1 to 2:1 to 1:1. Ammonium is widely reported to increase the SO_4 concentration in plants (Cox & Reisenauer, 1973; Kirkby, 1968; Haynes & Goh, 1978; Cao & Tibbits, 1998). This was found to be valid for maize grown at low sulphate concentrations in the soil, but the opposite was true for high soil-SO_4 concentrations.

(iii) Nitrogen utilization efficiency of wheat and maize was higher where N was applied as NH_4 compared to NO_3. Ammonium could have served as a supplementary N source when large SO_4 concentrations suppressed NO_3 uptake.

It can be concluded that the beneficial effect of an enhanced NH_4-N nutrition under sulphate salinity needs to be tested and investigated under field conditions. If the use of NH_4

fertilisers prove advantageous under sulphate saline conditions in the field, further experimentation would be needed to determine the optimal chemical form of ammonium fertilisers to be used, application rates, methods and timing of application. Anhydrous ammonia, aqua ammonia or urea may be used when considering fertigation, but urea would probably be the most preferable NH_4 source since it is the nitrogen fertiliser mostly used for foliar application and causes the smallest increase in the osmotic pressure of the soil solution. The timing and concentration of NH_4-application will be of particular importance, since free NH_4 in plants will instantly kill cells and thus needs to be metabolized rapidly (U. Kafkafi, The Hebrew University, Rehovot, Israel, personal communication, 1999). Fertilisation with NH_4 should thus be terminated during anthesis as the sugars, that are necessary for NH_4 metabolization in plant roots where NH_4 is stored, are translocated to the flowers or fruits during this period. Further experimentation with the injection of NH_4 into the irrigation water could be of great economic importance. The use of nitrification inhibitors may enlighten the mechanisms involved in the beneficial effect of NH_4 under sulphate saline conditions.

The precipitation of P as insoluble calcium phosphate complexes in the soil, might be the most serious nutritional problem that need to be addressed when irrigating with the sulphate saline water. The effectiveness of strip application of phosphate fertilisers or fertigation will, to a great extent, depend on the rate and kinetics of the precipitation process. Further experimentation is needed to determine the relationship between Bray I-P and plant available P in calcium and magnesium sulphate enriched soils, since soil- and plant-P concentrations were poorly correlated in the soil pot experiment. The hypothesis that low P concentrations in the top growth of maize was caused by the precipitation of calcium phosphate complexes between the free space of cortex cells of plant roots needs also to be investigated to put sensible guidelines in place for application methods, rates and timing of phosphate fertilisers.

The results of the soil pot experiment indicated that Ca^{2+} could become limiting for plant growth if the soluble Mg^{2+} and SO_4^{2-} concentrations are in excess. It is not anticipated that wetting of leaves with the Ca enriched waste water during irrigation of crops will alleviate Ca deficiencies that result from unfavourable Ca:Mg ratios in the soil solution, because of the immobility of Ca in plants and as Ca is moved to the younger leaves and grains almost exclusively in the transpiration stream (Mengel & Kirkby, 1987). The management of the soluble Ca^{2+} and Mg^{2+} ion concentrations in the root medium will thus be of extreme importance when irrigating crops with sulphate saline water. Care should be taken if the Ca^{2+}:Mg^{2+} ratio in the soil solution is less than one. Results from the nutrient solution trial indicated that an enhanced NH_4 nutrition did not only reduce the Mg concentration in plants, but also Ca. Caution should thus be exercised when applying large amounts of NH_4 fertilisers when the Ca^{2+}:Mg^{2+} ratio in the soil solution is unfavourable for Ca uptake by crops.

Other prominent nutrient interactions that may influence crop production when irrigating with the sulphate saline waste water are those between Mg and K, Mg and Na, and Mg and Mn.

An antagonistic effect of K in soil and plants with the Mg in plants was observed under non-saline as well as under strongly inhibitory saline levels. This nutrient interaction could prove valuable, since it will only be possible to control the soluble Mg concentrations in the root zone to a certain extent by applying water management techniques when irrigating with the calcium and magnesium sulphate enriched waste water. Continuous leaching of $MgSO_4$ from the soil profile to water courses may result in health hazards like diarrhoea (Alberta Agriculture, Food and Rural Development, 1993). Further experimentation to elucidate the extent to which the antagonism between K and Mg can be harnessed under conditions of low, medium and high levels of $MgSO_4$ salinity could prove valuable.

The soluble Na levels in soil of the salinised treatments increased with increasing soluble Mg levels in the soil. Plant-Mn concentrations further increased with increasing Mg concentrations in wheat and maize. These apparent synergistic relationships may result in Na and Mn toxicity in crops when irrigating with the Kleinkopje mine waste water, since Na and Mn levels in this water are already higher than the target water quality ranges given by the Department of Water Affairs and Forestry (1996).

Many shortcomings can be identified in the design, execution and measurements of the two experiments that were conducted. The results obtained from the solution culture trial must be interpreted with caution since the effect of sulphate salinity on nutrient availability may differ in the field, particularly for P and K, since their concentrations are controlled by the solid phase and are difficult to measure or predict. The biggest shortcoming of the soil pot trial with maize was that the experimental soils were kept at field capacity, which resulted in an extremely unfavourable Ca:Mg ratio in the soil solution. An attempt was made with this experiment to simulate the worst possible case scenario in terms of salinity build-up. It is, however, not expected that $MgSO_4$ will accumulate to such high levels in the irrigated soils as in the soil that was used in the glasshouse experiment, since it can be readily leached from the soil profile.

The chemical composition of the gypsum source that was used in this trial did further not reflect the chemical composition of the mine water that will be used to irrigate crops, since it contained high levels of P, Al and trace elements. The erroneous use of phosphogypsum instead of a purer gypsum source, cancelled the P fertilisation treatment effects to a great extent. The trace elements could have caused poor growth and a reduction in the uptake of essential nutrients by the plants of the salinised treatments. The physical characteristics of the applied gypsum in the soil did also not reflect the distribution pattern, structure and consistency of the gypsum that will be precipitated in the soil when irrigating crops in the field. Another shortcoming was that specific nitrogen-containing compounds (e.g. protein amino acids, amides and diamines) that normally accumulate during stress conditions, molybdenum and boron were not determined in plant material.

Plant nutrient analysis results further indicated that the once-off application of N and K, was not sufficient for the seven-week duration of the soil pot experiment. It is also questionable whether the applied NH_4 had any direct beneficial effect on plant growth under sulphate salinity, since NH_4 was only applied once at the onset of the experiment and could have been nitrified or immobilised. If this trial is to be repeated or a similar trial conducted in the greenhouse, it is recommended that nutrient levels must be much higher than that used on a hectare basis in the field, nutrient doses should be split over the growth period, the containers should be larger and the amount of experimental treatments should preferably be small enough so that daily watering of pots can be done on a mass basis. Since the growing of crops in culture mediums under glasshouse conditions is somewhat artificial compared to field conditions where plants are normally grown, it is of extreme importance that the obtained results should first be tested under field conditions before it is used for fertiliser recommendations.

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APPENDIX A Chemical composition of nutrient solutions of the different treatments

Tmts.	Ions (meq ℓ^{-1})							Compound (meq ℓ^{-1})							
	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	NO_3^-	$H_2PO_4^-$	SO_4^{2-}	KNO_3	$NH_4H_2PO_4$	NH_4NO_3	$Ca(NO_3)_2.4H_2O$	$Mg(NO_3)_2$	$(NH_4)_2SO_4$	$CaSO_4.2H_2O$	$MgSO_4.7H_2O$
Control	6	8.0	4.0	1	14	0.50	4.5	6	0.5	0.5	7.5	-	-	0.50	4
3K	**3**	35.6	18.0	1	14	0.50	43.0	3	0.50	0.50	7	3.50	-	28.6	14.5
6K	**6**	33.6	17.0	1	14	0.50	43.0	6	0.50	0.50	5	2.50	-	28.6	14.5
8K	**8**	32.2	16.4	1	14	0.50	43.0	8	0.50	0.50	3.60	1.90	-	28.6	14.5
10K	**10**	31.0	15.6	1	14	0.50	43.0	10	0.50	0.50	2.30	1.20	-	28.6	14.5
0.25P	6	33.4	16.8	1	14	**0.25**	43.0	6	0.25	0.75	4.8	2.45	-	28.6	14.5
0.5P	6	33.6	17.0	1	14	**0.50**	43.0	6	0.50	0.50	5	2.50	-	28.6	14.5
0.75P	6	33.8	17.0	1	14	**0.75**	43.0	6	0.75	0.25	5.10	2.65	-	28.6	14.5
$7NO_3$	6	29.0	14.6	1	**7**	0.50	43.0	6	0.50	0.50	0.35	0.15	-	28.6	14.5
$14NO_3$	6	33.6	17.0	1	**14**	0.50	43.0	6	0.50	0.50	5	2.50	-	28.6	14.5
$20NO_3$	6	37.6	18.9	1	**20**	0.50	43.0	6	0.50	0.50	9	4.50	-	28.6	14.5
$1NH_4$	6	33.6	17.0	**1**	14	0.50	43.0	6	0.50	0.50	5	2.50	-	28.6	14.5
$7NH_4$	6	29.6	14.9	**7**	14	0.50	43.0	6	0.50	6.5	1	0.50	-	28.6	14.5
$9NH_4$	6	28.6	14.4	**9**	14	0.50	44.0	6	0.50	8	-	-	0.5	28.6	14.4

APPENDIX B Mean dry matter yield for the salinity and fertiliser treatments ranked from highest to lowest according to the Gupta Shortfall test

S0			S1			S2		
Fertiliser treatment	Ordered mean yield (g)	Significance level	Fertiliser treatment	Ordered mean yield (g)	Significance level	Fertiliser treatment	Ordered mean yield (g)	Significance level
N6 P2 K1	31.73	0.98*	N6 P2 K1	25.73	0.99*	N6 P1 K3	7.53	0.98*
N6 P1 K2	31.52	0.96*	N6 P1 K1	23.62	0.60*	N5 P1 K3	7.29	0.95*
N4 P2 K3	31.20	0.93*	N2 P1 K2	23.38	0.52*	N6 P2 K3	6.79	0.89*
N4 P1 K3	30.48	0.80*	N6 P2 K3	22.97	0.40*	N4 P2 K1	6.36	0.78*
N6 P1 K1	30.44	0.79*	N5 P1 K2	22.80	0.35*	N2 P1 K3	6.04	0.68*
N4 P2 K2	29.71	0.57*	N6 P1 K3	22.46	0.25*	N5 P2 K3	5.86	0.62*
N2 P2 K1	28.95	0.32*	N6 P1 K2	22.30	0.22*	N4 P1 K3	5.86	0.61*
N1 P1 K1	28.75	0.26*	N5 P1 K1	21.85	0.14*	N3 P1 K2	5.77	0.59*
N1 P2 K1	28.63	0.23*	N2 P1 K3	21.79	0.13*	N4 P2 K3	5.75	0.58*
N2 P1 K3	28.35	0.17*	N5 P2 K3	21.69	0.11*	N1 P2 K3	5.73	0.57*
N5 P2 K3	27.42	0.04	N4 P2 K3	21.65	0.11*	N6 P2 K1	5.66	0.55*
N6 P1 K3	27.18	0.03	N2 P2 K1	21.51	0.09*	N1 P1 K2	5.54	0.50*
N5 P1 K1	26.88	0.02	N4 P2 K1	21.10	0.05	N5 P1 K1	5.50	0.49*
N2 P1 K1	26.53	0.01	N3 P2 K3	20.66	0.02	N1 P1 K3	5.38	0.44*
N1 P1 K3	26.29	0	N5 P1 K3	20.03	0.01	N2 P2 K1	5.17	0.36*
N5 P2 K2	26.29	0	N5 P2 K1	19.93	0.01	N1 P2 K2	5.09	0.33*
N1 P2 K3	26.13	0	N1 P1 K3	19.88	0.01	N3 P1 K3	5.07	0.33*
N6 P2 K2	25.99	0	N4 P1 K3	19.73	0	N5 P2 K2	5.01	0.31*
N5 P2 K1	25.76	0	N1 P2 K2	19.64	0	N5 P2 K1	4.87	0.26*
N4 P1 K2	25.63	0	N2 P2 K2	19.54	0	N1 P1 K1	4.86	0.26*
N2 P2 K2	25.32	0	N2 P1 K1	19.28	0	N1 P2 K1	4.56	0.18*
N1 P1 K2	25.24	0	N4 P1 K1	19.18	0	N6 P1 K2	4.52	0.17*
N2 P2 K3	24.91	0	N5 P2 K2	19.15	0	N4 P1 K2	4.52	0.17*
N3 P2 K2	24.80	0	N4 P2 K2	18.96	0	N3 P2 K2	4.48	0.16*
N5 P1 K2	24.77	0	N2 P2 K3	18.83	0	N6 P2 K2	4.22	0.11*
N4 P2 K1	24.65	0	N4 P1 K2	18.72	0	N3 P2 K3	4.13	0.10*
N3 P2 K1	24.57	0	N1 P2 K1	18.46	0	N4 P2 K2	4.03	0.08*
N2 P1 K2	24.47	0	N3 P2 K2	18.00	0	N3 P2 K1	4.00	0.08*
N5 P1 K3	24.23	0	N3 P1 K1	17.39	0	N2 P2 K2	3.94	0.07*
N3 P1 K3	24.02	0	N3 P1 K3	17.17	0	N3 P1 K1	3.66	0.04
N4 P1 K1	23.98	0	N6 P2 K2	16.93	0	N4 P1 K1	3.47	0.03
N3 P1 K2	23.82	0	N1 P1 K1	16.85	0	N5 P1 K2	3.44	0.03
N1 P2 K2	23.77	0	N1 P2 K3	16.54	0	N2 P2 K3	3.32	0.02
N3 P2 K3	23.66	0	N3 P1 K2	16.34	0	N2 P1 K1	3.26	0.02
N3 P1 K1	23.26	0	N3 P2 K1	16.31	0	N6 P1 K1	3.00	0.01
N6 P2 K3	22.80	0	N1 P1 K2	14.16	0	N2 P1 K2	0.97	0

* Fertiliser treatments within each salinity treatment group with significantly higher dry matter yields than the rest in the same group.

APPENDIX C Equilibrated mass distribution calculations for the S1 and S2 treatment soils with the MINTEQA2 (version 3.10) chemical speciation model (Allison *et al.*, 1991)

```
 PC MINTEQA2 v3.10

S1 TREATMENT SOIL

--------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed for all solids in the thermodynamic database and
   the print option for solids is set to: 2
 The maximum number of iterations is:  40
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

--------------------------------------------------------------------------------
 INPUT DATA

    330  0.000E-01   -6.10 y
    150  1.394E-01   -0.86 y
    460  6.492E-02   -1.19 y
    732  2.043E-01   -0.69 y
    580  1.140E-02   -1.94 y
     30  4.714E-03   -2.33 y

 H2O has been inserted as a COMPONENT
  3   1
    330      6.1000      0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

   ID        NAME        ACTIVITY GUESS    LOG GUESS   ANAL TOTAL
    330  H+1                  7.943E-07       -6.100   0.000E-01
    150  Ca+2                 1.380E-01       -0.860   1.394E-01
    460  Mg+2                 6.457E-02       -1.190   6.492E-02
    732  SO4-2                2.042E-01       -0.690   2.043E-01
    580  PO4-3                1.148E-02       -1.940   1.140E-02
     30  Al+3                 4.677E-03       -2.330   4.714E-03
      2  H2O                  1.000E+00        0.000   0.000E-01


     Charge Balance: UNSPECIATED

       Sum of CATIONS=  4.228E-01 Sum of ANIONS =  4.428E-01

       PERCENT DIFFERENCE =  2.313E+00  (ANIONS - CATIONS)/(ANIONS + CATIONS)
```

Type I - COMPONENTS AS SPECIES IN SOLUTION

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK
330	H+1	1.076E-06	7.943E-07	-6.10000	0.73851	0.132
150	Ca+2	2.871E-03	8.541E-04	-3.06850	0.29747	0.527
460	Mg+2	3.499E-02	1.041E-02	-1.98258	0.29747	0.527
732	SO4-2	5.667E-02	1.686E-02	-1.77320	0.29747	0.527
580	PO4-3	3.417E-11	2.233E-12	-11.65112	0.06535	1.185
30	Al+3	5.808E-11	3.796E-12	-11.42071	0.06535	1.185

Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK
3305801	H2PO4 -	6.816E-05	5.034E-05	-4.29812	0.73851	19.685
3305802	H3PO4	5.370E-09	5.609E-09	-8.25112	1.04451	21.681
3300020	OH-	1.700E-08	1.256E-08	-7.90115	0.73851	-13.866
4603300	MgOH +	2.896E-08	2.139E-08	-7.66984	0.73851	-11.652
4607320	MgSO4 AQ	2.987E-02	3.120E-02	-1.50578	1.04451	2.231
4605800	MgPO4 -	1.222E-07	9.022E-08	-7.04469	0.73851	6.721
4605801	MgH2PO4 +	2.312E-05	1.707E-05	-4.76769	0.73851	21.198
4605802	MgHPO4 AQ	2.934E-05	3.064E-05	-4.51369	1.04451	15.201
1503300	CaOH +	3.647E-10	2.694E-10	-9.56965	0.73851	-12.466
1507320	CaSO4 AQ	2.808E-03	2.933E-03	-2.53271	1.04451	2.290
1505800	CaHPO4 AQ	1.764E-06	1.842E-06	-5.73462	1.04451	15.066
1505801	CaPO4 -	7.431E-09	5.488E-09	-8.26062	0.73851	6.591
1505802	CaH2PO4 +	1.486E-06	1.097E-06	-5.95962	0.73851	21.092
303300	AlOH +2	1.632E-10	4.855E-11	-10.31385	0.29747	-4.463
303301	Al(OH)2 +	6.377E-10	4.710E-10	-9.32700	0.73851	-9.968
303302	Al(OH)4 -	1.254E-10	9.262E-11	-10.03329	0.73851	-22.868
307320	AlSO4 +	9.073E-11	6.700E-11	-10.17391	0.73851	3.152
307321	Al(SO4)2 -	1.215E-10	8.972E-11	-10.04712	0.73851	5.052
303303	Al(OH)3 AQ	7.095E-10	7.411E-10	-9.13015	1.04451	-16.019
3307320	HSO4 -	1.760E-06	1.300E-06	-5.88614	0.73851	2.119
3305800	HPO4 -2	1.323E-05	3.934E-06	-5.40512	0.29747	12.873

Type III - SPECIES WITH FIXED ACTIVITY

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
2	H2O	-2.431E-01	-0.614	0.003	0.000
330	H+1	1.766E-02	-1.753	6.100	0.000

Type IV - FINITE SOLIDS (present at equilibrium)

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
2003002	DIASPORE	4.714E-03	-2.327	-6.873	24.630
7015003	HYDRAPATITE	3.755E-03	-2.425	44.199	0.000
6015001	GYPSUM	1.149E-01	-0.940	4.848	-0.261

----------- EQUILIBRATED MASS DISTRIBUTION -----------

IDX	NAME	DISSOLVED		SORBED		PRECIPITATED	
		MOL/KG	PERCENT	MOL/KG	PERCENT	MOL/KG	PERCENT
580	PO4-3	1.372E-04	1.2	0.000E-01	0.0	1.126E-02	98.8
460	Mg+2	6.492E-02	100.0	0.000E-01	0.0	0.000E-01	0.0
732	SO4-2	8.936E-02	43.7	0.000E-01	0.0	1.149E-01	56.3
150	Ca+2	5.682E-03	4.1	0.000E-01	0.0	1.337E-01	95.9
30	Al+3	1.906E-09	0.0	0.000E-01	0.0	4.714E-03	100.0
330	H+1	2.327E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
2	H2O	5.040E-08	100.0	0.000E-01	0.0	0.000E-01	0.0

Charge Balance: SPECIATED

Sum of CATIONS = 7.576E-02 Sum of ANIONS 1.134E-01

PERCENT DIFFERENCE = 1.992E+01 (ANIONS - CATIONS)/(ANIONS + CATIONS)

EQUILIBRIUM IONIC STRENGTH (m) = 1.891E-01

EQUILIBRIUM pH = 6.100

S2 TREATMENT SOILS

Temperature (Celsius): 25.00
Units of concentration: MOLAL
Ionic strength to be computed.
If specified, carbonate concentration represents total inorganic carbon.
Do not automatically terminate if charge imbalance exceeds 30%
Precipitation is allowed for all solids in the thermodynamic database and
the print option for solids is set to: 2
The maximum number of iterations is: 40
The method used to compute activity coefficients is: Davies equation
Intermediate output file

INPUT DATA

330	0.000E-01	-6.10	y
150	2.791E-01	-0.55	y
460	1.298E-01	-0.89	y
732	4.089E-01	-0.39	y
580	2.282E-02	-1.64	y
30	9.429E-03	-2.03	y

H2O has been inserted as a COMPONENT
330 6.1000 0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	NAME	ACTIVITY GUESS	LOG GUESS	ANAL TOTAL
330	H+1	7.943E-07	-6.100	0.000E-01
150	Ca+2	2.818E-01	-0.550	2.791E-01
460	Mg+2	1.288E-01	-0.890	1.298E-01
732	SO4-2	4.074E-01	-0.390	4.089E-01
580	PO4-3	2.291E-02	-1.640	2.282E-02
30	Al+3	9.333E-03	-2.030	9.429E-03
2	H2O	1.000E+00	0.000	0.000E-01

Charge Balance: UNSPECIATED

Sum of CATIONS= 8.461E-01 Sum of ANIONS = 8.863E-01

PERCENT DIFFERENCE = 2.319E+00 (ANIONS - CATIONS)/(ANIONS + CATIONS)

Type I - COMPONENTS AS SPECIES IN SOLUTION

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK
330	H+1	1.111E-06	7.943E-07	-6.10000	0.71488	0.146
150	Ca+2	2.129E-03	5.562E-04	-3.25479	0.26118	0.583
460	Mg+2	6.082E-02	1.588E-02	-1.79902	0.26118	0.583
732	SO4-2	1.006E-01	2.627E-02	-1.58056	0.26118	0.583
580	PO4-3	9.383E-11	4.575E-12	-11.33957	0.04876	1.312
30	Al+3	7.898E-11	3.852E-12	-11.41436	0.04876	1.312

Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK
3305801	H2PO4 -	1.443E-04	1.031E-04	-3.98657	0.71488	19.699
3305802	H3PO4	1.066E-08	1.149E-08	-7.93957	1.07825	21.667
3300020	OH-	1.744E-08	1.246E-08	-7.90432	0.71488	-13.852
4603300	MgOH +	4.532E-08	3.240E-08	-7.48945	0.71488	-11.638
4607320	MgSO4 AQ	6.882E-02	7.420E-02	-1.12958	1.07825	2.217
4605800	MgPO4 -	3.946E-07	2.821E-07	-6.54959	0.71488	6.735
4605801	MgH2PO4 +	7.468E-05	5.338E-05	-4.27259	0.71488	21.212
4605802	MgHPO4 AQ	8.886E-05	9.581E-05	-4.01859	1.07825	15.187
1503300	CaOH +	2.436E-10	1.741E-10	-9.75912	0.71488	-12.452
1507320	CaSO4 AQ	2.760E-03	2.976E-03	-2.52636	1.07825	2.276
1505800	CaHPO4 AQ	2.280E-06	2.458E-06	-5.60936	1.07825	15.052
1505801	CaPO4 -	1.024E-08	7.322E-09	-8.13536	0.71488	6.605
1505802	CaH2PO4 +	2.048E-06	1.464E-06	-5.83436	0.71488	21.106
303300	AlOH +2	1.872E-10	4.890E-11	-10.31068	0.26118	-4.407
303301	Al(OH)2 +	6.588E-10	4.710E-10	-9.32700	0.71488	-9.954
303302	Al(OH)4 -	1.277E-10	9.128E-11	-10.03964	0.71488	-22.854
307320	AlSO4 +	1.482E-10	1.059E-10	-9.97492	0.71488	3.166
307321	Al(SO4)2 -	3.092E-10	2.211E-10	-9.65548	0.71488	5.066
303303	Al(OH)3 AQ	6.823E-10	7.357E-10	-9.13332	1.07825	-16.033
3307320	HSO4 -	2.833E-06	2.025E-06	-5.69350	0.71488	2.133
3305800	HPO4 -2	3.087E-05	8.062E-06	-5.09357	0.26118	12.929

Type III - SPECIES WITH FIXED ACTIVITY

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
2	H2O	-4.998E-01	-0.301	0.006	0.000
330	H+1	3.521E-02	-1.453	6.100	0.000

Type IV - FINITE SOLIDS (present at equilibrium)

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
2003002	DIASPORE	9.429E-03	-2.026	-6.873	24.630
7015003	HYDRAPATITE	7.493E-03	-2.125	44.199	0.000
6015001	GYPSUM	2.367E-01	-0.626	4.848	-0.261

----------- EQUILIBRATED MASS DISTRIBUTION -----------

IDX	NAME	DISSOLVED		SORBED		PRECIPITATED	
		MOL/KG	PERCENT	MOL/KG	PERCENT	MOL/KG	PERCENT
580	PO4-3	3.434E-04	1.5	0.000E-01	0.0	2.248E-02	98.5
460	Mg+2	1.298E-01	100.0	0.000E-01	0.0	0.000E-01	0.0
732	SO4-2	1.722E-01	42.1	0.000E-01	0.0	2.367E-01	57.9
150	Ca+2	4.894E-03	1.8	0.000E-01	0.0	2.742E-01	98.2
30	Al+3	2.192E-09	0.0	0.000E-01	0.0	9.429E-03	100.0
330	H+1	5.679E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
2	H2O	6.706E-08	100.0	0.000E-01	0.0	0.000E-01	0.0

Charge Balance: SPECIATED

Sum of CATIONS = 1.260E-01 Sum of ANIONS 2.014E-01

PERCENT DIFFERENCE = 2.303E+01 (ANIONS - CATIONS)/(ANIONS + CATIONS)

EQUILIBRIUM IONIC STRENGTH (m) = 3.272E-01

EQUILIBRIUM pH = 6.100

APPENDIX D Soil saturation extract analysis data

Treatment no.	Salinity Treatment	Fertiliser Treatment	pH (H_2O)	EC	Bray I P	Ammonium acetate extractable cations				SO_4
						Ca	K	Mg	Na	
				mS m^{-1}	mg kg^{-1}					
1	S0	N1:P1:K1	6.70	68	12.3	753	57	654	7	400
2	S0	N2:P1:K1	6.36	88	15.2	693	78	483	3	653
3	S0	N1:P1:K2	6.42	110	9.9	711	57	556	0	788
4	S0	N2:P1:K2	6.40	146	12.8	729	92	541	4	962
5	S0	N1:P2:K1	6.19	140	21.8	822	100	638	6	1398
6	S0	N2:P2:K1	6.19	103	20.5	658	98	469	13	509
7	S0	N1:P2:K2	6.60	82	36.3	844	62	523	7	510
8	S0	N2:P2:K2	6.27	131	13.6	729	57	560	15	784
9	S0	N1:P1:K3	6.55	90	19.0	722	93	531	9	492
10	S0	N2:P1:K3	6.50	111	12.7	760	72	637	8	479
11	S0	N1:P2:K3	6.16	62	13.8	663	66	475	5	327
12	S0	N2:P2:K3	6.57	112	12.9	706	53	566	13	180
13	S0	N3:P1:K1	5.92	80	12.3	707	54	561	10	434
14	S0	N4:P1:K1	5.90	109	16.0	714	67	478	3	639
15	S0	N3:P1:K2	6.21	122	14.2	706	73	496	4	1100
16	S0	N4:P1:K2	5.95	89	10.9	630	55	462	10	490
17	S0	N3:P2:K1	5.75	58	10.6	551	44	445	11	318
18	S0	N4:P2:K1	5.77	100	11.9	593	51	452	5	559
19	S0	N3:P2:K2	6.09	118	12.6	666	56	496	12	614
20	S0	N4:P2:K2	6.32	109	13.8	672	68	499	25	544
21	S0	N3:P1:K3	6.05	76	11.6	758	63	545	23	472
22	S0	N4:P1:K3	6.08	69	34.0	696	53	475	4	372
23	S0	N3:P2:K3	6.02	89	16.2	684	75	467	4	521
24	S0	N4:P2:K3	6.18	113	20.8	714	87	511	0	506
25	S0	N5:P1:K1	6.27	121	21.4	746	66	483	0	496
26	S0	N6:P1:K1	6.47	107	39.6	891	49	473	11	451
27	S0	N5:P1:K2	6.23	101	17.1	710	65	482	7	389

Treatment no.	Salinity Treatment	Fertiliser Treatment	pH (H_2O)	EC	Bray I P	Ammonium acetate extractable cations				SO_4
						Ca	K	Mg	Na	
				mS m^{-1}	mg kg^{-1}					
28	S0	N6:P1:K2	5.92	120	19.7	696	62	452	12	618
29	S0	N5:P2:K1	6.17	111	20.6	713	74	477	9	477
30	S0	N6:P2:K1	6.32	83	36.3	791	60	480	9	494
31	S0	N5:P2:K2	6.49	78	25.0	743	47	537	8	521
32	S0	N6:P2:K2	6.31	84	22.1	684	51	524	0	360
33	S0	N5:P1:K3	6.06	75	16.4	693	51	508	0	419
34	S0	N6:P1:K3	6.19	88	14.4	816	89	492	13	400
35	S0	N5:P2:K3	5.97	102	14.4	724	51	538	8	484
36	S0	N6:P2:K3	6.15	77	12.3	721	52	557	7	580
37	S1	N1:P1:K1	5.99	761	40.9	5847	60	1943	18	18225
38	S1	N2:P1:K1	6.12	765	43.6	6187	73	1811	9	19925
39	S1	N1:P1:K2	6.11	749	37.5	5518	64	2021	14	23975
40	S1	N2:P1:K2	6.17	723	54.9	6327	117	2025	8	20025
41	S1	N1:P2:K1	6.00	815	56.9	5878	119	1997	8	19875
42	S1	N2:P2:K1	6.07	667	48.3	5798	86	1763	16	19650
43	S1	N1:P2:K2	6.40	379	64.6	4938	64	975	9	18750
44	S1	N2:P2:K2	6.10	472	46.9	5798	62	1123	8	15075
45	S1	N1:P1:K3	6.26	711	52.9	6438	101	1757	12	19550
46	S1	N2:P1:K3	6.19	724	40.5	6558	69	1967	17	19275
47	S1	N1:P2:K3	6.20	750	47.1	6218	75	2043	9	18775
48	S1	N2:P2:K3	6.27	756	41.9	5998	66	2179	18	24150
49	S1	N3:P1:K1	6.21	568	40.8	6198	67	2379	13	25500
50	S1	N4:P1:K1	6.22	684	42.4	5118	64	2359	14	21750
51	S1	N3:P1:K2	6.31	700	45.7	10538	68	2025	10	18900
52	S1	N4:P1:K2	6.19	738	45.9	5678	58	2175	12	20775
53	S1	N3:P2:K1	6.17	879	50.9	6378	51	2107	15	19825
54	S1	N4:P2:K1	6.00	805	50.6	5918	58	2083	10	24325
55	S1	N3:P2:K2	6.00	796	47.9	5998	64	2111	12	22550

Treatment no.	Salinity Treatment	Fertiliser Treatment	pH (H_2O)	EC	Bray I P	Ammonium acetate extractable cations				SO_4
						Ca	K	Mg	Na	
				mS m^{-1}	mg kg^{-1}					
56	S1	N4:P2:K2	6.26	598	42.8	6918	52	2153	7	20750
57	S1	N3:P1:K3	6.17	752	44.7	6378	76	2141	15	24230
58	S1	N4:P1:K3	6.03	692	60.9	6498	51	2057	9	21905
59	S1	N3:P2:K3	6.14	740	47.8	5638	84	1979	14	21270
60	S1	N4:P2:K3	6.12	680	49.6	7238	93	2159	20	22150
61	S1	N5:P1:K1	6.25	686	59.8	6198	62	2055	12	29155
62	S1	N6:P1:K1	6.17	713	51.9	6498	73	2191	11	24040
63	S1	N5:P1:K2	5.93	619	60.9	6498	61	1971	0	23845
64	S1	N6:P1:K2	6.12	746	61.3	7478	81	2101	7	23800
65	S1	N5:P2:K1	6.30	749	73.6	7258	87	2105	20	23075
66	S1	N6:P2:K1	6.11	721	96.5	7898	54	2153	7	23470
67	S1	N5:P2:K2	6.29	762	60.2	6278	63	2087	15	23755
68	S1	N6:P2:K2	5.61	779	66.3	5658	60	2299	15	27245
69	S1	N5:P1:K3	6.12	711	51.4	6118	90	1979	6	21495
70	S1	N6:P1:K3	5.85	752	48.3	5918	51	2005	7	24405
71	S1	N5:P2:K3	5.92	800	55.9	5598	64	2043	15	21955
72	S1	N6:P2:K3	6.07	727	49.7	6158	63	2017	15	24195
73	S2	N1:P1:K1	6.03	1435	66.1	9658	135	3879	14	47670
74	S2	N2:P1:K1	6.03	1401	67.1	8398	195	3479	17	47030
75	S2	N1:P1:K2	6.11	1775	58.5	9578	104	4479	15	50690
76	S2	N2:P1:K2	6.31	1412	81.6	10297	267	3119	6	45210
77	S2	N1:P2:K1	6.05	1261	74.4	10857	211	3159	20	46980
78	S2	N2:P2:K1	6.05	1475	82.6	10517	125	3479	11	50440
79	S2	N1:P2:K2	6.32	1344	85.9	11137	143	3359	26	49610
80	S2	N2:P2:K2	6.15	1545	67.4	10817	173	3579	49	47900
81	S2	N1:P1:K3	6.30	1395	75.3	10917	205	3379	16	48030
82	S2	N2:P1:K3	6.23	1323	59.5	10917	135	3399	10	52680
83	S2	N1:P2:K3	5.91	1405	63.4	10597	131	3919	6	48510
84	S2	N2:P2:K3	6.22	1560	56.8	10837	181	3719	18	53000

Treatment no.	Salinity Treatment	Fertiliser Treatment	pH (H_2O)	EC	Bray I P	Ammonium acetate extractable cations				SO_4
						Ca	K	Mg	Na	
				mS m^{-1}	mg kg^{-1}					
85	S2	N3:P1:K1	6.04	1540	57.4	10497	121	3479	14	50670
86	S2	N4:P1:K1	6.06	1425	65.2	10637	167	3199	16	45740
87	S2	N3:P1:K2	6.04	1560	67.4	10917	153	3359	16	48940
88	S2	N4:P1:K2	5.70	1466	63.9	11517	121	3279	10	45570
89	S2	N3:P2:K1	5.58	1665	67.7	10397	109	3979	26	47750
90	S2	N4:P2:K1	5.89	1740	70.8	10677	137	3439	9	43880
91	S2	N3:P2:K2	6.05	1575	62.4	9837	157	3479	29	39960
92	S2	N4:P2:K2	6.17	1715	69.7	9777	165	3259	14	41730
93	S2	N3:P1:K3	6.03	1475	66.9	10017	151	3379	0	44710
94	S2	N4:P1:K3	6.12	1355	99.1	9897	157	3499	11	42120
95	S2	N3:P2:K3	6.13	1510	81.7	9677	219	3479	9	40810
96	S2	N4:P2:K3	6.15	1505	78.9	10597	221	3479	21	43430
97	S2	N5:P1:K1	6.38	1590	102.8	11737	155	3739	24	46440
98	S2	N6:P1:K1	6.00	1550	62.7	8817	145	3419	14	45180
99	S2	N5:P1:K2	5.93	1650	73.9	12717	195	3239	16	48770
100	S2	N6:P1:K2	5.79	1555	82.9	10417	193	3479	26	43050
101	S2	N5:P2:K1	6.07	1540	85.9	9577	147	3279	12	42050
102	S2	N6:P2:K1	6.12	1395	102.9	11777	155	3459	21	44280
103	S2	N5:P2:K2	6.23	1220	80.4	11517	127	3459	21	45630
104	S2	N6:P2:K2	6.00	1310	73.3	10977	139	3439	18	45870
105	S2	N5:P1:K3	6.17	1455	77.8	10217	203	3479	24	39530
106	S2	N6:P1:K3	5.85	1265	66.4	10137	127	3519	20	39940
107	S2	N5:P2:K3	6.00	1485	65.1	9017	133	3719	23	45530
108	S2	N6:P2:K3	6.09	1215	66.4	9197	123	3239	14	41060

APPENDIX E Soil analysis data: soluble and exchangeable cations

Treatment no.	Salinity Treatment	Fertiliser Treatment	Soluble cations				Exchangeable cations			
			Ca	K	Mg	Na	Ca	K	Mg	Na
			$cmol_c\ kg^{-1}$				$cmol_c\ kg^{-1}$			
1	S0	N1:P1:K1	0.196	0.002	0.206	0.007	7.335	0.143	5.175	0.042
2	S0	N2:P1:K1	0.316	0.003	0.261	0.006	6.615	0.197	3.713	0.026
3	S0	N1:P1:K2	0.349	0.002	0.396	0.007	6.762	0.143	4.179	0.010
4	S0	N2:P1:K2	0.575	0.005	0.574	0.008	6.716	0.231	3.877	0.030
5	S0	N1:P2:K1	0.218	0.015	1.441	0.034	7.001	0.242	3.808	0.011
6	S0	N2:P2:K1	0.324	0.005	0.333	0.006	6.259	0.247	3.525	0.070
7	S0	N1:P2:K2	0.270	0.002	0.201	0.006	8.168	0.157	4.102	0.042
8	S0	N2:P2:K2	0.432	0.003	0.466	0.008	6.859	0.144	4.141	0.077
9	S0	N1:P1:K3	0.267	0.004	0.217	0.006	6.954	0.235	4.151	0.054
10	S0	N2:P1:K3	0.359	0.004	0.434	0.030	7.241	0.180	4.807	0.025
11	S0	N1:P2:K3	0.173	0.002	0.137	0.006	6.460	0.167	3.771	0.035
12	S0	N2:P2:K3	0.305	0.002	0.350	0.006	6.757	0.135	4.307	0.071
13	S0	N3:P1:K1	0.207	0.002	0.189	0.007	6.865	0.137	4.426	0.058
14	S0	N4:P1:K1	0.293	0.003	0.250	0.008	6.849	0.168	3.682	0.024
15	S0	N3:P1:K2	0.330	0.003	0.349	0.006	6.731	0.184	3.732	0.032
16	S0	N4:P1:K2	0.246	0.002	0.199	0.006	6.057	0.138	3.602	0.057
17	S0	N3:P2:K1	0.142	0.001	0.122	0.006	5.372	0.112	3.539	0.059
18	S0	N4:P2:K1	0.249	0.002	0.219	0.005	5.685	0.128	3.500	0.036
19	S0	N3:P2:K2	0.297	0.002	0.279	0.008	6.365	0.140	3.802	0.064
20	S0	N4:P2:K2	0.252	0.002	0.216	0.005	6.470	0.172	3.889	0.344
21	S0	N3:P1:K3	0.197	0.002	0.176	0.006	7.383	0.159	4.308	0.274
22	S0	N4:P1:K3	0.186	0.001	0.135	0.005	6.775	0.135	3.773	0.031
23	S0	N3:P2:K3	0.280	0.003	0.237	0.006	6.561	0.190	3.605	-0.013
24	S0	N4:P2:K3	0.357	0.004	0.379	0.007	6.784	0.218	3.825	0.014
25	S0	N5:P1:K1	0.343	0.003	0.339	0.007	7.117	0.166	3.635	0.012
26	S0	N6:P1:K1	0.313	0.001	0.220	0.006	8.595	0.123	3.671	0.060
27	S0	N5:P1:K2	0.280	0.002	0.233	0.006	6.821	0.163	3.732	0.045

Treatment no.	Salinity Treatment	Fertiliser Treatment	Soluble cations				Exchangeable cations			
			Ca	K	Mg	Na	Ca	K	Mg	Na
			$cmol_c\ kg^{-1}$				$cmol_c\ kg^{-1}$			
28	S0	N6:P1:K2	0.362	0.003	1.931	0.007	6.599	0.155	1.787	0.065
29	S0	N5:P2:K1	0.327	0.003	0.282	0.007	6.804	0.185	3.643	0.051
30	S0	N6:P2:K1	0.262	0.002	0.192	0.006	7.648	0.152	3.757	0.051
31	S0	N5:P2:K2	0.201	0.001	0.166	0.004	7.230	0.118	4.252	0.052
32	S0	N6:P2:K2	0.219	0.002	0.198	0.006	6.623	0.129	4.113	0.011
33	S0	N5:P1:K3	0.205	0.002	0.172	0.005	6.727	0.129	4.007	0.014
34	S0	N6:P1:K3	0.230	0.003	0.191	0.006	7.929	0.223	3.857	0.069
35	S0	N5:P2:K3	0.293	0.002	0.267	0.006	6.948	0.130	4.159	0.047
36	S0	N6:P2:K3	0.188	0.002	0.165	0.004	7.023	0.130	4.418	0.045
37	S1	N1:P1:K1	0.784	0.009	7.469	0.015	28.393	0.144	8.521	0.081
38	S1	N2:P1:K1	0.910	0.010	9.371	0.017	29.964	0.177	5.533	0.040
39	S1	N1:P1:K2	1.028	0.010	7.232	0.013	26.505	0.154	9.398	0.049
40	S1	N2:P1:K2	1.006	0.019	7.080	0.013	30.566	0.280	9.585	0.041
41	S1	N1:P2:K1	1.022	0.022	7.904	0.015	28.307	0.281	8.529	0.018
42	S1	N2:P2:K1	0.913	0.011	5.735	0.013	28.018	0.208	8.772	0.056
43	S1	N1:P2:K2	1.087	0.007	2.747	0.007	23.552	0.155	5.274	0.034
44	S1	N2:P2:K2	1.074	0.009	3.542	0.010	27.857	0.151	5.698	0.024
45	S1	N1:P1:K3	1.055	0.016	6.925	0.016	31.069	0.241	7.533	0.036
46	S1	N2:P1:K3	1.198	0.012	7.276	0.018	31.524	0.165	8.910	0.057
47	S1	N1:P2:K3	1.063	0.012	7.553	0.015	29.963	0.181	9.259	0.025
48	S1	N2:P2:K3	1.104	0.011	8.776	0.017	28.824	0.158	9.155	0.060
49	S1	N3:P1:K1	0.535	0.007	5.733	0.011	30.391	0.164	13.844	0.044
50	S1	N4:P1:K1	0.238	0.005	2.382	0.006	25.299	0.158	17.030	0.056
51	S1	N3:P1:K2	0.567	0.007	5.310	0.012	52.016	0.167	11.354	0.032
52	S1	N4:P1:K2	0.676	0.007	6.088	0.012	27.655	0.141	11.810	0.042
53	S1	N3:P2:K1	0.719	0.008	8.231	0.016	31.106	0.122	9.107	0.049
54	S1	N4:P2:K1	0.699	0.010	7.236	0.015	28.830	0.139	9.905	0.028
55	S1	N3:P2:K2	0.839	0.009	7.085	0.017	29.089	0.155	10.287	0.033
56	S1	N4:P2:K2	0.677	0.007	6.295	0.015	33.842	0.126	11.422	0.015

Treatment no.	Salinity Treatment	Fertiliser Treatment	Soluble cations				Exchangeable cations			
			Ca	K	Mg	Na	Ca	K	Mg	Na
			cmol$_c$ kg^{-1}				cmol$_c$ kg^{-1}			
57	S1	N3:P1:K3	0.795	0.009	5.993	0.014	31.029	0.187	11.625	0.051
58	S1	N4:P1:K3	0.718	0.007	6.231	0.012	31.705	0.123	10.696	0.026
59	S1	N3:P2:K3	0.746	0.010	6.868	0.016	27.386	0.204	9.417	0.044
60	S1	N4:P2:K3	0.739	0.011	6.476	0.015	35.376	0.227	11.290	0.072
61	S1	N5:P1:K1	0.812	0.008	6.675	0.016	30.115	0.152	10.235	0.037
62	S1	N6:P1:K1	0.752	0.009	6.709	0.014	31.671	0.179	11.321	0.032
63	S1	N5:P1:K2	0.985	0.010	7.755	0.022	31.438	0.144	8.464	0.023
64	S1	N6:P1:K2	0.861	0.011	7.902	0.015	36.452	0.194	9.387	0.017
65	S1	N5:P2:K1	0.778	0.011	7.222	0.015	35.438	0.212	10.099	0.071
66	S1	N6:P2:K1	0.712	0.007	7.001	0.014	38.697	0.130	10.715	0.018
67	S1	N5:P2:K2	0.581	0.008	6.445	0.012	30.744	0.153	10.728	0.052
68	S1	N6:P2:K2	0.819	0.009	8.531	0.018	27.412	0.145	10.387	0.045
69	S1	N5:P1:K3	0.820	0.012	7.381	0.015	29.707	0.218	8.904	0.009
70	S1	N6:P1:K3	0.826	0.007	7.811	0.018	28.703	0.123	8.688	0.013
71	S1	N5:P2:K3	0.844	0.009	7.948	0.018	27.088	0.154	8.864	0.046
72	S1	N6:P2:K3	0.885	0.009	8.318	0.021	29.842	0.153	8.279	0.042
73	S2	N1:P1:K1	0.723	0.034	18.205	0.046	47.469	0.311	13.718	0.013
74	S2	N2:P1:K1	0.753	0.062	18.335	0.042	41.151	0.436	10.295	0.030
75	S2	N1:P1:K2	0.790	0.024	23.988	0.044	47.002	0.241	12.872	0.020
76	S2	N2:P1:K2	0.707	0.088	16.940	0.035	50.673	0.595	8.730	0.023
77	S2	N1:P2:K1	0.770	0.061	17.010	0.039	53.405	0.479	8.988	0.079
78	S2	N2:P2:K1	0.680	0.025	18.148	0.039	51.798	0.295	10.484	0.040
79	S2	N1:P2:K2	0.730	0.029	17.232	0.039	54.841	0.337	10.412	0.105
80	S2	N2:P2:K2	0.787	0.041	20.530	0.043	53.188	0.402	8.925	0.200
81	S2	N1:P1:K3	0.737	0.057	17.661	0.041	53.737	0.468	10.148	0.061
82	S2	N2:P1:K3	0.865	0.030	18.235	0.046	53.609	0.316	9.739	0.028
83	S2	N1:P2:K3	0.763	0.039	18.077	0.041	52.114	0.296	14.176	0.016
84	S2	N2:P2:K3	0.821	0.046	22.292	0.045	53.253	0.417	8.315	0.062
85	S2	N3:P1:K1	0.733	0.024	19.888	0.039	51.645	0.286	8.745	0.051

Treatment no.	Salinity Treatment	Fertiliser Treatment	Soluble cations				Exchangeable cations			
			Ca	K	Mg	Na	Ca	K	Mg	Na
			$cmol_c$ kg^{-1}				$cmol_c$ kg^{-1}			
86	S2	N4:P1:K1	0.703	0.036	16.505	0.039	52.374	0.391	9.822	0.060
87	S2	N3:P1:K2	0.795	0.034	21.847	0.045	53.679	0.358	5.797	0.055
88	S2	N4:P1:K2	0.845	0.032	22.792	0.054	56.623	0.278	4.194	0.021
89	S2	N3:P2:K1	0.770	0.024	25.256	0.054	51.110	0.255	7.491	0.089
90	S2	N4:P2:K1	0.707	0.023	20.979	0.046	52.569	0.328	7.324	0.026
91	S2	N3:P2:K2	0.898	0.044	25.731	0.053	48.187	0.358	2.901	0.073
92	S2	N4:P2:K2	0.783	0.037	16.830	0.044	48.002	0.385	9.992	0.048
93	S2	N3:P1:K3	0.987	0.036	18.847	0.051	48.996	0.351	8.962	0.027
94	S2	N4:P1:K3	0.887	0.030	17.842	0.043	48.497	0.372	10.954	0.037
95	S2	N3:P2:K3	0.907	0.069	21.524	0.048	47.379	0.491	7.108	0.024
96	S2	N4:P2:K3	0.937	0.073	22.722	0.056	51.940	0.493	5.910	0.068
97	S2	N5:P1:K1	0.958	0.034	23.057	0.055	57.608	0.363	7.715	0.078
98	S2	N6:P1:K1	0.863	0.041	24.248	0.056	43.132	0.330	3.890	0.034
99	S2	N5:P1:K2	0.665	0.057	19.249	0.049	62.791	0.443	7.407	0.053
100	S2	N6:P1:K2	0.602	0.048	18.519	0.048	51.377	0.446	10.113	0.096
101	S2	N5:P2:K1	0.734	0.032	17.853	0.042	47.053	0.345	9.133	0.039
102	S2	N6:P2:K1	0.867	0.044	16.826	0.048	57.898	0.353	11.642	0.074
103	S2	N5:P2:K2	0.981	0.024	13.465	0.041	56.487	0.302	15.002	0.081
104	S2	N6:P2:K2	0.867	0.027	13.906	0.041	53.906	0.329	14.397	0.066
105	S2	N5:P1:K3	0.761	0.045	16.964	0.049	50.220	0.475	11.668	0.085
106	S2	N6:P1:K3	0.701	0.022	17.303	0.047	49.881	0.303	11.659	0.073
107	S2	N5:P2:K3	0.780	0.032	21.462	0.051	44.213	0.309	9.146	0.079
108	S2	N6:P2:K3	0.862	0.024	16.315	0.044	45.029	0.291	10.342	0.048

APPENDIX F Analysis data of nutrients in maize plants

Tmt. No.	Salinity treatment	Fertiliser treatment	Nutrient concentration in plant										
			N	P	K	Ca	Mg	Na	SO_4	Cu	Fe	Mn	Zn
			%							mg kg^{-1}			
1	S0	N1:P1:K1	0.74	0.16	1.90	0.23	0.37	0.006	0.16	12	51	27	45
2	S0	N2:P1:K1	0.94	0.16	2.01	0.63	0.23	0.008	0.20	6	93	21	27
3	S0	N1:P1:K2	0.62	0.14	1.98	0.26	0.32	0.004	0.23	12	12	29	29
4	S0	N2:P1:K2	0.63	0.12	2.30	0.53	0.31	0.004	0.12	2	39	41	128
5	S0	N1:P2:K1	0.55	0.13	2.49	0.25	0.25	0.005	0.24	14	27	32	33
6	S0	N2:P2:K1	0.82	0.15	2.05	0.26	0.22	0.004	0.09	3	29	39	18
7	S0	N1:P2:K2	0.78	0.17	1.51	0.28	0.33	0.005	0.13	6	47	26	12
8	S0	N2:P2:K2	0.60	0.11	1.79	0.23	0.34	0.006	0.15	6	14	27	24
9	S0	N1:P1:K3	0.55	0.12	2.41	0.25	0.21	0.004	0.15	2	87	26	134
10	S0	N2:P1:K3	0.80	0.12	1.99	0.28	0.38	0.003	0.19	2	20	21	27
11	S0	N1:P2:K3	0.68	0.13	2.05	0.25	0.27	0.004	0.18	3	57	35	17
12	S0	N2:P2:K3	0.75	0.14	2.12	0.26	0.29	0.004	0.23	2	57	23	48
13	S0	N3:P1:K1	0.86	0.16	1.39	0.29	0.38	0.004	0.16	3	99	32	15
14	S0	N4:P1:K1	0.94	0.14	1.78	0.33	0.33	0.004	0.21	5	75	45	18
15	S0	N3:P1:K2	0.89	0.14	2.02	0.25	0.24	0.004	0.17	3	69	30	11
16	S0	N4:P1:K2	0.88	0.12	1.51	0.29	0.31	0.006	0.15	6	54	38	11
17	S0	N3:P2:K1	0.64	0.12	1.57	0.25	0.38	0.004	0.14	3	42	66	21
18	S0	N4:P2:K1	0.64	0.18	1.65	0.28	0.34	0.004	0.18	2	65	54	17
19	S0	N3:P2:K2	0.70	0.21	2.20	0.26	0.30	0.004	0.26	3	45	32	29
20	S0	N4:P2:K2	0.74	0.20	2.14	0.27	0.29	0.003	0.25	2	24	29	15
21	S0	N3:P1:K3	0.72	0.21	2.06	0.27	0.34	0.004	0.24	3	29	23	21
22	S0	N4:P1:K3	0.63	0.20	1.96	0.24	0.30	0.003	0.18	0	3	21	12
23	S0	N3:P2:K3	0.66	0.16	2.44	0.22	0.24	0.004	0.15	2	8	33	20
24	S0	N4:P2:K3	0.74	0.15	2.47	0.23	0.25	0.004	0.22	14	14	26	21
25	S0	N5:P1:K1	0.72	0.19	2.23	0.29	0.28	0.004	0.25	5	15	23	33
26	S0	N6:P1:K1	0.92	0.17	1.33	0.74	0.42	0.007	0.32	2	56	26	11
27	S0	N5:P1:K2	0.87	0.18	1.79	0.63	0.29	0.007	0.25	2	56	26	15
28	S0	N6:P1:K2	1.02	0.15	1.97	0.29	0.34	0.004	0.34	2	102	36	15

Tmt. No.	Salinity treatment	Fertiliser treatment	Nutrient concentration in plant										
			N	P	K	Ca	Mg	Na	SO_4	Cu	Fe	Mn	Zn
			%							mg kg^{-1}			
29	S0	N5:P2:K1	1.07	0.16	1.73	0.22	0.26	0.006	0.19	9	84	30	17
30	S0	N6:P2:K1	0.98	0.17	1.45	0.27	0.37	0.004	0.24	3	48	30	6
31	S0	N5:P2:K2	0.87	0.17	1.48	0.24	0.37	0.004	0.26	9	53	27	29
32	S0	N6:P2:K2	1.03	0.15	1.75	0.28	0.37	0.004	0.36	2	72	30	15
33	S0	N5:P1:K3	0.75	0.18	1.86	0.27	0.34	0.004	0.35	3	20	35	20
34	S0	N6:P1:K3	0.98	0.17	2.06	0.25	0.30	0.005	0.34	3	54	33	26
35	S0	N5:P2:K3	0.91	0.13	1.61	0.27	0.33	0.006	0.27	9	62	36	18
36	S0	N6:P2:K3	0.99	0.19	1.81	0.59	0.28	0.007	0.39	3	47	20	17
37	S1	N1:P1:K1	0.93	0.21	2.37	0.10	0.56	0.003	0.95	2	18	24	30
38	S1	N2:P1:K1	1.03	0.20	1.88	0.13	0.66	0.004	1.29	6	89	26	23
39	S1	N1:P1:K2	0.85	0.17	2.08	0.12	0.72	0.004	1.43	3	8	42	30
40	S1	N2:P1:K2	0.79	0.18	3.03	0.11	0.59	0.004	1.20	0	41	27	41
41	S1	N1:P2:K1	0.95	0.21	3.15	0.14	0.61	0.003	1.35	2	20	29	21
42	S1	N2:P2:K1	1.08	0.17	2.15	0.15	0.61	0.004	1.23	3	65	29	12
43	S1	N1:P2:K2	0.90	0.18	1.59	0.13	0.57	0.004	1.13	0	74	18	21
44	S1	N2:P2:K2	1.08	0.15	1.53	0.16	0.79	0.004	1.26	3	65	27	15
45	S1	N1:P1:K3	0.74	0.15	2.75	0.12	0.44	0.004	1.18	5	42	21	18
46	S1	N2:P1:K3	1.11	0.17	1.74	0.14	0.70	0.004	1.44	9	39	32	17
47	S1	N1:P2:K3	0.90	0.22	2.58	0.14	0.72	0.007	1.51	0	45	33	23
48	S1	N2:P2:K3	0.90	0.17	2.20	0.14	0.72	0.003	1.60	6	44	29	20
49	S1	N3:P1:K1	0.87	0.15	1.66	0.17	0.82	0.003	1.60	3	78	30	15
50	S1	N4:P1:K1	0.88	0.15	1.83	0.15	0.78	0.004	0.20	2	39	32	12
51	S1	N3:P1:K2	0.90	0.13	2.02	0.17	0.68	0.005	1.09	5	122	30	72
52	S1	N4:P1:K2	0.94	0.18	2.20	0.13	0.75	0.005	1.59	0	24	35	26
53	S1	N3:P2:K1	0.88	0.16	1.63	0.14	0.98	0.004	1.78	0	48	50	27
54	S1	N4:P2:K1	0.90	0.19	2.20	0.10	0.62	0.003	1.35	2	27	35	24
55	S1	N3:P2:K2	1.02	0.23	2.53	0.13	0.69	0.004	1.30	3	38	27	21
56	S1	N4:P2:K2	0.94	0.20	1.99	0.11	0.72	0.003	1.30	2	36	21	24
57	S1	N3:P1:K3	0.88	0.19	2.47	0.13	0.69	0.004	1.23	2	15	27	27

Tmt. No.	Salinity treatment	Fertiliser treatment	Nutrient concentration in plant										
			N	P	K	Ca	Mg	Na	SO_4	Cu	Fe	Mn	Zn
			%							mg kg^{-1}			
58	S1	N4:P1:K3	0.82	0.21	2.19	0.11	0.67	0.005	1.3	2	54	32	101
59	S1	N3:P2:K3	0.70	0.21	2.74	0.13	0.47	0.004	0.97	2	90	21	42
60	S1	N4:P2:K3	0.81	0.17	2.84	0.10	0.52	0.003	1.24	0	36	27	15
61	S1	N5:P1:K1	0.96	0.21	2.28	0.14	0.64	0.004	1.16	2	14	21	17
62	S1	N6:P1:K1	0.85	0.16	2.22	0.13	0.55	0.002	1.23	3	18	26	15
63	S1	N5:P1:K2	0.78	0.17	2.23	0.15	0.59	0.003	1.24	3	59	30	15
64	S1	N6:P1:K2	0.95	0.16	2.61	0.14	0.56	0.002	1.23	5	29	32	30
65	S1	N5:P2:K1	0.91	0.22	2.95	0.13	0.49	0.003	1.19	3	3	26	20
66	S1	N6:P2:K1	0.91	0.21	1.69	0.12	0.58	0.003	1.13	5	48	23	15
67	S1	N5:P2:K2	0.90	0.19	2.23	0.15	0.60	0.002	1.11	3	71	30	17
68	S1	N6:P2:K2	1.17	0.18	1.99	0.17	0.70	0.005	1.37	5	57	44	21
69	S1	N5:P1:K3	0.83	0.17	2.55	0.13	0.48	0.002	1.23	3	5	38	17
70	S1	N6:P1:K3	0.96	0.19	2.04	0.10	0.69	0.003	1.35	0	9	35	21
71	S1	N5:P2:K3	1.06	0.23	2.60	0.12	0.66	0.003	1.4	0	3	30	24
72	S1	N6:P2:K3	0.88	0.18	2.05	0.11	0.56	0.003	1.14	3	18	32	15
73	S2	N1:P1:K1	1.99	0.19	3.08	0.19	1.57	0.002	2.79	8	45	48	27
74	S2	N2:P1:K1	2.50	0.19	3.64	0.18	1.46	0.003	3.23	6	54	48	27
75	S2	N1:P1:K2	1.70	0.19	2.31	0.22	1.81	0.003	3.19	5	56	86	30
76	S2	N2:P1:K2	2.85	0.29	4.72	0.24	1.47	0.004	2.48	8	51	48	33
77	S2	N1:P2:K1	2.18	0.18	3.37	0.19	1.28	0.002	2.56	6	45	42	26
78	S2	N2:P2:K1	2.29	0.17	2.31	0.21	1.82	0.002	2.6	6	53	44	21
79	S2	N1:P2:K2	2.01	0.21	2.83	0.19	1.18	0.002	2.19	5	63	54	20
80	S2	N2:P2:K2	2.61	0.19	3.40	0.18	1.41	0.002	2.34	5	24	41	26
81	S2	N1:P1:K3	2.09	0.20	3.94	0.15	0.98	0.002	1.95	5	54	32	33
82	S2	N2:P1:K3	2.39	0.17	3.22	0.18	1.26	0.002	2.24	6	48	41	30
83	S2	N1:P2:K3	2.05	0.15	3.09	0.18	1.32	0.002	2.62	5	41	47	27
84	S2	N2:P2:K3	2.44	0.19	3.01	0.19	1.43	0.003	2.71	5	98	53	26
85	S2	N3:P1:K1	2.41	0.13	2.35	0.20	1.91	0.003	2.78	6	63	45	26
86	S2	N4:P1:K1	2.63	0.21	2.78	0.21	1.63	0.002	2.34	5	80	39	29

Tmt. No.	Salinity treatment		Nutrient concentration in plant										
			N	P	K	Ca	Mg	Na	SO_4	Cu	Fe	Mn	Zn
			%							mg kg^{-1}			
87	S2	N3:P1:K2	2.13	0.15	3.21	0.19	1.26	0.003	2.16	5	30	41	30
88	S2	N4:P1:K2	2.58	0.15	2.81	0.18	1.74	0.002	2.56	5	48	36	35
89	S2	N3:P2:K1	2.29	0.13	2.36	0.19	1.48	0.003	2.44	3	36	68	32
90	S2	N4:P2:K1	2.07	0.15	2.36	0.18	1.37	0.002	2.44	3	26	36	32
91	S2	N3:P2:K2	2.40	0.19	3.15	0.17	1.19	0.003	1.77	3	23	39	24
92	S2	N4:P2:K2	2.51	0.16	3.49	0.16	1.15	0.003	2.01	3	15	33	26
93	S2	N3:P1:K3	2.27	0.14	3.61	0.17	1.15	0.003	1.97	5	35	36	27
94	S2	N4:P1:K3	2.05	0.21	3.10	0.19	1.51	0.002	2.36	3	45	53	24
95	S2	N3:P2:K3	2.28	0.22	3.40	0.17	1.17	0.003	2.60	6	104	39	21
96	S2	N4:P2:K3	1.84	0.19	3.33	0.17	1.10	0.002	2.40	2	26	59	21
97	S2	N5:P1:K1	2.23	0.21	2.65	0.18	1.32	0.004	2.20	6	62	41	20
98	S2	N6:P1:K1	2.72	0.19	3.61	0.19	1.36	0.003	2.27	6	21	42	30
99	S2	N5:P1:K2	2.86	0.20	3.86	0.18	1.27	0.003	2.06	5	108	47	33
100	S2	N6:P1:K2	2.73	0.22	3.93	0.19	1.49	0.002	2.38	3	29	45	38
101	S2	N5:P2:K1	2.52	0.21	3.28	0.18	1.44	0.002	1.50	6	36	48	26
102	S2	N6:P2:K1	2.46	0.21	2.95	0.18	1.39	0.005	2.38	9	66	38	24
103	S2	N5:P2:K2	2.57	0.21	2.92	0.18	1.33	0.005	2.02	6	87	54	27
104	S2	N6:P2:K2	2.61	0.21	2.49	0.21	1.55	0.007	2.21	11	96	33	35
105	S2	N5:P1:K3	1.30	0.22	3.61	0.16	0.86	0.003	1.80	5	72	62	21
106	S2	N6:P1:K3	2.10	0.18	2.77	0.18	1.35	0.004	2.56	8	63	48	27
107	S2	N5:P2:K3	1.69	0.20	2.84	0.17	1.30	0.002	2.15	2	14	54	20
108	S2	N6:P2:K3	2.13	0.21	2.56	0.16	1.39	0.002	3.09	3	20	47	27