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Some fertility problems associated with Kuwaiti calcareous soil and brackish irrigation water.

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SOME FERTILITY PROBLEMS ASSOCIATED WITH KUWAITI CALCAREOUS SOIL AND BRACKISH IRRIGATION WATER

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SUMMARY

The study was undertaken to improve phosphorus (P), iron (Fe), zinc (Zn) and manganese (Mn) availability and crop uptake in Kuwaiti calcareous soils. Field, glass-house and laboratory studies investigated the effectiveness of i) pyrophosphate (PP) mixed with orthophosphate (OP) fertilizers and ii) elemental sulphur (S°) as a soil acidulent.

In the field PP was incorporated with OP at a PP:OP P ratio of 0:100, 5:95 and 10:90 and applied at recommended agronomic P rates to *Zea mays* (corn) and *Triticum spp* (wheat) with micronutrients as subtreatments. Crop yields did not differ for all treatments receiving P probably due to high P residual levels in the soil but plant P uptake and P-tissue concentrations were significantly higher with PP treatment and Zn-tissue concentrations increased above the control treatments by 17% and 34% for the corn and wheat respectively, whereas with OP only treatments there was a slight decline in Zn-tissue concentrations.

A further two experiments were conducted in the glass-house utilising a similar soil and experimental design to grow *Zea mays* and *Avena sativa* (oat) under distilled or brackish water irrigation regimes. PP amended treatments increased plant yields in the glass-house experiments by 15-18% and 20-25% for the corn and oats, respectively, while plant P-uptake increased by 83% and 32% when PP was incorporated with OP for the corn and oats respectively. Similarly, PP treatments stimulated higher plant Zn-uptake. In the glass-house Zn concentrations in plant tissues were higher by 24-40% for treatments with PP than with OP only. These findings were supported by $NaHCO_3$-P and DTPA-Zn soil extraction, where levels moved from "marginal" to "adequate" ranges with the inclusion of PP with OP. Generally there were no significant improvements when PP/OP ratio increased from 5 to 10%. Furthermore, brackish water irrigation had no direct influence on PP soil reaction or hydrolysis.

Elemental sulphur (S°) was applied in quantities that could theoretically neutralise 0, 25, 50, 100 and 200% of the soil $CaCO_3$ with two rates of P and micronutrient combinations in a split-split plot design. In the field experiment corn and wheat were grown as test crops, while in the glass-house corn was grown with distilled or brackish water after the soil/S° mixture was incubated at 30°C and approximate field moisture capacity for six months.

The oxidation of S° to H_2SO_4 did not proceed in a linear fashion; there were lower rates of S° oxidation at the high S° application, better monitored by the generated SO_4^{2-} than the decline in either soil pH or $CaCO_3$ content. Soil pH decline was moderate until soil $CaCO_3$ content dipped below 6%. At these levels soils became acidic. The dissolution of soil $CaCO_3$ was proportional to the S° applied, but its effective size distribution changed from coarse clay/fine silt to that of coarse silt/fine sand with the highest S° rates. This would have profound effects on its surface area and activity. The S° treatment also resulted in higher soil salinity; EC increased from 3-4 to as high as 12 dSm^{-1}. Simultaneously there was a build up of gypsum which under SEM examination revealed that soil particle surfaces were shielded by gypsum crystals.

Plants did not respond favourably to S° inclusion, and yield declined by 35% with the highest S° rates. However, at moderate rates the yield was similar to the control. Soil-P increased ($NaHCO_3$-P extraction) at moderate levels of S° and then declined at higher rates. Extractable soil-Fe (DTPA) significantly increased only at higher S° rates, while Zn (DTPA) did not have a clear response and DTPA-Mn steadily increased even with the lowest S° rate. Plant tissue concentration and element uptake were difficult to assess in the light of declining plant growth and changed soil nutrient availability. Nevertheless S° treatment equivalent to 25% $CaCO_3$ neutralisation maintained yield, P and Zn uptake while significantly increasing Fe and Mn uptake by 63 and 12% respectively for the field grown wheat.

In none of the studies was there consistent response to micronutrient fertilisation. Furthermore, brackish irrigation did not interfere with the soil nutrient extractions or plant uptake.

DEDICATION

TO FREE KUWAIT

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1. General Introduction

1.1 Statement of the Problems

Kuwait is a country in a rapid transition from small subsistence agriculture to modern technological practices. With the advent of commercial oil production in the late 1940's , demands for food production and new products have developed. Imports of various agricultural commodities have increased to meet the growing market. The consumption of dairy products specially that of milk has grown with imports of reconstituted milk covering most of the market. However, local dairy herds for fresh milk production have increased and captured 15% of the market (A.F.R.A., 1985). This was achieved by import of high performance dairy breeds mainly of the Friesian varieties from the E.C. countries. The last available estimate put the herd size at about 16,000 expected to double by the year 2000 (A.F.R.A., 1985).

Although 95 % of Kuwait land was classified as range land available for animal grazing, it is of poor quality producing about 2 tonnes per hectare annually of dry matter (Abo-Aquad *et al.*, 1984). Furthermore, lack of rainfall uniformity renders landuse for grazing unreliable. Local production of animal feed has increased to meet the increasing animal requirements. Alfalfa and barley are produced under irrigation and are used as green fodder and for hay production. However, these only cover about 4% of local market needs (A.F.R.A.,1985). Imports of animal feeds as green fodder or hay and concentrates mainly cereal grains cover more than 60 % of animal requirements (Sheep and dairy). It was estimated that in the 1980-1984 period, there were annual imports of about 1,300,000 tonnes of roughage together with about 340,000 tonnes of concentrated feed. These were mainly to supplement sheep and dairy production. The cost of roughage was relatively high due to bulkiness in transport and storage.

Plans to increase forage production were established in the late 1970's to attempt to bridge the gap in animal feed requirements especially in roughage supplies. To implement these ambitious plans many difficulties had to be overcome. Lack of water resources both in quantity and quality, harsh climatic conditions and poor soil fertility were some of the accepted constraints. Work on increasing water resources has met with limited success, as new ground water aquifers are saline (brackish) with their salt content varying from moderate to high levels and these aquifers have no natural recharge rendering their long term use questionable. Their was some good quality irrigation water, produced from municipal waste, extensively used in forage production but this was limited in supply.

Although altering the climatic conditions is considered impractical, moderating the local environment by having more wind shelter or using glass-houses might improve plant production. However, wind breaks provide only some protection mainly from sand storms, whereas glass-house technology is too expensive to be used in forage production.

Kuwaiti soils being part of the extensive Arabian desert are generally of poor fertility. Their characteristics of high sand and low organic matter contribute to their low productivity. Their salinity, rockiness and high calcite content further add to the difficulties in utilising most of the Kuwait's land in agricultural production. Soil salinity varies from one position to another, while gravel and rocks near the surface are abundant in certain areas. Calcite or the presence of calcium carbonate ($CaCO_3$) is a feature of all Kuwaiti soils. In some soils levels are moderate while in others very dominant. Some $CaCO_3$ occurs in calcite horizons locally known as Gatch, where it restricts water permeability and plant root penetration. Their thickness and degree of cementation differ form place to place, some lying deep in the soil profile while others are exposed at the soil surface . Therefore only restricted areas of Kuwait land were considered suitable for agriculture.

The calcareous soils of these areas beside having some physical and chemical problems associated with the presence of hard pans or high salinity, are characterised by basic reaction (high pH) and poor bio-availability of some plant nutrients notably nitrogen, phosphorus and iron. Nitrogen responses in fertility trials were mostly positive, while limited success was encountered in the cases of P and Fe. Preliminary field trials had indicated poor P fertiliser recovery and a wide deficiency of Fe caused chlorosis. In some studies conducted in the area, high yield was only obtained with high doses and frequent applications of P fertiliser. Although some of these preliminary fertility trials were conducted for extension services and their results were not published, other published studies have indicated similar findings. It was reported that a high application rate of 50 kg P_2O_5 per hectare per month to similar soils could yield almost 40 tonnes per hectare per annum of Hassawi alfalfa (Farnworth and Ruxton, 1974a). In a study on barley, yields also responded to a high dosage of P_2O_5 (160 kg P_2O_5 per hectare) (Farnworth and Ruxton, 1974b). No local studies were carried out to assess the degree and spread of Fe chlorosis. However, visual signs of Fe deficiencies were clearly present in many field crops.

1.2 General Literature Review

Calcareous soils cover over 30 % of the world land surface (Chen and Barak, 1982). Their presence is due to :

1) The rock that formed the soil, that is parent materials which contain appreciable amounts of calcium i.e. basalts (Ruellan, 1973) 2) The climate, prolonged dry seasons favouring the prevention of leaching of base cations from the soil profile. Therefore, this definition was suggested by Kadry (1973) :

"Calcareous soils are those soils with high calcium carbonate content whose physical problems of land and water use for crop production are primarily dominated by the high content of $CaCO_3$, especially the active fraction with high specific area."

Most of the soils of the Arabian plateau and those of North Africa would be included in this definition including those of Kuwait. It is the dominating influence of calcium carbonate on any system in which it is present due to its properties such as its solubility, high buffer capacity and basicity which gives it controlling power on the soil reactions and plant root responses (Loeppert, 1986). The influence of $CaCO_3$ would depend on its reactivity. Drouineau (1942) developed a measurement of oxalate-precipitable calcium that was expressed as "active lime". This fraction was used to describe the most reactive soil calcium carbonate which was related to its particle-size distribution. and has been shown to be roughly equal to the $CaCO_3$ content of the <20 µm soil particles (Yaalon, 1957, Chen and Barak, 1982). Beside its size distribution, $CaCO_3$ composition or more its incorporation of other ions would also affect its reactivity. Calcite ($CaCO_3$) and dolomite ($Ca_{0.5}Mg_{0.5}CO_3$) are the two major carbonate phases identified in soils with other minerals in between (Inskeep and Bloom, 1986). The incorporation of Mg and/or heavy metals were found to reduce the solubility of the $CaCO_3$ mineral (Hassett and Jurinak, 1971).

Calcium carbonate in the soil reaches a dissolution equilibrium which is affected by levels of soil solution CO_2 and ionic composition and strength (Lindsay, 1979). This maintains soil pH at an approximate range of 7.4 to 8.5 (Loeppert, 1986) and elevated levels of bicarbonate concentrations. Simultaneously released Ca ions, for example from $CaCO_3$ dissolution would influence the equilibrium concentration of bicarbonate. As its activity increases it would reduce bicarbonate activity. Nevertheless, the generated bicarbonate would be accompanied with OH^- which gives rise to a basic soil reaction.

Soil $CaCO_3$ would also react with other soil solution components. This could take the form of specific adsorption (ligand exchange) at surfaces or ion exchange on charged surfaces, where there has been element substitution of the calcite phase (Lindsay, 1974; Madrid and Diaz-Barrientos,1992). Furthermore, co-precipitation of $CaCO_3$ with other soil constituents would form other solid phases of variable solubility (Suarez and Rhoades, 1982).

Due to these major influences that are exerted by $CaCO_3$ on soil chemical properties, the reactions and plant availability of some nutrients can be greatly affected. Phosphorus and heavy metals are among the most important. Their reactions in calcareous environments will be further discussed below.

1.2.1 Phosphorus Reaction in Calcareous Soils

Phosphorus has long been recognised as an important element in plant nutrition. It is necessary for such life processes as photosynthesis, building and metabolism of carbohydrates, energy transfer and genetic reproduction. Plants obtain their P from soil by root adsorption. Soil-P is seldom in abundance. It was estimated that the soil top layer contains on average about 1000 kg P/ha (Khasawneh, *et el.*, 1980). Only a small fraction of this P, however, would be in the plant available form. Soil-P occurs in both organic and inorganic forms and the former is of little importance in calcareous soils due to its small amount except where heavy manuring is practised.

The supply of P to plants depends directly on the concentration of phosphate in the soil solution, which can be influenced by many factors. Soil moisture, temperature optimisation and fertilising methods would be the main agronomical practices implied in maintaining adequate P-supplies. Moreover, soil conditions such as its reaction (pH), adsorption potential, precipitation rates and P cycling would have a major effect on the fate and plant availability of soil P. Only a fraction of fertiliser P applied to soils would be available to plants due to its adsorption and/or precipitation. In calcareous soils adsorption on $CaCO_3$ surfaces and the precipitation of insoluble Ca-P compounds would greatly reduce P-plant availability. The reactivity of $CaCO_3$, which depends on its surface area, increases as affective $CaCO_3$ particle size distribution decreases (Holford and Mattingly, 1975c). This factor rather than total soil $CaCO_3$ content was found to correlate with P adsorption (Holford and Mattingly, 1975a). The adsorption of P onto $CaCO_3$ surfaces conforms to the Langmuir adsorption isotherm (Kuo and Lotse, 1972) with possibly two adsorption mechanisms or two bonding energy states as the Langmuir adsorption is better described by a two-region equation (Griffin and Jurinak, 1973). Initial P adsorption was by chemisorption reactions of high bonding energy, followed at higher concentration by the very low bonding energy physical adsorption (Holford and Mattingly, 1975b) usually on top of chemisorbed P. These P bonds, however, will only cover a small fraction of the $CaCO_3$ surface area (Griffin and Jurinak, 1973; Freeman and Rowell, 1981). Nevertheless these sites of P adsorption would form nucleation centres for further P adsorption followed by transformation of these compounds from an amorphous Ca phosphate structure to crystal forms. The initial formation was shown to be di-calcium phosphate (DCP) slowly changing into octo-calcium phosphate (OCP) (Freeman and Rowell, 1981).

The nature and modification of $CaCO_3$ by other ionic imperfections would affect adsorption of P. The presence of an Fe-oxide coating on the $CaCO_3$ would have greater effect on P adsorption (Hamad *et al.*,1992) but separate Fe-oxide had still much higher affinity for P adsorption. Other investigations have found that P sorption was strongly influenced by Fe-oxides even in the presence of $CaCO_3$ (Holford and Mattingly, 1975a; Ryan *et al.*, 1985a,b). In contrast, in arid zone soils $CaCO_3$ and not Fe or Al- oxides were shown to correlate better with P adsorption (Lajtha and Bloomer, 1983). This was attributed to the fact that arid-land soils are less weathered and therefore pedogenically younger than soils developed in temperate areas and thus they may have a lower content and less reactive free Fe and Al-oxides.

Phosphorus can also directly precipitate with Ca^{2+} ions in solution. This process can proceed by nucleation or seed formation of Ca/P compounds followed by crystal growth and finally by transformation of these small crystals into large ones (Brown, 1981). They change from amorphous calcium phosphate compounds into more basic calcium phosphates (Larsen, 1967) that have very low water solubility and with time they form precipitates of hydroxyapatite (HAP) or flourapatite (FAP) (Brown, 1981).

1.2.2 Iron Reaction in Calcareous Soils

Plants require iron (Fe) for many essential enzymes but perhaps the most important function is associated with the role of chlorophyll photosynthetic processes. Deficiency of Fe in plants manifested by a yellowing of the leaves (chlorosis) would result in greatly reduced photosynthetic potential and thus lower crop productivity . Although Fe is the fourth most common element in the earth's lithosphere after oxygen, silicon and aluminium, it is locked up in various extremely insoluble compounds. In calcareous soils where pH would be buffered between 7.4 and 8.5, the solubility of inorganic Fe would reach the lowest levels of approximately $10^{-10.4}$ mol L^{-1} (Lindsay, 1984). This would be controlled by ferrihydrite [$Fe(OH)_3^0$] (Norvell and Lindsay, 1982) a poorly crystallised or amorphous ferric hydroxide. Plant Fe requirements are rather low; a wheat or corn crop would remove about 1 kg of Fe ha^{-1} (Marschner, 1978). However, for plants to be able to obtain their Fe needs for optimum growth a minimum concentration of $10^{-7.7}$ M would be required (Lindsay and Schwab, 1982). The way soil $CaCO_3$ could effect Fe availability would be by direct surface reaction or indirectly by influencing soil reaction and HCO_3^- levels. Both forms of Fe oxides (Fe^{II},Fe^{III} salts) would react with $CaCO_3$ (Loeppert *et al.*, 1984a) consuming 2 and 3 $CaCO_3$ equivalent for each mole of Fe(II) and Fe(III) respectively (Loeppert and Hossner, 1984). This reaction would largely be influenced by the reactivity of the $CaCO_3$ surface area and the maintenance of an oxidising environment (Loeppert *et al.*,1984a; Loeppert and Clark, 1984; Clark *et al.*, 1985). Faster reactions favour the formation of less crystalline phases (Loeppert *et al.*, 1984a), and with the presence of silicate ions, these reactions could be blocked and the siliceous ferrihydrite formed would generally be of poor crystallinity with no or very little transformation into more crystalline phases (Vempati and Loeppert, 1986). It has been proposed that Fe(II) reactions with $CaCO_3$ would result in the formation of lepidocrocite or goethite (Ô-FeOOH,Ó-FeOOH respectively), with the former being unstable and transitionary (Loeppert and Clark,1984; Vempati and Loeppert, 1988). Goethite is the most dominant of Fe-oxide crystals in calcareous soils (Chen and Barak, 1982). Ferric (FeIII) reactions with $CaCO_3$ on the other hand would give rise to the poorly crystalline or amorphous ferrihydrite (Loeppert and Clarks, 1984). The structure of this compound is not fully understood, but its small dimension and large surface area (Vempati and Loeppert, 1988) is thought to make it play a large role in controlling Fe solubility and plant availability. Furthermore, this compound was found to be common in all soils. The presence of this Fe-oxide designated as "soil-Fe" by Norvell and Lindsay (1982) would control the solubility of all other Fe-oxide crystals in well aerated soils, since it is the most dissolvable form (Schwertmann and Taylor, 1987). Moreover, as this Fe-oxide hydrolyses, its product would be dominated by $Fe(OH)_2^+$ at pH below 7.4 and by $Fe(OH)_3^0$ between pH 7.4 and 8.5, while at higher pH $Fe(OH)_4^-$ would predominate (Lindsay and Schwab, 1982). The solubility levels would be lowest for $Fe(OH)_3^0$ and would increase by 1000 fold for every one unit drop in pH (Lindsay, 1979). It should be noted that organic matter/Fe complexes which are present in all soils to varying degrees have higher solubility and they can play an important role in improving Fe mobility and plant availability (Lindsay, 1974). Another factor that can effect Fe solubility would be that of redox potential. At lower redox potential Fe solubility would increase (Lindsay, 1979; Lindsay and Schwab, 1982), however, to reach the critical level needed by plants, i.e. 10^{-8}, M, Schwab and Lindsay (1983a) had calculated that pe+pH had to drop below 9.75. Furthermore, they had shown that ferrosic hydroxide, a metastable $Fe_3(OH)_8$, would control Fe solubility at pe+pH range of 6 to 16. Although under conventional agriculture soil bulk pe+pH would not drop to 9.75 levels, perhaps in protected microsite environments, such as around decomposing organic matter particles or in the vicinity of respiring plant roots, such conditions may arise. Also Fe stressed plants may contribute to the reduction of redox potential by acidifying the rhizosphere or increasing root exudates that could stimulate microorganism activities (Marchner *et al.*,1986).

In calcareous soils increased CO_2 gases would allow the formation of increased levels of HCO_3^-. Soil solution that contain 1-5% CO_2 could have 4-20 mM HCO_3^- concentration (Olsen and Watanabe, 1959; Schinas and Rowell, 1977). The way HCO_3^- can accentuate plant-Fe deficiency has been attributed to its influence on reducing soil solution Fe concentration via the effect it has on raising the pH (Wallace and Abou-Zamzam, 1984). Other research has identified that higher HCO_3^- affects plant physiological responses by interfering with Fe absorption and translocation from roots to shoots (Romheld *et al.*, 1982; Fleming *et al.*, 1984) or by weakening the plant Fe-response mechanism (Fleming et al., 1984).

It could be said in summary that Fe solubility in calcareous soils is controlled by a combination of reactions involving Fe solid phases, pH, redox, CO_2 and $CaCO_3$ activity. Furthermore, plant abilities to respond to Fe-stress conditions by reducing rhizosphere pH or creating reducing environments or exuding chelating agents with the possibility of increased rooting density or the formation of rhizodermal transfer cells would reduce the impact of calcareous soils in limiting Fe availability in some cultivars.

1.2.3 Zn Reaction in Calcareous Soils

Zinc plays some important roles in protein synthesis, numerous enzymatic functions, production of chlorophyll and RNA. It is absorbed by plants by an active process that is influenced by biological and environmental factors (Bowen, 1969). In soils that are derived from limestone or calcareous sandstone Zn content tends to be quite low (<150 μg g^{-1}) (Wedepohl, 1978). However, total Zn content in soil is an unreliable indicator of Zn plant availability. In calcareous soils the presence of $CaCO_3$ can affect Zn solubility directly and indirectly due to its over dominance on soil reactions. It has been suggested that $CaCO_3$ is involved in Zn adsorption directly on its surfaces by a covalently bonded (chemisorption) mechanism (McBride and Blasiak, 1979). At low Zn concentration, the adsorption could be described by the Freundlich isotherm equation. However it deviates at high Zn concentration (Elrashidi and O'Connor, 1982). Therefore, this adsorption relationship may suggest that other soil constituents besides $CaCO_3$ are involved in Zn adsorption or there is more than one mechanism of Zn sorption. Other workers had described this reaction by the Langmuir adsorption equation (Udo *et al.*, 1970), they further added that when Zn adsorption maxima were exceeded, Zn precipitated probably as carbonate. Also Mg substitution for Ca ions in the $CaCO_3$ structure such as dolomitic materials had shown a higher affinity for Zn adsorption (Jurinak and Bauer, 1956).

Zinc precipitation in the presence of $CaCO_3$ could result in the formation of $Zn(OH)_2$ or $ZnCO_3$. This, however, has been disputed due to the fact that these compounds' solubilities are much higher than those found in soils (Lindsay, 1979). Other research has shown that Zn had declined by the same molar content of released Ca, thus suggesting the substitution of Zn^{2+} for Ca^{2+} ions in the $CaCO_3$ structure (Madrid and Diaz-Barrientos, 1992). Similarly, reaction of Zn solution with $CaCO_3$ was proposed to start as an adsorption reaction forming a surface-solid solution, then continuing into precipitation possibly as hydroxycarbonate (Papdopoulos and Rowell, 1989). Retention of Zn by soil $CaCO_3$ may be a result of surface adsorption and/or precipitation. It could be the adsorption reaction operates at lower Zn concentration, while at higher concentration precipitation occurs (Udo *et al.*, 1970). Others, had postulated that the former mechanism was associated with soils of pH<7, whereas in soils of a neutral to alkaline reaction precipitation may be more dominant (Brummer *et al.*, 1983). Regardless of the nature of Zn soil reaction, pH is a major factor governing its solubility. It has been repeatedly shown that Zn solubility and plant availability declines as pH increases (Iyengar *et al.*, 1981; Jahiruddin *et al.*, 1985; Sims, 1986; Jahiruddin *et al.*, 1986). In calcareous soil where pH is buffered above 7.3 Zn solubility is quite low and this has been correlated with Zn deficiency in many soils in U.S.A. (Boswell *et al.*, 1989).

1.2.4 Manganese reaction in calcareous soil

Manganese is associated with the photosystem II of photosynthesis process, and some enzymes (Cheniae, 1970). Plants obtain their Mn by passive and metabolic processes (Moore, 1972). Mn deficiencies have been observed on well-drained soils of a calcareous nature (Murphy and Walsh, 1972). The reaction of Mn is similar to that of Fe in soils. Both elements have strong oxide/hydroxide precipitation reactions and interact strongly with soil $CaCO_3$ (Jauregui and Reisenauer, 1982). The way $CaCO_3$ influences the reaction of Mn in soil is through its affect on pH and through surface adsorption of Mn^{2+} (Bromfield and David, 1978). Plant available Mn was in those fractions identified as exchangeable and organic matter bound (Shuman, 1979). As soil pH increased as the case with calcareous soils the water soluble or exchangeable forms would shift to the less available oxide fractions (Sims and Patrick, 1978) or became complexed with organics or strongly bonded with Fe-oxides (Sims, 1986). Precipitation of Mn^{2+} as $MnCO_3$ is thought to be a relatively slow process described as starting with chemisorption on the surface of $CaCO_3$ and these initial nucleated centres act to attract the formation of $MnCO_3$ coating of the $CaCO_3$ particles (McBride, 1979). The high affinity of $CaCO_3$ for Mn^{2+} ions appears to be a function of ionic radius, divalent metal ions such as Mn^{2+} have similar size to that of Ca^{2+}; 8.0×10^{-2} and 9.9×10^{-2} nm for Mn and Ca ions respectively; whereby at accessible surface sites Mn^{2+} can readily substitute for Ca^{2+} (McBride, 1979). The formed $MnCO_3$ (rhodichrosite) characterised by low solubility would in reducing conditions, such as flooding or high organic matter amendments become the controlling fraction of Mn solubility (Schwab and Lindsay, 1983_b). However, as the oxidative environment is restored, released Mn would be oxidised to MnO_2 (pyrolusite) (Lindsay, 1979), through a chemical oxidation catalysed by MnO_2 already present (Ross and Bartlett, 1981).

1.3 Aims and scope of the study

Increasing forage production to meet local needs requires the input of many factors. Selection of the appropriate plant genotypes and providing the growth conditions that can facilitate their optimum growth, must be the most important. With calcareous soils, deficiencies in P, Fe, Zn and Mn as stated from the literature would limit the crop potential. Furthermore, these nutrients, fertilisation efficiency would be lowered.

To reduce the impact of soil $CaCO_3$ on the availability of these essential nutrients and improve the recovery of applied fertilisers two approaches were undertaken:- First, modification of the effect that the $CaCO_3$ can exert on the immobilisation of P and other trace elements by incorporating small amounts of pyrophosphate (PP). Moreover, the nature of these nutrient reactions be it by direct adsorption or precipitation with $CaCO_3$ or indirect influence that $CaCO_3$ can have on their reaction due to its effects on soil pH and/or organic matter would be examined in the presence of PP. Furthermore, the agronomical effectiveness of such treatment amendment with orthophosphate type fertiliser in improving plant growth or nutrient absorption would be investigated in a field trial and the more controlled glass-house environment.

The second approach is to counter the effect of $CaCO_3$ by directly lowering its presence. Elemental sulphur (S°), which is biologically oxidised in the soil to sulphuric acid can be effective in generating acidity that may shift soil pH down thus increasing the solubility of nutrient ions or at least lessening their soil fixation. Also, soil $CaCO_3$ activity (active lime content) would be depressed by direct degradation of $CaCO_3$ by the generated acid. Elemental sulphur is abundant in Kuwait (by-product of oil-refining) and its use as soil acidulent to improve such soils was investigated. Beside the indirect effects that S° oxidation would have on nutrient availability, its oxidation rates and changes to some chemical and physical soil parameters could be examined. Plants that are sensitive to nutrient availability under calcareous conditions were evaluated, where S° was used.

2 METHODS

The work of this study was conducted in a field site at an experimental station in Kuwait. Soils from the site were also brought to the University of Wales and used in glass-house growth experiments . Soil and plant samples from the field and glass-house experiments were analysed at the university facilities. Moreover additional support experiments were carried out in the laboratory. The materials and methods used in these studies will be presented separately in field, glass-house and laboratory sections. This presentation is general since more detailed explanation of the pyrophosphate (PP) and elemental sulphur (S^0) studies will be given in their respective sections (5 and 6).

2.1 Field Investigation and Sampling

Kuwait Institute for Scientific Research "KISR" agriculture station at Sulaibiya was the location of the field study. The site which has been developed within the last ten years contained an overhead sprinkler irrigation system (converted central pivot) and all the required facilities. An area of 3000 m^2 divided in three blocks was allocated for the study. There were two seasons of field experimentation; the first was preliminary and encompassed the following main treatments: 1) Soil amended with manure compost at a rate of 60 m^3/ha. The manure was not of commercial quality and contained a high percentage of sand. Moreover, it contributed to a problem of weed contamination. 2) Use of S^0 as a soil acidulent at a rate of 65 t/ha. The available S^0 was not in a powder form and needed to be milled. A small fire incident however stopped the milling process and only 2/3 of the S^0 was powdered. The remaining two tonnes were disced to a size fraction of 2-5 mm. Nevertheless the S^0 was incorporated in the soil in a uniform manner. 3) Soil compaction; Soil bulk density was increased from 1.17 to 1.42 g/cm^3 by the use of surface rollers to compress moist soil. 4) and a check treatment as a control. These main treatments were designed to manipulate some of the soil physical and chemical properties so as to increase plant availability of phosphorus and metallic essential elements. Therefore, the sub-treatment was of P fertiliser at 0 and 300 kg triple superphosphate, 46% P_2O_5 or 20% P (T.S.P.)/ha and sub-treatment with or without the following nutrients; $FeSO_4.7H_2O$, $ZnSO_4.7H_2O$, $MnSO_4.4H_2O$ and $CuSO_4.5H_2O$ at 27.5, 11.0, 5.0 and 2.5 kg/ha respectively. Urea was applied uniformly at a rate of 1000 kg/ha. Corn was used as a test crop.

The difficulties obtaining sulphur (6.0 tonnes) in the right powder form, caused a delay in planting the corn. Germination occurred by first week of November, however early cold weather later that month depressed plant growth . Some plant samples were collected and later analysed but they could not be statistically assessed. Soil samples were collected form all plots at the start of the experiment and again 80 days later.

Chemical analyses of soil focused on the changes in $CaCO_3$ content especially in relation to sulphur treatments. Soil pH, $NaHCO_3$-extractable P and DTPA-extractable Fe, Zn, Mn and Cu were measured for soils which had received various treatments. The result of these analyses are presented in Appendix II with some comments on features which influenced the design of the second season experiment.

The second season of field study used the same area allocated in the first season. Sulphur treated soil had been under irrigation for about a year and it was assumed that changes to some of its properties would be more detectable. Additional powdered sulphur was applied to increase treatments to a total of 5 including the control. More detailed information about the second season S^0 field trial is provided in the S^0 study(section 6.2.3) including treatment design and rates of application. Moreover, plant sampling , soil collection and crop harvest are described in sections 5.2.1.2 and 6.2.3.2.

Soil compaction as a management practice to improve nutrient availability was eliminated since it did not show any significant results in the first season.

Organic matter application on the other hand had a favourable effect on the growth of plants and it was expanded so that all plots received manure compost at a rate of 20 m^3/ha.

In addition to the sulphur study, the remaining field area was utilised for pyrophosphate evaluation as an additive to orthophosphate fertiliser. Pyrophosphate (NaPP, 23% P) was incorporated into triple superphosphate (T.S.P.) at a rate of 0, 5 and 10 % pyrophosphate P as a part of total P. Also a control with no P treatment was included. A split plot design was used with micronutrient as sub treatment. A more detailed description of the pyrophosphate field study is outlined in section 5.2.1.

Crop harvesting, soil and plant sample collection are described in section (5.2.1.2). As mentioned earlier the incorporation of animal manure resulted in some weed problems, which had to be removed manually throughout the duration of the experiment. No chemical herbicides were used . Furthermore, all treatments and seed sowing were carried out mechanically, with the exception of micronutrient distribution which was done manually.

2.2 Glass-House Investigation

As already mentioned a consignment of Kuwaiti soil was brought to Bangor and used in laboratory and glass-house studies. The experiment, however, encountered some difficulties with the behaviour of the soil in pot conditions. Slumping of the soil after irrigation and surface hardening upon drying made it impossible to have adequate plant growth. Sub-surface rather than surface irrigation reduced the problem but caused unacceptable salinization.

Trying various structure building materials (polyvinyl alcohol and poly acrylamide "soil tex") resulted in some improvement but was shortlived. Mixing inert particles to improve the physical conditions on the other hand proved to be adequate. A combination of soil, gravel and vermiculite in equal volume proportions (soil-gravel-vermiculite at 46-47-7 by weight) gave the best response. Water infiltration , aeration and surface hardening were modified to contribute reasonably to a healthy plant growth.

An experiment to investigate the impact of PP as an additive with OP fertiliser and to assess its effects on plant growth, P and micronutrient uptake were conducted in the glass-house. Moreover changes on the transformation of added PP, OP and metallic micronutrients in the soil as a result of PP inclusion were also monitored. Two test plants were used under both distilled and brackish water irrigation. The brackish water was made in the laboratory to resemble in composition and concentration the ground irrigation water available in the field station. More details about Kuwaiti ground water are presented in section 4. A more detailed description of soil treatments, rates of amendments, planting and growth conditions are provided in the PP study section 5.2.2.

A second set of glass house experiments was conducted utilising Kuwaiti soil that had been incubated for 6 months with 5 rates of S^0. A description of rates and incubation conditions are given in detail in section 6.2.2.1. Soils were mixed with gravel and vermiculite in the same proportions as in the PP experiment. As with the PP studies , the S^0 trials were irrigated with distilled and brackish water. Corn (Zea mays) was the test plant utilised. Plant harvesting and soil sample collection described in section 6.2.2.2. were similar to the procedure conducted in PP study (section 5.2.2).

2.3 Support Laboratory Investigation and Analyses

In support of the field and glass-house investigation on the effectiveness of PP inclusion in OP fertilisation, other experimental exercises were conducted in the laboratory to investigate the following areas: i) Soil adsorption of OP as influenced by incorporation of small proportion of P as PP, ii)PP hydrolysis, iii) OP mobility as affected by PP presence and iv) P-Zn interaction as influenced by PP. More detailed information regarding the experimental design and conduct are provided in PP study section 5.2.3.

Similarly experimentation conducted in support of S^0 study isoutlined in more detail in section 6.2.1. These included investigations about i) S^0-oxidation, ii) Some general soil physical and chemical parameters effected by S^0-oxidation iii) Scanning electron microscope (SEM) and EDAX examination of S^0 affected soils. iv) Measurement of $CaCO_3$ size distribution in relation to changes brought about by S^0-oxidation both directly and indirectly and v) Investigation of P-soil retention as affected by acidification.

Soil samples from the field and glass-house studies for both PP and S° treatments were analysed for their $NaHCO_3$ extracted P and DTPA-extractions of Fe, Zn and Mn. Similarly plant tissues were analysed for their contents of P, Fe, Zn and Mn. Basic soil and water analyses for general description or those needed for the field, glass-house and laboratory support exercises for both PP and S^0 studies are outlined here:-

2.3.1 Saturated Soil paste extraction and its ionic composition

A paste of 200 g air-dried soil was prepared as described in Richards (1954). Solution extracts were then used to obtain measurements of soluble Ca^{2+} and Mg^{2+} by a PYE UNICAM SP2900 atomic absorption spectrophotometer. For Ca^{2+} measurements a 1:1 dilution with a La^{3+} solution of 5000 µg/ml was used to suppress phosphate interference. Soluble Na^+ and K^+ were measured by UNICAM SP-90 atomic adsorption spectro-photometer in flame emission mode. Immediately after extraction pH was measured (pHs) by a Kent Ell 7055 pH meter, and electrical conductivity (ECe) measured by Solubridge model P 335. Soluble CO_3^{2-} and HCO_3^- were measured by pH titration of solution extracts by a standard acid (HCl 0.0200M) at inflection points of pH=8.3 for CO_3^{2-} and pH=4.5 for HCO_3^- (Rhoades, 1982). Extractable Cl^- was determined by chloride meter (Model Corning EEL-920). Soluble SO_4^{2-} was estimated as a $BaSO_4$ suspension and turbidity was measured by spectrophotometer (Cecil) (Rhoades, 1982). All the soil used in soil extraction was air dried and all measurements were calculated on an oven dried basis (104^{0}C). Saturation percentage (SP) was also obtained.

2.3.2. Soil pH (1:1) and EC (1:2)

All soil pH in the PP and S^0 studies were of 1:1 soil water suspension rather than 1:2.5 soil:water due the sandy texture of the soil. The same soils were diluted to 1:2 soil:water suspension for EC determination (EC 1:2). When these suspensions (1:2) were re-examined, their pH gave similar readings after equilibration. Measurements of pH were obtained by a Kent Ell 2055 pH meter, and EC by Solubridge Model P335.

2.3.3. Free $CaCO_3$ Content

Calcimeter method (Bascomb, 1961) was used to measure $CaCO_3$ equivalence.

2.3.4. Particle Size Distribution

The mechanical analyses of the soil was carried out by both Day's hydrometer method (Day, 1965) and by the Pipette method (Bascomb, 1982). Some measurements were preceded by repeated distilled water washing to remove gypsum especially in the S^0 treated soils. $CaCO_3$ was removed by acid digestion in another set of soils (See section 6.2.1.4). The two methods with the accompanied sieving were used to estimate the following fractions; 2000-600, 600-200, 200-63, 63-20 and <2 µm.

In preparing $CaCO_3$ standard for the procedure used in section 6.2.1.5., a further two sizes of clay were collected representing coarse clay (0.2-2.0 µm) and fine clay (<0.2 µm) by a Beckman-14 refrigerated centrifuge at 10^{0}C employing a rotor speed of 2000 and 3000 rpm (Shahid, 1988).

2.3.5. Gypsum and Soluble SO_4^{2-}

Since S^0 treatment builds up the gypsum content of the soil, a 1:20 soil water dilution was used to dissolve gypsum from the soil. A 1:2 and 1:10 dilution were also used to estimate Na_2SO_4 contents in non S^0 treated soils and soluble SO_4^{2-}

for the S^0 treated soils. All soil suspensions were allowed 24 hours equilibration time after 12 hours overnight shaking. There is difficulty in distinguishing gypsum-SO_4^{2-} from that of other sources, however for comparative estimations it was concluded that the dilutions employed here were reasonable. Extracted SO_4^{2-} separated from soil using Whatman filter paper (No 42) was first estimated by its precipitation as $BaSO_4$ measured by turbidity using a spectrophotometer. Extracted SO_4^{2-} in later work was measured by Dionex ion chromatography. However, only selective soil extracts representing the major S^0 soil treatments, measured at 1:10 dilution and 1:20 dilution, were carried out.

2.3.6 Soil Extractable Phosphorus

Phosphorus was extracted according to the method proposed by Olsen et al. (1954). A modification using a 1:10 soil to extractant (0.5 M $NaHCO_3$, pH 8.5) ratio instead of 1:20 was found to result in more reliable estimation. The extreme sandy characteristic of the soil (inert particles) had a built in bias against P extraction. Extracts were examined for P content by the colormetric method of Watanabe and Olsen(1965) measured by spectrophotometry (Cecil).

2.3.7 Determination of Plant available Fe, Zn, Mn and Cu by DTPA-Soil extraction method

Soils were extracted by the DTPA (diethylene triamine penta acetic acid) procedure (Lindsay and Norvell, 1978) using 1:2 soil:extractant and Fe, Zn and Mn were then measured by atomic absorption spectrometry (PYE UNICAM SP 2900). The limitation of instrument error prevented the study of Cu in this work, but copper is not widely reported to be deficient in calcareous soils and its removal should not compromise the objective of the study.

2.3.8. Plant Sample Preparation

Samples (1.0 g) of coarsely milled dried plant material were ashed in porcelain crucibles first at 200°C for 2 hours followed by a further 5 hours at 500°C. The cooled ash was wetted by 10 ml 2M HCl acid and after 24 hours the acid-ash suspensions were transferred to stoppered glass vials with the aid of another two 5 ml portions of 2M HCl acid.

2.3.9 Phosphorus content of Plant

A suitable aliquot (0.2 ml) of the ashed plant-acid suspension was analysed for P by the Watanabe and Olsen (1965) method.

2.3.10 Plant Tissue content of Fe, Zn, and Mn

Ashed plant-acid suspensions were directly used to determine Fe, Zn and Mn contents by aspirating the solution into the atomic absorption spectrophotometer, (PYE UNICAM SP 2900) using an air-acetylene flame.

2.3.11 Soil Mineral identification by XRDA

Some soil was used directly for diffraction by a Philips wide range gonimeter (PW 1050/23) by preparing a glass slide covered by a film of soil. Another similar sample was prepared from calcite particles that had been ground. For clay analysis, specimens were collected after mechanical analysis dispersion and several glass slides were prepared from Na-clay for XRDA as follows:

i. Mg-clay; MgAOC was used to convert Na-clay into Mg-clay.

ii. K-clay; KCl was used to convert Na-clay into K-clay.

iii. Mg-clay (E.G.); Mg-clay on a slide glass was saturated with ethylene glycol. This specimen is useful for identifying montmorillonite.

iv. K-clay (550°C for 1 hour); K-clay on a slide glass was heated at 550°C for 1 hour. This specimen is useful for identifying kaolinite clay.

Type of clay and other minerals were then identified from the various diffraction peaks on a glass slide.

2.3.12 Soil examination by Scanning Electron Microscopy (SEM)

Soil stubs for SEM were gold and carbon coated. These were then examined by using a SEM/EDAX instrument, Hitachi Instruments Company model (S520).

3. General Description of Kuwaiti Soils

In this section the main features of Kuwaiti soils are introduced, with some description of the conditions that may have contributed to their development. A summary of soil survey data with more detailed descriptions of some physical and chemical properties of the soil used throughout this study are included.

3.1 General Geographical Description

Kuwait lies at the north-west corner of the Arabian (Persian) Gulf between Latitudes 28^0 and 30^0 N and between longitudes 46^0 and 48^0 E. It comprises an area of approximately 18000 km^2. The topography is generally characterised by an undulating plain, gradually sloping down from about 300 m above sea level in the south-west to the sea in the east. Its apparent flatness is occasionally interupted by hills, escarpments and depressions.

Due to the location of Kuwait in the Sahara geographical region, the climate of the country is characterised by long hot and dry summers, short warm and sometimes rainy winters. Dust storms are frequent. The highest temperature recorded was 51^0C in July 1978, whilst the lowest -6^0C was recorded in January 1964. Mean temperatures however, were reported to be 37^0C in July and August and 14^0C in January (Omar *et al.*, 1990). Features of this desert climate also include a high rate of evaporation and an intermittent low annual rainfall of about 115 mm mainly between November and January (Al-Abdul-Razzak, 1984). Rainfall however, is quite unpredictable with reported annual rates as low as 22 mm and as high as 352 mm.

3.2 General Geological Description

Kuwait is situated on the eastern part of the Arabian Shield. The underlying materials consist of various metamorphic and igneous rocks of pre-cambrian age. Kuwait itself has a simple geological structure characterised by broad, gentle N-NW trending, doubly-plunging folds and some normal faults. Epeirogenic movement resulting from basement rock dislocations or from salt tectonism

(Kassler, 1973; Murris, 1980) were suggested to have caused the growth of these folded structures. This may have been formed during the upper Jurrassic and continued until the late tertiary period (Kamen-Kaye, 1970; Behbehani, 1980). Some of these folds were later displaced by normal fault formation (Omar *et al.*, 1981). Moreover during these times, upward lifting and erosion were common (Al-Awadi, 1988). In the later cretaceous period stable shelf conditions (Kamen-Kaye, 1970; Dewey et al., 1973) allowed the formation of a thick, shallow-water sequence dominated by platform carbonates through sediment supply and subsidence (Al-Awadi, 1988).

The geology of upper strata is dominated by the Kuwait group which has a thickness of about 150 to 210 m (Al-Awadi, 1988)(Appendix IV). Its composition is dominated by basic clastic sediments with secondary evaporites and limestones frequently present in many parts (Loutfi, 1971). Three formations are recognised in this group, Ghar, Lower Fars and Dibdibba (Owen and Nasr, 1958). The deeper formation, Ghar, was thought to have been formed during the Late Oligocene/early Miocene age, whereas the next formation, Lower Fars, was of Miocene age and the Dibdibba formation was of upper Miocene to Pleistocene age (Owen and Nasr, 1958). This last formation in a few places is covered by recent alluvial deposits (Al-Awadi, 1988). The lithological composition of these formations is quite similar with miner differences due to terrestrial effects (Appendix IV). They consist of mostly sand and gravel intercalated with sandy limestone, calcareous sandstone and marl with a little shale and other clays (Al-Awadi, 1988). In some localised areas calcite and/or gypsum cementation can be present.

3.3 General Pedological Description

The soils of Kuwait have general features common to all of them, these include sandy texture, very low organic matter content, presence of calcite and levels of salinity that in some places are extremely high. The build-up of salinity is mainly due to the fact that the greater part of Kuwait was covered by sea-water in the past; some salt-marshes still exist. The scarcity of rainfall coupled with high evaporation rates resulted in concentrating these salts. Moreover, seepage of sea water with capillary action introduced further salinity to the soil especially in the coastal areas.

Four great soil groups were recognised (Ergun, 1969):

i) Desert soils covering about 78 % of total area with main characteristics of very weak profile development. Drainage for most parts is excessive but restricted in some places due to cementation (lime and/or silica pan). In some areas gravel may cover the surface of the soil (desert pavement). These soils are moderately to strongly calcareous with some gypsiferous layers which may be exposed at the surface at some places. There is no structural development in this soil, or very weak platy structure in the surface layer with weak blocky in the subsoil. Wind erosion of the removal type is very active in this group, with occasional young sedimentation in some depressions. Five soil associations with a further nine soil series were recognised in this group.

ii) Desert-Regosol Intergrade Soils dominating 14 % of the land. The soils of this group are similar to the desert soils with the difference largely the lack of any profile development. They have developed on unconsolidated material and are characterised by lack of hardpan, lower gypsum and salt contents and no desert pavements. Generally they have good drainage, no structure, and sandy texture with calcite present throughout the profile. The soils were probably formed from wind blown depositions. There are two associations divided into four series in this group.

iii) Lithosol Soils: This group represents a shallow soil developed on top of consolidated rocks. They are confined to Jal Az Zor escarpment east of Kuwait Bay on steep topography, accounting for less than 1 % of the total land. They consist of A and C horizons, with weak development of the A horizon usually followed by semi hard and quite thick calcite and/or gypsum layers. The C horizon is basically fragments of the consolidated rocks. Only one association with one soil series was described in this group.

iv) Alluvial soils: These are predominantly young soils formed from marine deposition around coastal regions. They represent about 7 % of Kuwaiti land mostly in the north of the country. Their textures vary from sand to clay and they are very saline and gypsiferous. They are characterised by high water table and poor drainage with little horizon development. There are two soil associations representing four soil series.

The soils utilised in this study were from the Desert-Regosol Intergrade great group, they belong to the Sandy Desert Association within the Sulibiya series. A representative profile of this series is listed in Appendix V. These soils were developed from sandstone and limestone parent material. They have sandy to loamy sand texture with excessive drainage

3.4 Some Physical Soil Properties

Soils from experimental station "Sulaibiya" were collected from undisturbed sites and from the irrigated areas used in the field investigations. Table 3.1 present the mechanical analyses of the soils and the equivalent composition of calcite and gypsum.

It is clear that the soils are predominantly sandy with more than half in the 200-600 μm medium sand range. This would have great influence on soil water behaviour especially excessive infiltration and low water holding capacity. However, this could have some advantages in regard to plant desert ecology. The sandy texture could allay surface evaporation by preventing capillary movement, thus allowing the deep rooted plants to find water in the sub-strata. Moreover, scanning electron microscopy (SEM), indicated semi-spherical morphology (Appendix I), and this may suggest transported grains probably wind blown deposits (loess). Soil XRDA traces (Appendix VI) confirmed the overall

Table 3.1 Some physical properties of Sulaibiya soil

Site	Depth (cm)	% particle size distribution			Texture class	Calcite % equi.	Gypsum % 1:2
		sand	silt	clay			
	0-20	91	5	4	sandy	14	0.6
1	20-50	93	4	3	"	16	0.5
	50-100	92	5	3	"	22	0.9
	0-20	90	5	5	"	11	0.5
2	20-50	91	4	5	"	13	0.5
	50-100	93	4	3	"	16	0.8
	0-20	92	4	4	"	17	0.7
3	20-50	94	3	3	"	22	0.4
	50-100	92	5	3	"	28	0.9
4	0-10	89*	6	5	"	16**	2.0

Samples were collected from "KISR" experimental station. Sites 1,2 and 3 are virgin soil sites while 4 is from the area of field trials.

* sand fraction distribution (% of total soil)

particle size (µm)

2,000-600	600-200	200-63	63-20 (estimated)
7.2	47.5	26.7	7.6

** calcite fraction distribution (% of total soil)

particle size (µm)

2,000-600	600-200	200-63	63-20	20-2	<2
-	5.9	3.9	5.8	2.3	1.9

dominance of quartz (0.4215 nm peak) accompanied by calcite (0.303 nm peak) and some feldspar minerals (0.324,0.32,0.318 nm peak). Mineralogy of the clay fraction (<2 µm e.s.d.) by XRDA investigation has shown that the predominant clay mineral in these soils is montmorillonite; 1.55 nm peak (Mg^{2+} saturated) expands to 1.75 nm on ethylene glycolation (appendix VI). Palygorskite is found in appreciable amounts (1.05 nm and 0.64 nm peaks) and its presence is confirmed by shifting of the 1.05 nm peak to 1.00 nm after 550^0C treatment for one hour. Palygorskite has also been observed by SEM (appendix I). In addition to the montmorillonite and polygorskite there is indication of the presence of hydrous mica as suggested from XRDA traces where a peak at 1.00 nm is formed as a shoulder of the 1.05 nm peak of palygorskite. Also the disappearance of the 0.72 nm peak after heating the K-saturated clay (550^0C for one hour) confirmed the presence of kaolinite. Traces of feldspar, quartz and chlorite were also found within the clay fraction.

Soil calcite fractions ranged from 10-28 % $CaCO_3$ which would indicate that the soils of the area are moderate to highly calcareous. Furthermore, an increase in $CaCO_3$ content with profile depth may indicate some downward movement. The existence of about 20 % of the calcite in the clay and fine silt size fraction (<20 µm) is indicative of the presence of pedogenic secondary carbonates. However, crystalline calcite has been identified (SEM examples in plate 1,2 in S^0 section after page 165) which occurred in the silt and sand size fractions suggesting inheritance from the parent materials. It is plausible that both processes had contributed to the built up of $CaCO_3$ in the soil. Furthermore, mineralogical investigation of calcite nodules by XRDA revealed that they were predominantly $CaCO_3$ (0.303 nm) with traces of orthoclase, muscovite and K-feldspar (appendix VI). The presence of dolomite could not be ruled out especially if it was of pedogenic origin, since only large lime particles were investigated.

Gypsum is present in low amounts (<1 %) in the non disturbed soil whereas in the adjacent irrigated plots there was more than double that amount. It could be that SO_4^{2-} introduced by the irrigation water had contributed to the increase in its presence.

3.5 Some Chemical Soil Properties

Chemical analyses of the soil are presented in table 3.2 for undisturbed soils and those in the irrigated fields. Soil pH is around 8.0 which is expected form the calcareous nature of the soil. Soil salinity is low with levels of around EC_e 1.0 dSm^{-1} in the top layer. Both pH and salinity did not vary much with profile depth. Field soil (site 4) had a 1:2 extract to measure its EC and even though it is more diluted than the saturation extract, its salinity was three times that of the undisturbed soil, probably due to long term effects of saline irrigation. The EC (1:2) of the soil used in the glass-house studies (site 5) was unusually high up to about 4.5 dSm^{-1}. This soil was never under irrigation and the higher salinity could be localised variation, but it is more likely that the grinding of cemented particles (>2 mm) had released or increased the solubility of some salts, especially if they contained Na or K sulphate.

From the soil saturation extracts (Table 3.2) it is clear that SO_4^{2-} dominates the salts that are contributing to soil salinity followed by Cl^-. Base cations that contributed to the soluble constituents of soil solution are present with following declining order, $Ca^{2+}>K^+>Na^+>Mg^{2+}$. The solubility of Ca^{2+} would be controlled by the dissolution product of gypsum ($CaSO_4.2H_2O$), 4.9 mM L^{-1} at 25^0C (Arslan and Dutt, 1993). Therefore, if the glass-house soil salinity had increased due to introduction of precipitated salts, then these were probably not of $CaSO_4$, but they could be K_2SO_4 and/or Na_2SO_4.

The saturation extracts contained no or undetectable CO_3^{2-} levels which are expected in the pH range of the solution, and HCO_3^- levels were quite low. This may reflect the low biological activity of the soil but on the positive side this soil

Table 3.2 Some Chemical Properties of Sulaibiya Soil

Site	Depth (cm)	pH_e	% sat	EC_e dSm^{-1}	Saturation extract me/l								SAR
					CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	Na^+	
	0-20	8.1	18.5	1.0	nil	neg	2.16	7.03	3.78	1.08	3.78	1.62	1.0
1	20-50	7.9	16.6	1.2	"	"	4.22	7.83	4.82	1.20	3.61	2.41	1.4
	50-100	8.2	18.7	1.4	"	"	4.81	10.2	6.42	1.07	4.28	2.67	1.0
	0-20	8.1	16.7	1.1	"	"	nil	12.0	4.19	0.60	4.79	2.40	1.1
2	20-50	7.9	18.2	1.0	"	"	2.20	6.59	3.85	0.55	2.75	1.65	0.8
	50-100	8.1	17.0	1.4	"	"	3.53	8.82	5.29	1.18	2.94	2.94	1.2
	0-20	8.1	16.5	0.9	"	"	nil	7.88	3.64	0.61	2.42	1.21	0.7
3	20-50	8.2	14.8	1.0	"	"	2.03	8.11	4.05	0.68	2.70	2.03	0.9
	50-100	8.2	18.5	1.2	"	"	1.62	9.73	4.32	1.08	3.78	2.16	0.9

	Depth (cm)	pH 1:1		EC 1:2	$NaHCO_3$-P µg g^{-1}	DTPA-Fe µg g^{-1}	DTPA-Zn µg g^{-1}	DTPA-Mn µg g^{-1}
4	0-10	7.7	-	3.7	21.6	2.3	0.8	2.5
5	0-20	8.0	-	4.5	1.8	1.7	0.5	2.6

would not be expected to have bicarbonate induced Fe chlorosis.

Magnesium levels were lower than the other cations which may suggest that the controlling salt for Mg^{2+} dissolution is epsom salt minerals. This does not rule out the presence of dolomite but this mineral has much lower solubility.

Potassium levels of the soil are relatively high, second only to those of Ca^{2+} within the base cations. Their level amounts to 20-25 $\mu g\ g^{-1}$ soil estimated from saturation extracts.

Soluble sodium in the saturation extracts was relatively low and its ratio within the base cations as expressed by SAR values was estimated around 1.0. Using SAR values to extrapolate soil ESP indicated that this soil had no sodicity problems.

$ESP = [100(-0.0126+0.01475\ SAR)/1+(-0.0126+0.01475SAR)]$ (Richards, 1954)

Soil extractable levels of P, Fe, Zn and Mn that reflect their plant availabilities and indicate that the P "availability" ($NaHCO_3$-P) in the irrigated field soil was high, while that of the undisturbed soils utilised in the glass-house experiment was extremely low. The soil in the irrigated plots had been heavily fertilised by both organic and inorganic sources over about 10 years. Carry over effects are the cause of these high P levels. It is not clear how long it would take for the soil available-P to decline to levels of the undisturbed soil.

Metal ions extracted by the DTPA plant availability test indicate that this soil contains "low" to "marginal" levels of Fe and Zn, while those of Mn were "adequately" supplied.

Nitrogen levels were not measured but they were expected to be extremely deficient and therefore it must be added to any irrigated crop for reasonable growth. In this soil excessive drainage and the lack of appreciable organic content would require special attention to this major plant nutrient.

4. GENERAL DESCRIPTION OF KUWAIT GROUND WATER

Kuwait is a desert country with no rivers. Fresh water supply is provided by desalination of sea water which is then blended with 10% of brackish (aquifer) water. Distillation capacity from various plants was about 215 million imperial gallons per day (MIG/D) in 1987 expected to reach 250 MIG/D by the end of the century. In 1987 daily fresh water consumption was around 130 MIG/D thus generating some surplus resevoirs. This water, however is mainly for domestic use and very little is used in agriculture. Only treated sewage effluent is used for irrigation, apart from the ground brackish water.

Although about 200,000 hectares of Kuwait land was designated as suitable for irrigated agriculture, less than 5% is currently under cultivation owing to a shortage of irrigation water.

4.1 Aquifer Supplies

A total of about 290 MIG/D of brackish water is produced from various fields throughout the country (M.E. & W., 1989). This water, from various layers that are associated with certain geological formations, is used for the landscaping, agriculture and oil sectors, and its salinity varies in TDS from 3,000 to 9,000 $\mu g\ l^{-1}$. The aquifer complex consists of sedimentary rocks of the Kuwait group, as well as the formation of Dammam, Rus and Radhuma of the Hasa Group (M.E. & W., 1981). In Appendix IV, stratigraphy of these layers is provided. In general, the ground water flow shows hydraulic continuity through the saturated part of the Kuwait group and Dammam formation, while it is almost confined at the base of the Dammam and on top of the Radhuma formations by the impervious layers of the Rus formation. When considering the quality and quantity of the ground water only the Kuwait Group and Dammam formation aquifers appear to have reasonable potential. Therefore, these two aquifer complexes will be briefly described (M.E. & W., 1981).

The Kuwait Group aquifer has many hydrological characteristics that are influenced by the lithological variation within this group, the relatively pervious and semi-pervious zones show limited persistence over the area. Although gravel, sand, silt and clay materials with different degrees of cementation are the constituents of this group, it is the position of the clay zones that contribute most to the hydrology of the aquifer. The upper saturated part of the aquifer lies some 4 to 150 m in relation to land elevation. Its saturated thickness varies from one place to another and is confined by the structure of the Dammam formation, but in general it gradually increases towards the northeast of the state. In the central and southwestern parts of the state where the aquifer water quality is moderate (i.e. TDS 3,000-7,500 $\mu g\ l^{-1}$), the saturated thickness is more than 150 m. It increases to more than 350 m in the northeast, where the aquifer water becomes very saline.

The second aquifer complex, located in the Dammam formation, is the most productive in the state. It is distributed within the rocks of the Dammam structure which consist of stratified marine limestone deposits. This lies underneath the Kuwait group and on top of the Rus formation. Its saturated thickness ranges from 150 to more than 350 m, and generally increases towards the northeast. The hydrological characteristics of this aquifer are mainly affected by secondary with little contribution from primary porosity. It is the cumulative effects resulting from faults, fractures, solution channels, dolomitization etc. that appears to control the hydraulytic continuity and therefore the productivity of the aquifers.

The aquifers of the Kuwait group are hydraulically connected with the underlying Dammam aquifer. The mean directions of flow in these main aquifers resemble each other. The flow occurs in a dynamic equilibrium state in a northeastern direction towards the sea. The Kuwait Group aquifers get most of their recharge through leakage from the Dammam formation aquifer. Some water replenishment is also acquired from surface infiltration and from lateral flow due to higher hydraulic head in Saudi Arabia.

4.2 Ground water quality

Aquifer water quality varies from one location to another. In general the Kuwait Group aquifers are less saline than the Dammam formation. Furthermore, both appear to have their water salinity increase as they approach the northeastern or coastal parts of the country. Table 4.1 presents a chemical analysis of Sulaibiya ground water collected from various sources. The water is mildly saline (E.C. 4.8 dSm^{-1}; TDS 3,500 mg l^{-1}) and with most agronomical crops it should not be a major problem. However, with the high evaporation rate of the area, soil salinization may rapidly become a problem if no adequate drainage measures are undertaken. As has been already discussed in section 3, the field soil had higher EC values than the adjacent undisturbed soil. When these soils were collected the field had been irrigated for less than 10 years. Presuming similar trends the soil could become very saline (EC>10 dSm^{-1}) within 15-20 years. Use of higher levels of irrigation under these free drainage soil conditions could go some way to limiting the salinity build up. However, the major constituents of the ground water are SO_4^{2-}, Cl^-, Na^+, Ca^{2+} and Mg^{2+} (Table 4.1). The chloride salts and those of Na_2SO_4 would probably leach out, while those of Ca or Mg sulphate would precipitate due to their lower solubility product ($CaSO_4$ $4.9x10^{-3}M$, $MgSO_4$ $5.9x10^{-3.5}$ at 25°C) (Arslan and Dutt, 1993). Furthermore, capillary action between irrigations could re-introduce some of the leached salts.

Another aspect would be the deterioration in the aquifer water quality. With the limited recharge conditions, it is probably just a matter of time before this water would become more saline. Aquifer water has been mined since 1941 in the oil sector and furthermore, the Sulaibiya field has been in production for some 40 years with other fields exploited in the 1970's and 1980's. Monitoring of their productivity and water quality had been carried out by M.E. & W., and their .pn35assessments for 1988-1989 concluded that pumped water quality from various fields was generally constant since pumping started with a minor decline

4.1 Chemical analysis of Sulaibiya irrigation water

Parameter	M.E.& W. (range of 19 wells, 1988-89)	AAFRA 1984-85	KISR (range at different times of the year 1984-85	field irrigation water analysed at Bangor
TDS	3,500-5,000 mgl^{-1}	4560 mgl^{-1}	2827-2944 mg^{-1}	3506 mgl^{-1}
pH	7.2-8.0	7.6	7.3-7.8	7.0
EC	-	6.6 dSm^{-1}	3.7-4.6 dSm^{-1}	4.8 dSm^{-1}
CO_3^{2-}	-	nil	<1-11.4 mgl^{-1}	nil
HCO_3^-	80-150 mgl^{-1}	171 mgl^{-1}	153-176 "	131 mgl^{-1}
Cl^-	800-1600 "	1143 "	572-612 "	709 "
SO_4^{2-}	1100-1500 "	1498 "	1238-1350 "	1325 "
Ca^{2+}	350-550 "	464 "	298-316 "	373 "
Mg^{2+}	120-160 "	190 "	121-138 "	156 "
K^+	-	16 "	17-19 "	22 "
Na^+	550-900 "	626 "	405-460 "	435 "
B	-	-	1 "	-
NO_3^-	-	-	<0.03 "	-
NH_4^+	-	-	0.03-0.18 "	-
PO_4^{3-}	-	-	-	0.02 "

in some field discharge rates. The only exceptions were some wells located in the eastern part of the Sulaibiya field where there was a marked deterioration in the water quality. These included some of the earlier wells under production. It would be hard to draw a firm conclusion as to the longevity of Kuwait ground water supplies from the information presently available.

4.3 Glass-house brackish water

The following salts were used to generate for glass-house experiment irrigation water that resembled in concentration and composition Sulaibiya brackish water. Only distilled water was used so that dissolved organics would be avoided.

	made to 1 litre
$NaHCO_3$	180 mg
KCl	42 mg
$NaCl$	980 mg
$MgSO_4.7H_2O$	1605 mg
$CaCl_2.2H_2O$	197 mg
$CaSO_4$	1088 mg

5. Use of Pyrophosphate as a Soil Amendment

5.1 Introduction

The efficiency of phosphorus (P) fertilization in calcareous soils is known to be low. Added fertilizer (P) is quickly immobilized by $CaCO_3$ and progressively deposited as water insoluble calcium phosphate compounds. The major primary product of this reaction of the water-soluble usually orthosphosphate (OP) fertilizer in calcareous soil is dicalcium phosphate dihydrate (DCPD) (Bell and Black, 1970; Lindsay *et al*, 1962). With time DCPD is subsequently transformed into octacalcium phosphate (OCP) (Amer and Ramy, 1971; Larsen, 1967), and the more basic hydroxyapatite (HA) (Griffin and Jurinak, 1974; Lehr and Brown, 1958). One technique developed to reduce the precipitation of fertilizer P in calcareous soils is the incorporation of small amounts of sodium pyrophosphate (NaPP) into orthoposphate (OP) fertilizer. Application of ammonium phosphate fertilizer containing 10% of its P in form of PP to a calcareous soil has prevented the appearance of DCPD or HA (Larsen and Widdowson, 1966). Moreover, the addition of NaPP in small amounts to a solution supersaturated with DCPD has shown a remarkable inhibitory effect on the growth rate of DCPD crystals (Marshall and Nacollas. 1969).

5.1.1 Effect of Pyrophosphate on Phosphate

Orthophosphate P was shown to have a quick and sharp drop in its concentration when exposed to unlimited free $CaCO_3$ or calcareous soil high in $CaCO_3$. El-Zahaby and Chien (1982) found that after one hour a drop of more than 95% in the soluble-P-concentration had occurred when reacted with $CaCO_3$. They attributed this drop to the sorption of P by $CaCO_3$. Kuo and Lotse (1972) pointed out that 80% of the P absorption of $CaCO_3$ could be completed within 10 seconds. This rapid P adsorption will be followed by calcium phosphate heterogeneous nucleation on the $CaCO_3$ surface (Griffin and Jurinak, 1973). Amer and Mostafa (1981) found that there were two periods in the precipitation of soluble P in $CaCO_3$ suspension. A large drop in P concentration in about 5 minutes followed by a period of relatively little change, and then by a second drop. The first drop showed a Langmuir absorption maximum whereas the period when there was little change in P concentration was interpreted as time needed for the induction of precipitation by amorphous nucleation. The second drop in P concentration proceeded gradually and corresponded to crystal formation and their growth. During monitoring of the experiment for a further 360 hour period, the soluble P transformed to the more basic calcium phosphate.

Upon the addition of small amounts of pyrophosphate (PP) this process of P adsorption and precipitation could be altered. Incorporating NaPP at 2% P to the total P in OP almost entirely prevented the OP adsorption by $CaCO_3$ (El-Zahaby and Chien, 1982). This inhibitory effect of NaPP was only effective if added before or with OP. NaPP added 5 minutes after OP failed to stop the sorption of P by $CaCO_3$. However, the amount of PP was too small to compete effectively with OP for sorption sites on the $CaCO_3$ surface. El-Zahaby and Chien (1982) further indicated that PP may act by distorting the $CaCO_3$ surface thus hindering the formation of DCPD nuclei, which in turn inhibits additional adsorption of OP. Moreover, this inhibition was only for a short time, and dependent on the ratio of $CaCO_3$ to NaPP and OP. Amer and Mostafa (1981) compared various ratios of PP to the P content of OP. They found that low rates of NaPP were ineffective in preventing the reduction of soluble P content, but on the other hand, higher rates considerably increased the soluble P. This was attributed to the effect of PP in prohibiting the DCPD crystal growth. Amer *et al.* (1985) explained that PP had not prevented OP sorption by $CaCO_3$ but had in some other way inhibited its precipitation. Furthermore, they concluded that the quantities of PP required depended upon the surface area of $CaCO_3$, its reactivity (Zeta potential) and on the concentration of OP present in solution. It is important to note that the effectiveness of PP, be it in hindering the OP adsorption onto

$CaCO_3$ surfaces or preventing DCPD nuclei formation or reducing the growth rate of the DCPD crystals, lasts only for a short period. El-Zahaby and Chien (1982) reported that the inhibitory effect of PP was only effective for 3.5 hours for the soils they studied with the exception of one soil, however there were slightly higher P concentrations maintained in solution after one day.

Similarly, Amer and Mostafa (1981), studying the effect on two soils with different $CaCO_3$, detected a sharp drop in soluble P levels after one day. However the drop was less severe for the low $CaCO_3$ soil and for high PP rate treatments. Furthermore, the DCPD crystals formed in soil treated with NaPP were much smaller than those found in non-treated soils (El-Zahaby and Chien, 1982). This formation of micro-crystalline DCPD in calcareous soils treated with NaPP may result in less demand on the soluble P, thus maintaining a higher P content in soil solution even after a four week incubation period.

5.1.2 Agronomical Evaluation of Pyrophosphate Ammendment

If the inclusion of PP in a small amount with fertiliser P added to calcareous soils could reduce or postpone the fixation of P in the soils then this should have a positive effect on plant growth under a P stress environment. The addition of NaPP at rates 2% and 10% of the P content of the phosphate fertilizer, improved the plant yields grown on two calcareous soils in a pot experiment (Amer *et al.*, 1982). When fertilizer P was applied at a rate of 50 ppm, the inclusion of 2% PP improved the recovery of the fertilizer P by successive crops from 48.1% to 55.4% and from 57.5% to 71.6% for soils containing 39% and 4.1% $CaCO_3$, respectively (Amer *et al.*, 1982). In the same study, it was observed that NaPP had increased the mobility of monocalcium phosphate in soil columns, and to a lesser extent the mobility of diammonium phosphate.

5.1.3 Zinc-Phosphorus interaction

Phosphatic fertilizers have been identified as responsible for the induction or accentuation of zinc (Zn) deficiency symptoms in some crops (Burleson *et al.*, 1961; Ellis *et al.*, 1964; Ward *et al.*, 1963). This antagonism was attributed to the precipitation of P/Zn complex in soil solution (Lindsay, 1979; Spencer, 1960). This was refuted by Barrow (1987) who detected two ways by which fertilizer P can effect Zn sorption, on one hand indirectly by the effect of P in altering soil pH, this can vary depending on the type of P fertilization and its effect on the direction of pH changes (Barrow, 1987; Shuman, 1988c), and on the other hand directly by the effect of P sorption increasing the number of reactive sites for Zn sorption (Barrow, 1987; Xie and Mackenzie, 1989). Other investigations have reported that P/Zn interaction was a plant physiological phenomenon due to the interference of the two at the root surface absorption sites or in translocation within the plant (Burleson *et al.*, 1961; Burleson and Page, 1967; Khan and Zende, 1977; Langin *et al.*, 1962; Stukenholz *et al.*, 1966; Warnock, 1970).

5.1.4 Effect of Pyrophosphate on Zinc

Pyrophosphate either as a major constituent of polyphosphate fertilizer or as an amendment to orthophosphate fertilizer has been found to affect Zn solubility and availability to crops. Mortvedt and Osborn (1977) reported that treating acid soil with (PP) based fertilizer increased Zn concentration in the soil solution in comparison to its concentration in the (OP) treated or untreated soils. Asher and Bar-yosef (1982) have similarly shown that Zn concentration in clay suspension treated with PP but free from organic matter was higher than the Zn concentration in a suspension not treated with PP. This positive effect of PP on soil Zn solubility was explained as a consequence of the capacity of PP to solubilize organic matter which in turn chelates Zn, or by the sequestration properties of PP on the native or applied Zn (Asher and Bar Yosef, 1982; Mortvedt and Osborn, 1977). Furthermore, Bar-Yosef and Asher (1983) found that the efficiency of PP complexation of Zn was greater at soil pH of 8 or more and at higher initial PP concentrations. In this condition of high soil pH (greater than 7.5) Zn solubilization by PP was found to be comparable to or almost four fold better than, the organic ligands EDTA or DTPA, but only at PP molar concentrations much greater than that of EDTA and DTPA. At the same initial molar concentration for all three, PP had less than 2% of the effect of EDTA and DTPA in solubilizing Zn (Asher and Bar-Yosef, 1982; Bar-Yosef and Asher, 1983). These results are in agreement with the findings of Giordano *et al.* (1971), which indicated that high concentrations of Zn in soil solution were obtained after one day at a high rate (2000 ppm, P) of PP containing polyphosphate fertilizer. However, since PP hydrolysis in soil solution is relatively fast, then the sequestering of Zn by PP must only be effective for short periods. Therefore, it was suggested that the effectiveness of PP as a Zn carrier must be doubtful due to the need for high levels and frequent applications of PP (Bar-Yosef and Asher, 1983). Further, they added that applying PP and Zn together to the soil in solution form would be preferable to applying each separately.

5.1.5 Pyrophosphate hydrolysis

Pyrophosphate hydrolysis in soil is a reaction of both chemical and biochemically mediated processes (Dick and Tabatabai, 1986; Hons *et al.*, 1986; Stott *et al.*, 1985). Factors which dictate the rate of (PP) hydrolysis have been reported and indicate an increase in the hydrolysis rate as a function of increasing temperature, H-ion concentration, enzymatic activity, colloidal gels, complexing cations, concentration and the ionic environment in the solution (Dick and Tabatabai, 1986 and 1987; Stott *et al.*, 1985 Sutton *et al.*, 1966; Van Wazer *et al.*, 1955). Other factors such as moisture content, soil texture and amounts of soil organic matter and their particular properties, such as the molecular size and composition will also effect PP hydrolysis (Gilliam and Sample, 1968; Hons *et al.*, 1986; Hossner and Phillips, 1971; Tabatabai and Dick, 1979). Laboratory study has shown that the optimum temperature for PP hydrolysis is in the range of 30-35°C (Sutton *et al.*, 1966). Greater hydrolysis at high temperature is presumably due to increased microbial and enzymatic activity (Engelstad and

Allen, 1971; Sutton *et al.*, 1966). Non-conformity abounds in the literature with regard to pH effects on PP hydrolysis. Sutton and Larsen (1964) indicated a higher level of hydrolysis in higher pH soils. Hons *et al.* (1986), similarly found a greater PP hydrolysis in calcareous soils when compared to neutral or acidic soils. However others have shown that the rate and extent of hydrolysis of a PP containing condensed fertilizer decreased with rise in pH (Hossner and Melton, 1970; Philen and Lehr, 1967; Subbarao and Ellis, 1975). Tabatabai and Dick (1979) observed a decrease in PP hydrolysis in calcareous soils and attributed this decline to decreased magnesium ion activity.

Pyrophosphatase (PPase) is the enzyme that catalyzes the hydrolysis of PP to OP (Stott *et al.*, 1985). This enzyme is widely distributed within flora, fauna and soils (Tabatabai and Dick, 1979). The activity of this enzyme in soil has been shown to relate negatively to the levels of $CaCO_3$. This is due to the binding of the essential Mg^{+2} ion by $CaCO_3$ (Tabatabai and Dick, 1979). Other ions were found to restrict the activity of this enzyme. High levels of Cu (II) associated with organic soil caused a reduction in PPase activity (Parent *et al.*, 1985). Stott *et al.* (1985) measured an inhibitory effect of 30-35% in PPase activity in soils when exposed to Cu (II) and Fe (II), and less than 30% inhibition with the trace elements Cu (I), Mn (II), Zn (II) and Fe (III).

Soil physical paramters such as texture or organic matter content were found to be inconclusive in their effect on PP hydrolysis. Fine textured soil with large organic residues showed increased hydrolysis, whereas organically amended coarser soil showed depressed hydrolysis (Hons *et al.*, 1986), while Sutton and Larsen (1964) indicated no correlation between clay and organic colloids and the rate of PP hydrolysis. In comparison, Dick and Tabatabai (1987), have reported that the clay content has a significant positive correlation with PP hydrolysis rates.

Soil mositure content will also affect the rate of PP hydrolysis. Soils under flooded conditions have a higher hydrolysis rate than when at 1/3 bar moisture potential (Hossner and Phillips, 1971). Half-life values of applied PP under the flooded conditions ranged from about 0.5 to 4 days depending on other environmental factors. Under aerobic systems the half-life time required for PP hydrolysis varied from 4 to 100 days (Blanchar and Hossner, 1969; Sutton *et al.*, 1966). Hons *et al.* (1986) observed that PP hydrolysis in calcareous soils was marginally affected by soil moisture levels, with more hydrolysis under drier conditions.

Hydrolysis of (PP) in the soil is influenced by a combination of biological, physical and chemical factors, which are quite complex in nature. These factors are often interdependent, and the interaction among them will dictate the rate and total quantity of (PP) hydrolysis.

5.2 Materials and Methods

In this study the application of phosphorus fertilizer amended with small amounts of pyrophosphate on calcareous soil was agronomically assessed. This was approached by dividing the work into three distinct areas: a field trial carried out on a calcareous soil site in Kuwait; a series of glass-house experiments using a Kuwaiti calcareous soil irrigated alternatively by distilled or brackish water; and laboratory exercises to investigate the effectiveness of PP amendment on the solubility and plant availability of some soil nutrients, and the hydrolysis rate of the pyrophosphate under plant growth conditions in the same soil.

5.2.1 Field Experiment

5.2.1.1 Experiment Preparation

A field trial on the agronomic effectiveness of pyrophosphate as an amendment to triple super phosphate (T.S.P., Ortho-phosphate-based fertilizer) on calcareous soil was conducted at a desert site in Kuwait. Soil description and the methods of field preparation have been outlined earlier (sections 2.1, 3.5). A split-plot design was used with three adjacent blocks of similar soil and topographical characteristics. Phosphorus treatments were the main plot with the following composition:

a) Control = no phosphate added.

b) 0% PP = no pyrophosphate added to T.S.P. (100% T.S.P.).

c) 5% PP = 5% of the P is PP and 95% of the P is T.S.P.

d) 10% PP = 10% of the P is PP and 90% of the P is T.S.P.

All phosphorus plots, with the exception of the control, received 6.5 gP/m^2 in various combinations based on a rate of 150 kg P_2O_5/ha. Each main plot was divided into two subplots one with micronutrient application and the other without. The following shows the added micronutrients and their rates:

$FeSO_4.7H_2O$ = 50 kg/ha (1.00 gFe/m^2) Fe 5 ppm.

$ZnSO_4.7H_2O$ = 30 kg/ha (0.68 gZn/m^2) Zn 3.4 ppm.

$MnSO_4.4H_2O$ = 30 kg/ha (0.74 gMn/m^2) Mn 3.7 ppm.

$CuSO_4.5H_2O$ = 5 kg/ha (0.13 gCu/m^2) Cu 0.64 ppm.

In the above, part per million (ppm) estimation is a rough calculation of the amount of nutrients applied to a hectare furrow slice assumed to be 2,000,000 kg/ha soil, based on a soil depth of 15 cm and soil bulk density of 1.3 g/cm^3.

The randomization of the treatments assigned to main plots was carried out as prescribed for the design. In a similar way subplot treatments were then randomized within each main plot. Each block had separate randomization.

Two test crops were planted to ascertain the PP effect on their yield and their uptake of P, Fe, Zn, and Mn. A sweet corn (*Zea mays* L) of an Egyptian variety (Geza 107), and an American wheat (*Triticum* Spp) variety (Ukroge), were planted with spacing of 30x20 cm and 9.0x1.5 cm for the corn and wheat respectively. Each experimental unit was 5x7.5 meters. All plots were uniformly fertilized with urea at three intervals throughout the growing period with a total nitrogen application of 210 kg/ha. An over-head sprinkler system was utilized to deliver uniform irrigation to all plots whenever needed. Composition of the irrigation water has been provided earlier (table 4.1).

5.2.1.2 Crop Harvest and Analysis Preparation

Leaf samples from the corn plants were collected at 60-65 days after germination (start of tasseling). The third fully grown blade from the top was collected at random from ten plants for each experimental unit. In the laboratory each sample was individually washed by agitation in distilled water containing 0.05% Agral 90, then rinsed repeatedly in clean distilled water, shaken to remove excess water and placed in a labelled paper bag to dry in a forced air oven at 70°C. The air dried leaf samples were coarsely ground in a stainless steel hammer mill to a size of about 1 mm.

For the wheat, plants were harvested after the grains had hardened about 110 days from germination. From each experiment unit, ten plants were collected at random and combined. Roots and soil were discarded at ground level, and the samples were divided into grains and straw, then placed in polythene bags. In the laboratory samples were washed and oven dried in the same way as the corn leaves. Special care was needed in washing the wheat grains. Nylon sieves were used to prevent grains from floating and dispersing in the washing bucket.

Wheat yield was measured with the aid of wooden squares (25 cm). In triplicate for each experimental unit the above ground plants were harvested into polyethene bags. In laboratory the weight of straw and grains, from each bag, were measured separately to the nearest 0.1g. Small amounts from each sample were placed in beakers then weighed to the nearest 0.01g and oven dried at 107°C. After reweighing, dry matter yields in kg/ha were computed.

Soil samples were collected 30 and 90 days after planting. The earlier collections were of ten soil cores (taken by 3 cm auger) to a depth of 10 cm from each experimental unit. The second set of collections were at a later stage of crop growth, at depths of 0-30, 30-60 and 60-90 cm. Samples were air dried, sieved through 2 mm and stored for further analyses.

5.2.2 Glass House Experiment

5.2.2.1. Experiment Preparation

Surface (0-10 cm) calcareous soil, from the experimental station in Kuwait, was brought to Bangor and used in glass-house and laboratory studies.

A set of two growth experiments were conducted in the glass-house at the University, to test under more controlled conditions, the agronomic effects associated with amending orthophosphate fertilizer with a small amount of pyrophosphate. Soil, gravel and vermiculite were mixed as described earlier (section 2.2) and fertilized as following:

A : Control without micronutrient or phosphate addition.

A' : Control with micronutrient but no phosphate addition.

B : 100% (orthophosphate) without micronutrient addition.

B' : 100% (orthophosphate) with micronutrient addition.

C : 5% pyrophosphate with 95% orthophosphate without micronutrient addition.

C' : 5% pyrophosphate with 95% orthophosphate with micronutrient addition.

D : 10% pyrophosphate with 90% orthophosphate without micronutrient addition.

D' : 10% pyrophosphate with 90% orthophosphate with micronutrient addition.

Orthophosphate source was KH_2PO_4, Pyrophosphate source was $Na_4P_2O_7$ and all phosphate containing treatments had a rate of total P equal to 100 mg kg^{-1} of soil. Soil, gravel and vermiculite were mixed with the appropriate phosphate combination, and thoroughly homogenized before being divided into pots each containing approximately one kilogram of soil. The following micronutrient containing salts, were dissolved together in distilled water, and then an appropriate volume of solution was added to each pot assigned to have a micronutrient treatment so that the following micronutrient concentrations were delivered:

Salt used	Element and its concentration (μg/kg soil)
$FeSO_4.7H_2O$	Fe (II) = 20
$ZnSO_4.7H_2O$	Zn = 5
$MnSO_4.4H_2O$	Mn = 5
$CuSO_4.5H_2O$	Cu (II) = 0.5

A completely randomized design was used in a heated glass-house with four replications. Two crops were planted, corn (*Zea mays* L. variety Early King), and oat (*Avena sativa* variety Peniarth). Corn seedlings were thinned to two plants per pot whereas seven to ten plants were maintained in the oat pots. Nitrogen and potassium were supplied in solution from one week after plant establishment. Ammonium nitrate and potassium nitrate were used to give a concentration of 200 and 150 mg/kg soil of N and K respectively.

5.2.2.2 Plants and Soil Sample Preparation

Harvesting was done at plant age of about ten weeks, by collecting the aerial growth. Washing, drying and grinding of plants was carried out in the same manner as for the field experiment. Green yield and dry matter yield were tabulated before washing and after drying respectively.

In the first set of experiments distilled water was used to irrigate both corn and oat trials. In the second set of experiments, brackish water was used, reconstructed from laboratory salts to resemble the composition and salt concentration of Kuwaiti ground water (composition and salts used have been reported earlier (Section 4.3).

Soil samples were collected from each pot, air dried, and carefully sieved, to reduce the possibility of vermiculite sliping through, then stored in polythene bags for further analysis.

All plant samples obtained from field and glass-house studies, were ashed and dissolved in 2M HCl and then analysed for P, Fe, Zn and Mn as described earlier.

5.2.3 Laboratory Experiments

5.2.3.1 Pyrophosphate and P Sorption

Orthophosphate adsorption/precipitation by the native calcareous soil was studied to determine the possibility of PP inhibiting orthophosphate sorption. Triplicate 10 g soil samples were treated with KH_2PO_4 amended with 0,5 and 10% $Na_4P_2O_7$ to a total P concentration of 100.0 μg/g soil. A control treatment (no P added) also was included. 20 ml of distilled water was added to the soil and shaken for 24 hours. $NaHCO_3$ extractant (40 mls) was added and shaken for further 30 mins, then filtered through No. 42 filter paper. Aliquots were analysed for P as described earlier.

5.2.3.2 Pyrophosphate Hydrolysis

Soils from the glass-house studies were also used to test the amount of PP remaining after the growth period as an indication of its hydrolysis. This was done by adding enough 1 M HCl to a 10 ml aliquot of $NaHCO_3$ soil extract to change the pH to less than 7.0 and heating for one hour in a boiling waterbath. Volume was adjusted to 50 ml, and analysed for P as explained earlier. The difference between the P concentration before and after acidification of the solution and heating was taken to represent the amount of PP remaining in the soil that had not hydrolysed to OP.

5.2.3.3 Pyrophosphate Effect on P Mobility

A soil column experiment was conducted to investigate the effect of PP on the mobility of OP. Samples (200 g) of native air dried Kuwaiti calcareous soil were placed in clear glass tubes, 3 cm in diameter. One end of each tube was covered with a fine nylon cloth. On the opposite end a small amount of OP amended with PP mixed with little soil was carefully spread. The total P added was 1.0 g as KH_2PO_4 or a combination of KH_2PO_4 with $Na_4P_2O_7$. The ratios of P in OP:PP were 100:0, 95:5 and 90:10 for the three treatments. A control with no P addition was also included. A thin layer of acid washed coarse sand were carefully spread on top of the P treated soil in each column to reduce disturbance.

The study was carried out with three replicates of each treatment. The column was allowed to stand in distilled water overnight, and enough distilled water was added until the soil columns were completely wet. Columns were placed vertically on a stand watered from the top using a plastic tube and a funnel to lead the water flow just to the top of the sand to reduce disturbance of the soil columns. 50 ml of distilled water was applied once daily for two weeks. A sample of the leached water was collected at the end of the first and second week. The pH and P content of the leachates were measured. Columns were then stored for one week in a heated air cabinet (45°C) to dry. Dried soil columns were pushed out of the glass tubes and then they were segmented at 5 cm intervals downward from the amended band. A 5 gm sample from each segment was then analysed for $NaHCO_3$ - extractable P according to the method explained earlier.

5.2.3.4 Pyrophosphate Effects on P-Zn Interaction

A series of plastic bottles each containing 30g of Kuwaiti calcareous soil were incubated for eight weeks. These soils had the following amendments of Zn and P compounds:

1. control (no Zn or P added)
2. Zn + OP - PP.
3. Zn + OP + PP.
4. Zn - OP + PP.
5. Zn - OP - PP.

Zinc was applied in the form of $ZnSO_4.7H_2O$ at a rate of 10 μgZn g^{-1} soil and phosphate at a fixed rate of 150 μg P g^{-1} soil. KH_2PO_4 was used for the OP, while $Na_4P_2O_7$ was the PP source. The ratio of OP:PP where the two sources of P were present (treatment 3) was 9:1.

All soils were wetted with distilled water to approximately field capacity, sealed with polythene film and fastened with a rubber band, to maintain air exchange while preserving humidity. Bottles were stored in a dark heated (30°C) cabinet, and were shaken and remoistened every few days so that humid aerobic conditions were maintained through the eight weeks incubation.

At the end of the incubation period soils were allowed to air dry and were then analysed for DTPA-Zn and $NaHCO_3$-P as explained in (section 2.3.7 and 2.3.8). All treatments were run in triplicate.

5.3 Results

5.3.1 Field Experiment

The results of the field experiment are presented for wheat yield (kg/ha) both in the grain and straw portions separately in tables 5.1A and 5.1B respectively. Also included in these tables are the uptake/ha of the plant nutrients P, Fe, Zn and Mn by both plant parts. Moreover, total plant yield and elemental removal were compared in table 5.1C. Although the yield figures in this case might be unusual, since it includes both the grain and straw portions together, it was felt its relevent to the total removal by the whole wheat plant of the above mentioned nutrients. Table 5.2A and 5.2B show respectively the elemental concentrations of P, Fe, Zn and Mn in the wheat grain and straw portions. Similarly, table 5.3 shows the elemental concentrations for corn plant leaves. No corn yield data was obtained, since corn plants planted in the autumn started to die off with the advent of cooler temperatures without completing their life cycles. Nevertheless, full grown corn leaves were collected at the tasseling stage, and elemental content of these are presented in table 5.3.

Soil samples were collected from each experimental unit under wheat or corn cultivation. Since soil treatments (P, combined P/PP and micronutrients) were identical, data from soil analysis are presented together in tables 5.4A, 5.4B and 5.4C. $NaHCO_3$ extractable P and DTPA extracted Fe, Zn and Mn with soil pH are presented in table 5.4A for surface (10 cm) soils collected 30 days after planting. Data in table 5.4B reports the significant effects of incorporating micronutrient sulphate salts on the extractability of $NaHCO_3$-P and DTPA - Fe, Zn and Mn. These again were from the same soils reported in table 5.4A, while table 5.4C reveals data for soils collected at a later stage of plant growth (90 days after plant establishment). These explore the downward movement of P as indicated by $NaHCO_3$ extractable P at 0-30, 30-60 and 60-90 cm depth sections of soil profile.

The field experiments carried out in Kuwait using corn and wheat test crops have shown positive effects from the inclusion of pyrophosphate (PP) as an amendment to triple superphosphate (T.S.P). This response was in the increase in some plant elemental concentrations, as Table (5.1A) indicates there were no significant increases in yield of wheat grains grown with or without the addition of PP. Grain yields were more than four tonnes per hectare for all treatments containing phosphate, but only about three tonnes for the control (without P fertilization). Although this yield is low in comparison to irrigated wheat, it is however in the average range obtained in Kuwait, probably due to the poor quality of the irrigation water, specially the practice of exposing plant leaves to saline conditions by the sprinkler system. Elemental concentrations in the crops and their uptake per hectare, however, present another indication. Phosphorus concentration in the corn blades grown on soil treated with PP was about 50% higher than that accumulated in the blades of corn grown with or without T.S.P. fertilization (Table 5.3). The same highly significant increased accumulation of P was obtained with wheat both in the grain and straw portions (Tables 5.2A, 5.2B, respectively). However, the increases in the grain P content was only about 25%, compared to the straw where it was close to 60%.

Zinc uptake by corn and wheat showed a similar pattern to that of P uptake. In the corn blades as well as in the wheat grain and straw Zn concentration was increased as a result of PP inclusion. Highly significant Zn concentration increases in the range of 50% were observed in the wheat grain with the PP amended treatments (Table 5.2A). Wheat straw accumulated Zn in a similar pattern to that in the grains, but with concentration about half of that in the grains (Table 5.2B). The zinc concentration in the corn blades was raised by 15-18% when PP amended phosphate fertilizer was used (Table 5.3). However, this was only significant at the 5% level of probability. Moreover, there appeared to be no significant advantage in increasing the PP:OP ratio from 5% to 10% in regard to

Table 5.1A Yield and elemental uptake by wheat grains grown in Kuwaiti field. Means of 24 replicates.

Treatment of P (OP ± %PP)	Yield and Uptake by Wheat Grains				
	(kg/ha)		(g/ha)		
	Yield	P	Fe	Zn	Mn
Control (no P)	3053	7.41	121.0	60.5	125.8
OP + 0% PP	4285	10.67	166.6	78.8	199.5
OP + 5% PP	4337	13.88	174.7	132.3	173.7
OP + 10% PP	4470	14.42	180.1	127.9	160.7

L.S.D.	(.05) 1026	(.05) 3.22	(.05) 38.5	(.01) 45.0	N.S.
H.S.D.	(.05) 1385	(.05) 4.39	(.05) 51.9	(.05) 44.1	N.S.

Table 5.1B Yield and elemental uptake by wheat straw grown in Kuwaiti field. Means of 24 replicates.

Treatment of P (OP ± % PP)	Yield and uptake by wheat straw				
	kg/ha		g/ha		
	Yield	P	Fe	Zn	Mn
Control (no P)	2563	3.72	90.5	26.8	66.2
OP + 0%PP	2572	3.74	88.1	23.5	69.5
OP + 5%PP	2479	6.06	91.3	45.9	63.7
OP + 10%PP	2333	6.23	86.8	39.3	54.67

L.S.D.	N.S.	(.01) 1.87	N.S.	(.01) 16.1	N.S.
H.S.D.	N.S.	(.05) 1.90	N.S.	(.05) 16.4	N.S.

Table 5.1C Yield and elemental uptake by wheat plant grown in Kuwaiti field. Means of 24 replicates.

Treatment of P	Yield and uptake by wheat plant				
(OP ± % PP)	kg/ha		g/ha		
	Yield	P	Fe	Zn	Mn
Control (no P)	5616	11.3	211.5	87.3	192.0
OP + 0%PP	6857	14.4	254.7	102.3	269.0
OP + 5%PP	6834	19.9	266.0	178.2	237.4
OP + 10%PP	6803	19.7	266.9	167.2	215.3

Table 5.2A Elemental concentration of wheat grains grown in Kuwaiti field. Means of 24 replicates.

Treatment of P (OP ± % PP)	Elemental concentration (μg/g) in wheat			
	P	Fe	Zn	Mn
Control (no P)	2456	93	19.6	41
OP + 0%PP	2480	90	18.6	46
OP + 5%PP	3190	106	30.3	40
OP + 10%PP	3234	106	28.9	36
L.S.D.	(.01) 478	N.S.	(.01) 7.02	N.S.
H.S.D.	(.01) 601	N.S.	(.01) 8.82	N.S.

Table 5.2B Elemental concentration of wheat straw grown in Kuwaiti field. Means of 24 replicates.

Treatment of P	Elemental concentration (μg/g) in wheat straw			
	P	Fe	Zn	Mn
Control (no P)	1447	55	10.3	26
OP + 0%PP	1444	45	9.2	26
OP + 5%PP	2431	69	18.5	25
OP + 10%PP	2237	52	16.7	23
L.S.D.	(.01) 410	N.S.	(.01) 5.22	N.S
H.S.D.	(.01) 515	N.S.	(.05) 5.11	N.S

Table 5.3 Elemental concentration of corn blade grown in Kuwaiti field. Means of 24 replicates.

Treatment of P	Elemental concentration (μg/g) in corn leaves			
	P	Fe	Zn	Mn
Control (no P)	2350	85	31.9	58
OP + 0%PP	2221	82	27.6	48
OP + 5%PP	3413	77	38.0	60
OP + 10%PP	3622	80	36.4	55
L.S.D.	(.01) 501	N.S.	(.05) 5.22	N.S.
H.S.D.	(.01) 630	N.S.	(.05) 7.04	N.S.

the P or Zn concentration in the corn or wheat plant parts.

Iron (Fe) and managnese (Mn) concentration, in the three plant materials mentioned above, showed no significant response to PP treatments (Table 5.2A, 5.2B, 5.3).

In all the field fertility trials there were no significant responses to the application of micronutrient salts, containing $FeSO_4$, $ZnSO_4$, $MnSO_4$ and $CuSO_4$, in the yield or in elemental concentrations. On the other hand T.S.P. treatments significantly increased the grain yield of wheat but gave no significant improvement in the P grain concentration (Table 5.1A) when compared to that of the control. This is clearly shown in Table (5.1C). Although there was no improvement in the wheat yield due to PP amendment to T.S.P. there was a definite increase in the amount of P and Zn removed by the wheat crop. Phosphorus uptake by wheat plants increased from 14.4 kg/ha to almost 20 kg/ha when PP was incorporated with T.S.P. In the case of zinc, the increases were from 100 g/ha to a range of 160-180 g/ha. The failure of PP to improve yield when it was clearly able to increase P and Zn recovery could be attributed to the fact that the wheat crop was grown on a Kuwaiti desert site, where P and Zn availability were not the main restraining factors in crop yield. Other environmental and physical constraints may have a stronger role in limiting this crop yield. It could be speculated that if the other conditions for the wheat crop to reach its yield potential were present, then improved P and Zn availability might further increase that yield.

Soil extracts designed to indicate fertility levels available to plant growth, tend to support the results of plant tissue analysis. The data shown in the table (Table 5.4A) indicates clearly the improved "availability" of P and Zn in response to the treatments containing PP. $NaHCO_3$ extractable P more than doubled when PP amended T.S.P was used, even at the low levels of 5 and 10% PP when compared to treatments receiving the same overall P levels as T.S.P.

Table 5.4A Elemental content of $NaHCO_3$-P and DPTA extraction of Kuwaiti field soil. Means of 72 replicates.

Treatment of P (OP ± % PP)	pH 1:1 H_2O	$NaHCO_3$-P (µg/g)	DPTA extraction (µg/g)		
		P	Fe	Zn	Mn
Control (no P)	7.6	22	2	0.9	2
OP + 0%PP	7.5	33	2	0.8	2
OP + 5%PP	7.7	81	2	1.3	1
OP + 10%PP	7.6	87	2	1.8	2
L.S.D.	N.S.	(.01) 27.2	N.S.	(.05) 0.42	N.S.
H.S.D.	N.S.	(.01) 34.1	N.S.	(.05) 0.51	N.S.

Table 5.4B $NaHCO_3$-P and DPTA soil extractions with or without micronutrients addition. Means of 36 replicates.

Analysed Element	Elemental concentration (µg/g) from soils with or without micronutrients		Significance
	+	-	
P	53.60	57.80	N.S.
Fe	2.32	2.30	N.S.
Zn	1.34	1.06	N.S.
Mn	1.54	1.51	N.S.

Table 5.4C $NaHCO_3$-P extract (µg/g) at three soil depths. Means of 36 replicates.

Depth of soil section (cm)	Treatent of phosphorus			
	Control	OP+0%PP	OP+5%PP	OP+10%PP
0-30	20.8	31.5*	68.4**	73.6 **
30-60	18.9	17.8	17.2	19.7 N.S.
60-90	3.5	5.6	6.1	4.2 N.S.

*	Significant at (.05)
**	Significant at (.01)
N.S.	Non-significant

only. This highly significant improvement in the level of $NaHCO_3$-P could be the result of lower adsorption and/or precipitation of OP with the soil $CaCO_3$ and Ca^{2+} ions. It is interesting to note, that the level of $NaHCO_3$-P available in the control soil, not treated with any phosphate fertilizer, would be considered relatively "adequate" (minimum of 15.2 µg/g and average 21.5 µg/g). This could be attributed to the generous fertilization practised over several years on the field which was used and to the P contained in the FYM. Moreover, the T.S.P. only, (0% PP) treated soils had a high index value for $NaHCO_3$-P (> 30 µg/g) for corn and small grains. This could explain why wheat grain yield showed no significant response to the improved levels of "available" phosphate provided with the PP treatments. In such a situation it could be recommended that a scaled-down fertilization practice of applying only 50-100 kg P_2O_5 incorporating 5-10% PP would satisfy crop requirements.

Iron, zinc and manganese DTPA extractions in samples taken at 30 days after planting showed only zinc to behave positively to PP inclusion (Table 5.4A). DTPA-Zn extract was significantly increased by about 65% and 125% for the 5% and 10% PP amended T.S.P., respectively, when compared to the control or T.S.P. only treated soil extractions. The levels of DTPA-Zn for the non-PP treated soils were in the "marginal" range for crop growth, whereas the incorporation of PP increased the level to an "adequate" range for irrigated soils. Iron and Manganese DTPA extraction showed no relation to PP presence. Moreover, the levels of Mn in the studies soil were "adequate" for most agricultural crops. On the other hand DTPA-Fe levels were low, at about half the amount regarded as required for irrigated agriculture.

Table (5.4B), indicates the lack of any benefit from the practice of incorporating a combination of micronutrient salts on the availability levels of the plant nutrients in samples taken 30 days after planting. A possible Fe deficiency causing reduced yield potential was there since the resulting DTPA-Fe levels were in the lower marginal range for irrigated crops. Furthermore, the data in Table 5.4C for soil samples collected 90 days after planting indicates that the effect of PP in enhancing $NaHCO_3$-P availability is limited to the top 30 cm of the soil profile. Beyond that depth no significant variations exist between the extractable P levels. A relatively "adequate" level of $NaHCO_3$-P in the 30-60 cm portion compared to the 60-90 section could be explained by the physical downward movement of phosphate over the cropping years, and by the practice of deep ploughing which was practiced in alternate years on the site.

5.3.2 Glass-house Experiments

A series of glass-house experiments designed to investigate the potential benefit of incorporating PP with orthophosphate (OP) on phosphorus and some micronutrient plant availablity were conducted at the college heated glass-house. The effects of saline irrigation water on PP/soil behaviour were also studied. Corn and oats were used as test crops for their sensitivity to phosphorus and micronutrient deficiency. Tables 5.5, 5.6, 5.7 and 5.8 indicate the plant yields per pot both fresh and dry. They also indicate the elemental concentration of P, Fe, Zn and Mn in whole plant tissue, and the total element uptake per pot. Tables (5.9 A-D and 5.10) show the "extractable" elemental concentrations in the soil growing media as it was influenced by various fertilization treatments. Results in Table 5.5 clearly indicate that corn irrigated with distilled water and grown on soil treated with PP amended OP had its green and dry yield increased significantly when compared to the control or OP only treated soil. However only the high dosage of 10% PP did significantly increase the corn dry matter yield above that of OP treatments. Furthermore, the PP treatments also revealed a highly significant increase in the P and Zn plant tissue content (Table 5.5). The P content almost doubled, and the Zn content increased by about 30% with the PP treatments. These increases were similar at the 5 or 10% PP levels. Iron content (table 5.5), in corn and total uptake per pot (table 5.5) were found to be not

Table 5.5 Yield and elemental concentration of corn growth with distilled water. Means of 36 replicates.

Treatment of P	Yield (g/pot)		Element conc (µg/g)			
(OP ± % PP)	Fresh	Dry	P	Fe	Zn	Mn
Control (no P)	31.9	3.64	2258	49	29.8	43
OP + 0% PP	40.0	4.79	2322	47	31.5	40
OP + 5% PP	43.2	5.5	3854	46	42.2	44
OP + 10% PP	51.0	5.82	3898	47	40.6	45

L.S.D.	(.01) 9.6	(.05) 1.25	(.001) 528	N.S.	(.01) 7.46	N.S.
H.S.D.	(.05) 9.5	(.05) 1.67	(.001) 622	N.S.	(.01) 9.26	N.S.

Elemental uptake by corn grown with distilled water

Treatment of P	Elemental uptake (mg/pot)			
OP ± % PP)	P	Fe	Zn	Mn
Control (no P)	7.50	0.17	0.11	0.16
OP + 0% PP	11.88	0.23	0.15	0.20
OP + 5% PP	21.89	0.26	0.24	0.24
OP + 10% PP	22.76	0.27	0.24	0.27

L.S.D.	(.01) 7.12	N.S.	(.05) 0.066	(.05) 0.06
H.S.D.	(.01) 8.83	N.S.	(.05) 0.089	(.05) 0.08

Table 5.6 Yield and elemental concentration of corn grown with brackish water. Means of 32 replicates.

Treatment of P	Yield (g/pot)		Element conc (µg/g)			
(OP ± % PP)	Fresh	Dry	P	Fe	Zn	Mn
Control (no P)	32.1	3.63	2121	37	27.5	48
OP + 0% PP	44.6	4.78	2487	39	30.4	47
OP + 5% PP	59.2	6.12	3626	42	41.7	41
OP + 10% PP	55.4	5.74	3723	42	41.0	43

L.S.D.	(.05) 8.6	(.05) 0.89	(.01) 595	N.S.	(.01) 5.29	N.S.
H.S.D.	(.05) 11.4	(.05) 1.19	(.01) 739	N.S.	(.01) 6.57	N.S.

Elemental uptake by corn grown with brackish water

Treatment of P	Elemental uptake (mg/pot)			
(OP ± % PP)	P	Fe	Zn	Mn
Control (no P)	7.50	0.13	0.10	0.16
OP + 0% PP	11.88	0.19	0.15	0.22
OP + 5% PP	21.65	0.25	0.25	0.24
OP + 10% PP	21.23	0.24	0.23	0.25

L.S.D.	(.01) 3.10	(.05) 0.04	(.05) 0.034	(.05) 0.027
H.S.D.	(.01) 3.85	(.05) 0.053	(.01) 0.42	(.05) 0.036

related to the PP treatments. It was also found that the small differences in Mn content with various PP treatments were not significant. Although increased Mn uptake per pot was indicated at the 5% level of probability, this may be misleading and due to the improved yield effect of PP.

Results of the corn growth experiment utilizing brackish water are reported in Table 5.6. The improvement in green and dry weight, due to the addition of PP at 5 and 10%, are clearly shown (table 5.6) and were in the 28 and 24% range respectively. But more important findings were the highly significant increases in the content and uptake of P and Zn, 48% and 38% increases were observed in the corn tissue content of P and Zn; respectively, when OP was amended with 5 or 10% PP. Similar increases were obtained with total uptake of P and Zn per pot (table 5.6). As was observed with corn plants grown under the distilled water regime, the plant tissue content of Fe and Mn obtained with brackish irrigation had no significant relation to PP treatments. Their misleading increased uptake per pot was purely due to the significant increases in dry matter yield.

The duplicate growth experiments utilizing oats instead of corn as a test crop, gave similar results to those obtained for corn subjected to distilled or brackish irrigated trials. Table 5.7 for oats irrigated with distilled water reveals that there was a significant improvement in yield with OP fertilization, but no further increases from incorporating PP, while utilizing brackish irrigation (table 5.8) resulted in a significant, but small, dry matter yield increase with PP. Although there was a positive response in oat yields with OP fertilization, the lack of further yield improvement with the application of PP, especially with the distilled water trials, could be explained in that the spring oat variety used was grown out of season in late autumn. Although the glass house was temperature-controlled (16-18°C), it may be that reducing day light period (less growth degree light) could have hindered the growth vigour of the plants. Phosphate and Zn content of the oat plant tissue did respond strongly to the PP inclusion. The P content

Table 5.7 Yield and elemental concentration of oats grown with distilled water. Means of 32 replicates.

Treatment of P	Yield (g/pot		Element conc (µg/g)			
OP ± % PP)	Fresh	Dry	P	Fe	Zn	Mn
Control (no P)	17.62	2.73	4268	102	31.4	124
OP + 0% pp	25.55	3.92	4791	93	35.3	110
OP + 5% PP	26.75	4.32	5725	106	43.5	120
OP + 10% PP	25.55	3.97	6405	99	47.3	141

L.S.D.	(.05) 3.25	(.05) 0.81	(.01) 1239	N.S.	(.05) 6.9	N.S.
H.S.D.	(.05) 4.34	(.05) 1.09	(.01) 1537	N.S.	(.05) 9.3	N.S.

Elemental uptake by oat grown with distilled water

Treatment of P	Elemental uptake (mg/pot)			
(OP ± % PP)	P	Fe	Zn	Mn
Control (no P)	11.59	0.28	0.09	0.34
OP + 0% PP	14.58	0.36	0.14	0.42
OP + 5% PP	24.21	0.46	0.19	0.52
OP + 10% PP	24.89	0.33	0.18	0.53

L.S.D.	(.01) 6.52	(.05) 0.072	(.01) 0.039	(.05) 0.081
H.S.D.	(.01) 8.09	(.05) 0.096	(.01) 0.048	(.05) 0.108

Table 5.8 Yield and elemental concentrations of oats grown with brackish water. Means of 32 replicates.

Treatment of P	Yield (g/pot)		Element conc (µg/g)			
(OP ± % PP)	Fresh	Dry	P	Fe	Zn	Mn
Control (no P)	16.53	2.80	6018	95	25.2	108
OP + 0% PP	38.02	6.02	6174	94	29.0	109
OP + 5% PP	40.92	7.45	6684	102	41.8	111
OP + 10% PP	43.71	7.65	6631	102	44.5	112
L.S.D.	(.01) 10.29	(.05) 0.96	(.05) 465	N.S.	(.01) 6.37	N.S.
H.S.D.	(.01) 14.08	(.05) 1.29	(.05) 621	N.S.	(.01) 7.90	N.S.

Elemental uptake by oats grown with brackish water

Treatment of P	Elemental uptake (mg/pot)			
(OP ± % PP)	P	Fe	Zn	Mn
Control (no P)	16.87	0.26	0.07	0.32
OP + 0% PP	37.20	0.56	0.17	0.65
OP + 5% PP	49.57	0.76	0.31	0.83
OP + 10% PP	50.62	0.79	0.34	0.86
L.S.D.	(.01) 8.73	(.05) 0.14	(.01) 0.06	(.05) 0.15
H.S.D.	(.01) 10.82	(.05) 0.18	(.01) 0.07	(.05) 0.20

increased by 19.5-27% and about 8% with the application of PP for the distilled and brackish trials respectively (Tables 5.7, 5.8). On the other hand, Zn content increased by 23-34% and 44-53% when distilled and brackish irrigation water were utilized respectively (Tables 5.7, 5.8). Iron and managanese behaved in a similar way in oats to their behaviour in corn, and both did not respond to PP amendments.

Phosphate and zinc soil extractions by the $NaHCO_3$ and DTPA methods respectively, obtained after plants had been harvested (tables 5.9A-D), supported the plant tissue findings. In all growth trials with corn or oats, and under both distilled or brackish irrigation regimes, soil analyses were similar (Tables 5.9A-D). Soil pH was not affected by OP application or inclusion of PP and other micronutrient salts at the low levels used in these experiments. $NaHCO_3$-P indicated highly significant increases in response to the inclusion of PP at 5 and 10%. These $NaHCO_3$-P levels were more than doubled and in some instances tripled when compared to the control or OP only treated soils. Also there was more phosphate available with 10% compared to 5% PP (Table 5.9A, 5.9B, 5.9C and 5.9D) application with the exception of the distilled water oat experiment, in which there were no significant changes in P-extraction with the PP rates utilized (Table 5.9C). It should be noted, that OP only treated soils have had their $NaHCO_3$-P levels increased significantly ($p>.05$) in some cases, specially under distilled irrigation regimes (tables 5.9A,C) Generally, however, $NaHCO_3$-P levels with only OP fertilization would be agronomically regarded as being in a "marginal range", whereas the inclusion of 5 or 10% PP increased the levels to "adequate" contents for irrigated corn and small grains.

DTPA-Zn extracts also indicated a highly significant response to PP application. However the "available" Zn increases under brackish irrigation were lower than those obtained under distilled water (in the case of corn (tables 5.9A, 5.9B)), perhaps due to increased ionic interference, whereas in the oat

Table 5.9A Elemental concentration (µg/g) of soil extractions from glasshouse experiment utilising corn grown with distilled water. Means of 32 replicates.

Treatment of P	pH	$NaHCO_3$-P (µg/g)	DPTA extraction (µg/g)		
(OP ± % PP)	1:1	P	Fe	Zn	Mn
Control (no P)	7.7	5	2	0.2	2
OP + 0% PP	7.8	12	2	0.2	2
OP + 5% PP	7.7	34	2	1.0	2
OP + 10% PP	7.9	40	2	1.2	1
L.S.D.	N.S.	(.01) 6.29	N.S.	(.01) 0.21	N.S.
H.S.D.	N.S.	(.01) 7.81	N.S.	(.01) 0.26	N.S.

Table 5.9B Elemental concentration (µg/g) of soil extractions from glasshouse experiment utilising corn grown with brackish water. Means of 32 replicates.

Treatment of P	pH	$NaHCO_3$-P (µg/g)	DTP extraction (µg/g)		
(OP ± % PP)	1:1	P	Fe	Zn	Mn
Control (no P)	7.6	6	2	0.3	1
OP + 0% PP	7.6	9	3	0.2	1
OP + 5% PP	7.7	39	2	0.9	1
OP + 10% PP	7.7	36	2	1.1	1
L.S.D.	N.S.	(.01) 9.37	N.S.	(.01) 0.157	N.S.
H.S.D.	N.S.	(.01) 11.62	N.S.	(.01) 0.194	N.S.

Table 5.9C Elemental concentration (µg/g) of soil extractions from glasshouse experiment utilising oat grown with distilled water. Means of 32 replicates.

Treatment of P	pH	$NaHCO_3$-P (µg/g)	DTPA extraction (µg/g)		
(OP ± % PP)	1:1	P	Fe	Zn	Mn
Control (no P)	7.8	5	2	0.4	2
OP + 0% PP	7.7	9	3	0.4	2
OP + 5% PP	7.9	28	3	0.8	2
OP + 10% PP	7.8	36	3	0.8	2
L.S.D.	N.S.	(.01) 7.78	N.S.	(.01) 0.23	N.S.
H.S.D.	N.S.	(.01) 9.65	N.S.	(.01) 0.28	N.S.

Table 5.9D Elemental concentration (µg/g) of soil extractions from glasshouse experiment utilising oat grown with brackish water. Means of 32 replicates.

Treatment of P	pH	$NaHCO_3$-P (µg/g)	DTPA extraction (µg/g)		
(OP ± % PP)	1:1	P	Fe	Zn	Mn
Control (no P)	7.8	6	2	0.2	1
OP + 0% PP	7.9	6	3	0.2	2
OP + 5% PP	7.9	32	3	0.9	2
OP + 10% PP	7.9	36	3	0.9	2
L.S.D.	N.S.	(.01) 3.46	N.S.	(.01) 0.07	N.S.
H.S.D.	N.S.	(.01) 4.30	N.S.	(.01) 0.09	N.S.

experiments there were no differences due to type of irrigation. Furthermore, the levels of DTPA-Zn were "adequate" for the corn crops when distilled or brackish water was used, but at a "marginal" level for oat plants and could cause zinc deficiency, even with the 10% PP amendment. But, since these extractions were obtained from soils after plant harvesting, it could be that oats were more efficient in absorbing Zn and thus reducing its content in soil compared to corn. However, uptake data (tables 5.5, 5.6, 5.7, 5.8) do not support this hypothesis. A more probable explanation is that zinc was precipitated in oat roots and was not translocated to other parts of the plant. Unfortunately, no root analyses were carried out in this study.

DTPA extracts for Fe and Mn showed no response to the PP inclusions, and Fe levels were in a "deficient" range whereas the Mn levels were "adequate".

The inclusion of micronutrient sulphate salts has shown no effects on the $NaHCO_3$-P levels or any nutritional benefits in the DTPA extractable Fe, Zn and Mn (Table 5.10). DTPA-Mn from the distilled water irrigated corn and oat trials appeared to have significant increases on $MnSO_4$ addition, but it should be remembered that all soil extracts revealed "adequate" Mn supply.

5.3.3 Laboratory Experiments

5.3.3.1 Pyrophosphate and P sorption

The effectiveness of PP in maintaining a higher level of soil extractable P was tested. In this experiment P (OP and/or OP+PP) retention in calcareous soil was assessed after one day of vigorous shaking. The results (table 5.11) revealed a clear effect from OP addition, but no significant improvement in the $NaHCO_3$-P extraction due to PP treatments. Moreover, they indicate the strong reduction in extractable P; 89-94% of added P (OP±PP) was retained in the soil, even after only one day. This could be direct $CaCO_3$ adsorption of phosphate, or the formation of Ca-P compounds such as DCP which may with time transform to a more stable crystalline form(s). However, in this experiment PP failed to prevent

Table 5.10 Elemental concentration from soil extracts from glasshouse experiments. Means of 16 replicates.

Element	Plant	Type of irrig.	Element content from soil extract (µg/g)		
			with micro-nutrient	without micro-nutrient	
P	corn	distilled	22.5	23.4	N.S
P	oat	distilled	26.9	22.9	N.S
P	corn	brackish	19.8	20.5	N.S
P	oat	brackish	23.0	22.1	N.S
Fe	corn	distilled	1.99	1.83	N.S
Fe	oat	distilled	2.42	2.33	N.S
Fe	corn	brackish	2.76	2.63	N.S
Fe	oat	brackish	3.09	2.22	**
Zn	corn	distilled	0.66	0.63	N.S
Zn	oat	distilled	0.64	0.59	N.S
Zn	corn	brackish	0.56	0.62	N.S
Zn	oat	brackish	0.53	0.53	N.S
Mn	corn	distilled	1.87	1.39	*
Mn	oat	distilled	2.04	1.53	**
Mn	corn	brackish	1.03	1.26	N.S
Mn	oat	brackish	1.86	1.57	N.S

*	Significant at (.05)
**	Significant at (.01)
N.S	Non-significant

Table 5.11 Effect of pyrophosphate additions with orthophosphate on soil-P retention. Means of 3 replications.

Treatment of P (OP + % PP)	$NaHCO_3$-P (µg/g)	% of added P retained in the soil
Control (no P)	3.2	-
OP + 0% PP	11.7	91.5
OP + 5% PP	14.5	88.7
OP + 10% PP	8.9	94.3

L.S.D. (.05) 3.82

P adsorption/precipitation as had been observed in the field or glasshouse trials, even though in the field and glasshouse cases the soil P-extractions were conducted after much longer periods of soil-P (OP±PP) interaction. A possible explanation is that after the initial high P-soil retention, PP activities would with time cause more P to be released, but a more probable reason is that the artificial conditions of soil-P (OP±PP) suspension in diluted solution form in continuous agitation could have had increased soil $CaCO_3$ contact with the added P. Also, the more diluted environment coupled with the shaking probably caused many of the $CaCO_3$ particles to fracture thus increasing their reaction surface area with the possibility of greater amounts of dissolution which would also increase the levels of free Ca^{2+} ions in solution. This could eventually increase P adsorption/precipitation. As a note of caution, it should be pointed out that in these extractions the ratio of soil to extractant was 10g:60ml. This was much higher than the Olsen developed method and was twice the ratio that was used with the field or glasshouse extractions. The use of a higher ratio could have caused less P to be extracted. However, from previous work with this soil (>90% sand) the utilization of more soil to extractant gave more reliable results.

5.3.3.2 Pyrophosphate Hydrolysis

A test on the glass-house soils to determine the extent of PP hydrolysis, revealed almost complete conversion of PP into OP in the time allocated for crop growth. A technique using acidification and heat digestion (section 5.2.3.2), resulted in very little phosphate being diagnosed as PP (Table 5.12).

These levels representing PP remaining in the soil after ten weeks of plant growth should be observed with great care. The conditions and the techniques used had many limitations. The levels of PP applied to the soil were quite low to start with (5 and 10 mg kg^{-1}). Moreover, the ten ml aliquots that were acidified and heat digested were further diluted to 50 ml. These further dilutions resulted in readings at the lower sensitivity levels of the instrument. Since some of the

Table 5.12 P concentration differences in $NaHCO_3$-P extract after acidification and heat digesting as representing PP levels remaining in soils

µg PP/g soil corn/distilled irrigated	µg PP/g soil corn/brackish irrigated	µg PP/g soil oat/distilled irrigated	µg PP/g soil oat/brackish irrigated
-2.9	2.1	1.9	-2.4
4.0	8.6	-1.3	2.2
1.3	-3.3	1.2	3.8
0.5	0.4	-1.5	-0.8
1.9	3.4	1.7	-12.2
3.1	5.4	1.9	2.4
4.2	-5.6	-1.5	2.3
-4.0	-0.1	-1.4	-5.1
-1.8	-3.4	-2.1	1.8
-2.4	-4.8	2.5	2.3
1.6	1.6	1.2	-2.3
0.9	4.6	0.9	0.3
2.3	0.2	1.3	-2.6
-1.1	-2.2	-1.4	3.0
1.1	1.1	-3.3	1.5
0.6	-1.9	1.3	0.6
Mean: 1.3	1.7	0.9	1.3

** Mean values were tabulated from only positive values.

readings were negative (lower P after PP hydrolysis), it could be generalized that most of the PP had hydrolyzed within the ten week growing period. On the other hand, the levels could have been too low to be measured accurately as has been mentioned earlier or the technique may have failed to hydrolyse the remaining PP so it was not measured at all. Also there is a possibility that the $NaHCO_3$ extracts were assessing P "availability" from both OP and PP sources.

5.3.3.3 Pyrophosphate and P Mobility

In the column study that was designed to investigate any changes in P mobility in the presence of small amounts of PP, there were inconclusive results. The pH and P concentration of the leachates indicated no significant effect of including PP with OP (table 5.13). The pH of the leachates at the end of the first and second week were in the range of 7.6-8.1 and 7.4-7.7 respectively. The lowering of pH, after two weeks, was independent of the P treatments, though it was probably due to the leaching of any native Na_2CO_3 in the first week. The P concentration in the leachate was very low (0-0.9 $\mu g\ ml^{-1}$) and there were no clear variations due to any of the P treatments. $NaHCO_3$-P extractable levels from the various 5 cm sections produced from the dried soil column were also independent of the P treatments. Although $NaHCO_3$-P levels varied with depth, these results showed no significant response to the incorporation of PP with OP. Furthermore, there was great variation within the replications in the downwards movement of P, even in the columns receiving the same treatment. Since the soil was predominantly sand (> 90%) and most of the sand was in the medium to coarse range (200-600 um), this resulted in fairly rapid water infiltration through the columns. This fast water downward movement coupled with the appearance of cracks in the soil columns resulted in large portion of the applied powdery P and/or PP moving downward without much contact with the soil.

5.3.3.4 Pyrophosphate Effect on P-Zn Interaction

The antagonism of P/Zn has received a lot of attention in the literature.

Table 5.13 Effect of pyrophosphate addition with orthophosphate on P downward movement and leaching under heavy watering. Means of three replications.

Treatment of P	Leachate				Soil			
(OP ± % PP)	pH		P-cont µg/ml		$NaHCO_3$-P µg/g depth in cm			
	wk1	wk2	wk1	wk2	0-5	5-10	10-15	15-20
Control (no P)	7.9	7.6	0.2	0.0	1.0	0.9	2.3	1.1
OP + 0% PP	7.9	7.6	0.7	0.3	4.7	7.1	5.6	3.8
OP + 5% PP	7.8	7.5	0.4	0.8	7.8	7.2	3.9	2.5
OP + 10% PP	7.8	7.6	0.6	0.5	3.5	6.6	7.2	5.9
L.S.D.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.

Table 5.14 Effect of pyrophosphate on the P/Zn behaviour in Calcareous soil. Means of three replications.

Soil treatments	DTPA-Zn (µg/g)	$NaHCO_3$-P (µg/g)
Control (no P or Zn)	0.17	2.9
OP + 0% PP + Zn	0.39	8.4
OP + 10% PP + Zn	0.92	17.6
PP + Zn	1.04	27.5
No P + Zn	0.53	2.7
L.S.D.	(.05) 0.187 (.01) 0.259	(.05) 4.39 (.01) 6.09

However, the cause and site of this interaction is still the subject of controversy. In this experiment interactions between P and Zn in calcareous soil were measured after eight weeks incubation. Furthermore, the modification of that behaviour in the presence of PP as a small fraction (10%) of the total added P or as the sole P form were also observed. Results shown in table 5.14 represent the DTPA-Zn and $NaHCO_3$-P extractions for this experiment. The very low levels of DTPA-Zn and $NaHCO_3$-P in the non-amended soil (control treatment) confirms the deficiency of this soil with respect to these elements. Addition of $ZnSO_4$ salt significantly increased Zn-extractability over the control, but still in the "low" availability range (Lindsay and Norvell, 1969). The incorporation of OP with the Zn amendment to the soil also maintained significantly higher levels of DTPA-Zn in comparison to the non-Zn amended soil. This improved Zn extractability was less in the presence of OP than without it. However, the differences were not significant at the 5% level of probability. Incorporation of a small amount of PP with the OP resulted in a highly significant increase in DTPA-Zn not only over that of the control treatment, but also over the Zn amended soil with or without OP present. Use of PP as the only P source also improved the extractability of Zn, but the levels were not significantly different from those with only 10% PP.

$NaHCO_3$-P levels increased upon the addition of OP to the soil (table 5.14). Incorporation of 10% PP with OP further increased P extractability, moreover, the PP alone treatment gave the highest $NaHCO_3$-P levels. From these observations clearly the use of PP had increased P extractability, but this did not cause a reduction in Zn-extractability. In fact PP also increased the Zn extractable levels, suggesting that the P/Zn antagonism does not occur in the soil, at least not with this particular soil, and with phosphate enhancement caused by PP addition. This work is of course based on DTPA extractable Zn as a measure of "available" Zn and must be interpreted carefully in the context of Zn availability to plants.

5.4 DISCUSSION

5.4.1. Pyrophosphate Effect on Plant Growth and Uptake of P

Amending phosphatic fertilizer with pyrophosphate in amounts as small as 5% has shown a definite effect on the soil extractability of P and Zn, and more importantly, on the plant uptake of P and Zn. Figure 5.1 clearly indicates the improvement in the P concentration in the various parts of the plant tissue grown in the field experiment. Moreover, the concentration of P in plant tissue in the control did not differ from that receiving only OP, whereas, the incorporation of 5% PP into OP, while maintaining the same overall P levels, clearly improved P uptake. The increases in plant concentrations were about one third greater than those in the OP only or control treatment for the plant tissue. Yield of wheat grown in the field, however, did not improve with the inclusion of PP into OP fertilizer (tables 5.1, 5.2). As mentioned earlier, the field soil had a history of "rich" P fertilization and annual applications of FYM which probably was the reason for this lack of response to PP. Still the treatment containing a OP/PP mixture performed as well as or slightly better than the treatments where OP was the sole source of P. Similar findings were reported by Lathwell *et al.*, (1960); Stroehlein *et al.*, (1968) and MnKeni and MacKenzie, (1988). On the other hand, other studies found that plants absorbed more P from an OP than an OP/PP mixed source (Sutton and Larsen, 1964; Sutton *et al.*, 1966; Hughes and Hashimoto, 1971; Subbarao and Ellis, 1975). In their studies PP fertilizers were compared to OP and in such short term experiments (few days), that PP hydrolysis was not significant. Plant preferred HPO_4^{2-} and $H_2PO_4^-$ was more prevalent with OP than the polyphosphate fertilizers. This was reflected in the higher dry matter and P-uptake that they obtained.

When similar experiments were conducted utlizing severely P-deficient soil in the glasshouse, more favourable responses to PP inclusion were obtained. Green yield responses of corn and oat, with the incorporation of PP into OP are

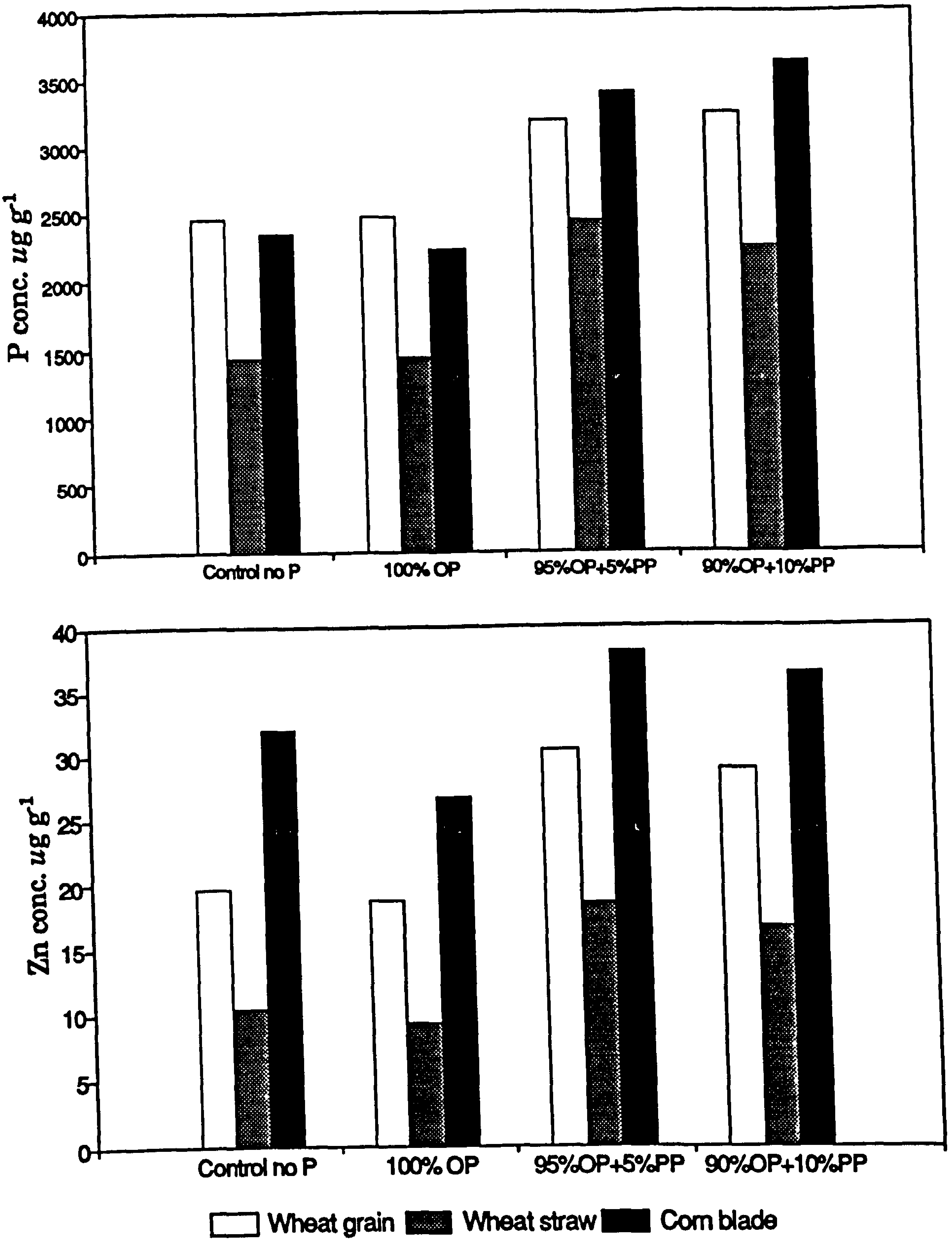


Fig. 5.1 Effect of amending T.S.P. with 0, 5 and 10% Pyrophosphate on the plant tissue concentrations of P and Zn for wheat and corn grown on calcareous soil in Kuwaiti field.

shown in Figure (5.2). Corn plants showed a clear and significant improvement in the green yield with the PP addition. This was even more apparent under the brackish irrigation regime. However, this has not indicated any advantages to saline irrigation. The higher green yield levels of brackish water irrigated corn in comparison to that of distilled water irrigated, was misleading and it may reflect more humid conditions when the crops were harvested. Dry matter yields (Fig. 5.2) clearly indicated no significant difference between brackish or distilled irrigation with respect to corn, and showed clear improvement in the dry yields with the addition of PP which ranged between 15% and 18%. This was in agreement with the finding of Amer *et al.* (1982), where a higher yield of corn was obtained with the incorporation of 2% PP. Increasing the ratio of PP to OP from 5 to 10% did not make any significant improvement in the dry yield (fig. 5.2). Amer *et al.* (1982), similarly found no positive yield responses when they increased the PP/OP ratios from 2% to 10%.

Oat plants behaved differently from those of corn. Distilled water irrigated oats had poor growth and did not respond to PP treatment, whereas the brackish water irrigated oats had an adequate growth and responded positively to PP amendment in both green and dry yields (Fig 5.2). The unsatisfactory growth levels of distilled water irrigated oats are probably due to growing the spring-oat variety Peniarth in the wrong season (grown during the autumn between September and November). The shorter day light had an adverse effect on the crop growth pattern, although it was grown in a heated glass-house. When considering the brackish irrigated oat an improvement in dry matter yield was achieved with the incorporation of PP. This increased yield was in the range of 20-25% (Fig. 5.2). Uzu *et al.* (1983) had similar results. They reported higher corn yields when their soil was fertilized with PP rather than OP, but only after liming the acid soils to a pH greater than 6.0. However, MnKeni and MacKenzie (1988) found that liming one of their soils resulted in NaPP being

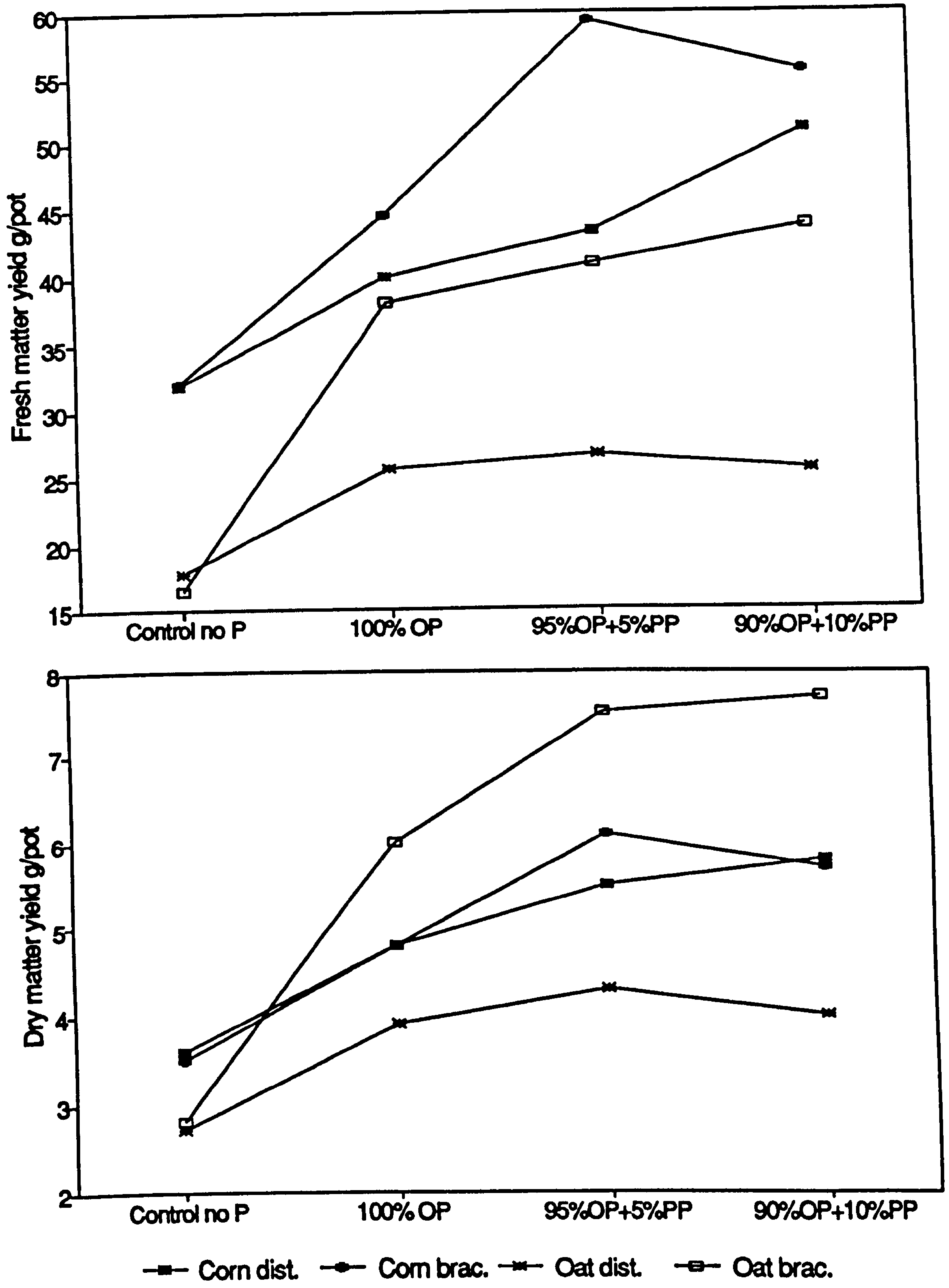


Fig. 5.2 Fresh and dry matter yields of corn and oat grown in a pot experiment, fertilized with OP amended with 0, 5 and 10% PP and irrigated with distilled and brackish water.

less effective than NaOP, while with other soils either source of P was equally effective. Several other studies were more in line with the results explained here. Corn and tomatoes performed better with PP containing fertilizer than OP in a pot experiment (Fourcassie and Gadet, 1966). Webb (1970) cited by MnKeni and MacKenzie (1978) also reported superiority of PP over OP type P fertilizer for corn when soils were basic or slightly acidic. Nevertheless, in another study on an alkaline soil, corn grew better with OP than PP (Subbarao and Ellis, 1975). This could have resulted from the formation of unavailable and stable PP compounds. However, if these compounds did dissolve with time, this could have a carry-over affect for subsequent crops. Stroehlein *et al.* (1969) showed that tomatoes yielded better with PP when it was the second crop, while OP was superior with the first crop of barley. The concept of PP having the properties of a slow-release P fertilizer has been suggested by Lehr *et al.* (1964). Singh and Dartigues (1970) reported that corn had given higher yields with PP containing fertilizer than an OP source, when grown on a Zn deficient soil. They concluded that Zn was more soluble with PP application which had resulted in higher Zn uptake and corn yield. However, Mortvedt and Osborn (1977) found that micronutrient solubilities including those of Zn were increased only for a very short time when PP was utilized as P fertilizer on neutral or calcareous soils.

These conflicting reports could be attributed to the fact that work has been conducted with different types of PP/OP sources and ratios which may have resulted in certain P ionic species being more abundant than others. Also, the length of experiments and environmental conditions could have had great influence on the way these compounds reacted. It seems that PP rates of hydrolysis, adsorption and precipitation vary greatly from one soil to another. Therefore, its effect on plant growth and nutrition would depend on these complex and inter-related circumstances.

Phosphate uptake by corn grown on the PP amended soil has indicated a large improvement in plant tissue P content and this was highly significant in both distilled and brackish water irrigated corn, averaging about 40 and 54% respectively (Fig. 5.3). On the other hand, the distilled water irrigated oat crop had poor overall yields, which has been attributed to growing the plant in the wrong season, but its P uptake responded positively to the addition of PP. The P tissue concentration increased by 15 and 25% with 5 and 10% PP treatments respectively (Fig. 5.3). The brackish water irrigated oat crop yielded more than the distilled water irrigated crop and its yield responded positively to the PP treatment, but its P tissue concentration had no significant variation due to the PP treatments. As indicated in Fig. 5.3 oats grown with brackish water had a higher P content for all the P treatments.

From the previous glass-house experiments, it could be said that P sensitive plants, such as corn, have reacted positively to the improved availability of phosphate in the growth media. The $NaHCO_3$-P levels extracted from PP amended soils were about twice the levels in the OP only treated soils (Fig. 5.4). Similarly, other plants like oats utilized in these experiments behaved favourably to the increased supply of soil P. Therefore, when the plant gowth vigour was strong it absorbed more P and as P soil levels were less limiting (fig. 5.4) when PP was added, this resulted in higher yields. On the other hand when growth conditions were unfavourable, such as declining day light hours, and plant vigour was weak, this resulted in an overall low yield. As these plants were relatively small, the increased levels of soil P (fig. 5.4) in response to PP treatments, resulted in more P accumulation in the plant tissue. But this additional P was not utilized to increase the plant growth because of other limiting factors, i.e. reduced photosynthetic activities, which in turn restrained the plant growth potential. Moreover, these experiments indicated that oats have higher requirements for P than those of corn and tend to accumulate higher levels of P in tissue at the growth stage that was analysed.

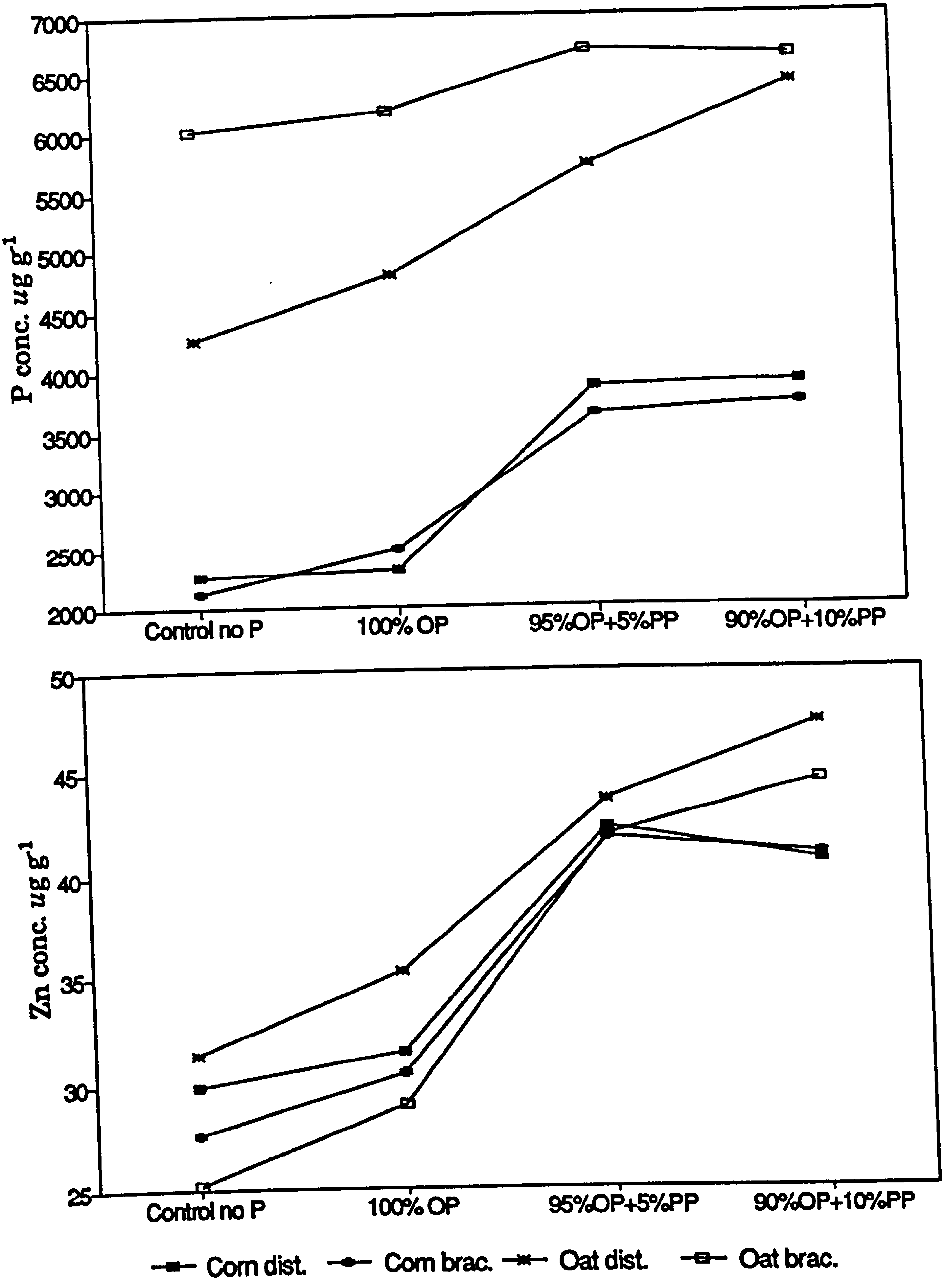
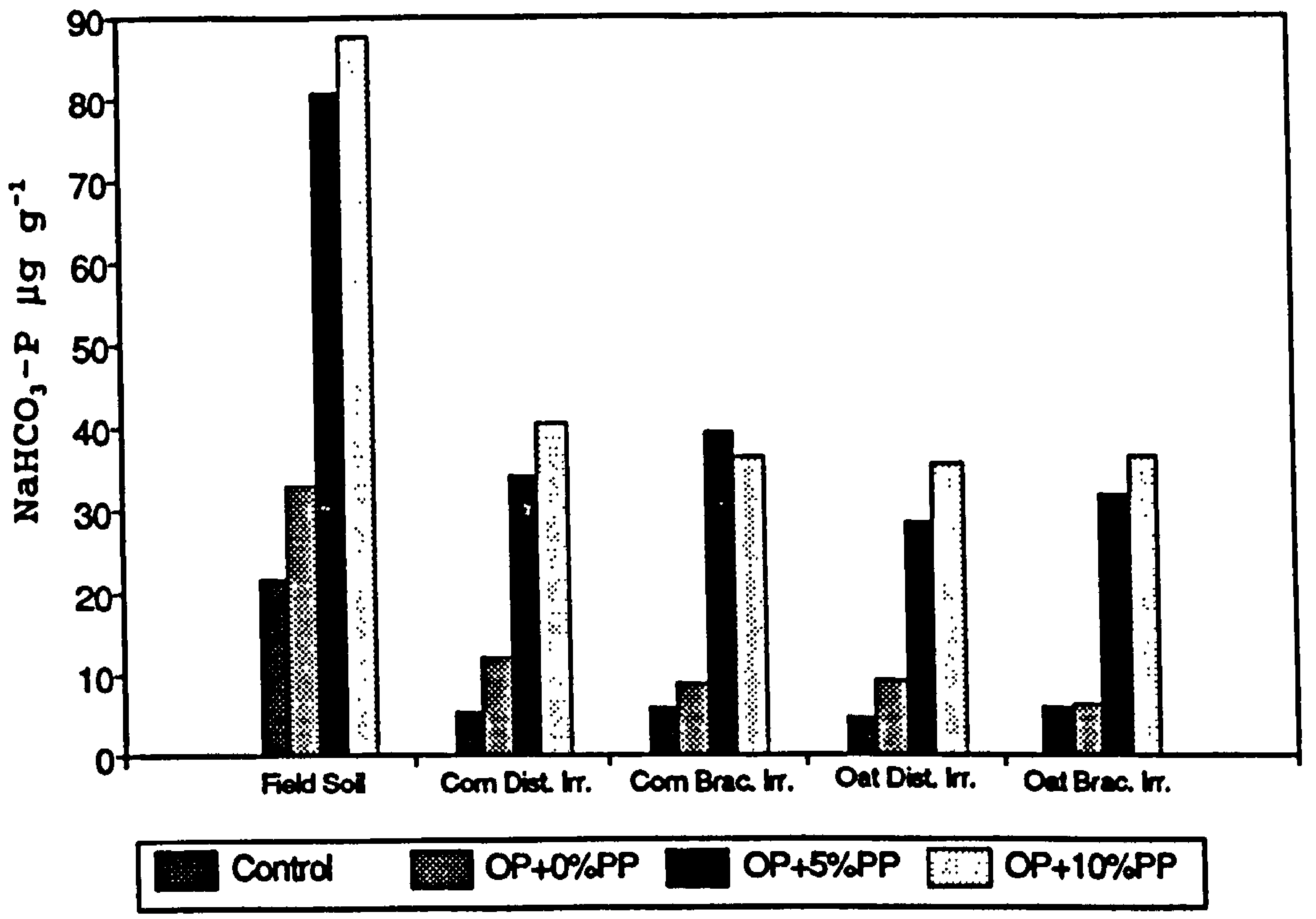


Fig. 5.3 Phosphorus and zinc tissue concentration for corn and oat grown in a pot experiment, fertilized with OP amended with 0, 5 and 10% PP and irrigated with distilled and brackish water.

5.4.2 Effect of Pyrophosphate on Zn Phyto-availability and Uptake

Pyrophosphate had a definite impact on zinc (Zn) recovery by the various plants tested and on the soil availability index (DTPA) of this nutrient. It was clearly shown in the field experiment (Fig. 5.1) that Zn plant tissue concentration was greatly enhanced by the impact of PP presence. This positive response was more apparent in the case of wheat, both in straw and grain, than in the corn. The effect of PP on soil Zn solubility could be explained by the capacity of PP to solubilize organic matter, which in turn can chelate Zn, as has been suggested by Mortvedt and Osborn (1977), although with questionable benefit on arid region calcareous soils of very low organic matter content. Since all the field received a good application of FYM compost, the concept of PP hydrolysing this organic source, thus increasing the amount of Zn loosely bonded to the organic coloids becomes conceivable, as has been revealed by the doubling of soil DTPA-Zn extractability (Table 5.4a). However, if PP influence was by enhancing organic chelation, then the levels of soil DTPA extractable Fe and Mn should also have increased, but this was not the case. The DTPA-Fe levels did not change with the addition of PP, although it was in a deficient range. Similarly DTPA-Mn levels did not have a significant response to PP. This brings into question the PP-organic solubilization theory. Giordano *et al.* (1971) have suggested that the PP affect on soil O.M. was indirect by raising soil pH. Although at higher pH Zn concentration usually decreased but the stability of Zn complexes reached maxima at about pH 8.0. This was in agreement with other work where it was reported that Zn-humic acid complexes had their highest stability constants at pH 8.0 (Randhawa and Broadbent, 1965). MnKeni and MacKenzie (1985) support the concept of PP solubilizing soil O.M. however depending on its content, it could increase soil retention by exposing more adsorption sites otherwise coated by O.M. Moreover, their finding had also shown increased solubilization of Fe, but to a very small extent of the potentially available amorphous or crystalline forms. In the glass-house studies the native Kuwaiti soil which was used contained insignificant amounts of organic matter, and only non-organic materials (gravel and vermiculite) were used to enhance its water percolation and aeration. Under such conditions the PP treatments resulted in a large increase in the Zn tissue concentration in both corn and oat plants (Fig. 5.3). Furthermore, the DTPA-Zn extraction from these soils were greatly enhanced in the presence of PP (Fig. 5.4). This supports the idea of Asher and Bar-Yossef (1982), that the increase in soil-Zn availability and enhanced plant uptake should be attributed to the sequesterization ability of PP for soil-Zn. Moreover, this PP-Zn relationship was specific to this element, and the sequesterization was applicable to neither (Fe) nor (Mn) (Table 5.9 a-d). The reaction of PP in soil and the way it affects the solubility of Zn could be by raising the soil pH (Xie and MacKenzie, 1989) and at higher pH the Zn-organic complexes increased in stability as has been discussed earlier. However in this soil, pH did not increase with PP amendments (tables 5.4a and 5.9) probably due to the initially high pH, buffered by soil effective levels of $CaCO_3$. Also other studies had shown no effect on soil pH by PP (Amer and Mostafa, 1981), while El-Zehaby *et al.* (1982) even reported lowering of pH upon addition of NaPP. Application of PP and its subsequent adsorption was found to increase soil cation exchange capacity (C.E.C.) and the associated amounts of Zn sorption (Xie and MacKenzie, 1990). However they also found less exchangable Zn as more PP was adsorbed and therefore they suggested that PP sorption could increase surface negative charge which would allow Zn^{2+} to get closer to soil colloid surfaces where it could eventually be specifically sorbed. Furthermore, they found that PP sorption was associated with Fe, Al, clay and O.M. and they speculated that Zn-PP complexes associated with them. Coarser soil, therefore would have less of these complexes sorbed, which could be the case in this Kuwaiti soil which was predominantly sandy with very little O.M.. Bar-Yosef and Asher (1983), supported the concept of direct



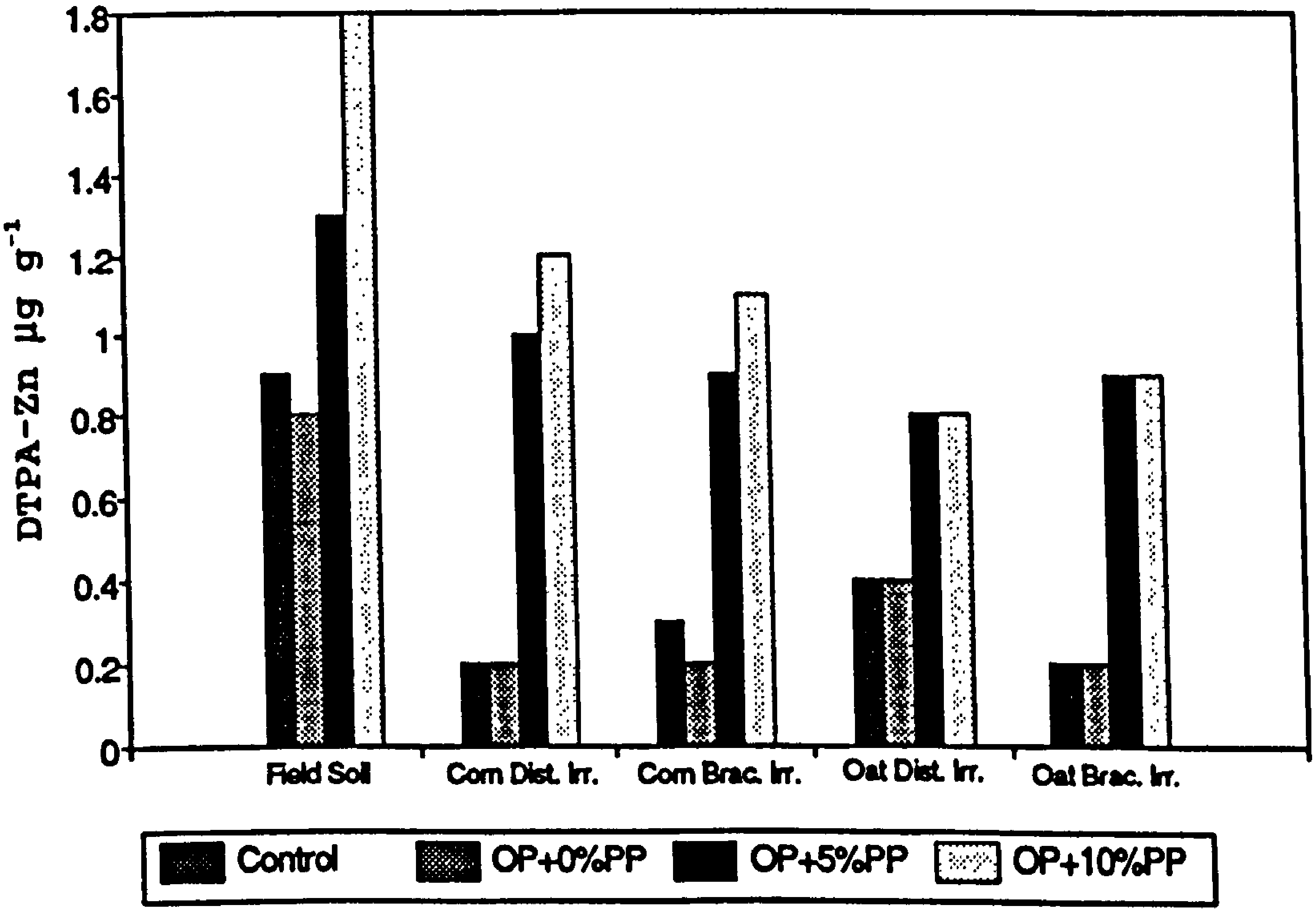


Fig 5.4 **$NaHCO_3$-P and DTPA-Zn soil extracts from the field and various glasshouse pot experiments where OP fertilized soils were ammended with 0, 5 and 10% PP.**

sequesterization of Zn by PP, but only at higher soil pH where the initial PP concentration was above a certain threshold of its specific sorption. In other words, if soluble PP were maintained in soil solution, this would increase soil soluble Zn. In these field or glasshouse experiments amounts of PP applied were very small and the duration of soil-PP contacts were of many weeks, nevertheless levels of DTPA-Zn were higher with PP than without. This suggests that soluble PP was maintained in soil with no appreciable hydrolysis, or that another mechanism existed by which the changed behaviour of soil Zn would continue long after the disappearance of PP.

5.4.3. Reaction of PP in the Calcareous Environment

The behaviour of applied PP to alkaline calcareous soil was found to be quite complex. In an over-simplification, several aspects will be discussed separately to try to yield a deeper understanding of how varous factors may have influenced its reactions. An overall assessment will then be drawn to explain the findings of this study.

PP in general was reported to be adsorbed by soil $CaCO_3$, Fe and Al oxides and some O.M. fractions (Xic and MacKenzie, 1990; MnKeni and MacKenzie, 1985; Uzu *et al.*, 1983; Amer *et al.*, 1985; Hughes and Hashimoto, 1971; Philen and Lehr, 1967). However, at higher soil pH less PP would be adsorbed by the soil (Bar-Yosef and Asher, 1983; Xie and MacKenzie, 1990), possibly due to competition by OH^- for adsorption sites, whereas at soil pH of 6.1 or below very little soluble PP was found (Smith and Martell, 1976). Moreover, the adsorption of PP in comparison to OP was reported to be higher, but with conflicting findings on the strength of this binding. Works by Sutton and Larson (1964) reported lower bonding energy for PP resulting in more of it being soluble, while Uzu *et al.* (1983) found more PP adsorption with stronger binding than OP. Furthermore, PP presence maintained higher levels of OP in solution (Amer and Mostafa, 1981) with findings that indicated a range of 17-34% of OP adsorption after one week (El-Zahaby *et al.*, 1982) in the presence of PP while without PP the adsorption was about 90% even after one day. It could be that PP was preferred on the adsorption sites of the $CaCO_3$, and due to its higher valence, it reduced the zeta potential to a greater degree thus reducing the amounts and strength of OP adsorption (Amer *et al.*, 1985). In the study carried out in the laboratory, there was no variation in the adsorption of OP with or without PP after one day, however this could be due to the conditions of the experiment (vigorous shaking had increased $CaCO_3$ adsorption sites). A more likely reason is that the amounts of PP used and its ratio to OP were too small to effectively compete with OP/$CaCO_3$ adsorption. Nevertheless, in the field and glasshouse experiments, similar amounts of PP were used and their ratio to OP were too small (5-10% PP of the total P in the fertilizers) to compete for the soil $CaCO_3$ adsorption sites, but still the results indicated higher $NaHCO_3$ extractable P (fig. 5.4) and crop uptake. Similarly in an incubation study (no prolonged shaking), incorporating 10% PP in OP led to doubling of the extractable P (fig. 5.5). Even for the field soils, which were collected 90 days after the application of the P treatments, the amounts of $NaHCO_3$-P extracted from the soil surface layer, were still higher for those receiving PP treatments than the control or T.S.P. treated soils (table 5.4C). The concept of PP reducing the adsorption sites available to the OP on the soil $CaCO_3$ surfaces and that this was the reason for its higher solubility, therefore seems to be weak. On the other hand, PP ions like those of OP were found to react with soil constituents. Calcium and/or magnesium carbonates, and to a lesser extent clay minerals, iron and aluminium hydroxides were found to react with the added P (Philen and Lehr, 1967). However, PP had a slower reaction with soil minerals than OP (Philen and Lehr, 1967) and it reacted in a markedly different way (Hughes and Hashimoto, 1971) with a lower tendency to precipitation. Furthermore, it seems that applied PP would interact with the soil native P with the possibility of increasing its solubility (Hughes and Hashimoto,

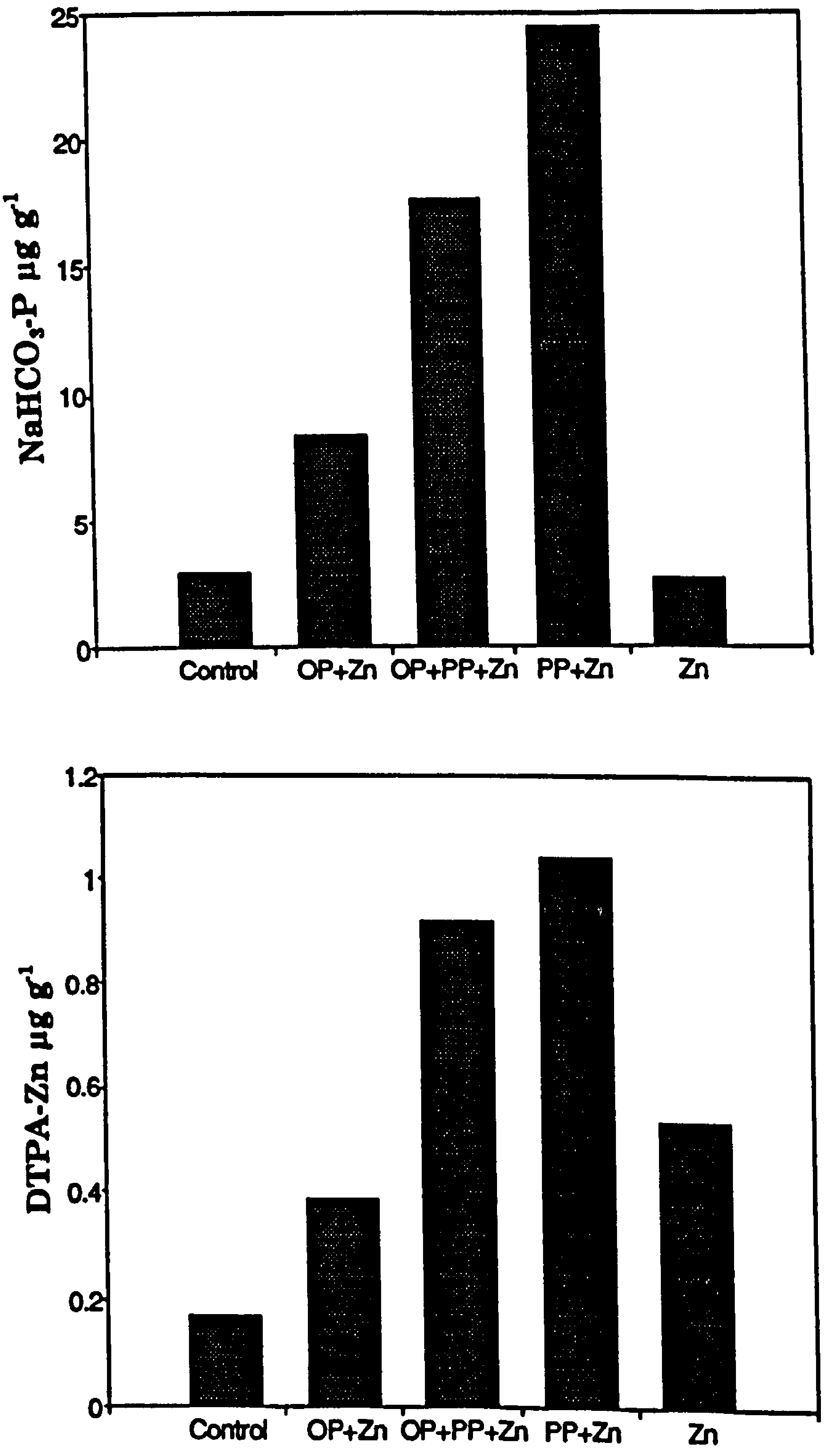


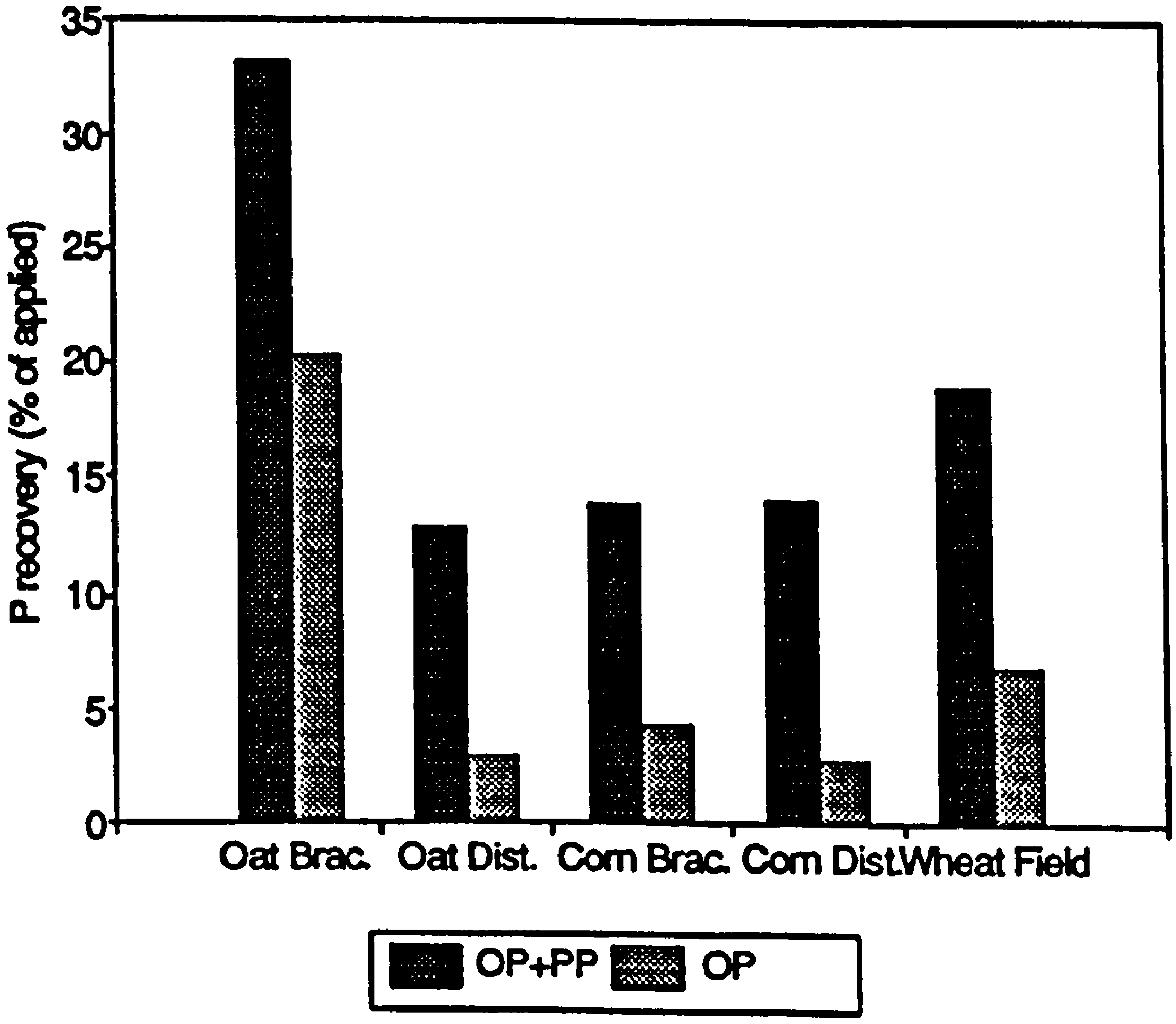
Fig 5.5 $NaHCO_3$-P and DTPA-Zn soil extracts from a laboratory incubation experiment showing the relationship of P and Zn in various combinations of OP, PP and $ZnSO_4$.

1971). The precipitate of PP would result in the formation of stable Ca-PP compounds incorporating other ions available in the soil or included within the applied fertlizers. Sodium, K and NH_3 were found to form such products that were reported to persist for long periods of 6-9 months (Subbarao and Ellis, 1975; Savant and Racz, 1973). Eventually these products would slowly dissolve and release their PP into soil solution.

PP was also found to prevent or reduce the precipitation of OP in a calcareous environment (Philen and Lehr, 1967; Amer and Mostafa, 1981; Amer *et al.*, 1985). If the action of PP were to prevent the adsorption of OP into $CaCO_3$ surfaces, thus hindering the formation of DCP nuclei which were found to be the pre-requisite for further OP direct precipitation, then this would also be a weak explanation, due to the low levels of PP used. Equally, the idea that PP would prolong the induction period required for the formation of DCP nucleation (Amer *et al.*, 1985) could not account for the higher levels of $NaHCO_3$-P. Since presumably this extended period would only be maintained in the active presence of PP, as PP hydrolysed to OP with time its direct effect on the solubility of OP becomes questionable. However, other reports had indicated differing hydrolysis rates in alkaline-calcareous soils. It was found that liming acid soil would enhance PP hydrolysis (Uzu *et al.*, 1983; Sutton and Larsen, 1964), but at high soil pH hydrolysis rates were low presumably due to the formation of stable products that were unavailable for the enzymatic mediated process (Philen and Lehr, 1967; Khasawneh *et al.*, 1979; MnKeni and MacKenzie, 1987). Lehr *et al.* (1964) had even found no appreciable conversion of PP into OP after more than four months monitoring of a PP type of fertilizer. It could be that biological activity was directly reduced by the high pH and $CaCO_3$ content, or that $CaCO_3$ had reduced available Mg^{2+} which was essential for the activation of PPase (Tabatabai and Dick, 1979). The Kuwaiti soil utilized in this study had very low organic content, and this may have resulted in low biological (and enzymic) activity necessary for active PP hydrolysis. Furthermore, the field experiments were conducted in the cool season where mean soil temperatures would be below 10°C, and this would probably reduce the activity of the enzyme PP-ase. Sutton *et al.* (1966) had reported low PP hydrolysis when temperature was as low as 7-12°C. Moreover, high concentration of OP was found to have a competitive inhibition on PP hydrolysis (Savant and Racz, 1972). In all the studies conducted here, high amounts of OP type salts, or fertilizers were used, which may have a product type inhibition on PP hydrolysis. Conjointly, it was shown repeatedly that not all added PP would hydrolyse (Gilliam and Sample, 1968; Hossner and Melton, 1970; Uzu *et al.*, 1983). Up to 10-20% of the PP was found to presist in soil. Also, high application of OP was found to result in the accumulation of polyphosphates (Pepper *et al.*, 1976). All these possibilities could maintain some PP presence in the calcareous environment for long periods.

5.4.4. Implications of PP for P/Zn Interaction, Solubility and Plant Nutrition

As has been reported earlier, plant concentration and uptake of P and Zn had increased when PP was amended into OP fertilizer (figures 5.1; 5.3). Moreover, the extractable $NaHCO_3$-P and DTPA-Zn from the associated soils was equally enhanced by the incoporation of PP (figure 5.4). Clearly there was no negative sinergistic effect of increased solubility of either P or Zn on each other. This was also observed by other workers, where no direct antagonism between extractable P and Zn was reported (Saeed and Fox, 1979; Brown *et al.*, 1970; Orabi *et al.*, 1981). Saeed and Fox (1979) indicated that high pH associated with calcareous soils was responsible for Zn precipitation as $Zn(OH)_2$, $ZnCO_3$ or Ca-Zincate. Ca^{2+} released from added P fertilizer was suggested as the reason for the presumed antagonisms of P on Zn solubility (Chandhry and Loneragan, 1972). However, there were some inconclusive reports that indicated a plant physiological mechanism by which soil deficient in P or Zn would intensify the



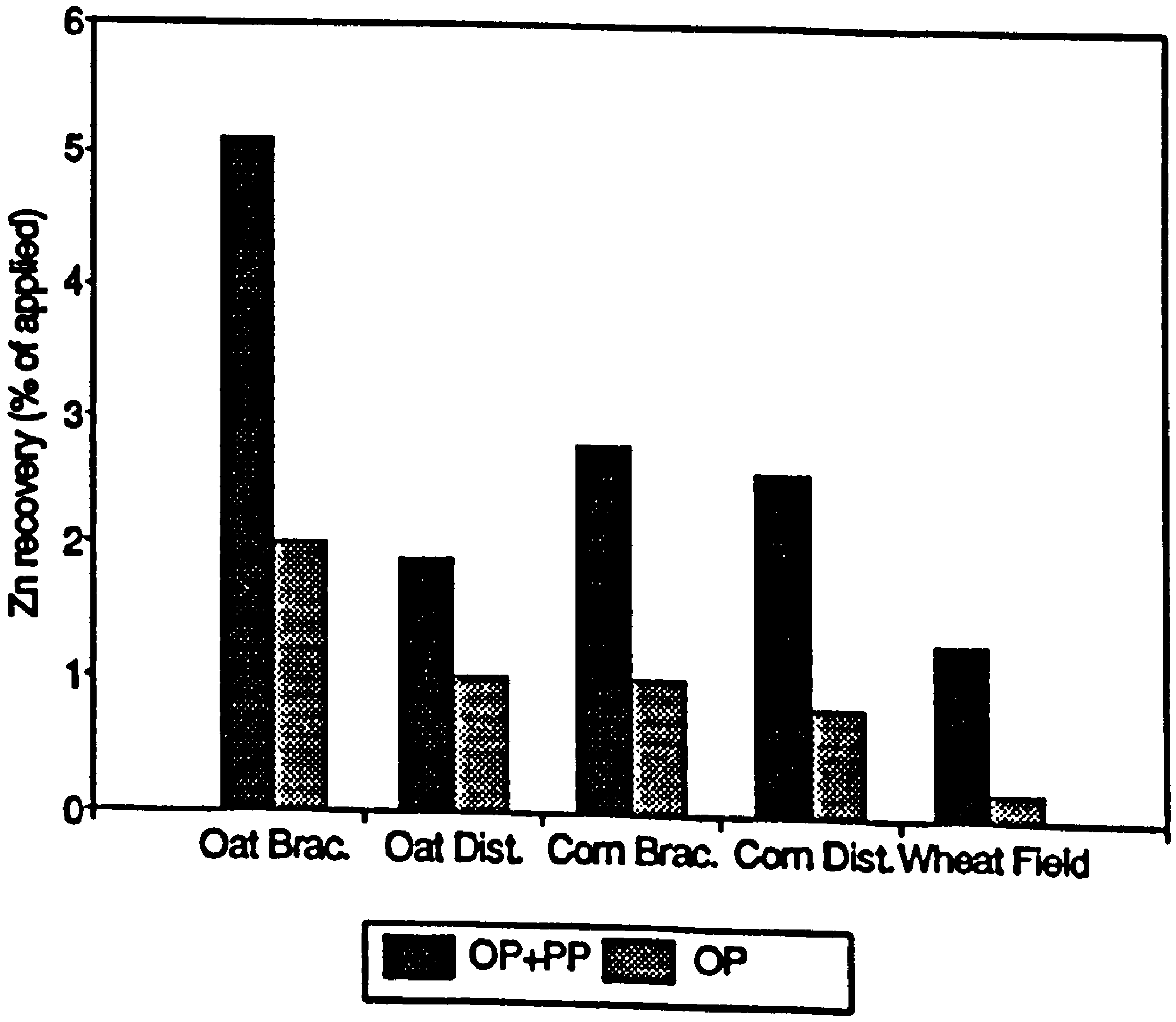


Fig 5.6 Phosphorus and zinc recovery as % of what been applied in response to OP or PP amended OP fertilizer for various pot experiments and for wheat grown in the field.

deficiency symptoms if the other element had increased in supply (Burleson *et al.*, 1961; Burleson and Page, 1967; Brown *et al.*, 1970), while other studies refuted this and reported increased plant P contents when Zn was added (Orabi *et al.*, 1982) to a calcareous soil. In the laboratory investigations on the effect of PP or PP/OP mixture on Zn extractability it was clearly shown that not only did the PP increase the DPTA-Zn, but simultaneously it increased the $NaHCO_3$-P. Also, there were no significant differences in DPTA-Zn levels with or without OP addition (fig. 5.5). This increased availability of P and Zn had resulted in corresponding increases in plant growth and their uptake of these two elements. The recovery of P or Zn as a percentage of that applied was calculated from the differences in the uptake of each element in the fertilized and control treatments. Figure 5.6 shows consistently higher P and Zn recovery when PP was added to OP. With the exception of brackish irrigated oats, the recovery of P was about 15% of added P-fertilizer when PP was included, while with only OP or similar type fertilizer the recovery was closer to 5% (fig. 5.6). In the case of Zn there were no significant responses to the fertilization with $ZnSO_4$. Nevertheless, incorporating PP with OP fertilizer had indicated a doubling of the % recovery of Zn, even though these were in the marginal range (fig. 5.6).

irregular shapes because of the condition and the way they were formed. These crystals therefore might not be efficient in attracting more OP and Ca^{2+} into their structure and thus smaller crystals would be formed, resulting in a higher proportion of the soil OP remaining in solution or weakly attached to the exchange complexes. However, this brings up a number of questions:

(i) How does and to what extent does the PP prevent the formation of DCP on the surfaces of soil $CaCO_3$?

(ii) Does any of the PP react with these small DCPD crystals and if so, how?

(iii) Why does the remaining soluble OP not form more DCPD crystals albeit smaller in size?

And lastly (iv) for how long does the effect of PP remain active on the behaviour of the soil P and Zn?

Due to time constraints and because the scope of this study was agronomical in nature, the soil chemical reactions of PP and especially their physical chemistry effects on OP were not further investigated.

6. Use of Elemental Sulphur as Soil Amendment

6.1 Introduction

One of the major constraints associated with alkaline calcareous soil must be its negative influence on the plant availability of phosphorus (P) and some micronutrients such as iron (Fe), zinc (Zn), and manganese (Mn). The presence of calcite ($CaCO_3$) and the accompanying high soil pH account for the low solubility of these elements. Therefore, it seems reasonable that an acidifying agent that lowers soil pH would increase the availability of these nutrients or delay their fixation in the soil when applied as fertiliser. Application of elemental sulphur (S^o) which would be oxidised and form a source of acidity might be an effective method of improving the nutritional status of such soils.

6.1.1 Elemental Sulphur Oxidation

Elemental sulphur (S^o) is oxidised in soils by chemical and biochemical reactions, which are influenced by many factors. Here some of these conditions that dictate the processes by which S^o is oxidised are briefly mentioned with emphasis on calcareous soil environments.

A purely chemical processes of S^o oxidation is usually slow and less important than biological oxidation (Chapman, 1989). S^o chemical oxidation was reported to take place in autoclaved soils (Nor and Tabatabai, 1977). Wiklander *et al.*, (1950) obtained a 73% oxidation of S^o into SO_4^{2-} by chemical means but only after about a year of incubation using autoclaved soils. More rapid S^o oxidation is carried out by the action of soil micro-organisms, of which the autotrophic bacteria of the genus Thiobacillus are thought to be the most important (Weir, 1975; Wainwright, 1984; Stevenson, 1986). Besides the chemolithotrophic bacteria, there are numerous other heterotrophic fungi, actinomycetes and bacteria that can oxidise S^o (Vitolins and Swaby, 1969; Wainwright, 1984). An extensive review of these heterotrophic organisms and their relative importance in oxidising inorganic sulphur compounds has been presented by Wainwright (1984).

It has been suggested that, in neutral to alkaline agricultural soils (pH 6.5 and above), the acidophilic Thiobacillus spp. are less important and heterotrophs are the predominant S° oxidisers (Vitolins and Swaby, 1969); Pepper and Miller, 1978; Lawrence and Germida, 1988). Higher organic carbon contents were shown to have a positive effect on the rates of S° oxidation (Skiba and Wainwright, 1984; Janzen and Bettany, 1987b). The addition of organic matter *in vitro* or in field trials has demonstrated an enhancement in inorganic sulphur oxidation and an increase in micro-organism populations and activity (Pepper and Miller, 1978; Wainwright *et al.*, 1986; Lawrence and Germida, 1988). This indicates that heterotrophic organisms were the primary S° oxidisers in these conditions, since chemolitotrophic oxidisers were inhibited by the presence of organic substrates (Vitolins and Swaby, 1969; Pepper and Miller, 1978).

The efficiency of S° as a soil acidulant would depend on the rate of its oxidation. It has been reported in many studies that the rate of S° oxidation accelerates with decreasing particle size (Li and Caldwell, 1966; McCaskill and Blair, 1987; Lee *et al.*, 1988a, Lee *et al.* 1988b; Chapman, 1989), due to the larger surface area available for oxidation associated with finer S° particles. Fox *et al.* (1964) demonstrated a linear relationship between plant sulphur recovery and the specific surface area of S° applied. Furthermore, the mixing of S° thoroughly in the soil would enhance the oxidation, by providing more contacts with the oxidising agents (Attoe and Olson, 1966; Stevenson, 1986).

Environmental factors would also have a great effect on the rate of S° oxidation. The most influential parameters would be soil temperature and moisture potential. S° oxidation takes place between 4° and 55°C, (Attoe and Olsen, 1966; Li *et al.*, 1966; Weir, 1975; Wainwright, 1984; Stevenson, 1986; Janzen and Bettany, 1987a). At temperatures of 45°C and above S° oxidation was reported to result in greater accumulation of intermediates such as thiosulphate, $S_2O_3^{2-}$, and tetrathionate, $S_4O_6^{2-}$, presumably due to abiotic S-oxidation or as the products of thermophilic organisms (Skiba and Wainwright, 1984).

A soil water content close to field capacity has been shown to be the optimum moisture potential for most rapid S° oxidation rates (Kittams and Attoe, 1965; Janzen and Bettany, 1987a). Moreover, soil texture could have an indirect effect on these rates. Sandy soil (>90%, sand) and heavy clay soil (>60% clay) characterised by extreme water retention capacities had other soil-moisture levels at which S-oxidation was more efficient (Janzen and Bettany, 1987a). This was attributed to the relationship in air to water ratios in these soils. In a further report they observed a significant relationship between oxidative capacity and soil clay or sand content; it was negative in the case of clay and positive with sand (Janzen and Bettany, 1987b). However, these soil parameters accounted for a small effect on the oxidation in comparison to other soil properties. Other studies had detected no relationship between soil texture and S° oxidation rates in soils of varying clay contents (Attoe and Olson, 1966; Rehm and Caldwell, 1969; McCaskill and Blair, 1987).

Oxidation of S° could occur over a wide range of soil pH [2-9] (Wainwright, 1984; Stevenson, 1986). Often the oxidation rates were found to be higher in alkaline than acidic soils (Attoe and Olson, 1966; Nor and Tabatabai, 1977; Janzen and Bettany, 1987b). However, others observed an increased rate of S° oxidation as sand dune pH decreased (Skiba and Wainwright, 1984). They further explained that soil pH was alone not a critical factor in S° oxidation, but the integrated effects of a number of parameters that support a prolific soil micro-organism population would favour a rapid oxidation (Skiba and Wainwright, 1984; Janzen and Bettany, 1987b).

Effects of other soil amendments on S° oxidation rates were less clear. With the exception of adding lime to acid soil (Attoe and Olson, 1966), all other inorganic additives did not greatly effect rates of S° oxidation (Weir, 1975; Wainwright, 1984). Sulphur oxidising micro-organisms had good tolerance to a wide range of soil ions (Keller, 1969). Also, their ability to withstand the presence of heavy metals was widely recognised (Weir, 1975).

Generally, a higher rate of S° application would provide more surface area available for oxidation, thus resulting in a linear increase in the amounts of S° oxidised (Weir, 1975; Janzen and Bettany, 1987b). However, at very high application rates the ratio of S° oxidised could be lower (Chapman, 1989), perhaps due to insufficient oxidisers for the large surface area available, or in case of heterotrophs limited organic substrate supply (Janzen and Bettany, 1987b), or the acid formed by oxidation of S° in localised areas around the S-particles might have an inhibitory effect on the heterotrophic population (Chapman, 1989), especially in poorly buffered soils.

Inoculation with Thiobacillus spp. and heterotrophs have been shown to enhance the S-oxidation capacity of various soils (Attoe and Olson, 1966; Violins and Swaby, 1969; Weir, 1975; McCaskill and Blair, 1987; Deluca *et al.*, 1989), but only in the initial short term period, whereas long time field trials have demonstrated no appreciable benefit due to inoculation (Weir, 1975).

Acidity (H^+ and $SO^{2-}{}_4$ ions) would be produced as a result of S° oxidation (Weir, 1975; Wainwright, 1984; Stevenson, 1986). The ability to lower soil pH would largely depend on the buffering capacity of the particular soil especially its base constituents, mainly the $CaCO_3$ content and its activity (Hassan and Olson, 1966; Modaihsh *et al.*, 1989). In general conditions that facilitate rapid S° oxidation and the rates at which S° were applied would determine the amount of sulphuric acid, H_2SO_4, generated. Calcite ($CaCO_3$) and/or $MgCO_3$ would react with H_2SO_4 and as a result dissolve, thus increasing the soil ionic composition of Ca^{2+} and Mg^{2+} and the CO_2 gas released (Hassan and Olson, 1966; Bole, 1986; Kalbasi *et al.*, 1988; Abo-Rady *et al.*, 1988). Moreover, the supply of SO_4^{2-} and the freed Ca^{2+} and Mg^{2+} would also produce the sulphate salts of these ions including gypsum, which, with its limited solubility (15 mM/L) would precipitate in the soil (Kalbasi *et al.*, 1986; Dawood, 1989). Since gypsum and other sulphate salts have characteristically greater solubility than the carbonates, the application of S° to a calcareous soil has often led to increased salinity measured by a higher electrical conductivity (E.C.) of the soil solution (Bole, 1986; Abo-Rady *et al.*, 1988; Modaihsh *et al.*, 1989).

6.1.2 Effect of S° Oxidation on Some Plant Nutrients

As a result of S° oxidation and the accompanied acidity, the soil pH and the $CaCO_3$ content would be expected to decline. This presumably would alter the solubility status and thus plant availability of P and micronutrients. Many reports have demonstrated increase of plant growth, higher yields when S° or direct H_2SO_4 were used on calcareous soils (Tisdale and Bertramson, 1949; Olson, 1950; Christensen and Lyerly, 1954; Sen Gupta and Cornfield, 1964; Hoeft and Sorensen, 1969; Mathers, 1970; Singh, 1970; Ryan *et al.*, 1975a; Ryan *et al.*, 1975b; Procopiou *et al.*, 1976; Wallace *et al.*, 1976; Clement, 1978; Wallace and Meller, 1978; Saroha and Singh, 1980; Shukla *et al.*, 1983; Soliman, 1987; Kalbasi *et al.*, 1988; Soliman, 1989; Deluca *et al.*, 1989; Falatah and Schwab, 1990). However, other investigations have revealed a growth reduction or no plant response in relation to S° addition (Hassan and Olson, 1966; Kashirad and Bazargani, 1972; Gupta and Mehla, 1980; Frank and Fehr, 1983; Bole, 1986; Abo-Rady *et al.*, 1988). This latter result was attributed to nutrient imbalances, with a possible sulphate/nitrate (SO^{2-}_4/NO^-_3) antagonism, (Kashirad and Bazargani, 1972; Abo-Rady *et al.*, 1988) or toxic build-up of SO_4^{2-} or Mn^{2+} especially at high S° application rates (Hassan and Olson, 1966; Gupta and Mehla, 1980). Others have detected no effects on soil pH, and thus lack of improvement in Fe availability to plants showing chlorotic conditions (Frank and Fehr, 1983). Increases in soil salinity have also been quoted as the cause for lower yields (Abo-Rady *et al.*, 1988). Similarly, there exist many discrepancies in the literature regarding the effect of S° on various soil nutrients, their solubility and availability to plant growth. Increases in available P indices have been demonstrated when S° or H_2SO_4 have been added to P deficient soils alone or with phosphates (Sen Gupta and Cornfield, 1964; Hassan and Olson, 1966; Procopiou *et al.*, 1976; Garcia and Carloni, 1977; Clement, 1978; Ryan and Stroehlein, 1979; Abo-Rady *et al.*, 1988; Modaihsh *et al.*, 1989; Soliman, 1989; Deluca *et al.*, 1989). However high S° application rates (> 5000 ug/g) were found to cause yield reduction (Hassan and Olson, 1966; Abo-Rady *et al.*, 1988; Soliman, 1989), and this was attributed to a possible nutritional disorders. Other studies have failed to show any increases in soil-P availability or plant-P uptake (Kashirad and Bazargani, 1972; Lindemann *et al.*, 1991). Lindemann *et al.* (1991) explained that a slow rate of S° oxidation in a highly buffered calcareous soil could be the reason, whereas Kashirad and Bazargani (1972) suggested an inhibition of plant-nitrogen (N) absorption due to high levels of SO_4^{2-} as the cause for the lack of significance in relation to P uptake.

Iron has shown contradictory behaviour where calcareous soils have been amended with S° or have been directly acidified i.e. H_2SO_4. Numerous reports have revealed a lack of Fe nutritional benefits due to S acidification (Hoeft and Sorensen, 1969; Gupta and Mehla, 1980; Lindemann *et al.*, 1991), with explanations varying from no increases in available soil Fe (Falatah and Schwab, 1990) to the formation of metabolically inactive Fe compounds within the plant tissue (Singh, 1970; Saroha and Singh, 1980; Gupta and Mehla, 1980). Others have reported an alleviation of Fe chlorosis with acidification treatments (Olson, 1950; Ryan *et al.*, 1975a+b; Razeto, 1982; Gaur *et al.*, 1971). Moreover, increases in soil available Fe were reported as being significant only at high S° application rates (Abo-Rady *et al.*, 1988; Modaihsh *et al.*, 1989). Similar findings by Ryan *et al.* (1974) reported a higher level in water soluble Fe only at

H_2SO_4 rates high enough to saturate 100% or more of the acid titratable basicity of calcareous soils. Wallace and Mueller (1978) have demonstrated that a complete neutralisation of a small portion of a calcareous soil was sufficient to rectify Fe deficiency.

Zinc solubility and plant availability resulting from acidification of calcareous soil by S° or directly by H_2SO_4 have had variable responses reported by various workers. Some studies indicated no significant effect of S° on Zn soil extractability (Hoeft and Sorensen, 1969; Modaihsh *et al.*, 1989; Lindemann *et al.*, 1991) and others attested that even at low rate of S° treatment there were significant increases in soil extractable and plant absorbed Zn (Hassan and Olson, 1966; Procopiou *et al.*, 1976; Shukla *et al.*, 1983; Kalbasi *et al.*, 1988; Soliman, 1989; Falatah and Schwab, 1990). However other reports concluded that great amounts of acidity in relation to the soil basicity were required to change the availability and uptake of Zn (Ryan *et al.*, 1974; Abo-Rady *et al.*, 1988).

In some cases there were releases of Mn^{2+} ions with the S° treatments and Zn/Mn antagonisms were observed (Soliman, 1987; Abo-Rady *et al.*, 1988).

The micro-nutrient that seemed to be most affected by S° treatment of calcareous soil was Mn. Low rates of S° or H_2SO_4 application, insufficient for total neutralisation of soil basicity, have been demonstrated to greatly increase soluble Mn. (Ryan *et al.*, 1974; Hassan and Olson, 1966; Soliman, 1987; Kalbasi *et al.*, 1988; Abo-Rady *et al.*, 1988; Soliman, 1989; Modaihsh *et al,*, 1989). Fertilization of $MnSO_4$ infused with as little as 0.5% S° was effective in eliminated Mn - deficiency on calcareous soil (Soliman, 1987). It has been suggested that the means by which S° affects the solubility of Mn in soil was that of a reductant of MnO_2 as S oxidises, rather than by acidification of the soil (Tisdale and Bertramson, 1949).

6.1.3 The Scope of this Study

In view of the conflicting information provided in the literature concerning the possible nutritional benefits of amending calcareous soils with S°, this study was undertaken to investigate the feasibility of using S° on Kuwaiti calcareous soil. This project aims to investigate rates of S° oxidation in such a soil and examine the effects on some chemical and physical properties, but more importantly evaluate the impact on some plant nutrients, and study their availability and uptake using test crops.

6.2 Materials and methods

In this study elemental sulphur (S°) applied at varying rates, from moderate to relatively high in relation to the total soil basicity of the Kuwaiti calcareous soil, were used in various experiments. Some were performed in the laboratories to examine the rate of S° oxidation and the resulting changes in some chemical and physical soil parameters. These were compared with a set of glass-house experiments using the same soil for growing test plants irrigated alternatively by distilled or brackish water. Added to these studies field trials (on an experimental site in Kuwait) assessing the agronomical effectiveness of the use of S° on test crops were conducted for two seasons.

6.2.1 Laboratory experiments

All the analysis carried out in the laboratories had utilized a calcareous virgin soil from Kuwait and with flowers of sulphur (BDH-Merck) as the source for S°. Some of the soils incorporating various rates of S° were incubated for six months at 30°C prior to their use as plant growing media in the glass-house. These and unincubated soils were utilized for the following laboratory exercises:-

6.2.1.1 Elemental sulphur oxidation

The purpose of this exercise was to investigate the rates of S° oxidation under controlled temperature and moisture conditions using Kuwaiti soil. The soil utilized had a mean $CaCO_3$ content of about 18.8% [range of 17.0-21.7%] (section 3.4). Based on this content the following rates of S° were used corresponding to the theoretical acidity required to neutralise 0, 25, 50, 100 and 200% of the soil equivalent $CaCO_3$.

Treatment	S° g kg^{-1} soil (oven-dry basis)	equivalent to % of $CaCO_3$ neutralised.
S_1	0	0
S_2	15	25
S_3	30	50
S_4	60	100
S_5	120	200

100 grams of air dried 2mm sieved soil mixed with the appropriate S°

[powdered S°] treatment were placed in a 250 ml plastic bottle, moistened with distilled water to about field capacity level, and covered with a tied polythene film. Bottles were stored in the dark at room temperature [approx. 21° C], and shaken once a week to maintain good aeration. These treatments were carried out in triplicate.

At 2, 4, 6 and 8 weeks soil samples were collected from each container [about 20 g.]. Allowed to air dry and then 5g of soil were used in [1:1] soil : water pH value measurement as in section 2.3.2. The same soil was then transferred to a larger bottle (250 ml) and further diluted to 1:10 , shaken for 30 minutes and filtered for SO_4^{2-} analysis as described in section 2.3.6. Some of the soil was used to measure $CaCO_3$ content by a calcimeter (section 2.3.4). A small amount of soil was oven dried to obtain the moisture content (2.3.1) for calculation. The data were statistically analysed and are presented in section 6.3.

6.2.1.2 Measurement of pH, E.C., $CaCO_3$, SO_4^{2-} and gypsum, for field and glass-house soil samples.

Soil samples [about 200 g.] were collected from each experimental unit in the field trials (6.2.3.2). Also soil was collected from each pot upon the termination of the glass-house plant growth experiment (6.2.2.2). A small amount of soil which was incubated with S° [same soil used for growing plants in the glass-house] was also analysed for the following:-

a) soil pH, 1:1 soil:water (2.3.2)

b) E.C. modified measurement (2.3.2) of 1:2 soil:water suspension

c) $CaCO_3$ content (2.3.4) by calcimeter method

d) $SO^{2-}{}_4$ by Dionex method 1:10 (2.3.5). Only selected samples were measured representing (1) soil SO_4^{2-} content with profile depth in the field.

(2) SO_4^{2-} in selected samples representing all main S° treatments [too many samples].

e) Gypsum content 1:20 (2.3.5). Selected samples from all S° treatments.

All the data were statistically analysed for significant variations with S° treatment and parameter correlations.

6.2.1.3 Soil mineral examination by SEM (Scanning electron microscope) and EDAX Analysis

Gold and carbon coated soil stubs were examined by the aid of SEM and EDAX to explore the possibility of the formation of a gypsum layer covering the dissolving $CaCO_3$ particles.

6.2.1.4 Soil mechanical analysis modified to measure the $CaCO_3$ fractions remaining after S° treatment

It was hypothesised that the smaller size $CaCO_3$ particles would react and dissolve faster than the larger particles with acidification resulting from S° oxidation. Therefore $CaCO_3$ surface area would be expected to decrease to a much greater extent than the reduction of $CaCO_3$ % content. For this purpose two sets of the same soil treatment (combined soil from different experimental units, however representing the same S° treatment from the glass-house growth experiment) were divided, one as it was and the other acid treated by 2M HCl to decompose all the $CaCO_3$. All mechanical analysis used soil equivalent to 100 g (oven-dry basis). All soils, especially S° treated ones, had to be washed to eliminate the gypsum which would interfere with soil dispersion. This was carried out by repeated distilled water washes in 1 litre centrifuge tubes, centrifugation being used to retain soil particles. $BaCl_2$ was used as an indicator of gypsum removal. Silt and clay fractions were measured by the hydrometer (2.3.5) and pipette (2.3.5) methods. Sand fractions were separated by sieves of 600, 200 and 63 um in size. This exercise was done in triplicate for the five S° soil treatments. The means of these data were plotted and the difference between the same sample before and after acid treatment was assumed to correspond to amount of $CaCO_3$ remaining in each soil fraction after S° oxidation.

To further check the values obtained in this exercise, the aliquots collected by the pipette method representing the clay and silt content, and the sieved sand fractions for the non-acid treated half of the exercise were re-examined. After drying and weighing, the various fractions were rewetted by 0.5 M HCl until all effervescence had stopped [5-10 mins.] then they were washed three times with distilled water, re-dried and weighed. The differences corresponded to the $CaCO_3$ in the various fractions.

6.2.1.5 Indirect measurement of $CaCO_3$ fractions by pH-time chart

An indirect method of measuring the various $CaCO_3$ size fractions was conducted by examining the time required for one gram of $CaCO_3$ to increase from 3 to 6 the pH value of dilute H_2SO_4 acid [0.005M]. A standard was made with various sized pure $CaCO_3$ corresponding to fine clay, coarse clay, silt, fine sand and coarse sand (<0.2, 0.2-2.0, 2-50, 63-200, 200-600 µm, respectively). These were obtained by grinding high quality marble for various times and obtaining a range of sizes by gravitational cylinder sedimentation and the use of the high speed centrifuge to collect the sediments.

The pH electrode was suspended in 2 L. of 0.005M H_2SO_4 with a magnetic stirrer and the pH meter was connected to a time chart. One gram of the standard $CaCO_3$ or a quantity of soil(S) containing 1 g. equivalent of $CaCO_3$ [based on calcimeter measurements] was added to the acid suspension. Time was recorded when pH reached 3 and again when it reached 6. The slope of the line between pH 4 and 5 was also measured.

The data were calculated to correspond to the mean effective size for the $CaCO_3$ fraction of each of the S° treated soil samples.

6.2.1.6 Column study for the effect of acidification on $CaCO_3$ fractions

A column study was conducted to investigate the changes to the soil $CaCO_3$ fraction distributions, in particular to investigate if small size fractions would dissolve more readily than the larger fractions thus reducing the $CaCO_3$ surface area in a larger proportion on acidification. Two hundred grams of air dried untreated Kuwaiti soil was placed in a clear glass tube, 3 cm in diameter. One end was covered with a fine nylon cloth. On the other end a thin layer of acid washed coarse sand was spread on top of the soil to reduce disturbance. After the columns were completely wetted by submerging in distilled water, they were placed vertically and 0.5 litre of distilled water or 0.5M H_2SO_4 was allowed to percolate through each set. The column then was allowed to dry in a heated air cabinet [45°C]. The dried soil was pushed out of the glass tubes and samples were analysed indirectly to determine the $CaCO_3$ fraction distribution as in section 6.2.1.5. A few soil samples were used to investigate the formation of gypsum layer around $CaCO_3$ particles as in section 6.2.1.3.

6.2.1.7 Column experiments on the leaching and retention of soil P exposed to weak acid percolation

It has been shown that phosphate ion adsorption to soil colloids can decrease as pH is lowered from alkaline to neutral, but also the presence of high Ca^{2+} content would enhance the precipitation of P in a Ca-P complex. As acidification of a calcareous soil would alter the status of soil pH and Ca concentration in solution, these two factors would be expected to have a direct effect on P availability and extractability.

This experiment was conducted on soils that had a history of P fertilization, high pH [8.0 +] and a $CaCO_3$ content of more than 15%. They were not exposed to acidification as samples came from control plots from the field trial site. Two treatments of P were used, 0 nd 400 ugg^{-1} soil. 10 g soil samples in plastic syringes were connected to a series of peristatic pumps. The soil surface was covered with rock wool fibre to reduce surface disturbance when a series of dilute H_2SO_4 acids [distilled H_2O, 10^{-1},10^{-2}, 10^{-3} and 10^{-4} M] were allowed to percolate through. After each 20 ml dose of the acid the leachates were analysed for pH. Accumulated leachates from all 5 runs [100 ml] were analysed for Ca^{2+} and P content. The soil was allowed to dry and then, $NaHCO_3$-P and the remaining $CaCO_3$ content were measured.

These trials were repeated three times.

6.2.2. Glass-house experiments

6.2.2.1 Experiment preparations

Soil brought from Kuwait was incubated with S° for some six months prior to its use as a growing medium. The soil [<2 mm] was mixed with S° at rates which have been described in section 6.2.2.1. About 3 kg samples of soil were placed in plastic bags with 3 perforated tubes inserted in the middle of each bag, to enhance aeration. The soil were wetted to about field capacity and placed in a heated cabinet [30°C]. Open water containers were maintained in the cabinet to increase humidity. The soils were also periodically sprayed with water to prevent their drying, during the six month incubation.

Two sets of growth experiments were conducted in the university glass-house. One set was irrigated with distilled water and the other with brackish solution prepared from laboratory salts to resemble Kuwaiti ground water. Its composition was reported in Table 4.1. Portions of S° treated soil were mixed with gravel and vermiculite as described in section 2.2.

A randomised complete block design was used, where the main treatment was the S°. The other treatment was P enrichment using KH_2PO_4 added at zero levels or a P equivalent of 100 mg/kg soil. The appropriate P amounts were thoroughly mixed with the S^0 treated soil - gravel - vermiculite mix. The mixture was placed in pots each containing about 0.5 kg soil. A further treatment, +/-

micronutrients was incorporated where + level applications consisted of the following:-

salt used	element concentration mg kg^{-1} soil
$FeSO_4.7H_2O$	Fe(II) = 20
$ZnSO_4.7H_2O$	Zn = 5
$MnSO_4.4H_2O$	Mn = 5
$CuSO_4.5H_2O$	Cu(II) = 0.5

These salts were dissolved together in distilled water and then an appropriate volume of solution was delivered to each pot assigned to have a micronutrient treatment.

All treatments were randomised with three replications, or blocks as required by the design.

Corn (*Zea mays* L. Variety Early King) was planted and thinned to two plants per pot. Nitrogen and potassium were applied uniformly to all treatments in solution one week after plant establishment. Ammonium nitrate and potassium nitrate were used to give a concentration of 200 and 150 mgkg^{-1} soil for N and K respectively.

6.2.2.2 Plants and soil sample preparation

Harvesting for the two experiment sets [distilled and brackish water irrigated] was done at plant age of 10 weeks, by collecting the above soil growth. Washing, drying and grinding of plant parts were carried out in the manner described in section 5.2.1 and samples were prepared and analysed for P, Fe, Zn and Mn content as in sections 2.3.9, 2.3.10 and 2.3.11.

Soil samples were collected from each pot and handled as mentioned in section 5.2.2. They were analysed for various properties, some of which have already been described in sections 6.2.1.2, 6.2.1.3, 6.2.1.4 and 6.2.1.5, while $NaHCO_3$ extractable P and DTPA extractable Fe, Zn and Mn were carried out as in sections 2.3.7 and 2.3.8.

6.2.3 Field experiment

6.2.3.1 Experiment preparation

In the first season field trial, treatments were initially examined (section 2.1). One of these was the incorporation of S° in the field soil at a rate of 60 tonnes / hectare or the theoretical acidity required to neutralize 50% of the soil equivalent $CaCO_3$ content, based on an average $CaCO_3$ content of about 18% and a soil depth of about 15 cm. Not all the S° was in powdered form, as about a third of the amount was fractured S° of about 2 - 3 mm^3. Although the first season corn crop had failed due to an early cold spell in November of that year, the soil analysed 100 days after S° application revealed a moderate reduction in soil pH and $CaCO_3$ content [not significant in the former and significant at 5% probability level for the latter] (Appendix II). Phosphorus levels (Bicarbonate extraction) did not change but they were in the moderate range of about 30 ug/g soil (Appendix II). However, Fe level and that of Mn significantly increased (Appendix II) while Zn slightly declined.

Based on these results a second trial in the same field was carried out a year later and incorporated the following rates of S°:-

S_1 control no S° added

S_2 15 tonnes/hectare of S° all in the second season

S_3 30 tonnes/hectare of S° all in the second season

S_4 60 tonnes/hectare of S° all in the first season

S_5 90 tonnes/hectare of S° 60 tonnes in first season
and 30 tonnes in second season

All treatments were of powdered S° for the second season treatments, and were applied as mentioned in the field preparation (section 2.1).

A split-split plot design was applied whereby the main treatment was that of S° rates. The sub-plot was that of P treatments at zero and 6.5 g P/m^2, based on a rate of 150 kg P_2O_5/ha. T.S.P. was the form of phosphate fertilizer. The sub-sub-plot, was two treatments levels, one with micronutrient application and the other without. The following were the micronutrients used and their rates:-

salt used	rate of application kg/ha	equivalent of nutrient element g/m^2
$FeSO_4.7H_2O$	50	1.0 Fe(II)
$ZnSO_4.7H_2O$	30	0.68 Zn
$MnSO_4.4H_2O$	30	0.74 Mn
$CuSO_4.5H_2O$	5	0.13 Cu(II)

All treatment in the main, sub-plot and sub-sub-plots within the three blocks were randomised in accordance with the experimental design.

Two test crops were planted to ascertain the effect of S° on their yield and their uptake of P, Fe, Zn and Mn. Sweet corn (Zea mays L variety Geza 107), and a wheat (Triticum spp variety Ukroge), were sown at spacing of 30 x 20 cm and 9.0 x 1.5 cm for the corn and wheat respectively. Each experimental unit was 2.5x7.5 metres. Urea based nitrogen fertilizer was uniformly applied to the whole field at three intervals throughout the growing period, giving a total N application of 210 kg/ha. Crops were uniformly irrigated whenever needed by an over-head sprinkler system. Composition of the irrigation water was reported in section 4.3.

6.2.3.2 Crop harvest and analysis preparation

Corn leaf samples were collected at tasselling stage about 60 - 65 days after germination. The procedure used in collecting the leaves and their subsequent preparation for analysis was as described in section 5.2.1.2.

Wheat was harvested at the grain hardening stage [about 110 days from germination]. Samples were collected and yield was measured as explained in section 5.2.1.2.

Similarly, soil samples were collected as in section 5.2.1.2 However, to these soil samples, first season soil collected in the first year was also added for analyses.

6.3 Results

The data for the laboratory experiments, glass-house and field studies were all statistically analysed and in this section will be presented separately.

6.3.1 Laboratory experimental results

In describing the soils used for various studies and analysis, the "incubated" and "non-incubated" soils refer to soil brought from Kuwait which had not been used to grow plants in the glass-house. "Glass-house" soils are those analysed after being used to grow corn for ten weeks, while "field" soil refers to the soil utilized for field trials. Distinction is made between the first and second season S° application whenever necessary.

6.3.1.1 Elemental sulphur oxidation

The results of this experiment clearly show that S° incubated in soil under favourable oxidation conditions can be oxidised and a surge in soluble SO_4^{2-} indicates this. Table 6.3.1.1.1 presents the effect of five S° treatments varying in rates from 0 to 200% of theoretical acidity required to neutralise the soil $CaCO_3$ with incubation periods of 8 weeks. Soluble soil sulphate was used as a measure for S° oxidation and it has indicated a progressive increase in the amount with increasing S° rates and longer incubation. The SO_4^{2-} values for the S° rates used after 8 weeks incubation indicate a highly significant increase for all rates above that of the control. However the increases between the various S° rates were only significant at the 5% level of probability. Exploring indirect effects of S° oxidation, soil pH has declined from about 8.0 to an average of about 7.2 for the highest S° rate. All the pH decreases were highly significant in relation to S° rate zero after 8 weeks incubation but this was not the case for shorter incubation periods. The $CaCO_3$ contents of the soil also declined with increasing rates of S° and longer incubation periods. This reduction was more apparent and highly significant ($p<0.01$) after 8 weeks incubation. Unlike soil pH, the $CaCO_3$ decline was significant after only 4 weeks incubation. Tables 6.3.1.1.2 and 6.3.1.1.3

Table 6.3.1.1.1 **Effect of S° treatments and incubation periods on soil pH, $CaCO_3$ percentage and soluble sulphate content. Reported data are means of 3 replicates**

	INCUBATION PERIODS IN WEEKS											
S° treatment	- 2 -			- 4 -			- 6 -			- 8 -		
	pH	$CaCO_3$	$SO2-_4$	pH	$CaCO_3$	SO^{2-}_4	pH	$CaCO_3$	SO^{2-}_4	pH	$CaCO_3$	SO^{2-}_4
% *	1:1	%	µg g^{-1}	1:1	%	µg g^{-1}	1:1	%	µg g^{-1}	1:1	%	µg g^{-1}
0 S_1	8.1	19	1447	8.1	19	1018	8.0	19	859	8.0	19	1239
25 S_2	8.0	18	1889	7.9	16	2662	7.7	14	3324	7.6	13	3815
50 S_3	8.1	18	2417	7.9	16	2969	7.7	12	3680	7.5	10	4735
100 S_4	7.9	18	2956	7.8	15	3606	7.6	12	4698	7.5	8	5299
200 S_5	7.9	16	2895	7.7	12	3631	7.4	9	4551	7.2	7	6526

	pH	$CaCO_3$	SO^{2-}_4
LSD .05	0.29	2.2	914.5
LSD .01	0.54	4.0	1678.7

* Equivalent % $CaCO_3$ dissolved by S° treatments if all oxidized.

Table 6.3.1.1.2 **Additive effect of S° treatments over 8 weeks of incubation on soil pH $CaCO_3$ and sulphate content. Means of 3 replicates**

S° treatment	pH 1:1	$CaCO_3$ %	SO^{2-}_4 µg g^{-1}
S_1	8.1	19	1141
S_2	7.8	16	2923
S_3	7.8	14	3450
S_4	7.7	13	4140
S_5	7.5	11	4401

LSD .05	0.10	0.8	313
LSD .01	0.14	1.1	439

Table 6.3.1.1.3 **Effect of incubation. Means of 3 replicates.**

Incubation wks.	pH 1:1	$CaCO_3$ %	SO_4^{2-} µg g^{-1}
0	8.0	19	1141
2	8.0	18	2321
4	7.9	16	2777
6	7.7	13	3422
8	7.6	12	4323

LSD .05	0.09	0.66	274
LSD .01	0.12	0.91	379

show the separate effect of S' treatments and incubation time(s) respectively. It should be noted, however that the values reported (pH, $CaCO_3$% and SO_4 content) were additive for the four incubation periods and the five S' treatments for tables 6.3.1.1.2 and 6.3.1.1.3 respectively.

6.3.1.2 General soil chemical analysis for field, incubated and glass-house experiments

As mentioned before soil samples were collected from every experimental unit in the field. Furthermore, other samples were collected from every main plot (S' treatments) with three incremental profile depth sections. Soils utilized in the incubation and glasshouse exercises were also collected. The following are some of the general soil chemical analyses carried out.

6.3.1.2.1 Sulphate (SO_4^{2-}) variation within field soil profile

Table 6.3.1.2.1 represents the soil SO_4^{2-} at three soil depths for each S° treatment. Although a large number of samples were analysed, the variation between them was inconsistent even for the same S° treatments and depth. It could be that soluble SO_4^{2-} had moved horizontally between the various experimental units, thus contaminating their levels of SO_4^{2-}. However, some observation was possible in that soil SO_4^{2-} levels increased significantly with the incorporation of S°, but not between various S° rates (table 6.3.1.2.1). Furthermore, there was clear downward movement of SO_4^{2-}, more apparent in the 30-60 cm horizon and at high S° levels (table 6.3.1.2.2)

6.3.1.2.2 Soil pH, $CaCO_3$, E.C., SO_4^{2-} and gypsum contents

All soil samples from the field, incubation and glasshouse experiment were analysed for some general soil chemical parameters which are presented in tables 6.3.1.3.1, 2, 3, and 4 for laboratory incubated, glasshouse distilled water irrigated, glasshouse brackish water irrigated and field trials soils, respectively. Table 6.3.1.3.1 represents soils with various S° levels incubated under favourable

Table 6.3.1.2.1 **Measurement of soil profile SO^{2-}_4 ug g^{-1} for field trials sites. Data are means of 9 replicates.**

S° treatment	Profile depth (cm.)		
	0 - 30	30 - 60	60 - 90
S_1	2613	1067	920
S_2	5104	1277	946
S_3	3202	1240	673
S_4	5641	3570	2072
S_5	5531	3669	2171

LSD$_{.05}$ 2310

LSD$_{.01}$ 4241

Table 6.3.1.2.2 **Means of SO^{2-}_4 ug g^{-1} accumulated according to S° rates and profile depth for field trials. Means of 9 replicates.**

S° treatment	SO_4^{2-} Conc	Profile Depth (cm)	SO_4^{2-} Conc
S_1	1535	0-30	4420
S_2	2440	30-60	2164
S_3	1704	60-90	1358
S_4	3761		
S_5	3790		

LSD$_{.05}$ 948 LSD$_{.05}$ 692

LSD$_{.01}$ 1362 LSD$_{.01}$ 958

conditions for six months. Soil pH had not changed significantly, although there was a significant drop in soil $CaCO_3$. Also there was a moderate but significant rise in salinity as measured by the E.C. readings. There were some increases in the SO_4^{2-} and gypsum contents, however these parameters were not statistically analysed due to the large number of samples required by the experimental design. Only 32 samples out of 180 (used in other parameters) were analysed representing the five S° treatments and three blocks with two replicates. But clearly there was an increase in the SO_4^{2-} levels when compared with control treatment (S_1). Similarly the gypsum content had doubled and tripled with the increases in S° additions. These results also indicated the ability of the incubated soil to oxidize S°. Tables 6.3.1.3.2 and 6.3.1.3.3 demonstrate the changes in various soil parameters as affected by progressively increasing S° additions for soils used to grow a test crop in the glass-house, which were irrigated by distilled and brackish water respectively. Soil pH declined in a highly significant way especially with the highest S° rates [S_4, S_5]. At rates S_2, S_3 representing respectively the theoretical acidity to neutralize 25% and 50% of the soil $CaCO_3$, the pH decline was smaller although at some rates significant. However, it was difficult to obtain a stable reading especially if the pH meter electrode touch the soil in the suspension. The presence of $CaCO_3$ at >10% and its ability to buffer against the increase in soil H^+, was expected to be the reason for that. $CaCO_3$ equivalent % also declined in a highly significant way. The decreases were consistent with the S° applications and at the highest rate [S_5] the remaining $CaCO_3$ was only a small fraction of what was the original amount [S_1]. It is important to notice that the soil became acidic < 7.0 even though, there was still some $CaCO_3$ remaining in the system. It could be that at these high S° rates, the remaining $CaCO_3$ particles were large with less surface area and therefore reduced buffering capacity. The drop in soil pH and $CaCO_3$ contents after only 10 weeks glasshouse growth trials [and a week for drying] were more pronounced

able 6.3.1.3.1 Effect of S^o on various soil parameters for the incubated soils prior to their use as a growing medium. Means of 3 replicates.

S^o treatment	pH 1:1	$CaCO_3$ % equi.	E.C. 1:2 dSm^{-1}	SO_4^{2-} 1:10 μgg^{-1}	gypsum 1:20 * % equi.
1	8.0	18	4.5	1214	0.9
S_2	8.1	17	6.1	1825	1.9
S_3	7.9	15	6.4	2307	2.1
S_4	8.0	17	6.5	2184	1.5
S_5	7.9	16	7.5	2581	2.3
LSD .05	0.26	1.63	0.91	* *	* *
LSD .01	0.37	2.29	1.28	* *	* *

Table 6.3.1.3.2 Effect of S^o on various soil parameters for the glass-house experiment irrigated by distilled water. Means of 12 replicates.

S^o treatment	pH 1:1	$CaCO_3$ % equi.	E.C. 1:2 dSm^{-1}	SO_4^{2-} 1:10 μg g^{-1}	gypsum 1:20 * % equi.
S_1	7.9	18	3.0	478	1.0
S_2	7.8	15	8.3	2188	1.7
S_3	7.4	12	7.8	2431	3.1
S_4	6.3	4	9.4	2716	3.0
S_5	5.5	2	9.9	3142	3.7
LSD .05	0.19	0.99	1.48	* *	* *
LSD .01	0.26	1.39	2.08	* *	* *

* Gypsum % calculated from soluble sulphate at that dilution.

* * Not enough samples were conducted for statistical analysis as required by the design. Only 2 samples for every S^o treatment from each block.

than the previous 6 months incubation. Although the incubations were at favourable temperature and moisture levels, it may be that aeration was inadequate especially in polythene bags containing about 3.0 kg soil. The wetting-drying cycles provided for plant irrigation increased the level of oxygenation and thus promoted faster S° oxidation. From visual observation there were salt deposits on the soil surface between irrigations and this was confirmed by the moderate to high measurements of soil salinity [E.C. readings], which doubled and even tripled as S° rates increased. The increases were more severe with brackish compared to that of distilled irrigation. This was expected since the practice of percolating more water through the soil in the pots to reduce salt damage to the growing plants had been more successful in the case of distilled water in solublizing and removing the salts.

A few soil samples, two from each S° treatment from every block, were used to measure increases in $SO^{2-}{}_4$ and gypsum contents, but were not appropriate for statistical analysis. However, there were increases in both of these as more S° was incorporated into the soils. For high S° treatments there could be higher amounts of gypsum present then these indicated by the 1:20 dilution due to the solubility limits of gypsum ie $2.63 gl^{-1}$ (Richards, 1954).

Field trial soils were also analysed for the same parameters as those of glass-house studies (table 6.3.1.3.4). However, there was an unfair comparison between treatments S_2 and S_3 and those of S_4 and S_5, since the former had only one season [4 months] of S° incorporation before they were collected and then analysed. Whereas, treatment S_4 had its S° added a year earlier and treatment S_5 had 2/3 and 1/3 of its S° added in the first and second year respectively. Soil pH from the field study had not changed with the incorporation of S°. Although there was a small decline in soil pH, this was not statistically significant. However there was a highly significant drop in the soil $CaCO_3$ content, even for the second season lowest S° rate [S_2]. Unlike the glass-house soils, the soil pH of

Table 6.3.1.3.3 **Effect of S° on various soil parameters for the glass-house experiment irrigated by brackish water. Means of 12 replicates.**

S° treatment	pH 1:2	$CaCO_3$ % equi.	E.C 1:2 dSm^{-1}	SO_4^{-1} 1:10 $\mu g\ g^{-1}$	gypsum 1:20 * % equi.
S_1	8.0	18	3.9	964	1.1
S_2	7.9	15	9.2	2182	2.8
S_3	7.5	12	8.1	3922	3.5
S_4	6.2	6	10.3	4449	3.8
S_5	5.9	1	11.7	4140	4.1
LSD .05	0.20	0.82	1.05	* *	* *
LSD .01	0.28	1.15	1.47		

Table 6.3.1.3.4 **Effect of S° on various soil parameters for the field trials. The data are means of 180 replicates.**

S° treatment	pH 1:1	$CaCO_3$ % equi.	E.C. 1:2 dsm^{-1}	SO_4^{2-} 1:10 $\mu g\ g^{-1}$	gypsum 1:20 % equi.
S_1	7.7	16	3.7	2613	2.0
S_2	7.7	15	7.2	5140	3.8
S_3	7.6	14	8.6	3202	3.5
S_4	7.7	8	10.8	5641	4.4
S_5	7.6	4	11.9	5531	5.6
LSD .05	0.098 (N.S.)	1.84	0.96	2310	* *
LSD .01	0.137 (N.S.)	2.58	1.35	4241	

N.S. Non significant

* Gypsum % calculated from soluble sulphate at that dilution.

* * Not enough samples were taken for statistical analysis as required by the design. Only 2 samples for every S° treatment from each block.

the highest S° rate [S_5] did not become acidic even though a high proportion of its $CaCO_3$ had dissolved. It could be that enough $CaCO_3$ remained to buffer the soil, but more likely that horizontal solute movements between the plots had diluted the acid strength. Soil salinity as indicated by E.C. measurement also increased and some of these increases were at the extreme range for crop growth. As has been noted there was an inverse relationship between the decline in soil $CaCO_3$ and the increase in E.C. This behaviour was more manifested in the field than the glass-house studies. It could be that the brackish water irrigation coupled with extremely high evapo-transpiration in the field trial in Kuwait had further concentrated the salinity released by the dissolution of $CaCO_3$. Soil SO_4^{2-} as expected also increased in response to S° addition. Although these changes were for most part significant, some were inconsistent, and even the control treatment S_1 had a high SO_4^{2-} content compared with the levels in the same field at a distance from S° treatments. Probably horizontal solute movement had contaminated various adjacent plots with the SO_4^{2-} released from S° oxidation. Gypsum content of the soil also increased in response to S° treatments. Although no statistical analyses were carried out the variation in gypsum % was not great. Furthermore, even the control had a reasonably high level of gypsum when compared to the previously virgin soils used in the glass-house experiments. Using ground water high in SO_4^{2-} content to irrigate soils naturally containing some free Ca^{2+} had over the years probably resulted in the built-up of gypsum.

6.3.1.3 Examination of $CaCO_3$ and gypsum particles by SEM and EDAX

The purpose of this particular examination was to explore the possibility of a gypsum layer being formed by the increased SO_4^{2-} levels due to S° oxidation and the release of Ca^{2+} by the subsequent $CaCO_3$ dissolution. If these ion concentrations exceeded the solubility product limits of $CaSO_4$, this would start to precipitate out of solution. The possibility of this precipitate covering other soil particles especially some of the active $CaCO_3$ could have a great influence on P and some trace element bio-availability. Some of the SEM photographs from the examination confirmed the presence of $CaSO_4.2H_2O$ particles covering other soil constituents. Not only $CaCO_3$ particles had $CaSO_4$ layers covering part of them but also some sand (quartz) particles had similar covering. This examination, however, was only qualitative and no firm conclusions could be drawn as to the degree of $CaCO_3$ surface shielding due to $CaSO_4$ precipitation. Plates of SEM photographs and their corresponding EDAX analysis will be presented and further comments will be provided in the discussion (section 6.4).

6.3.1.4 Soil and $CaCO_3$ mechanical analysis

This study was extremely difficult to conduct. With high levels of SO_4^{2-} in the soil, especially the highly S° amended treatments there was a need for many cycles of washing with distilled water. But as the ionic strength of the soil suspension got weaker it was difficult to precipitate the light soil fraction even after long, high speed centrifuging. A few drops of $Al_2(SO_4)_3$ were periodically needed to flocculate the suspension. As the exercise involved many washings to remove the soil SO_4^{2-} and in separating various sand fractions, some soil particles were lost especially from finer fractions. This was reflected in the poor reproducability of the data as indicated by a high standard of error in the statistical analysis. Table 6.3.1.4.1 presents the mechanical analysis of glass-house soils amended by five rates of S°. "A" fractions were those that still contain their $CaCO_3$, whereas "B" represents the same soil after its $CaCO_3$ had been removed by acid digestion. Some of the measurement of the coarse silt fraction, which were tabulated by balancing the amounts to the original 100 g oven-dried soil used, gave negative readings. It could be that averaging the three replicates was the reason, or that the soil was not adequately dispersed thus lowering the values of the silt and clay fractions, or that hygroscopic behaviour of the various fractions in absorbing humidity from the air while cooling after

Table 6.3.1.4.1 **Mean measurement of soil fractions where the same soil analysed before and after acid treatment. Means of 3 replicates for each set (A&B)**

% particle size distribution								
"A" fraction size in µm (non-treated)								
S° Treatment	course sand 2000 - 600	medium sand 600 - 200	fine sand 200 - 63	coarse silt* 63 - 20	silt 20 - 2		clay < 2	
					hydro	pipette	hydro	pipette
S_1	7.2	47.5	26.7	7.6	7.4	6.5	5.6	4.5
S_2	9.5	50.1	31.4	- 0.8	7.5	4.5	5.4	5.3
S_3	11.1	61.9	22.6	- 6.9	6.9	6.2	6.1	5.1
S_4	6.4	48.4	28.1	9.7	6.1	3.1	7.2	4.3
S_5	7.4	57.3	26.9	- 2.9	6.3	5.2	6.9	6.1

* added to 100% based on values of silt and clay by the pipette method

% particle size distribution								
"B" fraction size in µm (acid-treated)								
S° treatment	coarse sand 2000 - 600	medium sand 600 - 200	fine sand 200 - 63	coarse silt* 63 - 20	silt 20 - 2		clay < 2	
					hydro	pipette	hydro	pipette
S_1	8.3	41.6	22.8	1.6	3.3	4.1	4.7	3.6
S_2	7.9	43.4	26.5	- 1.3	5.1	4.8	5.1	4.1
S_3	9.1	49.5	19.1	3.2	5.9	4.2	6.2	4.9
S_4	8.6	54.1	20.9	2.1	6.2	4.9	6.8	5.4
S_5	7.3	53.0	29.4	- 1.4	6.4	5.0	7.4	5.7

* added to 100% based on values of silt and clay by the pipette method then subtracted from total $CaCO_3$ as measured by calcimeter

oven drying, could have been the cause for these discrepancies. The differences between the two sets representing the $CaCO_3$ amounts in each fraction for the three replicates were statistically analysed and their means were represented in table 6.3.1.4.2. Some of the data were negative reflecting a higher total of that particular fraction after acid digestion. The comparative analyses representing that fraction size content of $CaCO_3$ were insignificant due to the very high standard error estimation. Table 6.3.1.4.3 shows the $CaCO_3$ fraction measured by digesting it after separation by mechanical analysis and then tabulated to the original soil values, with a lower standard error estimation reflected by a smaller LSD. However, these findings expressing $CaCO_3$ fraction contents were only significant in the cases of 600-200 and 200-63 µm sand fractions. This was expected since these two fractions represent more than 75% of the soil and presumably a high proportion of the soil $CaCO_3$. The theory that slow acidification by S° oxidation would digest the smaller soil $CaCO_3$ fraction faster than the larger ones, thus reducing the surface area of $CaCO_3$ in a higher proportion to the reduction in the total $CaCO_3$ amounts could not be elucidated from this exercise. The samples measuring the silt and clay fractions by the pipette method use very small amounts (20 ml from 1.0 litre suspension). To use this to estimate its $CaCO_3$ content was misleading.

6.3.1.5 Indirect $CaCO_3$ fraction measurements by pH-time chart

Table 6.3.1.5.1 shows the time needed for 1.0 gram $CaCO_3$ to raise the pH of weak acid from 3-6 and the slope of the line between pH 4-5 for the various sizes of standard pure $CaCO_3$ ranging from fine clay to coarse sand. Using that standard as a guide, soils selected from the glass-house experiment were exposed to the same treatment whereby various consignments of soil all containing 1.0 gram $CaCO_3$ as measured by calcimeter were added to the weak acid. The time needed to raise the pH from 3-6 and the slope of the line between pH 4-5 were

Table 6.3.1.4.2 Mean measurement of % $CaCO_3$ distribution estimated by the differences between each soil particle size before and after acid treatment. Means of 3 replicates.

% particle size distribution						
$CaCO_3$ fractions (µm)						
S° treatment	2000-600	600-200	200-63	63-20*	20-2	< 2
S_1	-1.1	5.9	3.9	5.8	2.3	1.9
S_2	1.6	6.6	4.8	1.1	-0.3	1.1
S_3	2.0	12.3	3.4	9.7	1.9	0.3
S_4	-2.2	-5.6	7.3	-6.9	-1.8	0.4
S_5	0.1	4.4	-2.5	0.0	0.2	0.4
	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.

S.E.D. 2.481

* Estimated by subtracting 100 from total $CaCO_3$ as measured by calcimeter, all other soil fractions and the very fine sand fraction estimated before acid treatment for each S° rate.

N.S. Non significant at 0.05 probability

Table 6.3.1.4.3 Mean measurement of % $CaCO_3$ distribution tabulated by the diffrece in each fraction before and after acid digestion.Means of 3 replicates.

% particle size distribution						
$CaCO_3$ fractions (µm)						
S° treatment	2000-600	600-200	200-63	63-20*	20-2	< 2
S_1	0.1	8.1	6.7	1.7	0.8	0.0
S_2	1.3	7.9	5.2	-0.8	0.2	0.2
S_3	0.7	6.3	2.2	0.6	0.8	0.1
S_4	0.1	1.7	2.3	-1.2	0.7	0.0
&& S_5	0.2	0.8	0.4	-1.0	0.6	0.2

LSD

.05 0.892

* Estimated by subtracting all other $CaCO_3$ fractions from total $CaCO_3$ as measured by calcimeter for each S° treatment.

recorded and their analysis presented in table 6.3.1.5.1. As has been demonstrated in table 6.3.1.5.1, there were progressively longer periods needed to decompose $CaCO_3$ in a weak acid medium as its dimensions got larger. Treatment S_1 which contain no S° as a control had a time of 10.51 minutes corresponding to about the same time for the coarse clay in the standard. The time[s] in the case of treatments S_2, S_3 increased slightly indicating that the $CaCO_3$ particles still present were of the size between coarse clay and silt [1-20 um]. Treatment S_4 corresponding to the acidity needed to decompose all the soil $CaCO_3$ showed a time similar to the silt-sized standard [18 minutes] indicating that fewer fine $CaCO_3$ particles still pesisted. Treatment S_5 containing S° theoretically able to neutralize 200% of the soil $CaCO_3$ had a time of 23.3 minutes, a 25% increase on the silt standard time showing that only particles somewhat larger than silt size still persisted in the soil. Treatments S_4 and S_5 had highly significant increases in the time needed to raise the pH from 3-6 when compared to the control [S_1]. However, the slope of the line had non-significant variation between the S° treatments except in the case of S_5 although values did not correspond to those of the standard. This exercise showed conclusively that the remaining $CaCO_3$ after acidification due to S° - oxidation needed longer time to neutralise the acidity reflecting a lower surface activity due to larger particles size. However, interpretion of the data of the exercise has many limitations. It has been assumed that all soil $CaCO_3$ for the control and the acid treated soils had a uniform size, which might not be the case. Therefore a time requirement corresponding to a specific standard size could arise from a range of particles varying in size but collectively given a time similar to that of the standard. Furthermore, other soil components could have influenced $CaCO_3$ surfaces and so the rates of the acid reaction, for example the soil organic matter and clay content or other minerals naturally present or added as fertiliser. While these might be expected to have some effects, it would be safe to assume that the

Table 6.3.1.5.1 Time needed for 1.0 gram $CaCO_3$ (as measured by calcimeter) to raise the pH of weak H_2SO_4 acid from pH 3 - 6 and the slope of the line between pH 4 - 5 for glass-house soil containing various S° treatments.

Standard based on pure $CaCO_3$					
	F. Clay	C. Clay	Silt	F. Sand	C. Sand
Time (min)	5.17	9.50	18.70	85.42	----
Slope	>0.01	0.07	0.19	2.27	

S° treatment	Time needed for soil containing 1.0 gram $CaCO_3$ to raise pH from 3 - 6 in min.**	Slope of the line for pH rise from pH 4 - 5.
S_1	10.51	0.42
S_2	12.79	0.46
S_3	12.16	0.52
S_4	18.17	0.53
S_5	23.31	0.67

$LSD_{.05}$	3.07	0.123
$LSD_{.01}$	4.37	0.175

** Means of 5 replicates

$CaCO_3$ fraction of such calcareous soils would be the main factor in the direction and speed of pH change, but since high S° applications had greatly reduced the $CaCO_3$ content, these other factors would be expected to have proportionally enhanced roles. Any additional acidity produced by S° oxidation that had not been neutralised by the soil $CaCO_3$ would negatively influence the rise in the pH of the weak acid when soil was added. This would be expected in the high S° treatments. The physical characteristics of the standard $CaCO_3$ used [produced by grinding high quality marble rock] would probably be different than those of the $CaCO_3$ in the soil especially in its hardness and porosity, so to correlate such time requirement from the exercise to correspond to an exact size could be misleading.

6.3.1.6 Column study on the changes to $CaCO_3$ after slow acidification

Although the original intention was that the soils from this exercise would be mechanically analysed to explore the changes in the various $CaCO_3$ size fractions upon acidification, this had been abandoned in light of the difficulty in obtaining a sound result as was the case in section 6.3.1.4. Therefore, only indirect "pH-time chart" analysis as in section 6.3.1.5, and examination of $CaCO_3$ particles by SEM and EDAX analysis as in section 6.3.1.3 were carried out.

Table 6.3.1.6.1 contains the means of three replications for % $CaCO_3$ and time needed to raise the pH. As expected there was a highly significant drop in the $CaCO_3$ content, but more remarkably the remaining $CaCO_3$ required a significantly greater time to raise the pH of the weak acid when equal amounts of soil $CaCO_3$ [1.0 g] were added. Variation in the slope of the line however was insignificant. This exercise confirmed that the $CaCO_3$ particles remaining in soil from the columns after partial acid decomposition were of a larger size as recorded by the "pH-time chart". Since the soils used were identical and the acid utilized was diluted [0.5 M H_2SO_4] and since enough time was allowed for

Table 6.3.1.6.1 Effect of limited acidification on $CaCO_3$ content and the time needed for 1.0 gram of the remaining $CaCO_3$ to raise a pH of a weak acid from 3 - 6 and the slope of the line between 4 - 5. Data, means of 3 replicates.

Treatment	% $CaCO_3$	Time needed for 1.0gram $CaCO_3$ to raise pH from 3 - 6 (min)	Slope of the line between pH 4 - 5
Control 0.5 L of dist. H_2O	18.4	11.75	0.38
H_2SO_4 0.5 L (0.5M)	10.9	15.25	0.56

LSD .05	4.99	3.13	N.S.
LSD .01	7.56	4.74	N.S.

Table 6.3.1.7.1 Effect of acid leaching on soluble P and extractable P of calcareous soil. Means of 3 replicates.

	Leachate						Soil			
H_2SO_4 treat.	pH		Ca^{2+} μgg^{-1}		P ugg^{-1}		$NaHCO_3$-P $\mu g\ g^{-1}$		$CaCO_3$ % equi.	
M	-P	+P	-P	+P	-P	+P	-P	+P	-P	+P
10^{-1}	2.1	2.2	8.1	7.4	1.5	4.1	28.13	63.41	1.2	1.3
10^{-2}	7.2	7.5	4.1	5.3	1.3	3.8	30.33	68.08	10.2	8.9
10^{-3}	7.8	7.7	2.7	2.1	1.5	3.8	30.83	63.09	15.9	14.2
10^{-4}	8.7	8.2	1.3	1.2	1.1	2.8	31.10	76.35	16.7	17.1
Dist.	8.4	8.3	1.0	0.9	1.1	4.2	29.80	72.17	16.5	17.0

LSD .05	0.37	0.73	0.93	6.55	2.53
LSD .01	0.52	1.04	1.32	9.32	3.40

equilibration after treatment so that all acidity were consumed, the limitation indicated in the previous section (6.3.1.5) would be of no consequence in these findings. Even though on average about 40% less soil was used in the control compared to the treated soil to deliver equal amounts of $CaCO_3$, this variation was not so great that on its own it could drastically shift the pattern of pH-time equilibration.

Examination of the soil particles by SEM and EDAX analysis to find if there was masking of the remaining $CaCO_3$ by precipitation of a layer of $CaSO_4$ showed no such layers. It could be that dilute acid [0.5 M H_2SO_4] had leached the Ca^{2+} and SO^{2-}_4 ions out of the column, thus the formation of $CaSO_4$ precipitate did not occur.

6.3.1.7 P solubility and retention in relation to $CaCO_3$ slow decomposition by weak acid

The experiment was conducted to shed light on the simultaneous changes to soil pH, Ca^{2+} content and $CaCO_3$ activity when exposed to acidity and how this would affect the solubility and extractability of P. Table 6.3.1.7.1 presents the means of three replicates for leachate pH, Ca^{2+} and P content and extractable soil P and $CaCO_3$ content. These were presented separately for the P amended and non-amended soils. Leachate pH did vary with respect to the acid treatment and the more concentrated the acid the more significant and the larger the drop in pH. Acid treatment 10^{-1} M reduced pH to the greatest extent and its leachate became acidic; about 3.7; after only 40 ml of the acid. As weaker acid was used the drop in the pH was smaller and in the case of 10^{-4} M the drop compared to the distilled water was insignificant. There were no significant differences in the leachate pH due to the P addition. Ca^{2+} ions measured in the leachate and expressed in terms of that removed from the soil showed a highly significant variation when exposed to increasing strength of acidification. Again as with the pH the differences in Ca^{2+} did not respond to P treatment. As expected there was a clear drop in the soil $CaCO_3$ content in reaction to progressively stronger treatment and this was in many instances highly significant. P application did not effect $CaCO_3$ loss. All the above changes were expected and designed so that an exploration of their effects on P solubility as measured in the leachate and P bio-availability as measured in the $NaHCO_3$ extracts could be assessed. P solubility and extractability did not respond to the changes in pH, Ca^{2+} concentration and $CaCO_3$ contents for the non-P treated soils. The P amended soils did have significantly higher soluble and extractable levels of P when compared to the non-amended soils. In some cases the differences between the various acid treatments were also significant. However, this did not in a consistent way reflect acid strength. It could be that the newly added P did not have enough reaction time in the soil and it was more soluble and extractable independently of the changing conditions due to the acidification.

6.3.2 Glass-house experiments

The glass-house experiments were conducted using S° incubated soil treated with two levels of P and micronutrient combinations. Corn (Zea mays) was utilized as a test plant and allowed to grow for ten weeks. Distilled and brackish irrigation water were administered in two separate sets of experiments. See section 6.2.2.1 for details of experiment layout. Tables 6.3.2.1 and 6.3.2.2 show extractable P, Fe, Zn and Mn obtained from the soil after plant harvest for the distilled and brackish water irrigated sets respectively. $NaHCO_3$ - P extract showed a marked increase in extractability with the increasing rates of S°. However, the increase was only significant when the soil was fertilised with P. It could be that the reduction in soil pH and more importantly the reduction of $CaCO_3$ activity were ineffective in non-P treated soils due to low levels of native soil P components, whereas fertiliser P stayed longer in available forms in response to S° application. Lowering $CaCO_3$ activity and the acidity of S° micro-niches could be the reason for maintaining the higher extractability of P even

Table 6.3.2.1 Effect of S° treatment on NaHCO-P and DTPA-Ext. Fe, Zn, and Mn for the distilled irrigated soil. Means of 6 replicates.

S° treatment	$NaHCO_3$-P $\mu g g^{-1}$		DTPA-Fe $\mu g g^{-1}$		DTPA-Zn $\mu g g^{-1}$		DTPA-Mn $\mu g g^{-1}$	
	-P	+P	-Fe	+Fe	-Zn	+Zn	-Mn	+Mn
S_1	1.4	3.6	1.6	1.7	0.5	0.3	2.7	2.5
S_2	2.1	9.8	2.8	2.6	0.9	1.0	5.4	6.1
S_3	2.7	9.8	6.9	7.3	1.0	1.4	8.3	7.2
S_4	2.5	4.6	4.8	9.4	1.1	0.9	11.4	19.2
S_5	2.5	8.7	9.4	6.4	0.9	1.2	15.7	14.2

LSD .05	2.215	3.21	0.397	4.71
LSD .01	2.964	4.29	0.531	6.30

Table 6.3.2.2 Effect of S° treatment on NaHCO-P and DTPA-Ext. Fe, Zn, and Mn for the brackish irrigated soil. Means of 6 replicates.

S° treatment	$NaHCO_3$-P ugg^{-1}		DTPA-Fe ugg^{-1}		DTPA-Zn ugg^{-1}		DTPA-Mn ugg^{-1}	
	-P	+P	-Fe	+Fe	-Zn	+Zn	-Mn	+Mn
S_1	1.92	2.97	1.8	1.6	0.46	0.29	2.6	3.4
S_2	2.85	4.42	2.6	2.6	0.45	0.93	5.8	5.1
S_3	3.54	7.19	6.2	5.9	0.82	1.16	9.5	11.6
S_4	2.28	6.53	4.3	7.8	1.19	1.20	17.6	15.7
S_5	2.53	8.36	9.6	7.3	0.96	1.17	16.4	21.4

LSD .05	2.009	2.97	0.502	3.79
LSD .01	2.688	3.97	0.672	5.07

after a ten week growing period.

DTPA extractable-Fe levels for the native soil were low and would be expected to cause Fe-deficiency in growing corn. Soil acidification had a significant effect in increasing the DTPA-Fe and in many cases these increases were highly significant especially with the high rate S° treatments. At a S° treatment corresponding to 25% of the theoretical acidity required to dissolve the soil $CaCO_3$ (S_2), the S° did not significantly increase DTPA-Fe extractability. Lowering of soil pH and possibly direct reduction in $CaCO_3$ activity could be the reason for the higher extractability with higher S˚ rates. In a few cases there were positive effects from Fe fertilization, however these were inconsistent. Similar findings were observed with soil DTPA-Zn. There were significant improvements in Zn availability, apparent even with the lowest S° application. Moreover there was no significant variation in DTPA-Zn in response to greater doses of S°, and no benefits due to $ZnSO_4$ addition to the soil. The effects of S° on soil Mn were strongly manifested in the extremely large quantities of DTPA-extractable Mn. With the high S° rates, there were many cases which had extractable Mn levels more than five fold that of the control. In such circumstances, one might fear direct toxic effects on the growing plants or indirect problems due to nutritional imbalances due to possible inter-elemental antagonisms. As was the case with Zn, there were no apparent increases in DPTA-extractable Mn in response to Mn salt amendments.

From the two tables representing the same soil exposed to similar treatments, but differing in the type of irrigation they received, there appears to be no definite variation in the four nutrients measured in the extracts. It appears that the slightly saline irrigation utilised in one of the experimental sets has had no direct effect on the solubility or precipitation of the nutrients studied.

Plant yields and elemental concentrations of some nutrients and their uptake per plant are presented in tables 6.3.2.3 and 6.3.2.4 for the distilled and brackish

Table 6.3.2.3 **Effect of S° treatment on P, Fe, Zn, and Mn tissue concentration and on its plant uptake for distilled irrigated soil. Data of yield and P concentration and uptake are means of 6 replicates, while Fe, Zn and Mn concentration and uptake are means of 12 replicates.**

S° treat.	Dry weight g/plant		Plant tissue concentration ug g^{-1}					uptake ug $plant^{-1}$				
			P		Fe	Zn	Mn	P		Fe	Zn	Mn
	-P	+P	-P	+P				-P	+P			
S_1	2.15	2.26	1017	940	45.4	18.8	30.0	2237	2115	102.3	40.2	66.2
S_2	2.49	2.21	970	989	58.1	18.8	43.3	2411	2196	138.7	44.1	101.8
S_3	2.46	1.82	962	1021	63.9	19.1	45.1	2348	1860	138.8	40.3	96.4
S_4	1.63	1.46	1241	1378	72.0	18.7	49.7	2013	1999	110.2	28.3	76.7
S_5	1.34	1.45	1429	1495	79.4	21.5	49.8	1928	2187	109.8	29.1	69.6
LSD .05	0.56		188		9.3	N.S.	8.1	632		N.S.	8.0	33.7
LSD .01	0.76		252		12.4	N.S.	10.8	845			10.7	45.1

Table 6.3.2.4 Effect of S° treatment on P, Fe, Zn, and Mn tissue concentration and on its plant uptake for brackish irrigated soil. All data are means of 6 replicates except those of Mn concentration and uptake which are of 12 replicates.

S° treat.	Dry weight g/plant		Plant tissue concentration ug g^{-1}							uptake per pot(ug $plant^{-1}$)						
			P ugg^{-1}		Fe ugg^{-1}		Zn ugg^{-1}		Mn ugg^{-1}	P		Fe		Zn		Mn
	-P	+P	-P	+P	-Fe	+Fe	-Zn	+Zn		-P	+P	-Fe	+Fe	-Zn	+Zn	
S_1	1.84	3.54	933	1264	39.0	52.0	13.0	33.0	23.7	1708	3732	84.2	142.5	27.7	90.3	63.7
S_2	1.73	3.26	988	1892	42.1	64.1	16.0	21.0	34.5	1658	5928	117.2	138.7	42.2	47.5	86.1
S_3	1.90	3.24	1532	2505	55.0	60.6	15.6	23.1	48.2	2859	8104	125.5	157.2	36.0	60.8	124.0
S_4	1.88	2.05	2075	3488	70.7	56.5	22.3	26.5	42.1	3687	6567	119.2	118.3	35.7	55.2	82.7
S_5	1.54	2.19	1586	2496	83.5	72.0	16.9	30.4	37.5	2456	5428	149.5	134.5	31.3	54.8	69.9
LSD .05	0.59		493		15.3		6.8		7.3	1320		32.7		16.1	28.4	
LSD .01	0.80		660		20.5		9.1		9.8	1765		43.3		21.6	38.0	

water irrigated trials, respectively. Although the two sets of experiments were grown in the same glasshouses side by side, plant growth responded differently to the type of irrigation water used. From visual observation the set utilising the distilled water had a soil structure problem, whereby after irrigation the soil slumped and water percolation was restricted. In some cases it took more than 24 hours for the irrigation water to percolate through the soil. Treatments high in S^0 were less affected, but plant growth was stunted. In general the set that was irrigated by the distilled water had plants with poor growth which did not respond in their yields to P fertilization. Furthermore, their yields responded negatively to the S^0 treatments. However, the yield did not significantly decline with moderate rates of S^0 (S_2, S_3), but at high S^0 treatment (S_4, S_5) yield significantly dropped by 30-40%.

Nutrient concentration in plant tissue for the distilled water irrigated set (table 6.3.2.3) confirmed what was obtained from the yield responses. P concentrations were similar in all treatments receiving no S° or moderate amounts (S_1, S_2, S_3) and no difference occured if P fertilizer was incorporated, whereas treatments high in S° (S_4, S_5) lead to greater amounts of P in the plant tissue. This was perhaps a response to the stunted plant growth, since P uptake per plant was not statistically different in any of the S° or P treatments.

Iron tissue concentrations and uptake followed the same pattern as P. Fe concentration increased significantly in response to increasing S° treatment, however due to the lower yield with higher S°, the total Fe uptake per plant was about the same. Furthermore, there was no significant response to micro-nutrient fertilization neither in the plant tissue Fe concentration nor in the plant Fe uptake. From the DTPA-Fe soil ectracts (table 6.3.2.1) S° appeared to increase the bio-availability of Fe even at moderate levels such as S_3, but because of the soil physical problems the plants were unable to respond to this increased nutrient availability.

Zinc behaved differently. It did not respond to S° with regard to Zn plant tissue concentration (table 6.3.2.3) even though the soil DTPA-Zn extract had higher levels in relation to S° treatments (table 6.3.2.1). It could be that the restricted plant root growth had adsorbed only the limited Zn that it had encountered. It seems that Zn was not the limiting factor in plant growth and that was reflected in the lack of response to the increased Zn availability. The reduction in total plant Zn uptake with increasing S° rates was due to the smaller plant growth obtained at such rates.

Manganese concentrations in the plant tissue were only significantly higher when compared to the control (S_1) (table 6.3.2.3). It could be that the improved availability of Mn (table 6.3.2.1) due to the presence of S° was beyond that required for nutrition of the corn plant. The increased availability with higher S° treatments did not cause the plant to absorb greater quantities of Mn, but these higher levels could give rise to other nutritional problems. Plant Mn uptake reflected that finding. For example, plants of treatment S_2 which received S° corresponding to the amount needed to neutralize 25% of the soil $CaCO_3$ maintained their higher yield in comparison to other S° treatments, but with the improved Mn bio-availability, they accumulated significantly higher amounts of Mn compared to all other treatments (table 6.3.2.3) while the highest S° treatment (S_5) had plant Mn uptake similar to the control (S_1).

Brackish water irrigated plants had a relatively better growth than those distilled water irrigated and that was reflected in the yield responses (tables 6.3.2.3 and 6.3.2.4). It could be that the slightly saline water had prevented the collapse in the aggregation of soil particles thus maintaining good aeration and water percolation. Greater plant vigour and better root growth in the brackish water irrigated set compared to the distilled water set responded more to the various treatments. Yield (dry weight) reacted positively to the P fertilization (table 6.3.2.4) and this was in direct response to the increased bio-availability of

P as was expected from $NaHCO_3$-P extracts (table 6.3.2.2). S^0 effect on plant yield was negative at the high rates (S_4, S_5) where P was added. At the more moderate rates there was no statistical variation in plant yield due to S^0 treatments. Treatments that had no added P, all had low yield compared to the ones receiving P, and they did not respond to S^0 treatments.

Plant tissue P concentration had shown the positive effect of P fertilization. The concentration increased by more than 50% with the addition of P and this was in most cases highly significant. The effect of S^0 treatment was positive in enhancing the P tissue concentration even in moderate S^0 treatments (S_2, S_3). The reduced plant yield had resulted in a much higher concentration of P as observed in S_4 treatment. This was not due to enhanced uptake of P, but because other factors limited plant growth, possibly the toxic effects of high SO_4^{2-} as shown in S^0 treatment S_5. P uptake by plants was the highest with the S_3 treatment which increased P availability (table 6.3.2.2) and did not reduce yield (table 6.3.2.4). This P uptake level was more than 1/3 higher than the other treatments and this increase was highly significant.

Iron tissue concentration reacted to both S^0 treatment and Fe fertilization. Treatments S_1 and S_2 corresponding to the control and the lowest rate of S^0 had low Fe-tissue concentration, when no Fe fertilization applied. Upon the addition of $FeSO_4$ to the soil, concentration increased by 35-50%. However this was only significant in the case of the S_2 treatment. At high S^0 treatment (S_4, S_5), Fe-tissue concentration did not respond to Fe fertilization, but there levels were much higher than in the other treatments and in some cases were double those of the control. However with the decreased plant growth at high S^0 treatment, it was difficult to distinguish between the effect of higher Fe bio-availability (table 6.3.2.2) and reduced yield when evaluating Fe-tissue concentrations.

When observing the plant Fe uptake the variation mostly was not significant. It could be that S^0 and Fe fertilization had increased plant absorption of Fe, but this element was not the limiting factor in plant growth, and therefore it did not correlate with plant yield.

Zinc tissue concentration did not respond to S^0 treatment, but it did moderately to Zn fertilization. In some cases this was doubling of the Zn levels with fertilization and was highly significant (table 6.3.2.4). This finding was further confirmed from the plant uptake of Zn where the control S^0 treatment with Zn fertilization accumulated significantly greater amounts of Zn than all other treatments. This reflected the benefit of $ZnSO_4$ and the higher plant yield when S^0 was not incorporated (table 6.3.2.4).

Plant tissue concentration of Mn was higher with higher rates of S^0 treatment. There were no significant effects due to $MnSO_4$ amendments, but the increased bio-availability of Mn as observed in soil extracts (table 6.3.2.2) from the presence of S^0 was reflected closely in the plant tissue Mn levels. Treatments which received S^0 had significantly increased concentration of Mn compared to the S_1 control treatment. Mn levels were highest in S^0 treatment S_3, which reflect the combination of higher Mn bio-availability due to S^0 oxidation effects, and the more vigorous plant growth at such moderate levels of S^0 application. This was confirmed in the plant Mn uptake where that treatment (S_3) had significantly higher levels of Mn uptake than all other treatments.

From the statistical analysis of the experimental designs there were clearly some cases of nutrient antagonisms. There was a moderate but significant drop of P-tissue concentration with the presence of of micro-nutrient fertilizer. In a similar way P fertilization caused a highly significant decline in Fe-tissue composition. The same phenomenon was observed in the case of Zn-tissue levels, but less severely (only significant at the LSD .05 level of probability) than that of Fe. On the other hand, Mn levels were not affected by amendments other than S^0. However since this area of plant nutrition needs much more investigation and it is beyond the scope of this study no further work was applied to plant nutritional antagonisms.

6.3.3 Field Experiment

This field study (2nd season) consisted of five S^0 treatments ranging from 0 to as high as 90 tonnes per hectare. Furthermore, treatments of P and micronutrients were included in the split-split plot design. Two test crops were grown to examine the effects of the various soil treatments on their nutritional responses. Table 6.3.3.1 presents the soil extractable levels of P, Fe, Zn and Mn. These were obtained from soil collected randomly from each experimental unit about 12 weeks after second season S^0 application. $NaHCO_3$-extractable P levels revealed a positive response to P fertilization, but no effect due to S^0 treatments. However, this response was small and statistically insignificant. From the soil $NaHCO_3$-P obtained well into the plant growth season, the levels indicated a high bio-availability of P even from the control, reflecting fertilizer history at the site, and this could be the reason why the soil S^0 or P fertilization treatments did not improve these levels. Soils from S^0 treatment S_3 which had received P fertilizer had a statistically much higher level than all other treatments. However when examining the data, a few samples (six out of a total of 180) had an extremely high extractable P level, and when these were eliminated, the $NaHCO_3$-P levels were similar to the other treatments. It could be that those soil samples were collected from an area where accidently large amounts of T.S.P. were released from the mechanical fertilizer drill. In general the field had been receiving annual applications of fertilizer P and farm yard manure for the previous ten years and this seems to have built up the soil bio-available levels of P, thus no response to soil treatments was observed. When comparing the level of $NaHCO_3$-P in these soils with that utilized in the glasshouse experiments (tables 6.3.2.1 and 6.3.2.2) (virgin soil from the same area) the levels were much higher in the field soil.

DPTA-Fe, Zn and Mn data was unbalanced and needed to be transformed

Table 6.3.3.1 Effect of S^0 treatment on the NaHCO$_3$-P and DPTA-Ext Fe, Zn and Mn for field experiment soil. Data are means of 180 replicates except P ext (90 replicates)

S^0 Treatment	NaHCO$_3$-P		DTPA-Fe		DPTA-Zn		DPTA-Mn	
	µg g^{-1}		µg g^{-1}		µg g^{-1}		µg g^{-1}	
	-P	+P	S	T	S	T	S	T
S$_1$	21.6	32.9	2.3	0.34	0.83	-0.50	2.5	0.36
S$_2$	21.4	43.0	2.7	0.41	0.76	-0.41	4.6	0.53
S$_3$	36.2	53.0	2.9	0.40	0.79	-0.45	5.7	0.73
S$_4$	26.5	35.0	11.4	0.87	1.25	-0.11	13.5	0.92
S$_5$	18.6	26.2	17.9	1.13	1.10	0.03	18.1	1.06

LSD$_{.05}$	14.23	0.2555	0.1617	0.3619
LSD$_{.01}$	19.04	0.3418	0.2163	0.4843

S = skewed data
T = transformed into log$_{10}$
LSD values for DTPA - Fe, Zn or Mn are for the transformed data.

Table 6.3.3.2 Effect of S^0 treatment on P, Fe, Zn and Mn tissue concentration of corn leaf; third leaf from top at taselling. Data are means of 60 replicates.

S^0 treat.	Plant tissue concentration µg g^{-1}			
	P	Fe	Zn	Mn
S$_1$	2292	147.1	20.7	36.0
S$_2$	3484	164.0	23.9	44.3
S$_3$	3000	143.4	23.6	46.1
S$_4$	2856	167.9	23.6	52.3
S$_5$	3180	192.6	29.8	50.5

LSD$_{.05}$	397.9	26.6	N.S.	11.69
LSD$_{.01}$	532.4	25.6	N.S.	15.64

(log 10) so that they could be statistically analysed. The effect of S^0 treatments on these micronutrient solubilities and thus bio-availability seems to shift dramatically at the extremely high S^0 rates. It could be that at these S^0 levels corresponding to 100% and 200% of theoretical acidity required to neutralize soil $CaCO_3$, the acidity produced was above the soil buffering capacity and thus in micro-environments was enough to solubilize large quantities of soil micronutrients. This observation applies to DTPA-Fe and the extractable level quadruples with the high S^0 treatments (S_4, S_5). Thus increased levels were statistically highly significant when compared to the control or the low S^0 treatments (S_1, S_2, S_3) of the transformed data. Variation in the Fe-extractable levels between the control or the low S^0 rate treatments were insignificant. Furthermore, their levels were in the "marginal" region of availability for cereal crops (Lindsay-Norvell test), whereas the levels released at the high S^0 rates were more than "adequate".

Zinc behaviour was identical to that of Fe. DPTA-Zn levels did not change significantly from the control at low S^0 treatment rates. However, with the high S^0 treatments (S_4, S_5) there was a 50% increase in Zn extractability compared to the control (table 6.3.3.1) and this improvement was highly significant for the transformed data. These levels were "adequate" while the others were in the "marginal" range for cereal crops.

DPTA-Mn levels followed those of Fe and Zn. There were progressive increases in the extractable Mn levels in relation to S^0 treatments. However, these increases were quite large with the high S^0 rates (S_4, S_5) (table 6.3.3.1). When statistically comparing the transformed Mn data, there was a significant increase in DPTA-Mn levels for treatment S_3 at the 5% level of probability. Whereas for the S_4, S_5 treatments the increases were highly significant. Moreover all the DPTA-Mn levels were "adequately" available for cereal crops (Lindsay-Norvell test). However the high Mn released at high S^0 treatment might cause nutritional imbalances.

From the micro-nutrient soil extractions studied there appeared to be no benefits from their fertilizer addition in the sulphate forms of their respective salts, at least not at the rates which was applied.

The effect of S^0 treatment on plant tissue concentration of the elements studied did not follow soil extractable levels. Concentrations of P in corn leaf tissue responded positively to soil S^0 treatments (table 6.3.3.2). Their levels significantly increased by 30-50% above that of the control, but these increases were greater with the lowest S^0 rates (S_2) and declined with further higher S^0 applications. It could be that S^0 oxidation maintained more soil P in solution, but as the rates increased P availability to plants declined possibly due to microbial fixation by a flourishing population or to large amounts of SO_4^{2-} competing directly or indirectly with the plant P-uptake.

Fe tissue concentration in corn blades also increased in response to soil S^0 treatments. However, the increases were not significant except in the very high S^0 applications (S_5) (table 6.3.3.2). Reduced plant growth or actual higher ion absorption could not be distinguished from these observations for the higher Fe-tissue concentration. Furthermore, it should be noted that Fe-tissue levels were higher than the critical deficiency diagnoses for all treatments, although visual observations had clearly indicated that a high degree of plant chlorosis was present.

Zinc tissue concentrations did not vary in relation to soil S^0 treatments, whereas, Mn concentrations increased significantly (table 6.3.3.2). However none of the values for the control or S^0 treated were below the critical levels for corn plants.

Corn was used only as an indicator crop and no grain yields were obtained since it was grown out of season. Usually it is grown in the spring, but due to experimental constraints it was planted in autumn, and with the advent of cooler weather, plants started to die before completing their growth cycle.

The other test crop was wheat which performed much better. Plants were grown to harvest, and yields were collected at dough hardening stage of grain development. Grain and straw yields, elemental concentration and total plant uptake of P, Fe, Zn and Mn are presented in tables 6.3.3.3 and 6.3.3.4 for grain and straw respectively.

Grain yields responded negatively to S^0 treatments, but the yield decline was only apparent and significant in the high S^0 treatments (S_4, S_5), and it was more apparent where P fertilizer was added (table 6.3.3.3). Grain yield was slightly above 4 tonnes per hectare for the control and the low S^0 treatments (S_2, S_3), about the average obtained in Kuwait; however it declined by about 40 and 50% with S^0 treatments S_4 and S_5 respectively. The same general behaviour was also observed with the green crop yield.

Wheat straw yields reflected the same pattern that was found with grain yields (table 6.3.3.4), but the effect of P fertilization was more clear. On non-P fertilized plots the yield decline was insignificant, whereas on the P fertilized plots the yield dropped by 35% for the high S^0 rate treatments compared with the control.

Elemental concentrations in the grain and straw portions of the plant varied in relation to S^0 soil treatments. While there was no significant variation in grain tissue P concentration (table 6.3.3.3), the straw P concentrations were higher with S^0 treatments S_4 and S_5. This significantly higher P accumulation may be just a reflection of lower yields (table 6.3.3.4). There was a slight increase in P grain concentration due to P fertilization, but this increase was small, although significant, compared to the declining plant P uptake with increasing rates of S^0. Grain iron concentration behaved positively to S^0 treatments. Its concentration increased by 45-50% for treatments S_2, S_3 and S_4 and a massive 85% for treatment S_5 over that of the control S_1 (table 6.3.3.3), while, there were no

Table 6.3.3.3 Effect of S^0 treatment on yield, P, Fe, Zn and Mn plant tissue concentration and plant uptake for wheat grain. Means of 60 replicates except of yield and elemental uptake, they are of 30 replicates.

S^0 Treat.	Green wt kg/ha		Dry wt kg/ha		Plant tissue concentration $\mu g\ g^{-1}$				
	-P	+P	-P	+P	P	Fe	Zn	Mn S	Mn T
S_1	3624	4576	3349	4263	2445	79.5	19.4	44.4	1.64
S_2	4083	4561	3692	4285	2423	125.5	18.0	49.4	1.69
S_3	3297	4296	3022	3968	2455	106.5	17.3	43.6	1.64
S_4	3003	3304	2713	3077	2708	118.9	21.7	48.1	1.68
S_5	3268	2944	2834	2707	2457	149.1	21.8	64.8	1.8
LSD$_{.05}$	1207		882		N.S.	38.76	N.S		0.067
LSD$_{.01}$	1615		1180		N.S	51.86			0.090

S=skewed
T=transformed into $\log_{10}$

S^0 Treat.	Plant Uptake g ha^{-1}							
	P		Fe		Zn		Mn	
	-P	+P	-P	+P	-P	+P	-P	+P
S_1	8308	10352	259	344	67	85	147	192
S_2	8794	10583	456	536	65	78	183	212
S_3	7391	9814	221	419	54	72	137	168
S_4	7406	8516	328	362	57	69	132	153
S_5	6938	6691	415	401	62	58	179	176
LSD$_{.05}$	1726		162		27.1		58.9	
LSD$_{.01}$	2309		217		36.3		78.8	

Table 6.3.3.4 **Effect of S^0 treatment on yield, P, Fe, Zn and Mn plant tissue concentration and plant uptake for wheat straw. Mean of 60 replicates, except of yield and elemental uptake, they are of 30 replicates.**

S^0 Treat.	Green wt kg ha^{-1}		Dry wt kg ha^{-1}		Plant tissue concentration µg g^{-1}			
	-P	+P	-P	+P	P	Fe	Zn_s	Mn_s
S_1	2183	2797	2115	2672	1465	46.5	10.2	25.3
S_2	2282	2662	2162	2539	1713	87.7	10.4	32.7
S_3	1943	2498	1839	2382	1610	64.7	9.1	28.2
S_4	1861	1983	1745	1932	1826	78.2	11.1	36.0
S_5	2224	2137	2071	2003	1960	101.1	13.4	49.8
$LSD_{.05}$	526		459		301.5	N.S	N.S	N.S
$LSD_{.01}$	704		614		403.4			

S = skewed

S^0 Treat.	Plant Uptake (g ha^{-1})							
	P		Fe		Zn		Mn	
	-P	+P	-P	+P	-P	+P	-P	+P
S_1	3098	3914	103	148	22	25	56	71
S_2	3704	4349	198	267	22	26	69	82
S_3	2961	3835	113	141	17	22	52	67
S_4	3186	3528	146	158	20	23	64	70
S_5	4059	3926	197	203	27	26	101	96
$LSD_{.05}$	1327.4		95.7		N.S		32.4	
$LSD_{.01}$	1776.0		128.1				43.3	

significant variations in mean straw Fe concentrations. Although there was an observed increase in Fe straw values, these were inconsistent with great fluctuations for replicates of the same S^0 treatments (table 6.3.3.4).

Plant tissue Zn concentrations did not respond to soil S^0 amendment in either the wheat grain or in the straw portion (tables 6.3.3.3 and 6.3.3.4). Although there were small statistically insignificant increases in Zn grain or straw concentrations this could be due to the lower yields from stunted plants with the high S^0 rate Treatments.

Mn tissue concentrations for both the grain and straw wheat plant portions were unbalanced and needed to be transformed (log 10) before statistical analyses. However, the variations in concentration values were insignificant except in the case of grain Mn concentration with treatment S_5 (tables 6.3.3.3 and 6.3.3.4). It seems from these findings that neither Zn nor Mn were the limiting nutrients for plant growth. Roots were able to absorb all they require of these two elements. Other conditions possibly nutritional had more apparent effects on plant growth. This will be explored in more depth in the discussion.

Total plant uptake of P, Fe, Zn and Mn per hectare as measured in the wheat grain and straw portions has shown significant variation in response to S^0 and P fertilization (tables 6.3.3.3 and 6.3.3.4). However, these values representing elemental concentration multiplied by tabulated yield estimations for each treatment combination, could be misleading since there was a negative yield response to S^0 treatment, while a positive one to P fertilization. Furthermore, the effect of S^0 on nutrient plant tissue concentration was in a few cases effective in enhancing the concentration as in the case of grain Fe levels or the P-straw values. Moreover, the wheat grown in plots that had received high rates of S^0 (treatments S_4 and S_5) had a patchy growth, and in a few cases a total crop failure. Yield values reported for these plots were collected from locations that had plants within the experimental units. Units with no crop growth were treated

**Table 6.3.3.5 Wheat (grain and straw) plant uptake of P, Fe, Zn and Mn per hectare as affected by S^0 treatment.
All data are means of 90 replicates.**

S^0	P kg ha^{-1}		Fe g ha^{-1}		Zn gha^{-1}		Mn g ha^{-1}	
Treat.	-P	+P	-P	+P	-P	+P	-P	+P
S_1	11.4	14.3	362	492	89	110	203	263
S_2	12.5	14.9	654	803	87	104	252	294
S_3	10.4	13.6	334	560	71	94	189	235
S_4	10.6	12.0	474	520	77	92	196	223
S_5	11.0	10.6	612	604	89	84	280	272

as missing values. Table 6.3.3.5 presenting wheat uptake of P, Fe, Zn and Mn as influenced by S^0 and P fertilizer soil treatments, shows a clear demonstration that moderate S^0 application (S_2) with P fertilizer at an agronomically recommended rate consistently resulted in higher wheat uptake of P, Fe, Zn and Mn. This is probably due to higher nutrient bio-availability and no adverse effects on plant growth associated with high $S^{\bullet}$ application rates.

6.4 Discussion

Three general areas on the S^0 amendment of calcareous soil will be discussed: S^0 oxidation using the medium of Kuwaiti soil; second, the changes in some soil parameters as a result of S^0 oxidation; and lastly the effect of these changes on plant growth and nutrition.

6.4.1 Elemental Sulphur Oxidation

The oxidation of S^0 in soil was measured indirectly by observing changes in soil pH, $CaCO_3$ and sulphate. Also biological assessments were possible by plant dry matter yields and plant S contents. Here changes in the status of certain plant nutrients in the soil or in the plant tissue could be used indirectly to indicate S^0 oxidation. All these measurements, however, have their drawbacks and they could not be accurately used to reflect the rate of S^0 oxidation. A direct measurement of S^0 in soil could be more reliable in expressing the rate at which S^0 is being transformed. Of the several procedures developed to measure the soil S^0 content none could be routinely used due to their poor sensitivity, lack of selectivity, slowness or utilization of dangerous solvents (Tabatabai, 1982; Watkinson *et al.*, 1987). A method for measurement of S^0 in soil by high performance liquid chromatography (HPLC) has been developed which might offer greater sensitivity and accuracy (Lauren and Watkinson, 1985; Watkinson *et al.*, 1987; Watkinson, 1989). However, this facility was not available during the conduct of this study. Furthermore, the study was that of soil fertility and plant nutrition. Although a higher confidence in measuring soil-S^0 would be beneficial in studying S^0 oxidation, the subsequent changes in the soil environment and its effect on plant growth would require a more traditional procedure in assessing S^0 as a soil amendment.

Changes in soil pH, % $CaCO_3$ and SO_4^{2-} contents as affected by incubation with various applications of S^0 were presented in table 6.3.1.1.2. Although the three variables reacted significantly to S^0 treatments, these changes were not equally manifested in their magnitude (figure 6.1). Their correlation ($p<0.01$) with the amount of S^0 added were $R^2=0.37$, 0.45 and 0.71 for pH, % $CaCO_3$ and SO_4^{2-} contents respectively. The moderate pH drop was expected due to the buffering intensity associated with the presence of $CaCO_3$. At pH above 8 the buffering would be very small because pCO_2 would strongly decrease with increasing pH, while nearer to neutral pH the buffering increases in strength by a factor of 100 for each one unit drop in pH (Van Breeman and Wielmaker, 1974_a). This was reflected by an initial sharp drop in incubated soil pH to below 8 followed by smaller decreases with higher rates of S^0 (figure 6.1).

The dissolution of soil $CaCO_3$ was more responsive to the S^0 treatments. It was initially fast moderating in influence with increasing S^0 rates (figure 6.1). It could be that smaller and less dense $CaCO_3$ particles reacted first leaving the larger and harder particles requiring more acidity and a longer time to dissolve. This concept will be further discussed later. However, it could be that as S^0 treatments increased from 15 to 30 and then further to 60 and 120 g kg^{-1} soil that the rate of S^0 oxidation had slowed, probably due to less efficient soil contacts at higher concentration. This would result in increasing difficulty for the microbial population to colonize the S^0 surfaces. A lower percentage of S^0 oxidation with higher rates of application has been shown by micromorphological examination (Rida and Modaihsh, 1988). Due to this it would be difficult to calculate time requirement of S^0 oxidation from the dissolution of soil $CaCO_3$. Furthermore, dissolution of $CaCO_3$ would depend on the soil properties especially pH, clay and organic contents, and the characteristics of the $CaCO_3$ in question (Abo-Rady *et al.*, 1988). Miyamoto (1977) also faced difficulties in establishing a numerical relation for the amounts of H_2SO_4 required to dissolve $CaCO_3$ compounds.

The increase in soil SO_4^{2-} contents by three fold with S^0 treatment provided the highest correlation ($R^2=0.71$) of the three measured parameters (figure 6.1). The moderation in the increasing SO_4^{2-}-soil content with higher rates of S^0 could

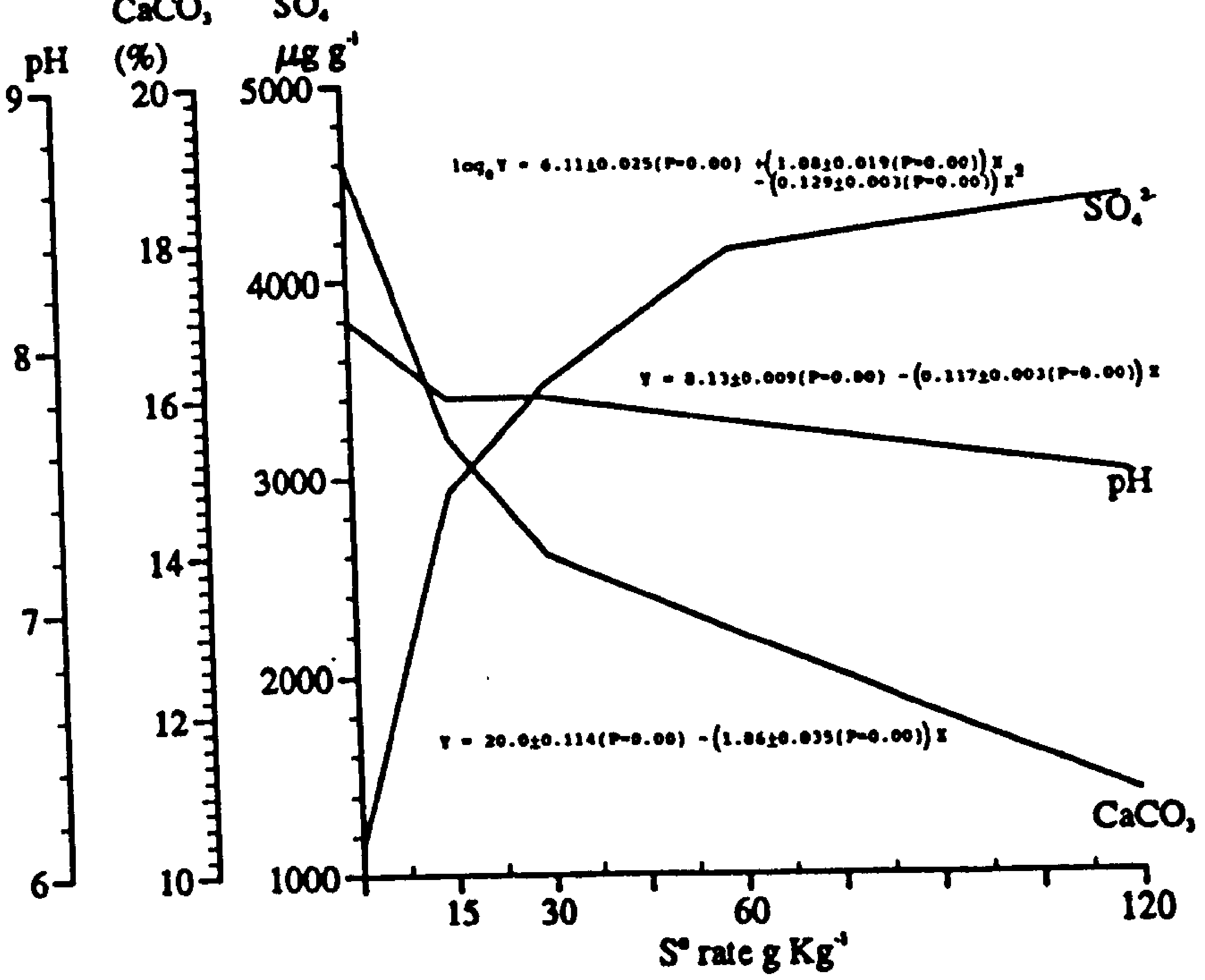


Fig.6.1 Effect of S° oxidation on soil bulk pH, $CaCO_3$ percentage and sulphate accumululation.

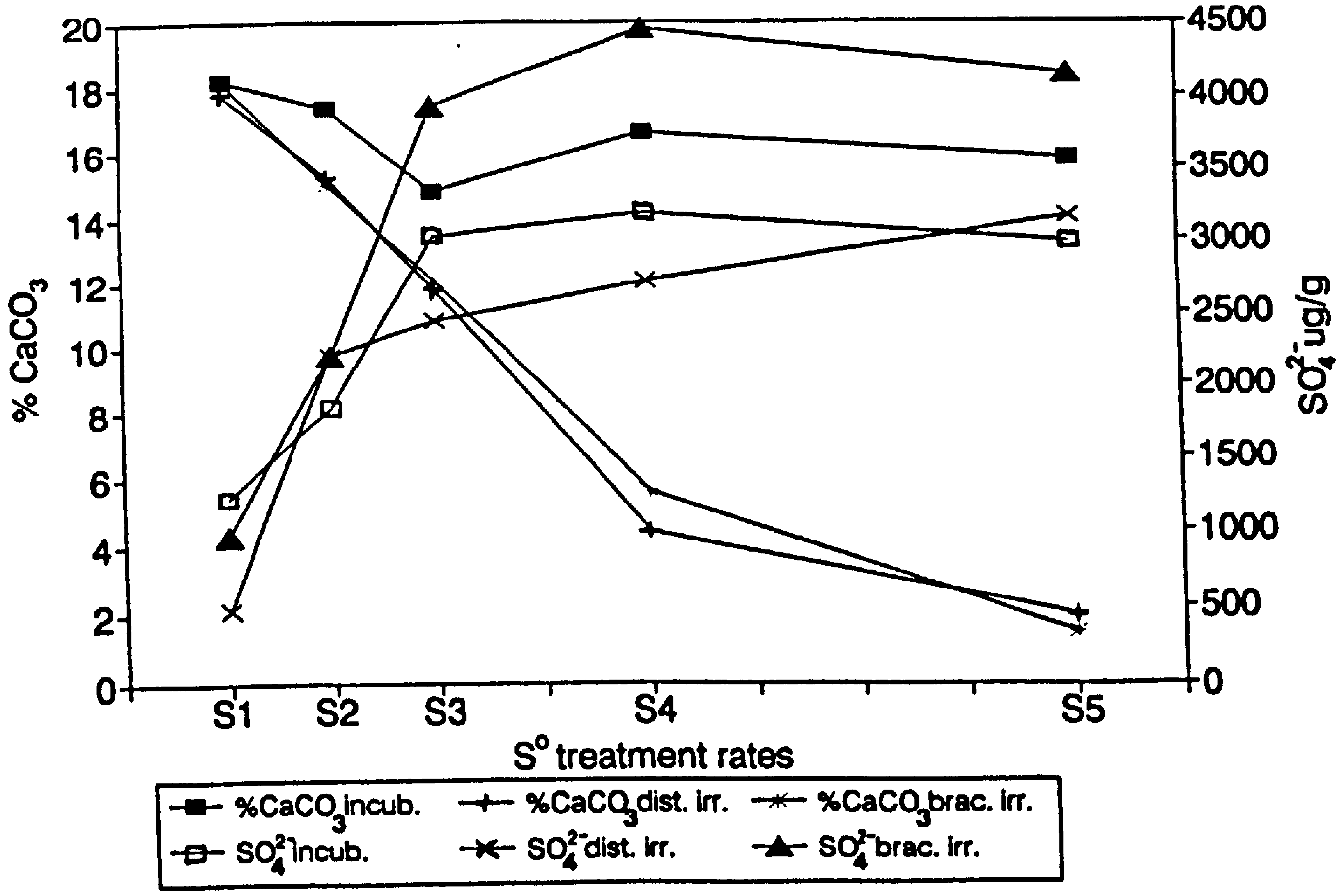


Fig.6.2 Percent $CaCO_3$ reduction by S° oxidation for soil treatments S_1, S_2, S_3, S_4 and S_5 (0, 15, 30, 60 and 120 g S°/kg soil, respectively) incubated for six months and then used in pot experiments irrigated with distilled water or brackish water.

be a further indication of a slow down in S^0 oxidation at higher concentrations, but it also could be that the SO_4^{2-} which was generated had coupled with free Ca^{2+} from the soil or the dissolved $CaCO_3$ reaching the solubility limits of $CaSO_4$ (15 mM/l) (Kalbasi *et al.*, 1986; Dawood, 1989) and precipitated out of solution. This would result in higher gypsum content and increased soil salinity, which will be discussed later. The procedure of obtaining soil SO_4^{2-} utilizes a high dilution factor of 1:10 soil to extracting solution. This would presumably dissolve all available SO_4^{2-}, but it could also dissolve some of the SO_4^{2-} in the naturally occurring gypsum and that recently formed. Although these discrepencies could be accounted for by the use of controls and checks, great difficulty has been associated with the removal of gypsum salt from soil suspension. Also, some of the SO_4^{2-} would be tied up in the soil microbial biomass, which would be expected to increase with the additional S^0. Under field conditions a further portion of the SO_4^{2-} produced would be metabolized by the growing plants. Therefore, the use of the SO_4^{2-} as an indicator for the rate of S^0 oxidation at best would be qualitative.

An application of S^0 at the theoretical amount needed to neutralize about 50% of $CaCO_3$ in the top 15 cm (average 16.0%) was monitored for 450 days. Soil pH and % $CaCO_3$ contents were tabulated and presented in figure 6.3. The soil pH declined significantly with time linear correlation ($p<0.01$) $R^2=0.512$, but %$CaCO_3$ decline was more dramatic, down to below 10% with linear correlation of $R^2=0.947$, $p<0.01$. The dissolution of soil $CaCO_3$ was expected with the S^0 application at a rate of 60 t ha^{-1}, but the moderate drop of soil pH from 8.0 to about 7.7 was considered small. This contrasted with the findings of Kashirad and Bazargari (1972), where the soil pH was reduced from its original 8.3 to 7.55 with a mere application of S^0 at 6750 kg ha^{-1}. Their soil originally contained about 20% $CaCO_3$ and with 100% efficient S^0 oxidation as they indicated (S^0 completed its transformation within 7 months) this would only neutralize about

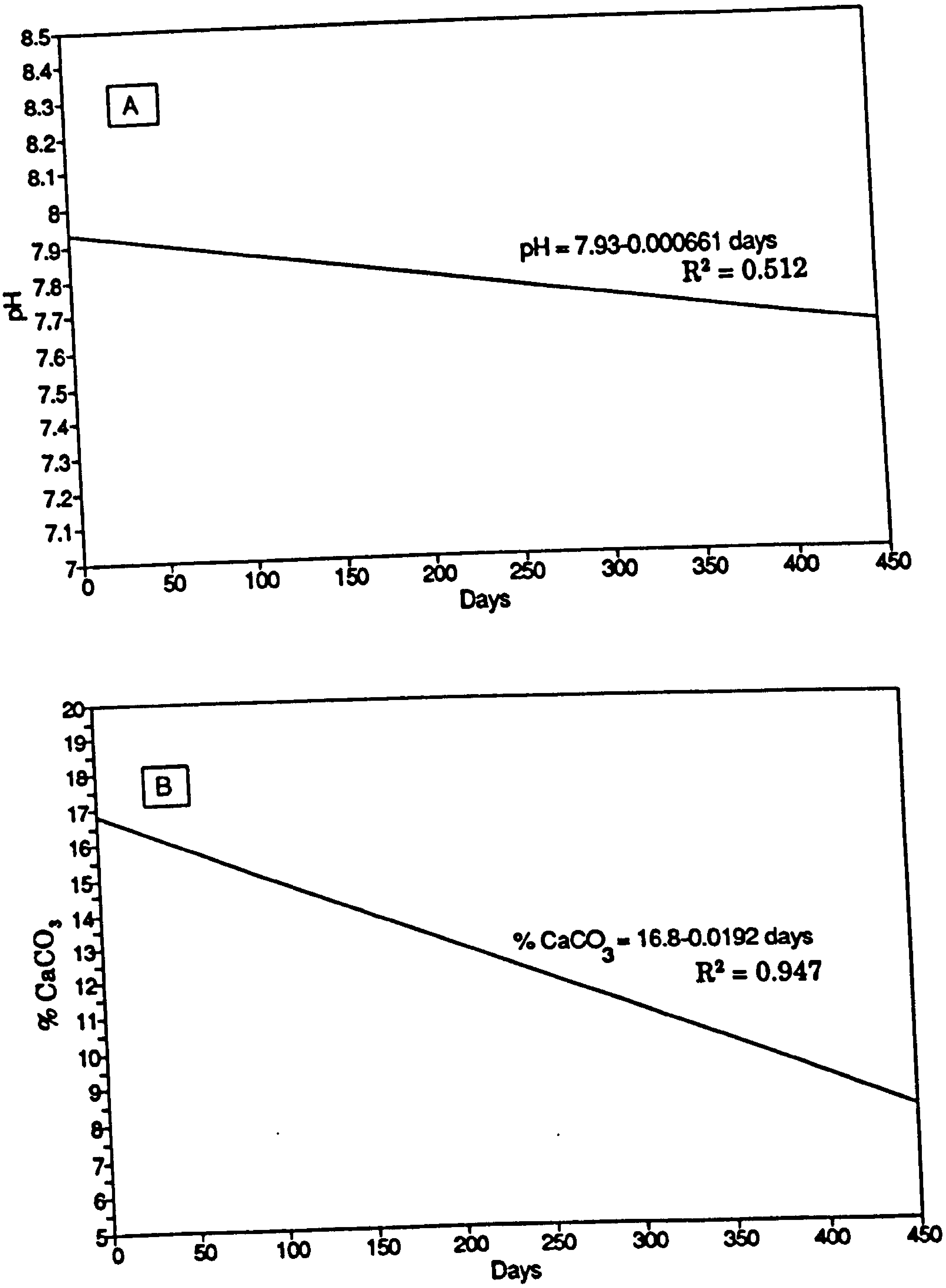


Fig.6.3 Time linear regression relationships for changes in soil pH (A) and reduction in $CaCO_3$ % (B) for field soil treated with S° at a rate of 60 tonnes per hectare.

21 tonnes of $CaCO_3$. Using average soil bulk density (not provided in the study) this would be equivalent to a reduction in the soil $CaCO_3$ to about 18-19%. Their observed soil pH drop with the little decline in soil equivalent $CaCO_3$ could only indicate that the $CaCO_3$ in question had a low activity, and therefore it would be expected that the drop in pH would be reversed with time. In simulation studies (Abo-Rady *et al.*, 1988; Modaihsh *et al.*, 1989) where two calcareous soils were incubated with S^0 at a rate 30 g kg^{-1}, one soil originally containing about 21% equivalent $CaCO_3$ had its pH drop from 8.4 to 7.2 whereas the other soil became slightly acidic from an original pH of 8.1 and $CaCO_3$ at 9.1%. A more careful scrutiny of their data shows that in the case of the first soil, assuming an incubation of 18 weeks adequate for complete S^0 oxidation, that would reduce the soil $CaCO_3$ content to no less than 11-12%. With the high buffering associated with $CaCO_3$ (Van Breeman and Wielmaker, 1974_a) a soil pH value in the range of 7-8.5 only proves the presence of $CaCO_3$. The pH of a calcareous soil will vary in a manner dependent upon the partial pressures of the dissolved CO_2 and the ionic strength of the soil suspension at the time of measurement (Yaalon, 1957). In the range of CO_2 in the soil atmosphere environment under calcite saturation the pH would range from 7.3-8.2 (Van Breeman and Wielmaker, 1974_b). Therefore, the indicated decline of soil pH as a result of S^0 oxidation and its interpretation to predict the rate of oxidation would not be appropriate. Only when the acidity produced from S^0 oxidation exceeded the required amounts to dissolve all $CaCO_3$ did the soil pH drop to below neutrality, as was the case with the second soil. From fig.6.3 the soil % $CaCO_3$ content went down only to about 8% after 450 days. This explains the maintenance of soil pH at a range of 7.7-8.0. The use of $CaCO_3$ % dissolution as an indicator of S^0 oxidation rates would be more accurate and it has been shown that the rate under Kuwaiti field conditions was slower than that reported in other studies. Although the conditions were different, some workers used low S^0 applications, while

others conducted their studies in laboratories. It could be the harsh environmental conditions in the field prevented the flourishing of a large microbial population necessary for an efficient oxidation of the S^0, especially at the high rates used.

The soil SO_4^{2-} content would be more accurate in measuring S^0 oxidation rates as it has been indicated earlier. However, under the field situation this was not appropriate. Leaching, precipitation and horizontal SO_4^{2-} movements coupled with SO_4^{2-} addition with the irrigation water made it difficult to present a value indicative of S^0 transformation.

From the previous findings, it could be said that slight soil pH changes would be misleading as a tool indicating acidification of calcareous soil, although they have been presented by numerous studies, providing that the soil $CaCO_3$ content did not dissolve to below 1.5%. The use of % reduction in $CaCO_3$ or the soil SO_4^{2-} content would be more representative. Figure 6.2 presents the relationship between increasing SO_4^{2-} content and the reduction in soil % $CaCO_3$ as a function of S^0 ammendment rates. Soils were incubated under favourable conditions for six months and were then used for growing a test crop in a heated glasshouse for 10 weeks, where some were irrigated with distilled water while others with saline (brackish) water. The changes in soil content of SO_4^{2-} paralleled changes in soil % $CaCO_3$. With higher application rates of S^0 there were greater quantities of SO_4^{2-} generated as a product of its oxidation. The acidity produced in the process caused a reduction in $CaCO_3$ content. However, the SO_4^{2-} generated and the drop in soil $CaCO_3$ were smaller in the case of the incubated soil than in the soil after glasshouse irrigation, even though the former was incubated for six months at 30°C under approximate field capacity moisture regimes. It could be all the conditions to maintain good aeration (section 6.3) were not adequate and subsequently oxygen diffusion was too slow for rapid oxidation. The process of plant irrigation and the wetting-drying cycles had probably enhanced soil aeration and therefore the rate of S^0 oxidation. This was clear from the SO_4^{2-} produced and $CaCO_3$ dissolved during a ten week growth period (fig.6.2). It was interesting to observe that brackish irrigated pots accumulated significantly greater amounts of SO_4^{2-} than distilled irrigated ones, even though the reduction in soil $CaCO_3$ was about the same (fig.6.2). Some of these SO_4^{2-} increases were introduced with the saline irrigation waters, but that alone could not account for the variations. Most likely, over irrigation which was used to reduce salinity damages, had in the case of distilled watering dissolved and leached some of the SO_4^{2-}, While the saline water which resembles Kuwaiti ground water was SO_4^{2-} saturated and did not remove the recently generated SO_4^{2-}. This would have great implications for soil reclamation in Kuwait, where the increased salinity associated with S^0 application could not be eliminated with the available ground water. This will be explored further in the following section on changes in soil parameters.

Higher SO_4^{2-} levels and greater $CaCO_3$ dissolution in the irrigated soil could have another possible explanation. As incubated soil was utilized for plant growth, there was probably a build up of organic substrate, a great increase in a naturally organic poor soil (section 3). As most recent findings indicate the predominant role of heterotrophs in S^0 oxidation in alkaline soils (Vitolins and Swaby, 1969; McCready and Krouse, 1982), this organic supply would enhance their activities. The contribution of the chemolithotrophic *Thiobacillus spp.* under alkaline pH range would be limited (Wainwright, 1984), until the pH was significantly reduced. As suggested by Vitolins and Swaby (1969) in neutral and alkaline soils the heterotrophs, which prefer a pH range of 6.0-7.5, were the primary S^0 oxidizers. However their S^0 metabolism was incomplete and produced little H_2SO_4. These would be followed by secondary autotrophic oxidizers such as *Thiobacillus thioparus* which thrive best at pH between 5 and 6.5 generating greater acidity for the autotrophic *T.thiooxidans* which flourishes at pH below 4.5. The irrigated soils did eventually have a low pH (5.5-6.0) with the highest S^0

application rates (tables 6.3.1.3.2; 6.3.1.3.3), but in most cases they were in the alkaline range. However, this was for bulk soil and did not represent the pH in micro-niches especially on the surface of S^0 particles, where possibly the pH was much lower, and sufficiently acidic for the autotrophic oxidizers.

The mechanism of S^0 oxidation is not completely clear. Many investigators have proposed different schemes. Vishniac and Senter (1957) have suggested the following pathway:

$$\underset{}{S^{\circ}} \rightarrow \underset{\text{thiosulphate}}{S_2O_3^{2-}} \rightarrow \underset{\text{tetrathionate}}{S_4O_6^{2-}} \rightarrow \underset{\text{trithionate}}{S_3O_6^{2-}} \rightarrow \underset{\text{sulphite}}{SO_3^{2-}} \rightarrow \underset{\text{sulphate}}{SO_4^{2-}}$$

The presence of these intermediates was confirmed in findings by later investigators on S^0 oxidation (Nor and Tabatabai, 1977; Skiba and Wainwright, 1984; Wainwright *et al.*, 1986). Some of these intermediates can be phytotoxic to some plant species (Nor and Tabatabai, 1977) but it has been shown that they are transitory in nature and largely converted into SO_4^{2-} in a matter of days (Nor and Tabatabai, 1977; Skiba and Wainwright, 1984; Wainwright *et al.*, 1986). However with large application rates, such as the ones used in this study, there could be a continuous presence of these compounds which might cause some problems on seed germination and subsequent root growth and development. In future studies some investigation on the build up of these intermediates and their possible adverse effects on plants should be included.

6.4.2 Effect of S^0 oxidation on some soil parameters

Oxidation of S^0, abiotic or biologically mediated by the *Thiobacilli*, would proceed as follows (Wainwright, 1984):

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 + \text{Energy}$$

The H_2SO_4 generated would react with the $CaCO_3$ of calcareous soil resulting in changes in some physical and chemical properties. As already mentioned, the effect on soil pH would be tied to the reaction of the soil $CaCO_3$. Therefore, the analysis of soil pH would be considered in relation to the changes on $CaCO_3$.

Soil %$CaCO_3$ declined with all treatments of S^0 to a varying degree. The reductions were influenced by rate of S^0 application, time of incubation and environmental factors such as temperature and aeration (tables 6.3.1.1.1, 6.3.1.2.3-6). However, the effect on soil bulk pH did not follow that of $CaCO_3$ content, it declined by a small amount from 8.0 to a range of 7.3-7.7 for most treatments. Glasshouse soils with the highest rates of S^0 did become acidic (tables 6.3.1.2.4, 6.3.1.2.5) with their pH ranging from 5.5 to 6.3 even though some contained as much as 5.6% $CaCO_3$.

Table 6.4.1 reveals how some soil samples selected from the glasshouse study exhibited acidic reactions while still containing more than 1.5% $CaCO_3$. Their pH increased upon fine grinding. One possible explanation for this shift was that the remaining $CaCO_3$ particles were large with low activity. As they were ground fine, their surface area increased and thus their buffering capacity shifted the pH upward. Another possible explanation is that the build up of free Ca^{2+} and SO_4^{2-} ions had passed the solubility product of $CaSO_4$ and precipitated out of soil solution. This precipitate would cover all soil particles including those of $CaCO_3$, and in the process decrease their activity. Milling of soil particles re-exposed the $CaCO_3$ and subsequently raised soil pH. These two concepts were further explored.

Techniques developed to measure the particle size distribution of soil $CaCO_3$ and thus reflect its activity could be divided into two general methods. One based on actual measurement of the various particles of the whole soil by fractionation using sieving and sedimentation procedures, and subsequently quantifying the amounts of $CaCO_3$ in each particular fraction. The other technique assessed the reactivity of the soil $CaCO_3$ in relation to a previously defined standard which could be used to estimate the effective $CaCO_3$ particle size.

Utilization of mechanical analysis techniques to separate the soil into its various size fractions and quantify the $CaCO_3$ content of each fraction yielded

Table 6.4.1 Changes in soil pH after grinding into fine powder soil samples which exhibited acidic reaction while containing some quantities of $CaCO_3$

% $CaCO_3$ in soil sample	pH	
	before grinding	after grinding
8	6.9	7.4
8	6.8	7.2
6	6.4	7.2
4	6.7	7.2
4	6.7	7.0
3	6.2	7.0
1	6.1	6.9
2	5.1	6.6

inconsistent results (tables 6.3.1.4.1, 6.3.1.4.2 and 6.3.1.4.3). Its reproducability was quite poor with a possible explanation due to the following conditions: (i) S^0 treated soil had accumulated gypsum salts which interfered with soil dispersion even with the use of a high dosage of calgon solution, (ii) successive distilled water treatment of the samples to wash out the excess amounts of $CaSO_4$ probably resulted in the loss of some clay especially when the ionic strength of the suspension got weaker and clay could no longer be precipitated by centrifuging, and last (iii) the sandy nature of the soil (sand>90%) had a built-in bias against the measurement of $CaCO_3$ in the finer fractions since very small amounts of silt and clay could be collected by sedimentation.

In view of these circumstances the indirect chemical estimation of effective particle size distribution through the assessment of $CaCO_3$ activity was used. The oxalate method (Drouineau, 1942) for determination of "active" $CaCO_3$ was considered inappropriate due to the large gypsum content of the sample and the non-specificity of the procedure in mixed mineral conditions. Other techniques such as the one developed by Von Tress *et al.* (1985) which was based on a stochasic model for the dissolution of mixed particle size clacite in conjunction with pH-stat titration was considered too complicated and requiring special apparatus and sample pre-treatments. Furthermore, the pH-stat procedure was reported to over estimate the clay size $CaCO_3$ compared to the sieving and sedimentation techniques (Moore *et al.*, 1990).

The procedure which was used in this work (section 6.2.1.5 had encompassed the ideas and limitations of earlier methods, but was characterised by simplicity, rapidity and the need for only some basic laboratory apparatus. Following are some of the more important assumptions and limitations of the exercise:

1. It has been shown that the dissolution of $CaCO_3$ in a stirred suspension follows first order reaction rates with respect to H^+ activity in a suspension pH range of

approximately 3.0 to about 5.0. At this pH range the relationship of pH to log dissolution rate were found to be linear (Berner and Morse, 1974, Plummer *et al.*, 1978). At pH values below 3.0 the diffusion of H^+ towards and Ca^{2+} away from the calcite surface would control the dissolution rate while at pH values approaching the equilibrium pH of calcite, the PCO_2 of the suspension would have a great influence on the dissolution rate and the above mentioned relationship would deviate from linearity (Von Tress *et al.*, 1985). Therefore the method which was used utilizes mild acid (H_2SO_4 0.005M) which naturally had a measured pH of about 2.85. Moreover, time measurement stopped when the suspension pH reached 6.0, thus ensuring that the dissolution reaction occurred in the linear phase with respect to time.

2. The ionic strength of the suspension would exert some effects on the rate of $CaCO_3$ dissolution. Ionic levels and composition would be expected to change upon soil addition and with the break down of $CaCO_3$ into its ionic consituents. However, the use of a relatively large amount of suspension (2.0L of 0.005M H_2SO_4) would minimize the relative changes to its ionic strength. Furthermore, it would eliminate the need of vigorous N_2 gas bubbling through the reaction mixture to maintain a constant PCO_2.

3. It has been observed that soil $CaCO_3$ usually occurs as a conglomerate of smaller sized particles cemented together by carbonate or silicate clays (Bui *et al.*, 1990). The practices used in soil dispersion, being violent shaking, shearing or ultrasonic vibration, were found to have a great influence on particle size distribution (Moore *et al.*, 1990). Therefore, the physical method used to measure the various size fractions of soil $CaCO_3$ would depend on the technique used in soil pre-treatment. The method utilized here could avoid that, since soil (<2.0 mm) could be directly used, and the results obtained would reflect the actual effective $CaCO_3$ particle size distribution in unaltered soils.

4. Soil $CaCO_3$ reactivity was compared to that of fractured $CaCO_3$ (marble slab).

However this could be misleading since the morphology of the $CaCO_3$ could be different. Even similar size fractions would have unequal surface reactivity depending on the smoothness and the shape of the calcite particles and the degree of cementation of the various aggregates. Furthermore, the time reactivity of the standard used in this study was that for semi-pure $CaCO_3$ (other standards use the highly pure geologic Iceland-spar calcite). Depending on the chemical composition of the soil calcite especially the degree of elemental substitution and/or the presence of dolomite, their dissolution rates could be different from those of the standard. Use of $CaCO_3$ fractions from calcite rocks from the parent materials of the tested soil could be a better standard and might avoid the chemical composition discrepancies.

5. Figure 6.4 taken from table 6.3.1.5.1 exhibits the time needed for one gram of $CaCO_3$ to raise the pH of weak H_2SO_4 acid from 3.0 to 6.0. The standard time (on the right) was obtained from crushed marble separated into the various fractions by sieving and sedimentation techniques. The S^0 treated soil was delivered in amounts that contained one gram of $CaCO_3$ based on calcimeter estimation. This could be problematical as the amounts of soil needed would increase as their $CaCO_3$ content decreased. However, since the $CaCO_3$ fraction is expected to be the most reactive with suspension H^+ and this would be fixed, the additional soil components would have limited effects. The Kuwaiti soil, which is extremely sandy in nature with very few organic constituents, would have low pH buffering activity apart from that of the $CaCO_3$, but as the % $CaCO_3$ got smaller the other soil components would have an enhanced role. It was considered that this procedure would not be accurate with soil containing less than 5% $CaCO_3$.

From figure 6.4, the effective particle size of $CaCO_3$ in the non-treated soil (S_1) was that approximating coarse clay to silt. This was similar to the findings of Bui *et al.* (1990) which indicated that about one third or more of the total $CaCO_3$

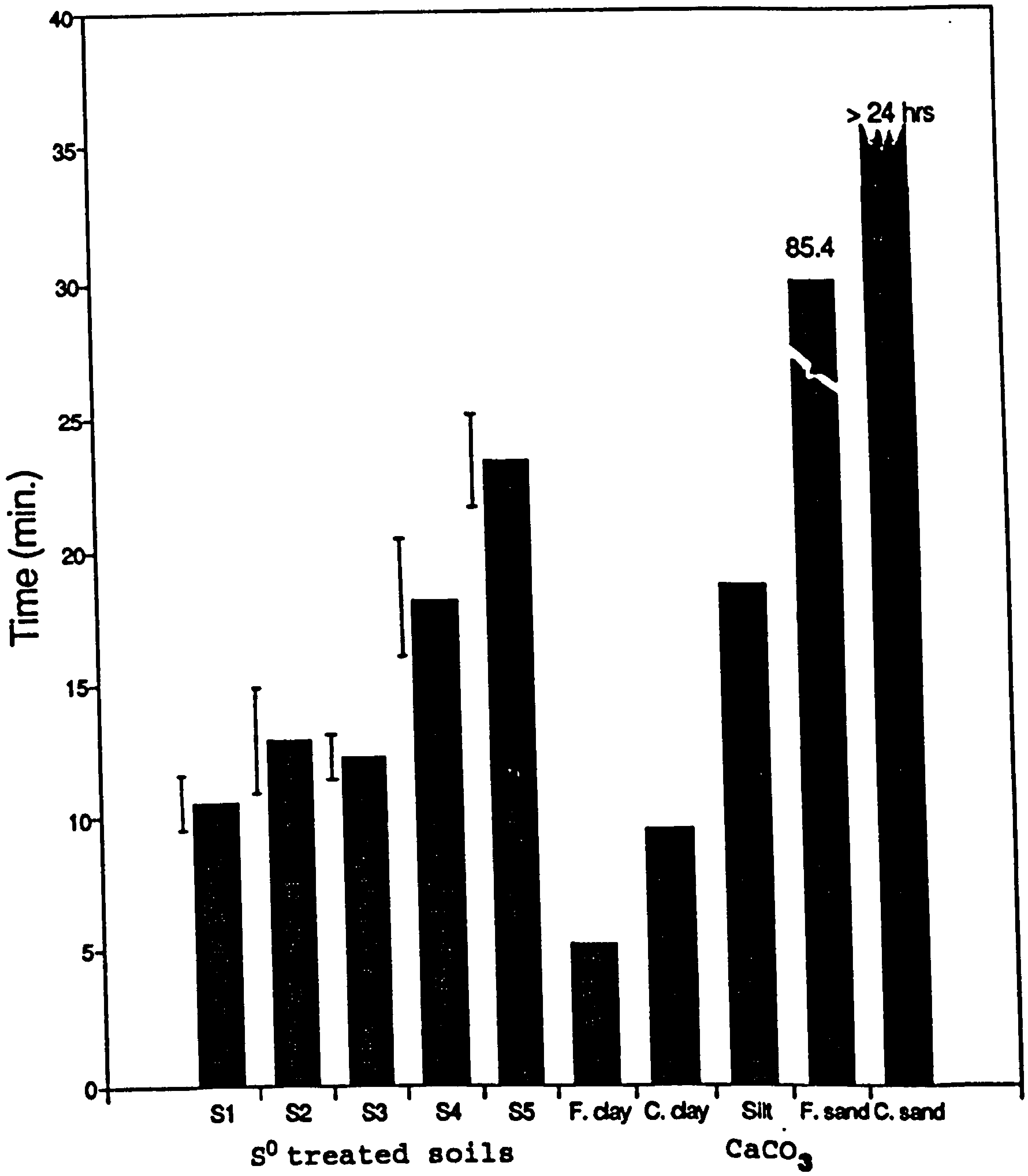


Fig.6.4 Time required to raise the pH of 0.005M H_2SO_4 from 3 to 6 for soils treated with S^0 but containing one gram $CaCO_3$ and those of standard one gram pure $CaCO_3$ in various fraction sizes.

content of the soils occurred in the silt fraction, while those of clay size varied in different soils by up to 60%. The $CaCO_3$ of the S^0 treated soil required more reaction time than non-treated soils. Those from the high rate S^0 treatments (S_4, S_5) indicated the effective sizes of $CaCO_3$ were close to the standard silt to fine sand. This could be explained, in that the acidity produced from S^0 oxidation reacted and dissolved the finer (clay size) $CaCO_3$ fractions leaving a relatively higher proportion in the coarser fractions compared to the non-treated soil. This soil treatment with S° would have a great effect on the activity of the soil $CaCO_3$, which would depend on its surface area, because a reduction in the finer sized fraction would reduce the total $CaCO_3$ activity far more than the levels reflected in the precentage reduction in total soil $CaCO_3$.

The other possible effect of S^0 oxidation on soil $CaCO_3$ particles would be that of amorphous $CaSO_4$ (possibly young crystals) formation that may cover these particles and in the process reduce their activity. To investigate this possibility the scanning electron microscope was utilized due to the fact that naturally occurring gypsum (about 1-2% in the non-treated soil) would be difficult to distinguish from newly formed $CaSO_4$ salts through chemical means. Moreover the oxidising S^0 and its intermediates including those of SO_4^{2-} would over estimate the amounts of gypsum if it was measured directly by the soluble SO_4^{2-}. Similarly, the measurement of Ca^{2+} in soil extract would not only include Ca^{2+} from gypsum but also derived from calcite and other dissolution products.

Scanning electron microscopy (S.E.M.) was used only for observation and no quantitative measurements on the degree of $CaSO_4$ shielding the $CaCO_3$ were undertaken. Plates 1,2 are those of calcite as indicated by the accompanied EDAX analysis (plates 8 and 9 show examples). The S.E.M. exposures of calcite indicated the crystal morphology (large with clear cleavage faces) of the particles which suggested that the calcite was of geological origin. Furthermore the variation in calcite sizes from particles larger than 300µm to some as small as 1µm

Calcite crystals
varying in size
from sand to silt.

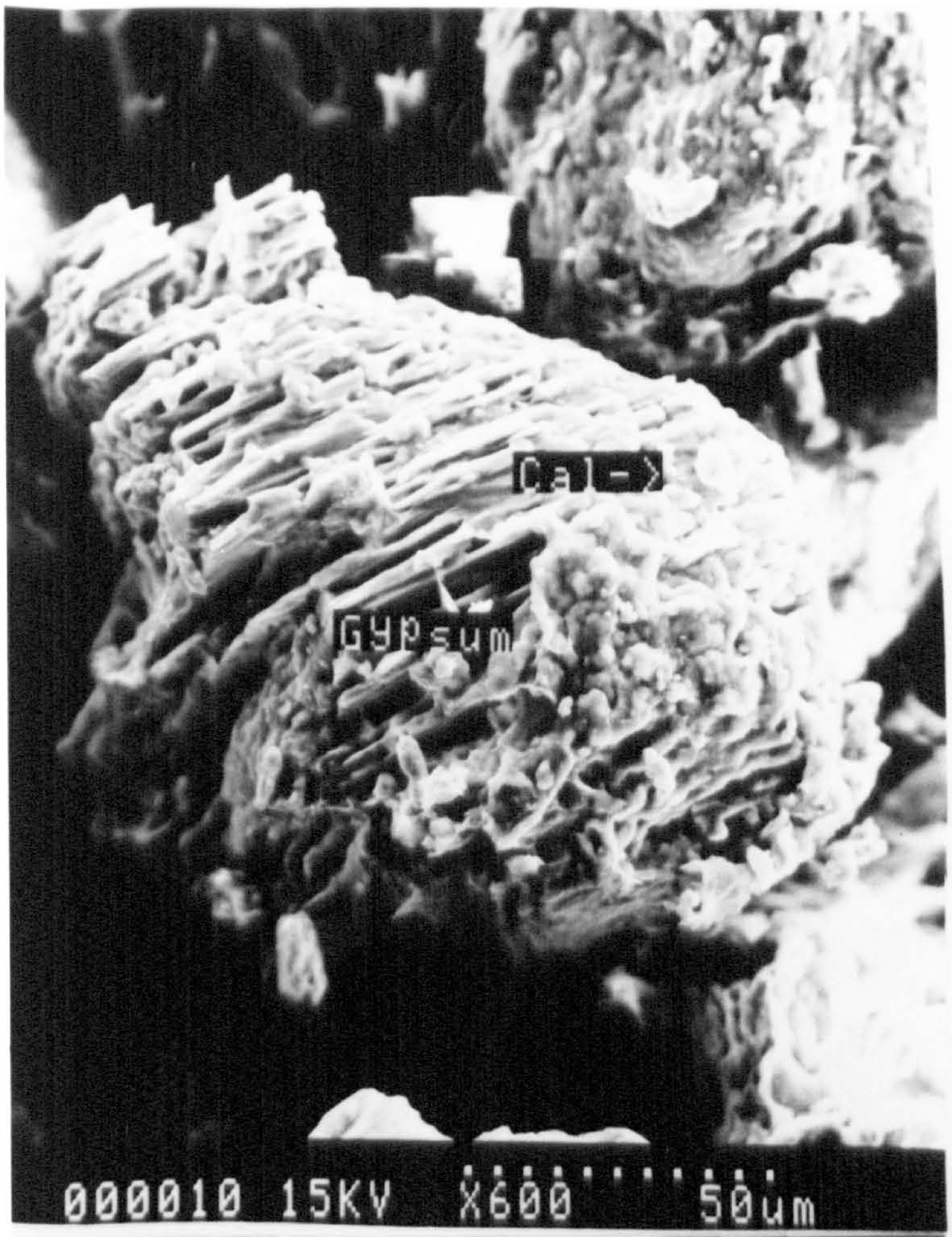
Clay size
calcite particles
within soil matrix.

PLATE 1

Calcite crystals
of various sizes.

Crystalline calcite,
shape indicating possible
geological origin.

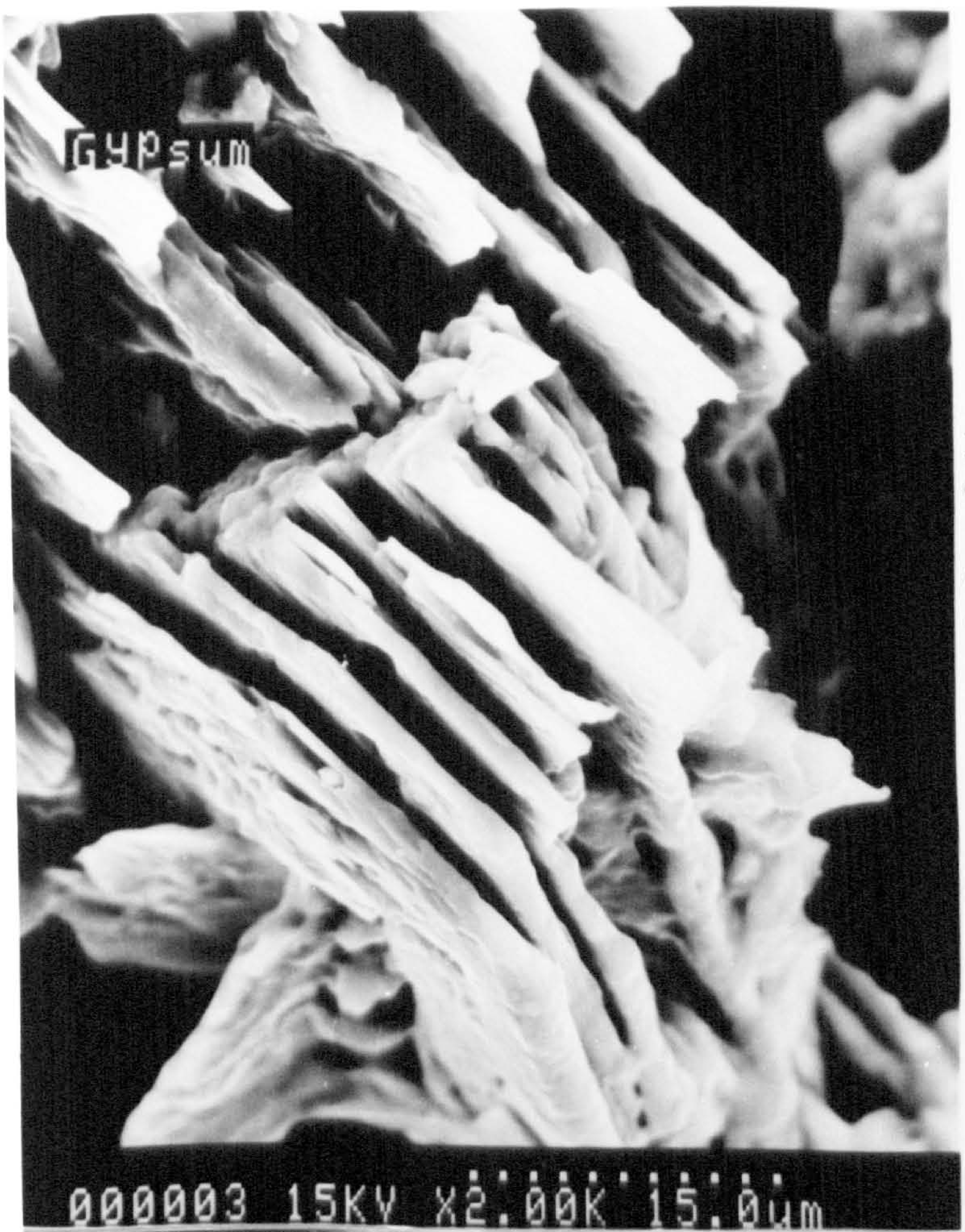
PLATE 2



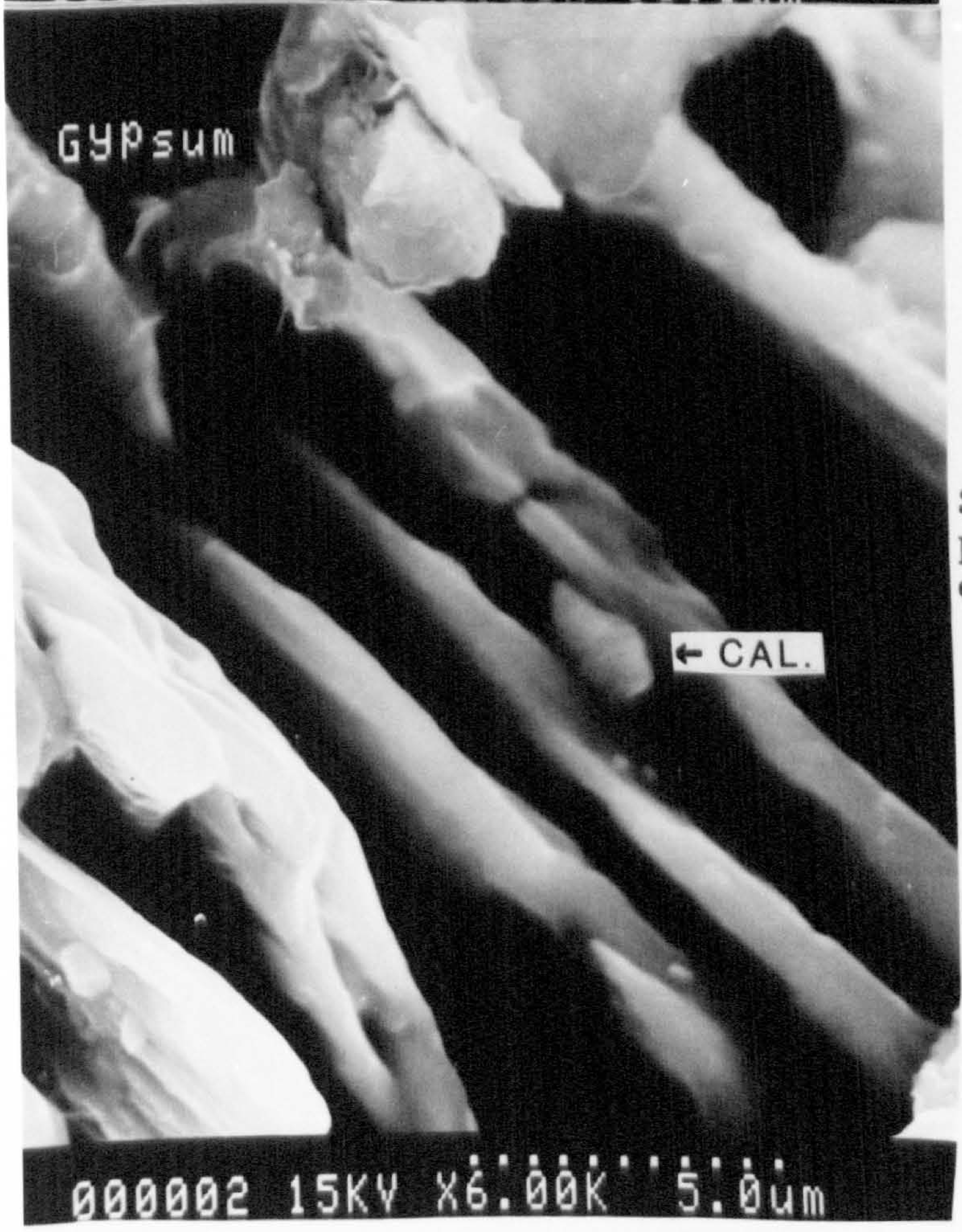
Gypsum particles from S° treated soils. The layered nature of these materials may incorporate other soil particles .

Gypsum ($CaSO_4 .2H_2O$); the poor crystallinity of particles may indicate recent deposition.

PLATE 3

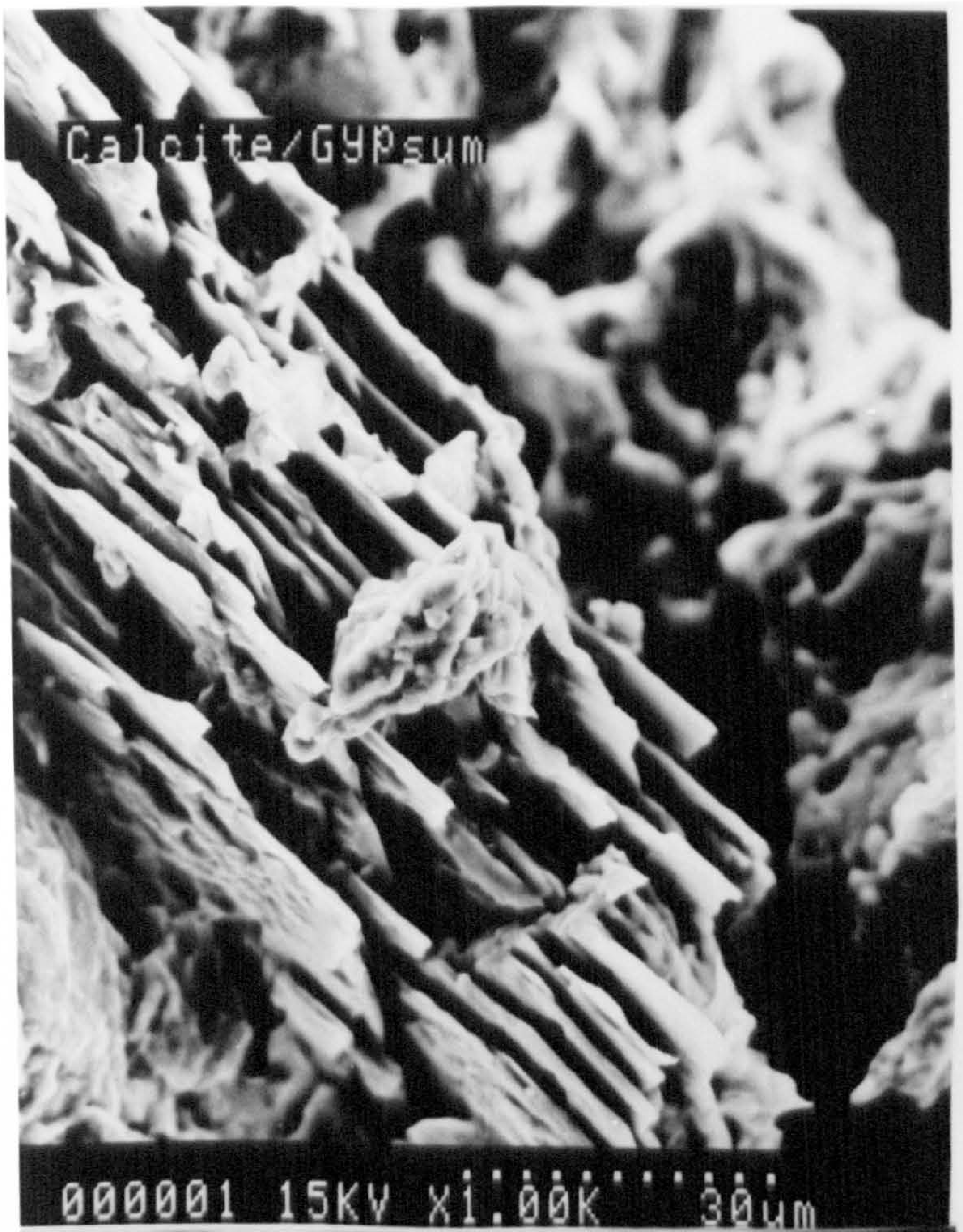


Layer formation of gypsum, which could incorporate other matrix grains especially of clay size.



Small clay size calcite particle wedged between gypsum layers.

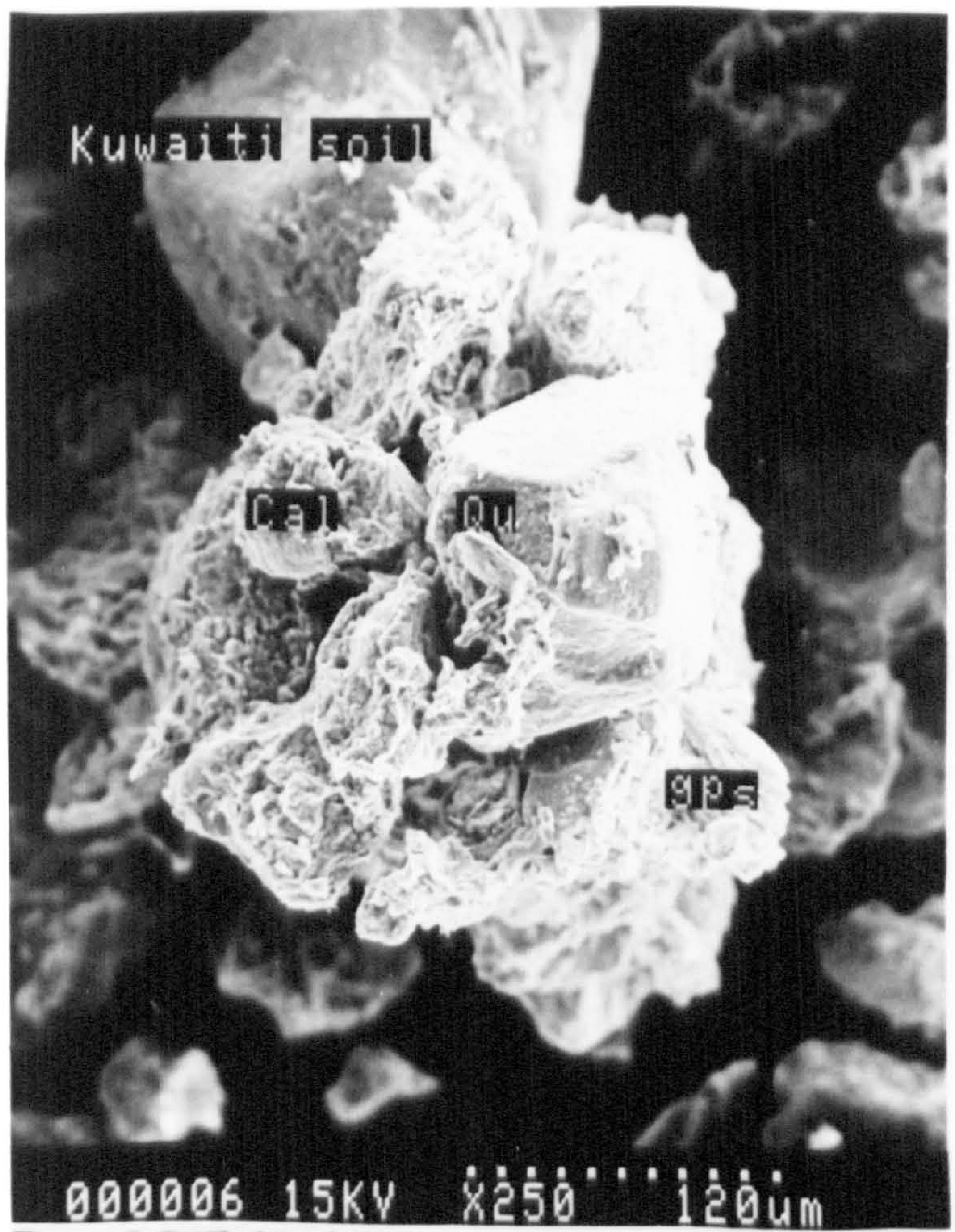
PLATE 4



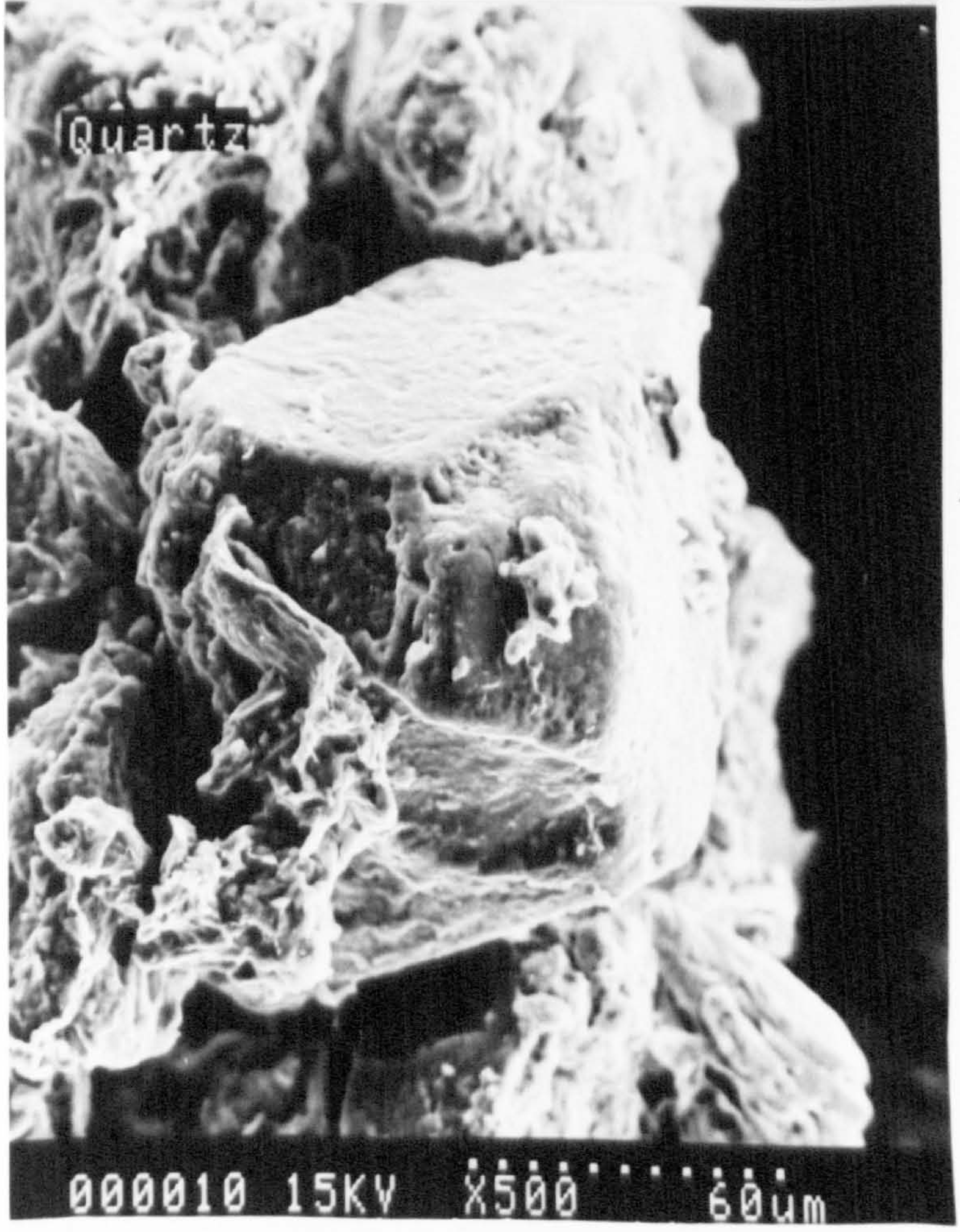
A broken formation of gypsum crystals with a calcite particle wedged between layers.

At higher magnification.

PLATE 5

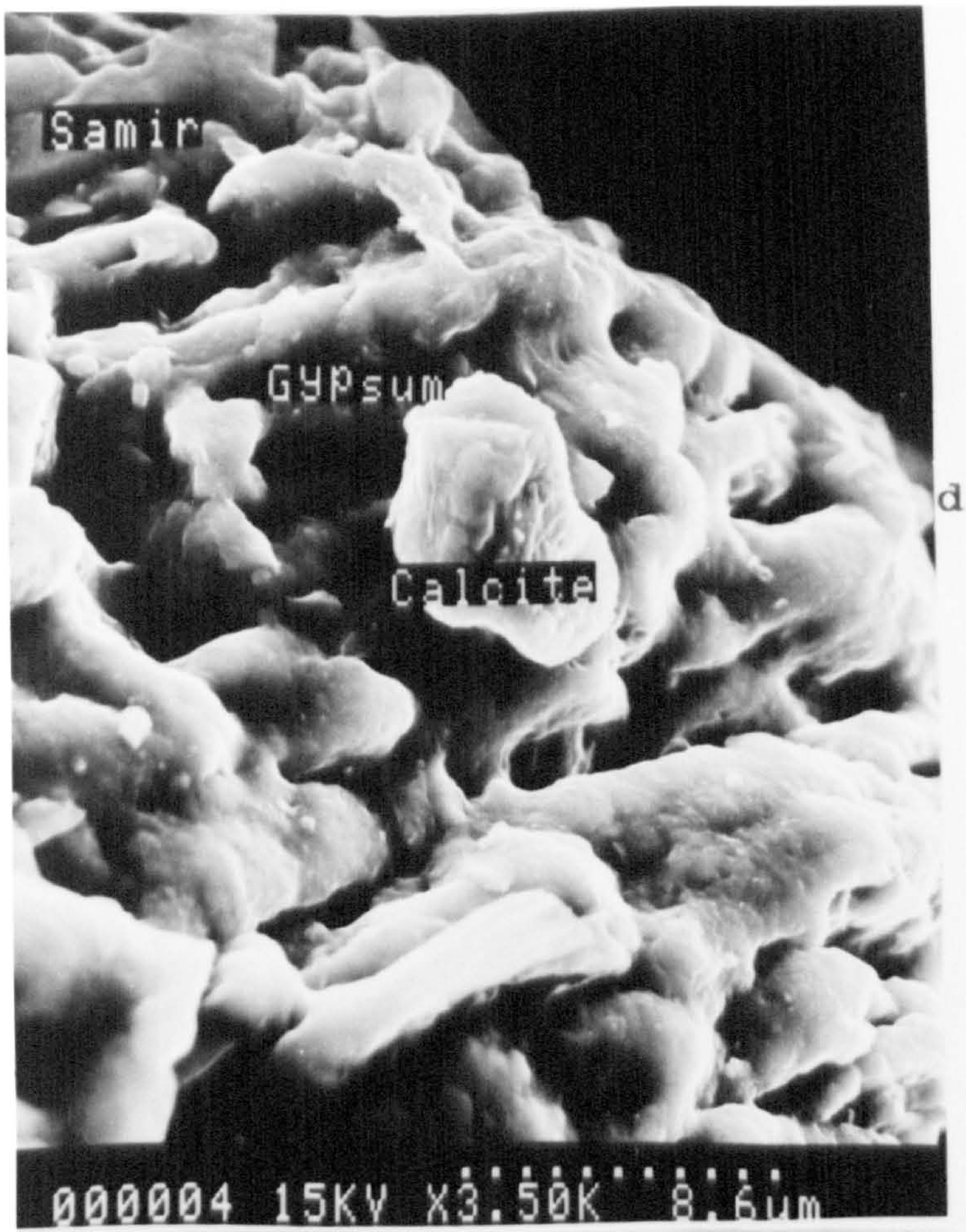


S° treated soil clearly showing deposits of gypsum (or $CaSO_4$) on other soil matrix grains including quartz and calcite.

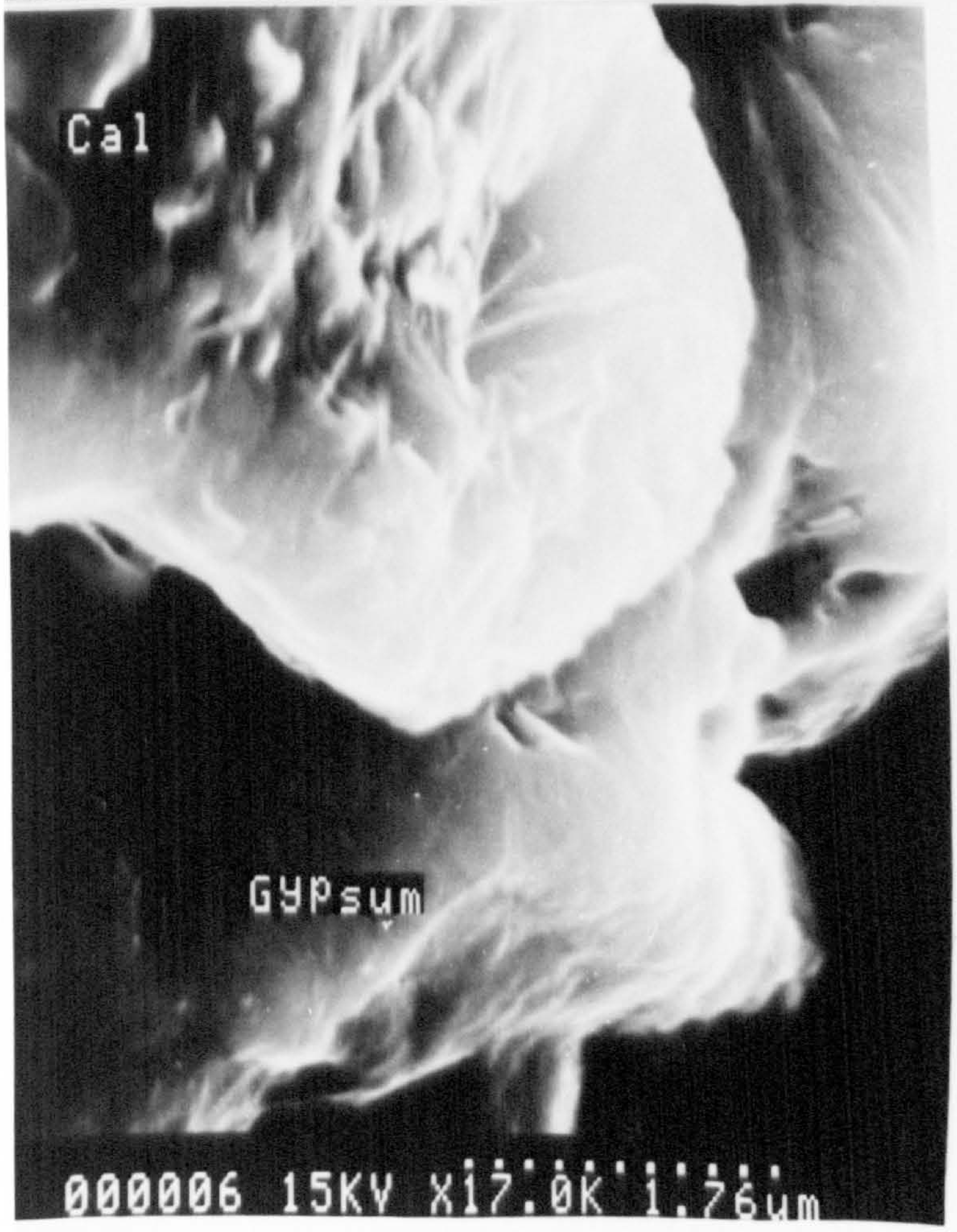


At higher magnification.

PLATE 6

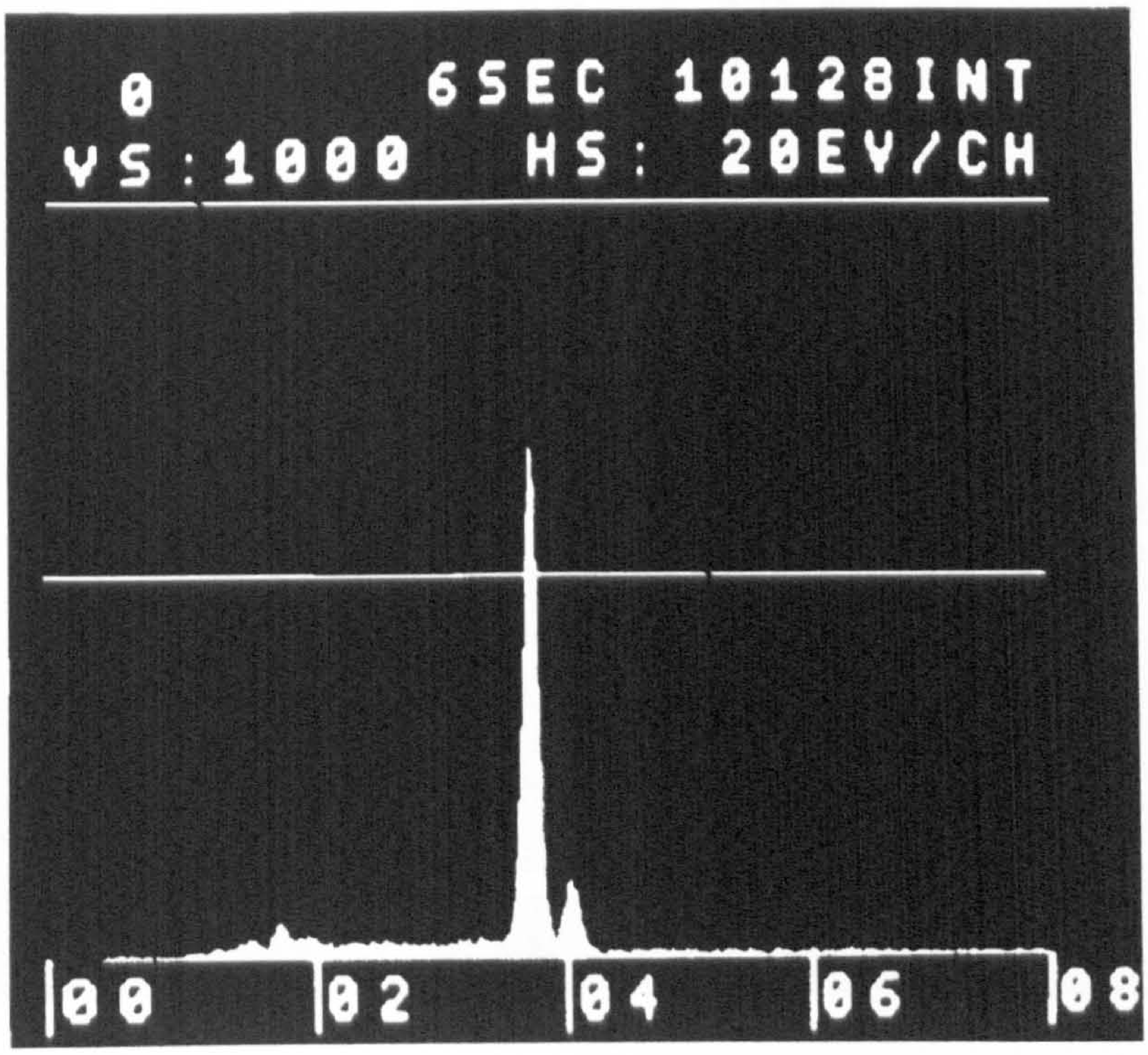


Calcite particle attached to partially dissolved gypsum crystal.

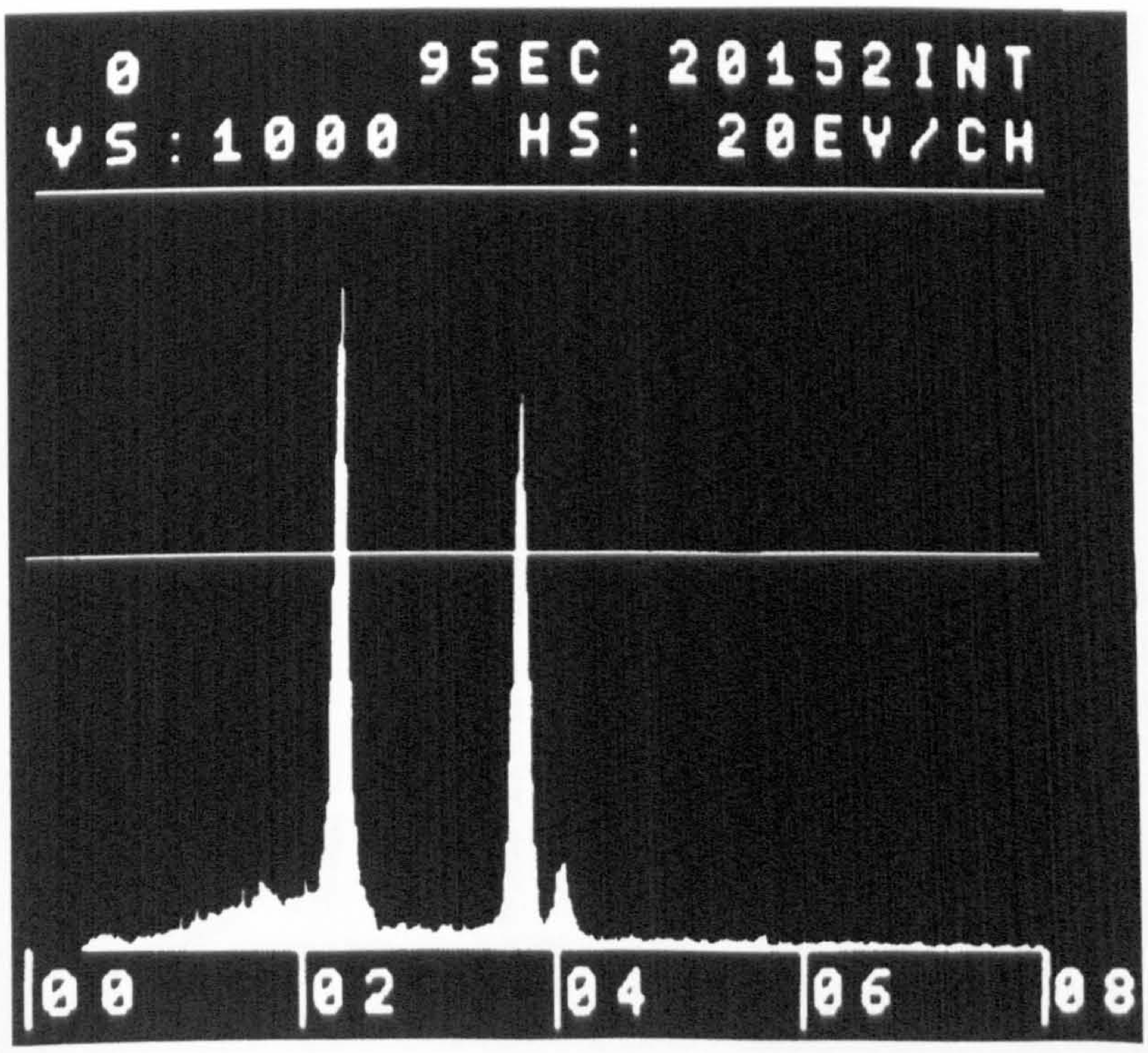


At higher magnification, a degree of reduction in calcite exposed surface area is shown.

PLATE 7

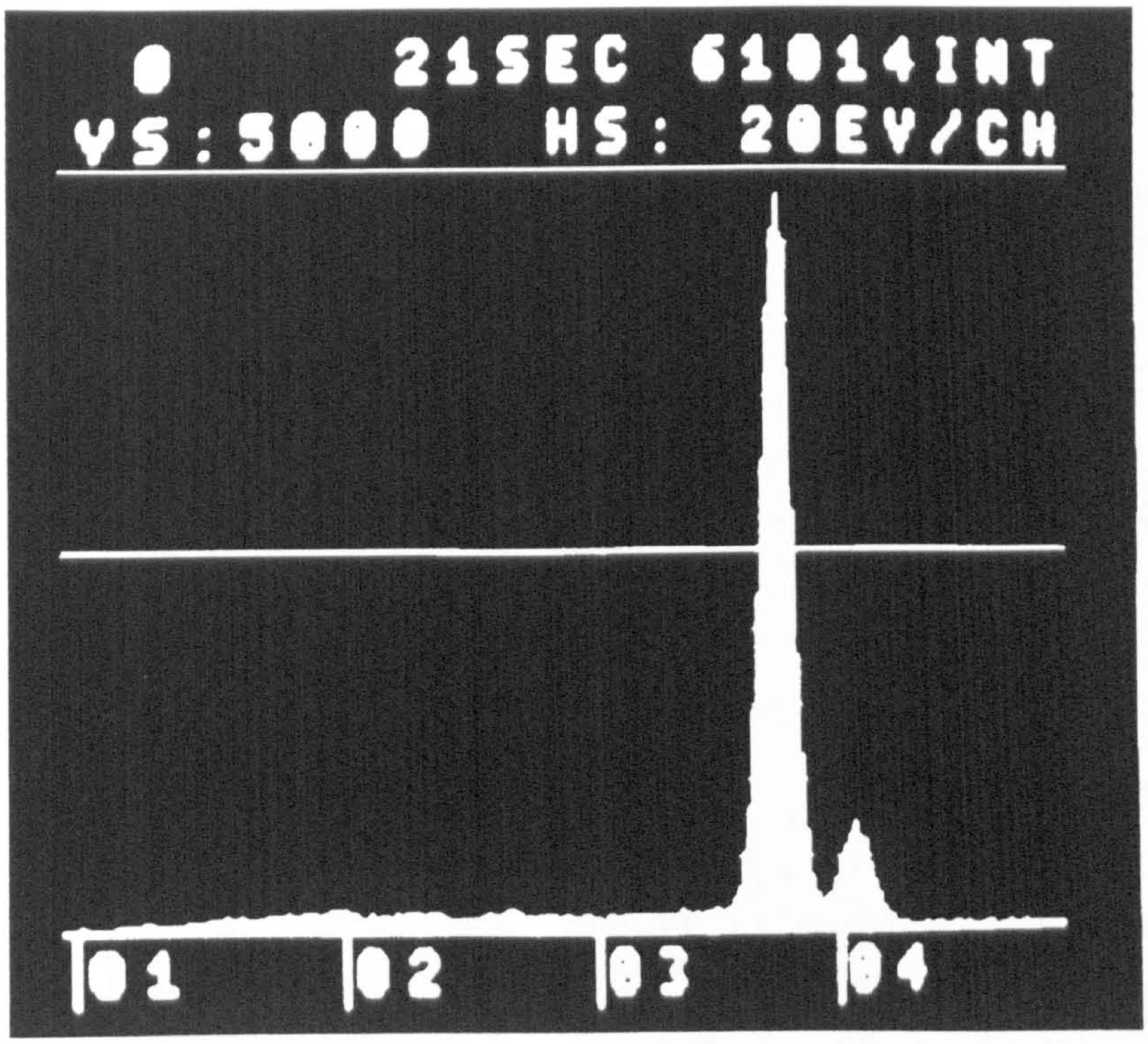


Example of EDAX
for calcite.
Showing Ca
(3.690 & 4.012 KeV)

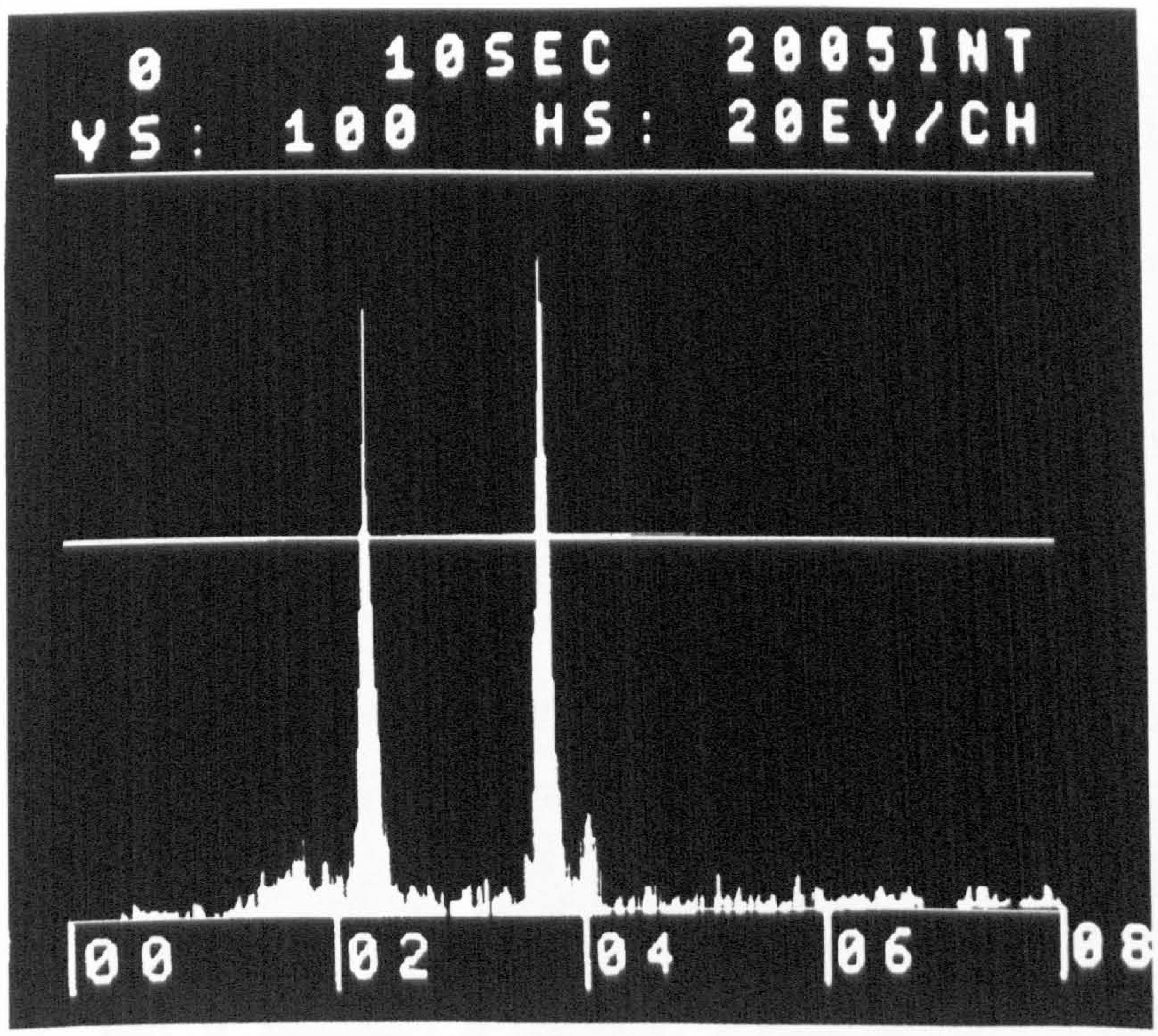


Example of EDAX
for gypsum.
Showing
S (2.307 & 2.322 KeV)
Ca (3.690 & 4.012 KeV)

PLATE 8

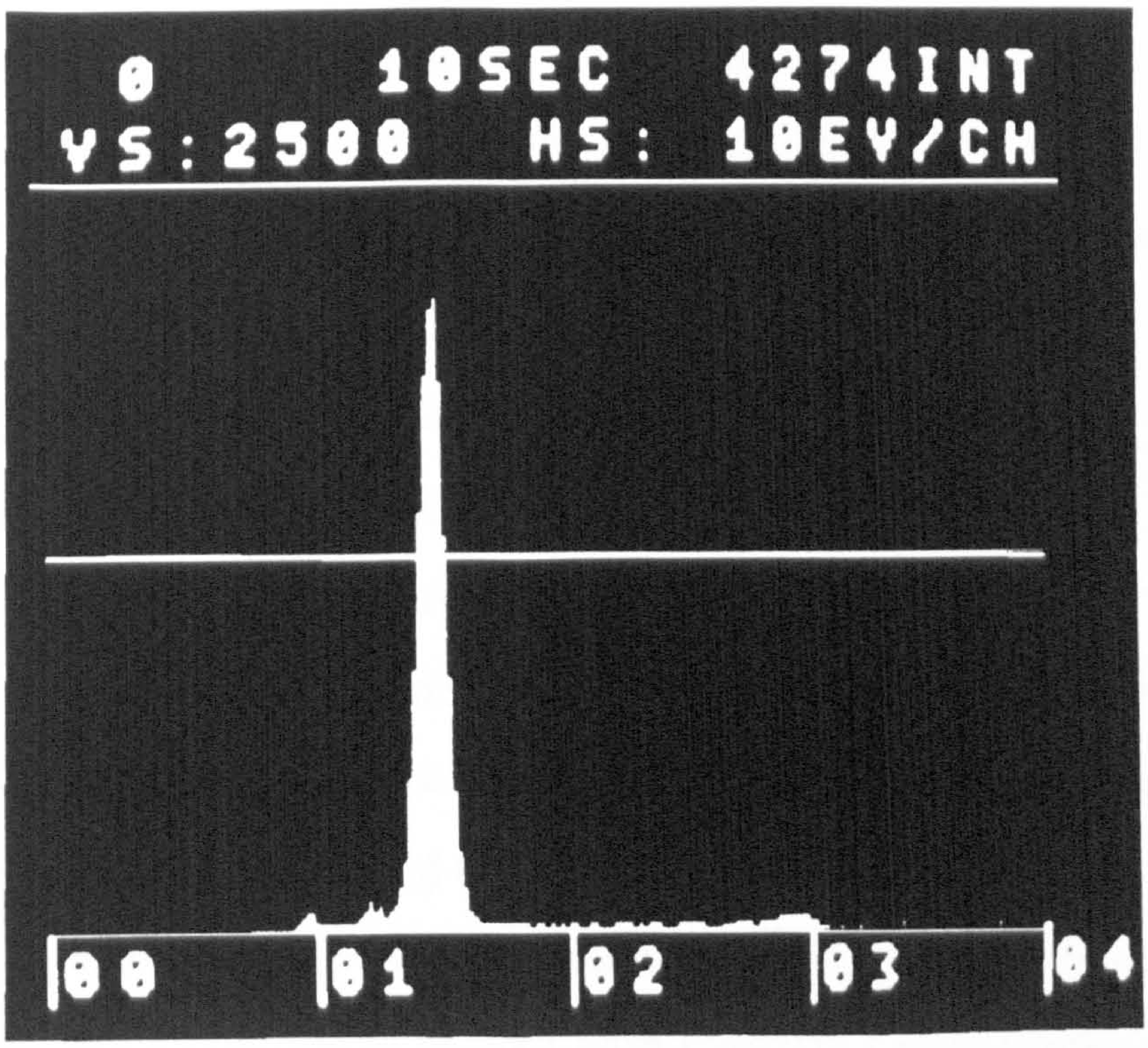


Example of EDAX
for calcite.
Showing Ca
(3.690 & 4.012 KeV)

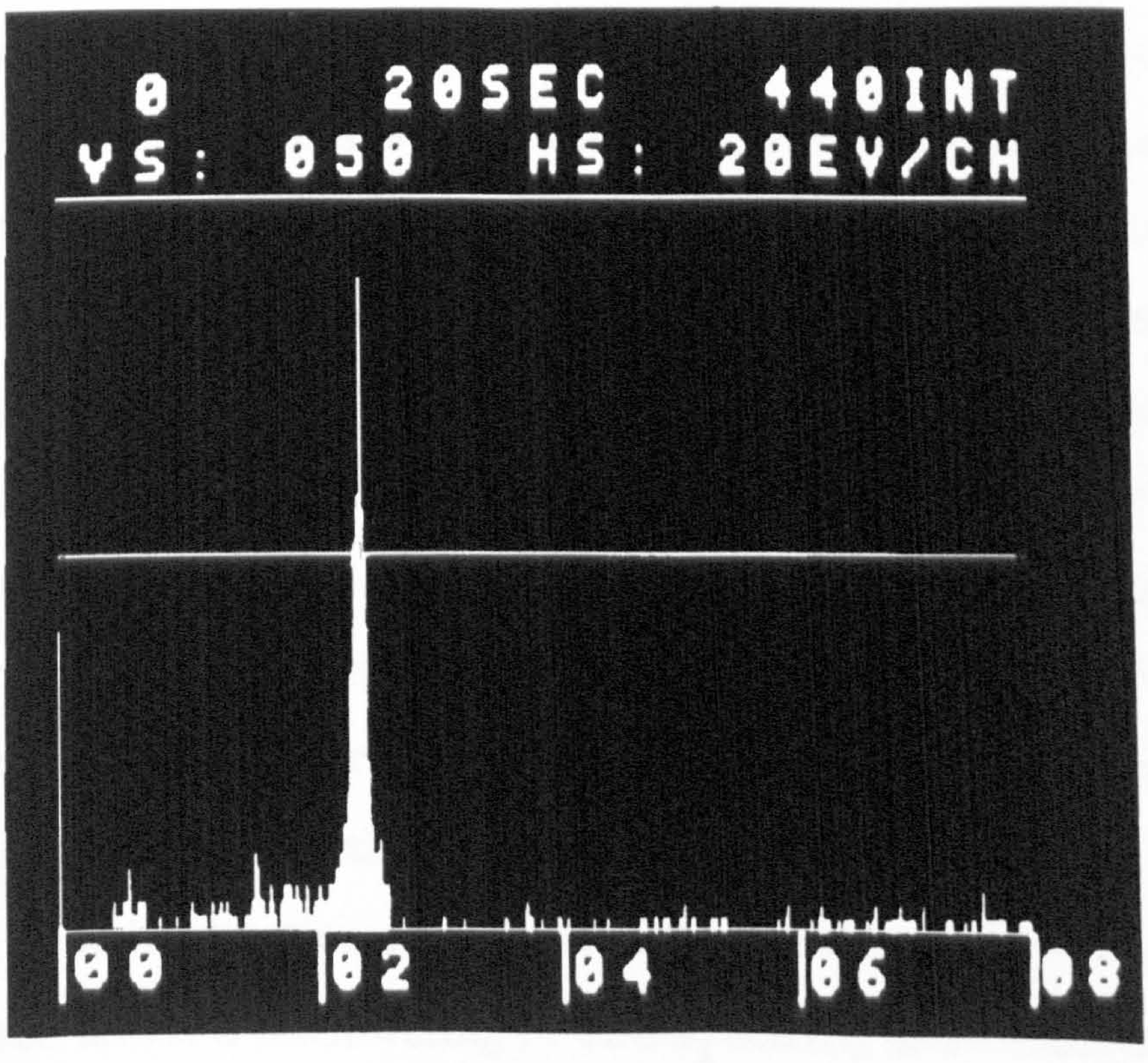


Example of EDAX
for gypsum.
Showing
S (2.307 & 3.322 KeV)
Ca (3.690 & 4.012 KeV)

PLATE 9



Example of EDAX
for quartz.
Showing only Si
(1.739 & 1.740 KeV)



Example of EDAX
showing only sulphur
from an unoxidised
S° particle.
S (2.307 & 2.322
KeV)

PLATE 10

proves its occurrence in all soil size fractions from coarse sand to that of clay.

Plates 3-7 demonstrate the presence of $CaSO_4$ particles; they could be crystalline gypsum; (confirmed by EDAX analysis, an example of which is presented in plates 8 and 9). This crystal formation (plate 3) may suggest that they were pedogenic. The time involved for the oxidation of S^0 would be sufficient for the development of large crystal formations. Furthermore, these crystals resemble what are commonly referred to as "sand or desert roses" albeit smaller in size (Jafarzadeh and Burnham, 1992). These were usually found to incorporate some matrix grains, typically sand. Kastner (1970) observed that these usually form during rapid, uninterrupted growth whereby ionic diffusion to the crystalline face was faster than the rate at which the host grains were pushed aside. Such conditions prevail with constant replenishment of water saturated with SO_4^{2-} and Ca^{2+} ions. Moreover, those $CaSO_4.2H_2O$ particles were present in layers with voids large enough to entrap other soil particles in the clay fraction. In plate 4 a clay size calcite particle was observed to be wedged between slightly weathered crystaline gypsum. Also some partially dissolved larger gyspum formations had exposed other soil particles embedded in them, as shown in plate 5, where a silt size calcite particle has surfaced from between layers of $CaSO_4.2H_2O$. At lower magnification, Kuwaiti soil that had received S^0 treatment clearly indicated the formation of a film composed of $CaSO_4$ layers covering various soil particles. In plate 6 this $CaSO_4$ layer had covered some quartz and calcite particles leaving less than 50% of their surface area still exposed. Plate 10 shows the Edax examination of quartz and sulphur. Sulphur particles do not naturally occur in Kuwaiti soil, but that examined was probably an unoxidized S^0 particle.

One implication of the material presented in these electron microscopic observations is the lowering of $CaCO_3$ activity as a consequence of shielding of the $CaCO_3$ surface by these particles. In plate 7, a calcite particle was partially covered by $CaSO_4$, and at higher magnification its surface is shown in contact with that of $CaSO_4$. This would indicate a degree of reduction in the exposed surface area of $CaCO_3$ and suggests a proportional reduction in its activity.

Figure 6.5 indicates a build up of % gypsum in the soil as % $CaCO_3$ declined when treated with various appliations of S^0 over a prolonged period. Therefore, the suggestion of the formation of layered gypsum crystals as has been observed in the S.E.M. examination (plates 3-7) was likely. Moreover, the other aspect of $CaCO_3$ activity, its surface area being shielded by the recent precipitation of $CaSO_4$, would be probable in the light of the increases in soil gypsum even with the low S^0 applications (S_2, S_3). The gypsum formed was proportional to the applied S^0 and the dissolution of $CaCO_3$ (figure 6.5). This was similar to the observations of Dawood (1989), who reported that about 66-76% of the SO_4^{2-} generated from S^0 oxidation had precipitated out of soil solution as $CaSO_4.2H_2O$.

Due to the dissolution of soil $CaCO_3$, large increases in soil solution ionic concentration occurred which resulted in increased salinity. Figure 6.6 presents the relationship between increased E.C. reading with the declining $CaCO_3$ contents as a function of S^0 applications. Similar observations were reported by other investigators (Modaihsh *et al.*, 1989; Abo-Rady *et al.*, 1988; Bole, 1986). However direct comparison with their results would be difficult since the E.C. measurements were not conducted uniformly. In this study E.C. readings were for 1:2 soil:water suspension whereas, others used a different ratio or soil saturation extract. Generally they all indicated an increase in the soil Ca^{2+}, Mg^{2+}, K^+ and Na^+ cations with the levels of SO_4^{2-}, Cl^-, CO_3^{2-} and HCO_3^- increased in a similar manner. This generated salinity would remain for some time in an arid area (Abo-Rady *et al.*, 1988), while, in more humid regions of Canada the E.C. increases due to S^0 oxidation were not in evidence after 2 to 3 years (Bole, 1986) probably as a result of ions leaching from the surface layers. Added to this, SAR (sodium adsorption ratio) declined from the top layer due to the increase in Ca

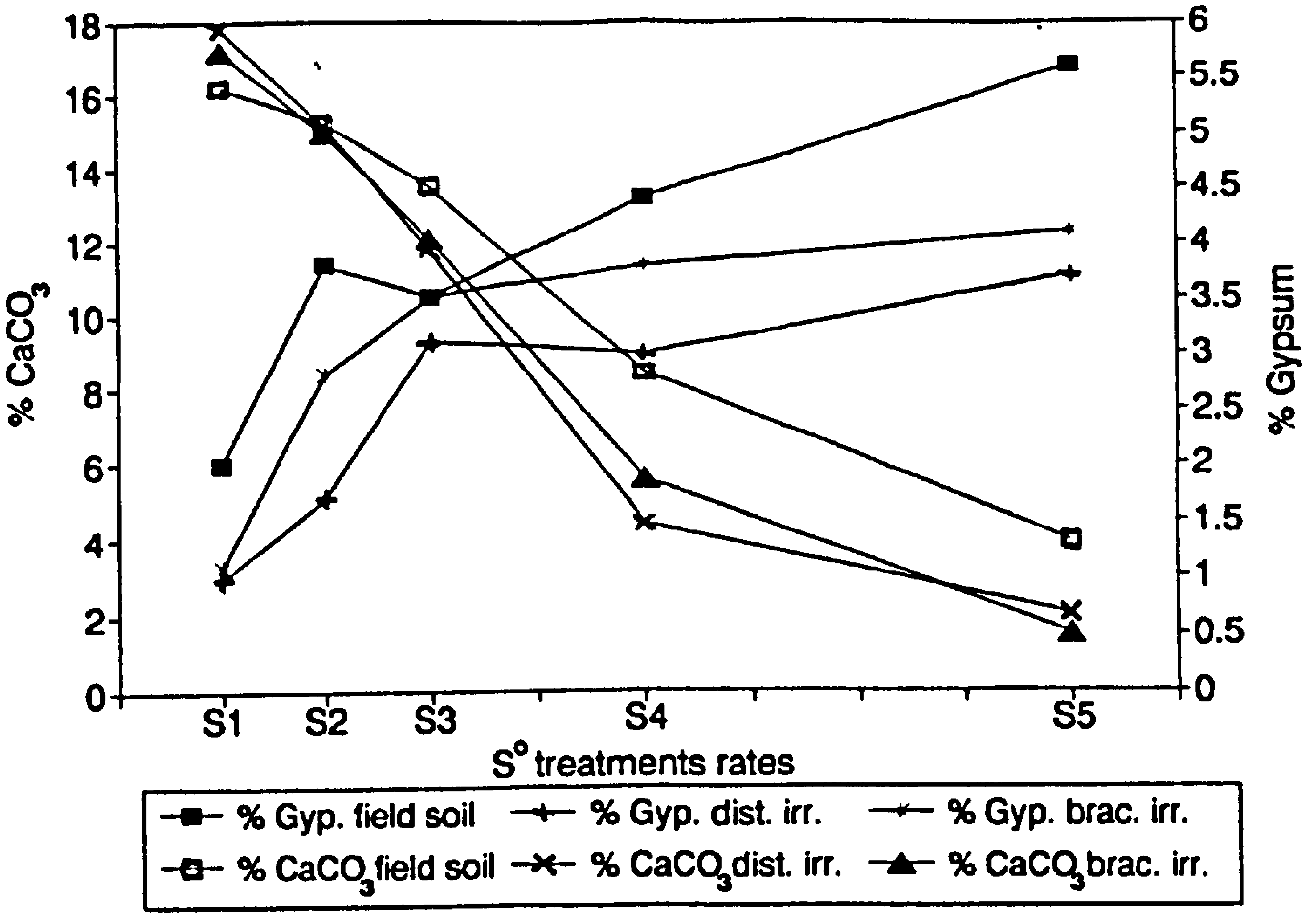


Fig.6.5 Relationships between CaCO$_3$ % reductions and increases in gypsum % in response to S° treatments of field soils and pot experiment soils irrigated with distilled and brackish water.

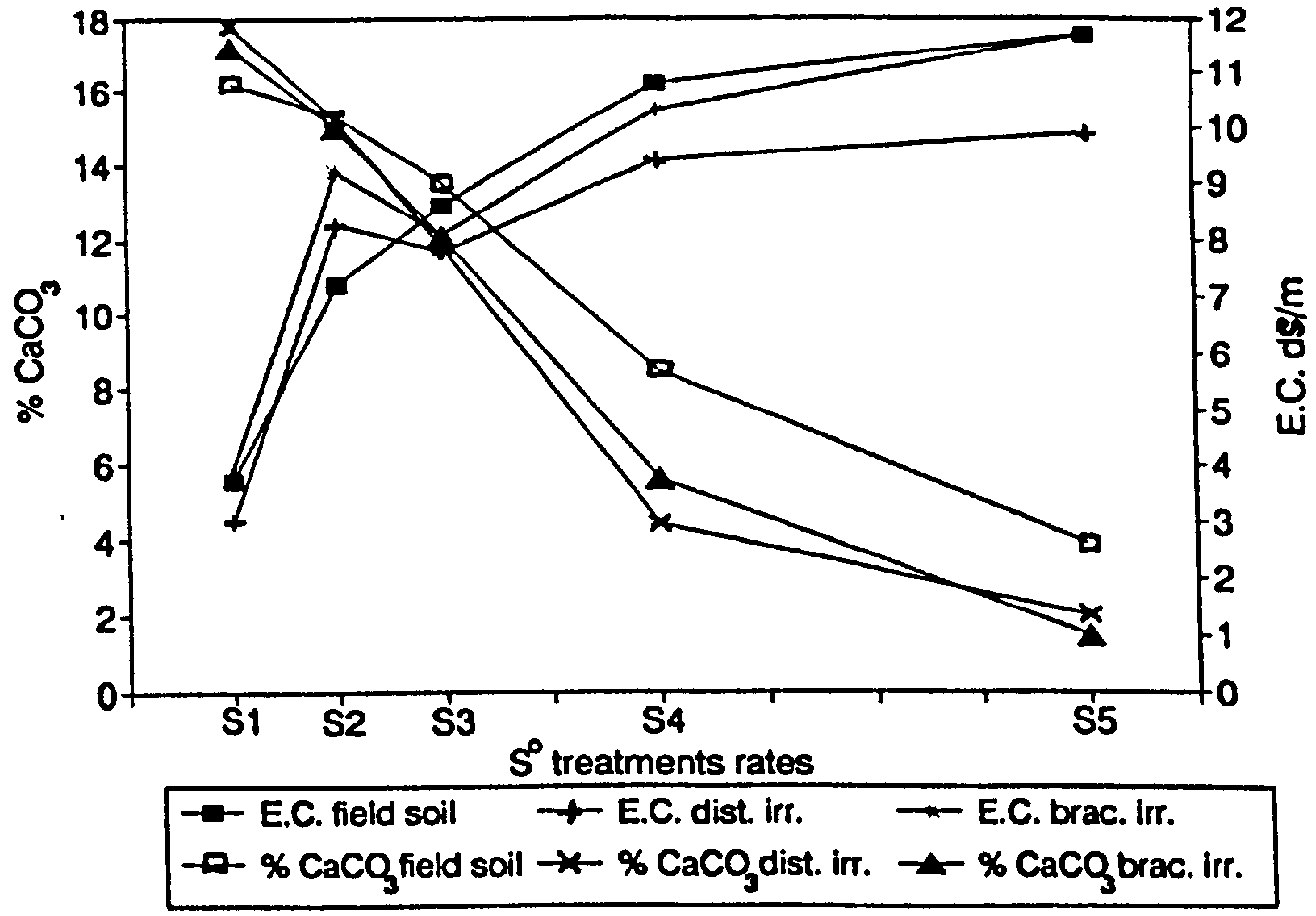


Fig.6.6 Relationships between CaCO$_3$ % reductions and increases in soil E.C. in response to S° treatments of field soils and pot experiment soils irrigated with distilled and brackish water.

and Mg solubility in S^0 treated soil (Bole, 1986). When water availability was limited or the quality of irrigation water used was poor, salinity accumulated and some salts would precipitate out of solution as has been the case with gypsum (figure 6.5). Modaihsh *et al.* (1989) showed that the high values of E.C. and soluble SO_4^{2-} were confined to the top 10 cm of a soil column, and in this layer gypsum formed as indicated in thin section soil examination. In this field study SO_4^{2-} had accumulated in the top 30 cm (figure 6.7) even though a high rate of irrigation was practised in the hope of reducing the build-up of soil salinity. It was thought that because of the poor quality irrigation water (T.D.S. >3,500 containing >1,300 $\mu g l^{-1}$ SO_4^{2-}) and with the increased solubility of Ca^{2+} and the recently oxidized SO_4^{2-}, the solubility product of $CaSO_4$ was exceeded and it precipitated probably as gypsum. This was the reason why the greatest SO_4^{2-} content of the field soil profile (figure 6.7) was confined to the top horizon, and only with the high S^0 treatments (S_4, S_5) did the SO_4^{2-} leach to lower depths. At these very high S^0 applications it was suspected that there were greater amounts of SO_4^{2-} produced than the amount of readily soluble Ca^{2+} and Mg^{2+} available in the soil solution of the top horizon, thus the excess SO_4^{2-} did not precipitate immediately but H_2SO_4 moved downward with drainage water. This concept was confirmed by studies in the glasshouse when comparing distilled water irrigated to brackish water irrigated soils. Gypsum content and E.C. values of the distilled water irrigated soil were lower than those of the brackish water irrigated soils (figures 6.5 and 6.6 respectively), although the soils had the same levels of S^0 treatment and were subjected to similar incubation conditions, with the practically identical levels of soil $CaCO_3$ reduction. The different values of E.C. and gypsum levels in the two soil sets were directly due to the inability of brackish water to remove the salinity from the soil with the drainage water as had been the case with the distilled water. This adds an additional constraint on the success of treating Kuwaiti calcareous soils with S^0. Salinity would increase and

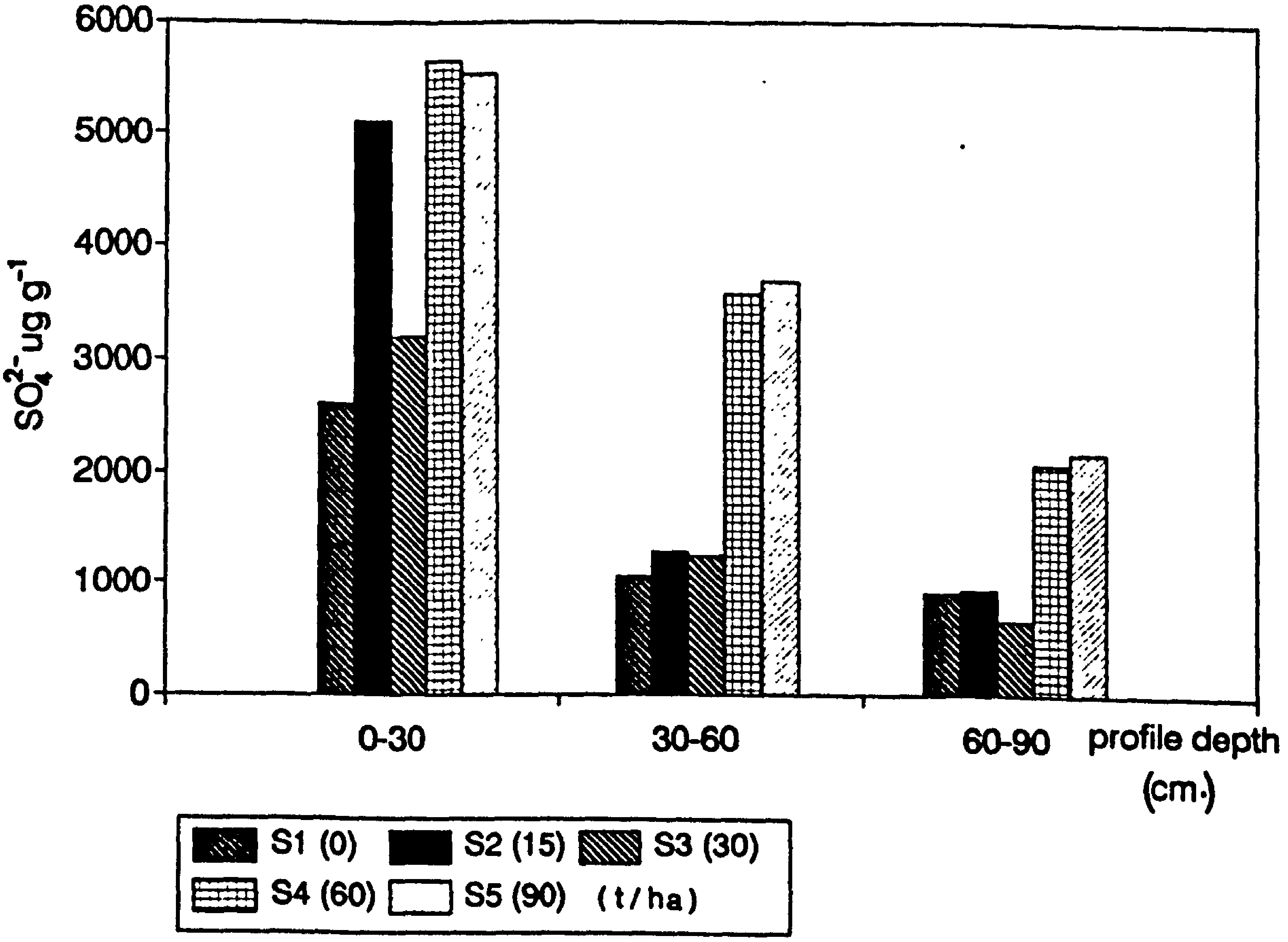


Fig.6.7 Effect of S° treatments (t per ha) on sulphate movement in soil profile at a field site in Kuwait.

it would not be possible to eliminate it easily using the available ground water.

6.4.3 Effect of S° on some element phyto-availability and plant responses

Soil dominated by the presence of $CaCO_3$ is characterized by high pH and low levels of plant available P and micronutrients, such as Fe. The use of acidifying amendments on these calcareous soils would result in changes in some parameters. In this study S° as an acidifying agent has reduced both bulk soil pH and $CaCO_3$ content and activity. Further, it has increased various ionic concentrations in soil solution, thus resulting in higher salinity. These changes would have a great effect on plant nutrition. The behaviour of P and trace elements in this changed environment were monitored. Their soil extraction and plant uptake were measured not only in a field experiment, but also in a glasshouse set of trials and some laboratory exercises.

6.4.3.1 Effect of S° treatments on P

Phosphorus availability as indicated by $NaHCO_3$ extracts first increased in response to S° inclusion at moderate rates (theoretical acidity to neutralize 25 and 50% of soil $CaCO_3$ contents). Then as S° rates were further increased, P availability declined (figure 6.8). In the early stages and at lower S° application rates, the reduction in $CaCO_3$ both as a percentage and its active surface area (tables 6.3.1.3.1-6.3.1.5.1) probably resulted in a reduction in $CaCO_3$ induced OP adsorption. It has been repeatedly found that P was adsorbed onto $CaCO_3$ surfaces in calcareous soils, following the Langmuir isotherm (Kuo and Lotse, 197; Holford and Mattingly, 1975a), with a better fit when described by a two linear region Langmuir isotherm (Griffin and Jurinak, 1973) corresponding to two different types of surface (Holford *et al.*, 1974) or two bonding energies (Holford and Mattingly, 1975a). Furthermore, this interaction has been described as a heterogeneous nucleation process ultimately resulting in about 5 per cent of the $CaCO_3$ surface being covered with P ions (Griffin and Jurinak, 1973).

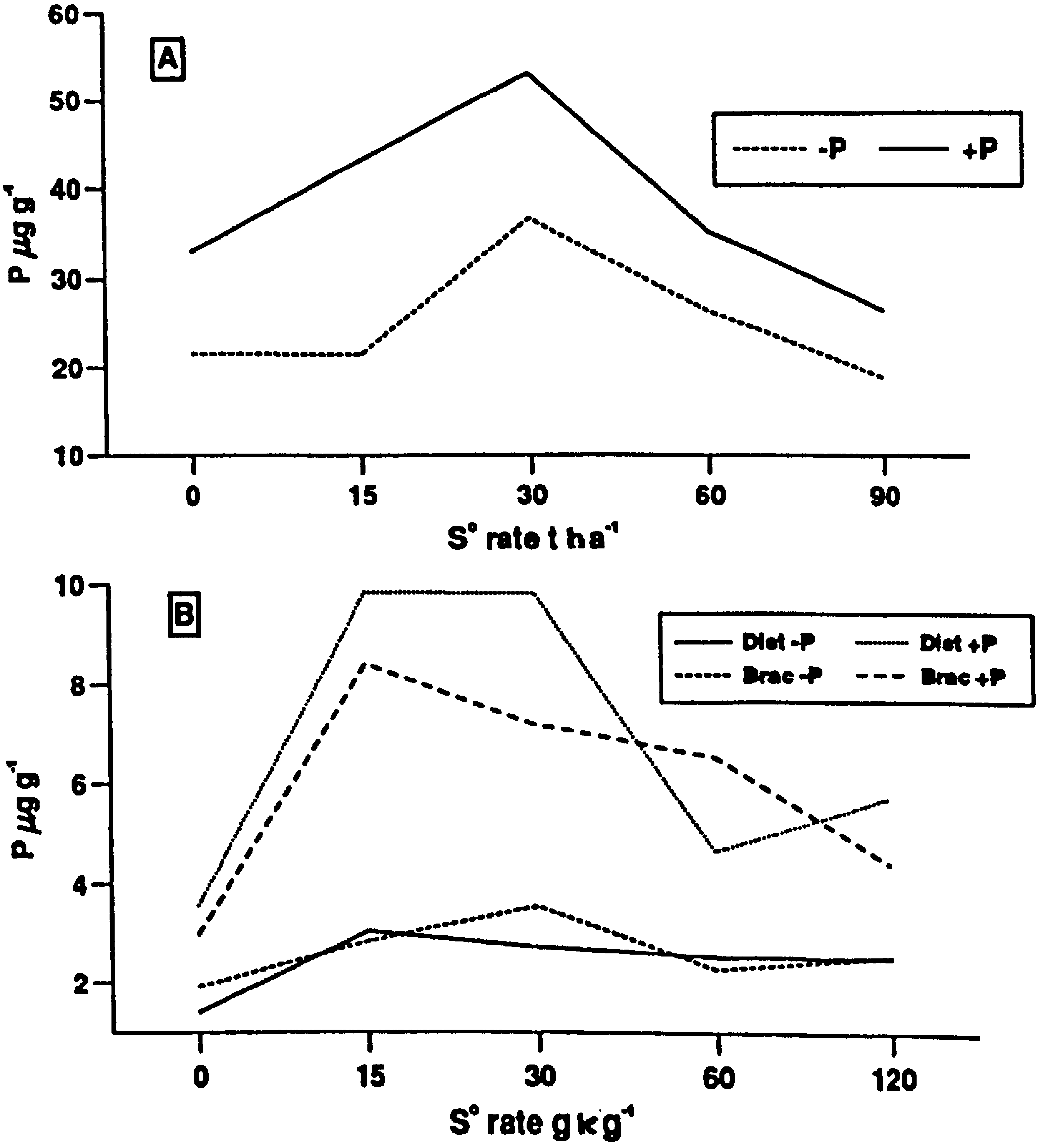


Fig.6.8 Effect of S° on $NaHCO_3$-P in field (A) and distilled or brackish water irrigated glasshouse soils (B) with or without P fertilizer.

Consequently, $CaCO_3$ surface area and not total soil $CaCO_3$ content would be correlated with P adsorption (Holford and Mattingly, 1975_a). Holford and Mattingly (1975_c) concluded that more weathered soil may have a lower content of $CaCO_3$, but of smaller particle size and therefore a higher specific surface, which determines its reactivity. In the indirect method to measure $CaCO_3$ particle size distribution as affected by S°, there was progressively a greater proportional dissolution of smaller particles (figure 6.6) indicating a greater reduction in specific surface and thus reactivity of the $CaCO_3$ than that corresponding to the total chemically determined $CaCO_3$. This would presumably reduce the amount of OP adsorption which may have contributed to the higher $NaHCO_3$-P availability (figure 6.8). Furthermore, the total amounts of P adsorbed by $CaCO_3$ would behave in such a way that there would be initial chemisorption directly on the $CaCO_3$ surfaces on the site of exposed Ca^{2+} ions where phosphate ions would replace other anions; i.e. HCO_3^-, OH^- or even H_2O molecules (Kuo and Lotse, 1972). This reaction would predominate when P ionic concentration was low and result in the formation of a monolayer (Griffin and Jurinak, 1973; Holford and Mattingly, 1975_b) on the $CaCO_3$ surfaces. As these sites are filled multilayers of physically adsorped P, characterized by very low bonding energy, may occur and be deposited on the initial chemisorbed layer (Holford and Mattingly, 1975_b). This later deposition would be more significant when P ionic concentration was relatively high. These conditions were clearly observed with the previously virgin glasshouse soils (figure 6.8B) where, the reduction in soil $CaCO_3$ surface area in response to increasing rates of S° resulted in no appreciable changes in $NaHCO_3$-P when no fertilizer P was applied. This suggests that the native P in these soils was so low that even with the decline in the available $CaCO_3$ surface area, there were still enough sites for that chemisorption to occur in a monolayer form. However, when P was added to the soil (100 µg/g soil), the extractability of soil P ($NaHCO_3$-P) after the termination of the growth experiment (total 11 weeks) reacted positively to S° and was strongest with the lowest S° rate (15 g/kg soil). This may suggest that under these conditions the combination of reduced $CaCO_3$ surface area and initially high P-ionic concentration resulted in the formation of the weakly held multilayered P deposits on the soil $CaCO_3$.

Another possible explanation for the increased extractability of P could be that in soil micro-niches, S° oxidation had resulted in much lower pH than that measured in the bulk soil (tables 6.3.1.3.1-4). This could be quite conceivable with active S° oxidation, so P solubility would be enhanced and may be expressed by higher $NaHCO_3$-P levels. In the P solubility diagram developed by Lindsay and Moreno (1960), they clearly indicated that at pH of 6.5, under the conditions used in their study, there would be supersaturation with respect to all Ca-P. These would be controlled by the precipitation of DCPD or OCP which would predominate in such equilibria at higher pH.

In the field experiment $NaHCO_3$-P had doubled, and in the glasshouse soils they increased by three fold in response to the moderate level of S°; 30 t/ha and 15 g/kg, respectively. It should be pointed out that S° field application at 30 tonnes per hectare would correspond to about 15 g/kg soil when considering the arable horizon (depth of about 20-30 cm). Other researchers had obtained similar trends when using S° at rates comparable to those mentioned above, especially when taking into consideration the nature of their soils (Kashirad and Bazargani, 1972; Ryan and Strochlein, 1979; Abo-Rady *et al.*, 1988); Modaihsh *et al.*, 1989). Even in a study where much lower rates of S° were used with T.S.P. there was significantly greater availability and recoverability of P in their observations (Deluca *et al.*, 1989).

At higher S° application rates, there were much more severe reductions in the soil $CaCO_3$ content (tables 6.3.1.3.1-4) and more importantly the effect it had on $CaCO_3$ surface area (figure 6.4). Furthermore, the soil pH started to decline significantly (tables 6.3.1.3.1-4) and in some glasshouse soils even becoming acidic. However, under these changes the $NaHCO_3$-P levels did not increase, but in fact started to decline and their levels with the highest S° rates were not different from those without S° treatments (figure 6.8). Therefore, it is safe to assume that factors other than the soil $CaCO_3$ had become the major constituent in controlling the soluble and labile P in these peculiar S° treated soils.

It has been recognised for a long time that the oxides, hydroxides and oxyhydroxides of Fe and Al are important in the sorption of P in many soils, particularly those characterized by being non-calcareous with neutral or acidic reaction (Lindsay and Moreno, 1960; Mattingly, 1975). The influence of amorphous or crystalline forms of Fe and/or Al on P adsorption are still not completely resolved. While some studies attributed this sorption to the Fe or Al crystalline fractions (Torrent, 1987; Pena and Torrent, 1984; Borggaard, 1983) others had found that the amorphous forms accounted for more reactions (Loganathan *et al.*, 1987; Borggaard *et al.*, 1990; Freese *et al.*, 1992). Moreover, although the adsorption also followed the Langmuir isotherm, it was characterized by stronger bonds (Holford and Mattingly, 1975_a), corresponding to about one third of all P sorption in the soils studied, when compared to the remaining P correlated with other soil factors including $CaCO_3$ surface area. Ryan *et al.* ($1985_{a,b}$) after investigating 20 mostly calcareous mediterranean soils indicated the involvement of the free Fe oxides (oxalate extracts) with P adsorption, even in the presence of $CaCO_3$.

These oxides would affect the P adsorption not only directly as just mentioned, but also indirectly by modifying the behaviour of other soil particles. This could be done by coating them including surfaces of soil $CaCO_3$ (Hamad *et al.*, 1992) or by being incorporated into the structure of these particles as impurities (Holford and Mattingly, 1975_b), and thus providing an adsorption site for P. In the S° treated soils there were steady increases in the DTPA-Fe and DTPA-Mn (figures 6.9, 6.10). Although these extractions do not directly correspond to a particular Fe, Al or Mn oxide or hydroxide, they represent that fraction which is chelated by the DTPA organic ligand. In the case of Fe they include the little that might be soluble or exchangeable and some of the poorly crystalline oxides. If the soluble and exchangeable forms were extremely sparse, then the large increases in the DTPA-Fe after the S° oxidation must be due to an increase in amorphous Fe. This amorphous Fe or possibly freshly crystallized oxide/hydroxide must have had an increasingly dominate role in the adsorption of P ions especially with the declining effects of soil $CaCO_3$. Hamad *et al.* (1992), after treating pure calcite with ferrous perchlorate solution to obtain its coating with Fe-oxide, had found that as the coating increased from 0.00 to 16.0g Fe_2O_3 per kg $CaCO_3$, the P maximum sorption had increased from 18.2 to 160 mg P per kg calcite. Furthermore, in their study on Sudanese soils they calculated, based on the adsorption model they used, that free Fe-oxide had contributed 30-40% of all P adsorption while Fe-oxide coated $CaCO_3$ contributed to less than 6%. Uncoated soil $CaCO_3$ had a negligible effect of less than 1%. However, these proportions were based on the P-adsorption of a pure system of Fe_2O_3, calcite or Fe coated calcite. This may not be the case for actual P-adsorption in a dynamic soil system. Moreover, the soil they studied was heavy clay (40-60%) and being from the Gezira region it was likely to be very rich in organic matter. This would further contribute to the behaviour of P. Nevertheless, if this concept of Fe_2O_3 directly or in association with the soil $CaCO_3$ having a prominent effect on P-adsorption is correct, than in the Kuwaiti soil subjected to acidification the release of Fe-oxide (indicated by higher DTPA-Fe values) must have had an enhanced effect on P-adsorption, especially with the low clay and organic matter characteristic of this soil. MnO which had been released by the effect of S° acidification (based on DTPA-extraction) (figures 6.9, 6.10 and 6.11) may also have had a similar effect on P-adsorption to that of Fe-oxide. Similar comments might apply to Al (no measurement was conducted).

In addition to the effect of metal oxides on P-retention, this increased P-adsorption (lower $NaHCO_3$-P extraction) at higher rates of S° application may be explained by the changes in the soil solution ionic strength and its contributers. In response to S° oxidation and its effect on the dissolution of soil $CaCO_3$, there was a consistent and measured increase in soil salinity (tables 6.3.1.3.1-4). This presumably was in direct response to increases in the concentration of SO_4^{2-} and Ca^{2+} ions. However, the solubility of these two ions would be controlled by the formation of $CaSO_4$ or its hydrated form (gypsum). Although gypsum content had increased in the soil in response to S° amendments (tables 6.3.1.3.1-4), the accompanied increases in soil salinity (up to about 10 dS m^{-1}) could not be due to SO_4^{2-} and Ca^{2+} ions alone due to their limited solubility in soil solution. The higher E.C. readings (tables 6.3.1.3.1-4) then could be as a result of other cations (i.e. Mg^{2+}, Na^+, K^+, NH_4^+ etc.) released into soil solution from the exchange sites which might have become dominated by Ca^{2+}. Nevertheless, these changes in ionic composition might increase or decrease P solubility due to their effect on its adsorption/desorption and precipitation/dissolution reactions.

Many studies have shown that higher salt concentrations present in soil solution would increase the level of P-adsorption in that soil, and was greater for Ca^{2+} than for Na^+ ions (Ryden and Syers, 1975; Helyar *et al.*, 1976; Ryden *et al.*, 1977; Barrow and Shaw, 1979; El-Mahi and Mustafa, 1980; Curtin *et al.*, 1992). However, the effects of the ionic strength of the solution and its cationic constituents on P adsorption were found to be related to the kinetics of the reaction and had no effect at infinite time equilibrium (Ryden and Syers, 1975; Ryden *et al.*, 1977). The short-term effect was attributed to the influence of the ionic strength of the solution on the surface charge of the adsorbing compounds and their effect on the thickness of the diffuse double layer. Divalent as compared to monovalent ions, therefore, would have a specific effect on the surface charge and the diffuse double layer in relation to the rate of P-adsorption.

Moreover, the initial chemisorbed layers formed by the P-adsorption onto the oxides/hydrous oxides were found to be independent of the solution ionic strength and composition, while the physically bonded P was dependent on the matrix solution (Ryden *et al.*, 1977). This last form of sorbed-P, therefore would tend to be affected by the increased ionic strength of the soil solution resulting from the S° oxidation. Furthermore, this physically-bonded P was closely related to both $NaHCO_3$ extractable P and that P-fraction referred to as labile-P (Ryden and Syers, 1977). This concept could explain the lack of changes in the $NaHCO_3$-P levels for the glasshouse soils when no phosphate fertilizer was added (figure 6.8B), whereas with the P treated soils the levels declined sharply with high rates of S°. It could be that the control soils had so little P, it was all held tightly by a chemisorption reaction and therefore the increased salinity from S° oxidation had no direct effect on its retention. On the other hand, the increased ionic strength of soil solution and possibly its domination by Ca^{2+} ions at higher S° treatments had increased both the amounts and strength of the physically bonded P, resulting in lower $NaHCO_3$-P extraction in the latter case (figure 6.8B). This did not happen with the field treated soil, where both P amended and non-amended soils had similar reaction to increasing rates of S° (figure 6.8A). In this case, however, the soil had high levels of P (long history of P fertilization) so that the physically sorbed P layer was present regardless of the recent P fertilization.

Calcium phosphate precipitation would also be expected to take place both in the soil solution and on the adsorbent surfaces such as that of $CaCO_3$. The adsorption/precipitation reactions may occur consecutively and/or simultaneously and therefore are difficult to distinguish. Nevertheless, the precipitation process usually proceeds in three stages: (i) the initial stage characterized by the formation of a Ca-P amorphous substance that does not change with time and acts as the nucleus for further precipitation, being referred to as nucleation. (ii) The second stage is marked by accumulation, deposition and progressive transformation of the amorphous pattern of the precipitate to that approaching crystalline apatite, thus resulting in crystal growth. (iii) The third stage involves the ripening of small crystals into larger ones (Eanes *et al.*, 1965; Brown, 1981). This precipitate of Ca-P compounds was thought to change from that of mono-calcium phosphate (MCP) to di-calcium phosphate dihydrate (DCPD) to octa-calcium phosphate (OCP) to hydroxyapatite (HAP) or fluorapatite (FAP) (Amer and Ramy, 1971; Holford and Mattingly, 1975_b; Griffin and Jurinak, 1974). As this transformation proceeded, the product became increasingly less water soluble and therefore resulted in P being less labile or plant available. The changes in the structure of DCPD to OCP to HAP would involve realignment of the elements and incorporation of further Ca^{2+} ions (Brown, 1981). The Ca-P molar ratios would correspondingly rise from 1 to 1.33 to 1.67, respectively. It was clear therefore, that increasingly higher Ca^{2+} levels in soil solution would promote P precipitation and its transformation to more basic compounds. The condition of high Ca^{2+} levels in response to the dissolution of soil $CaCO_3$ (table 6.3.1.7.1) would explain the lowering of $NaHCO_3$-P in that H_2SO_4 treated soil. The same phenomena could be the reason why $NaHCO_3$-P had declined with high rates of S° in both the field and glasshouse soils (figure 6.8).

6.4.3.2 Effect of S° treatments on iron, zinc and manganese

In this section the three micronutrients Fe, Zn and Mn will be discussed both collectively and individually. Their interaction with S°, P and amongst each other will be discussed where it is appropriate.

In general, all three elements (Fe, Zn and Mn) had a higher DTPA extraction with increasing rates of S° application. However, there were some differences in the magnitude and from field to glasshouse experiments (figure 6.9, 6.10 and 6.11). DTPA-Mn increased by a massive 5 to 7 fold, but DTPA-Zn had a slight increase that in most cases was inconsistent in relation to S° application rate. The release of soil Mn was beyond the usually accepted critical values required for

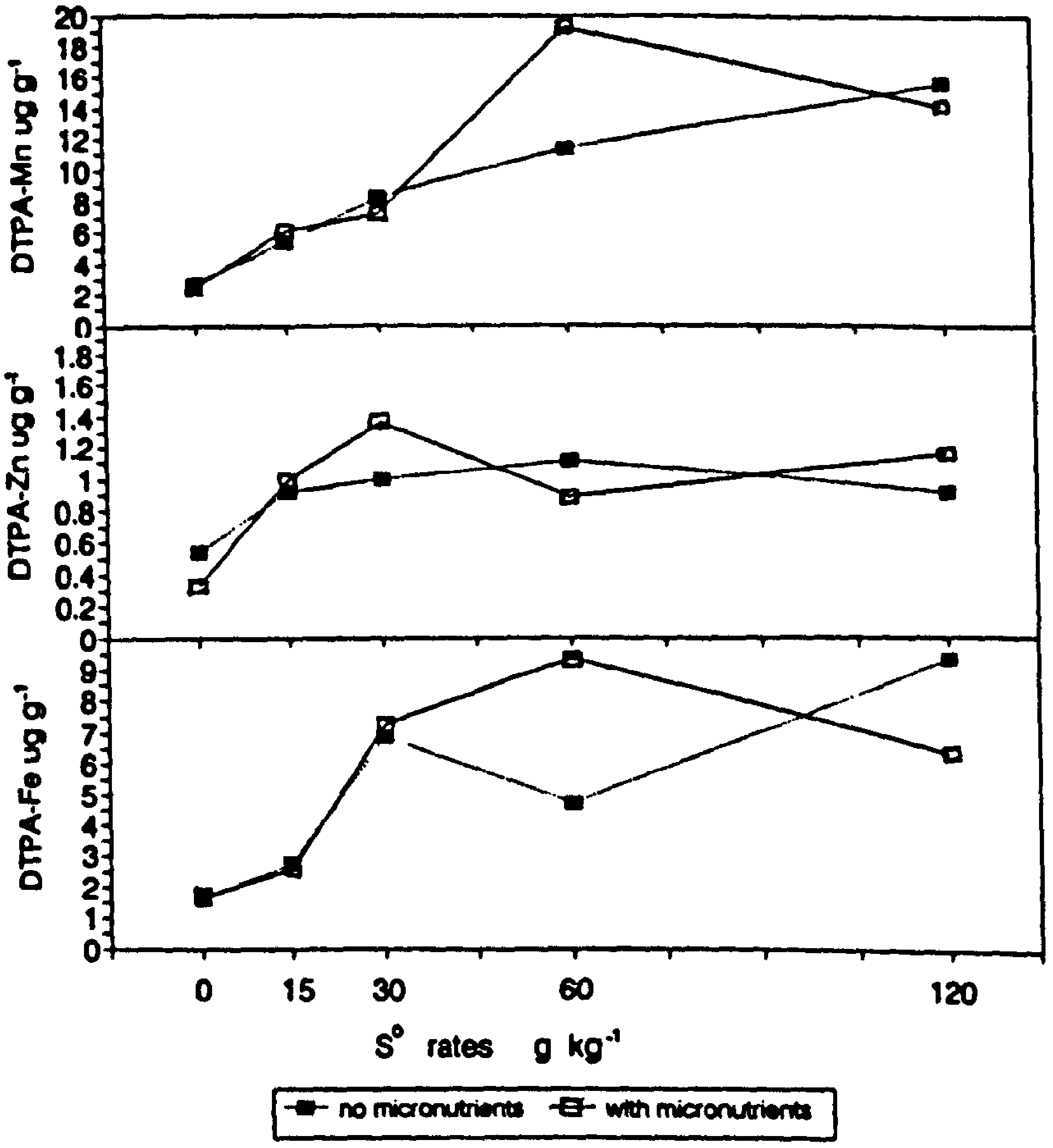


Fig.6.9 DTPA extractions of Fe,Zn and Mn from distilled water irrigated soils.

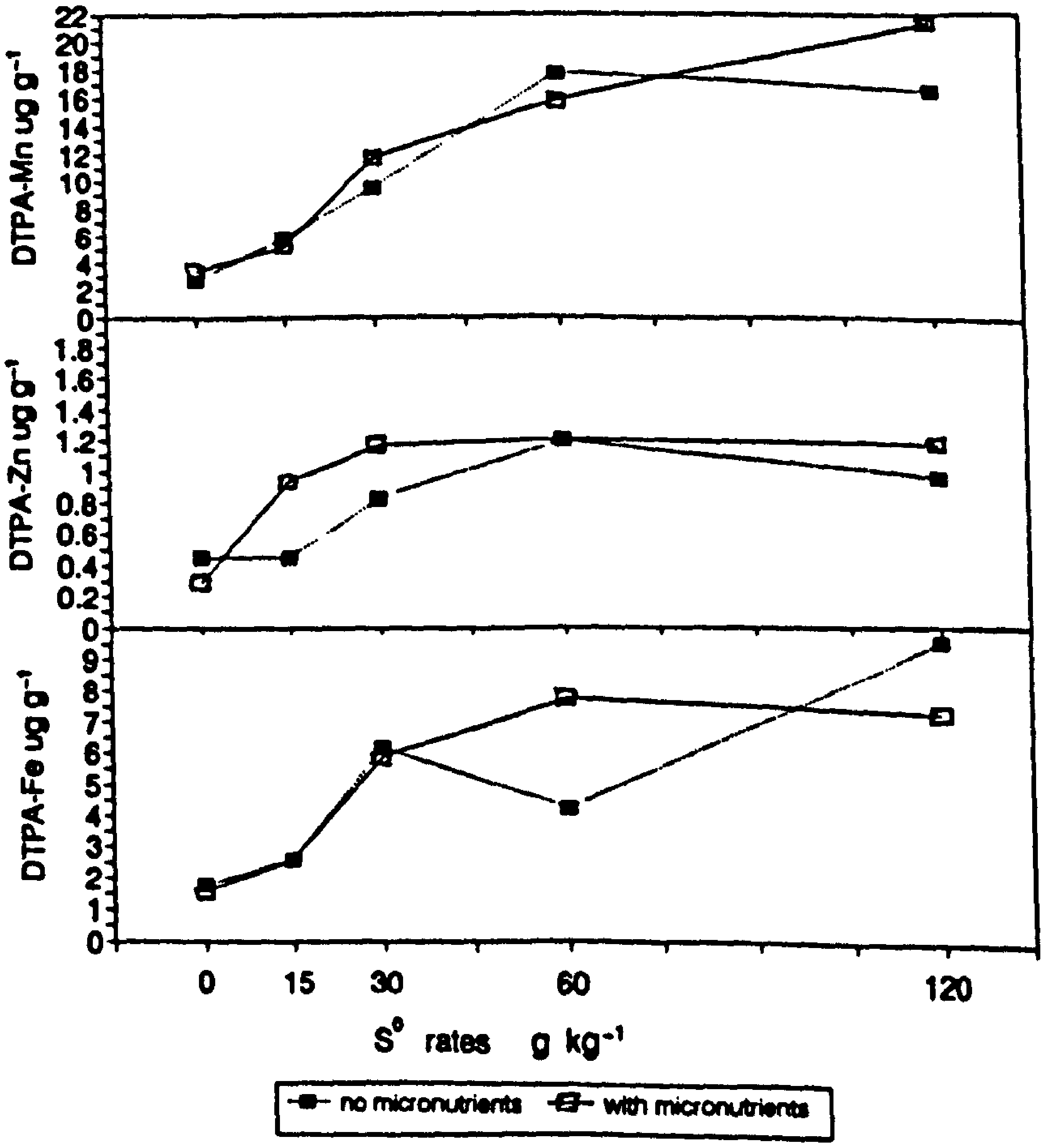


Fig.6.10 DTPA extractions of Fe,Zn and Mn from brackish water irrigated soils.

the growing crop. In some cases there was more than 30 μg DTPA-Mn per g of soil (critical nutrient range was reported as 3-5 μg/g) (Sillanpaa, 1982). Although there was more Mn available than that required by most crops, the DTPA-Mn contents were in the normal range found in agricultural soils. Zn levels were in the critical nutrient range (0.5 to 1.0 μg/g, Lindsay and Norvell, 1978) and occasionally they did increase to more than 1.0 μg/g, but not in linear response to levels of S° application.

Iron levels in the soil were originally low (average 2-2.5 μg/g, critical range depending on the crop grown was estimated at 3 to 4.5 μg/g, Lindsay and Norvell, 1978). Upon S° application DTPA-Fe extractions increased appreciably above the critical levels, but only with the high S° application rates. At 15 g/kg and 15 to 30 t/ha S° rates for the glasshouse and field soil respectively, there were hardly any changes with respect to DTPA-Fe. At higher S° dosages, however, the DTPA-Fe extraction increased dramatically to between 6 to 10 μg/g and 10 to 18 μg/g for the glasshouse and the field soils respectively (figures 6.9, 6.10, 6.11). Although the S° rates were higher in the glasshouse sets than those of the field soil (depending on the profile depth considered), the extractable DTPA-Fe levels in the field soils were about double those in the glasshouse soils. Since both soils were similar and had initial low DTPA extractable Fe levels (about 2 μg/g soil), then factors other than soil S° amendment rates increased the Fe extractability in the field compared to the glasshouse soils. It could be that compost manure had interacted with S° and directly or indirectly shifted Fe extractability. However this organic source on its own did not increase DTPA-Fe extractability (figure 6.11). Another possible explanation is that high rates of S° needed more time to be fully oxidized and show their effects on Fe-solubility. The highest Fe extractions from the field soils were from those plots which had received all or part of the S° in the first season. Perhaps if the laboratory/glasshouse incubated soils had been better aerated there may have been more efficient S° oxidation and

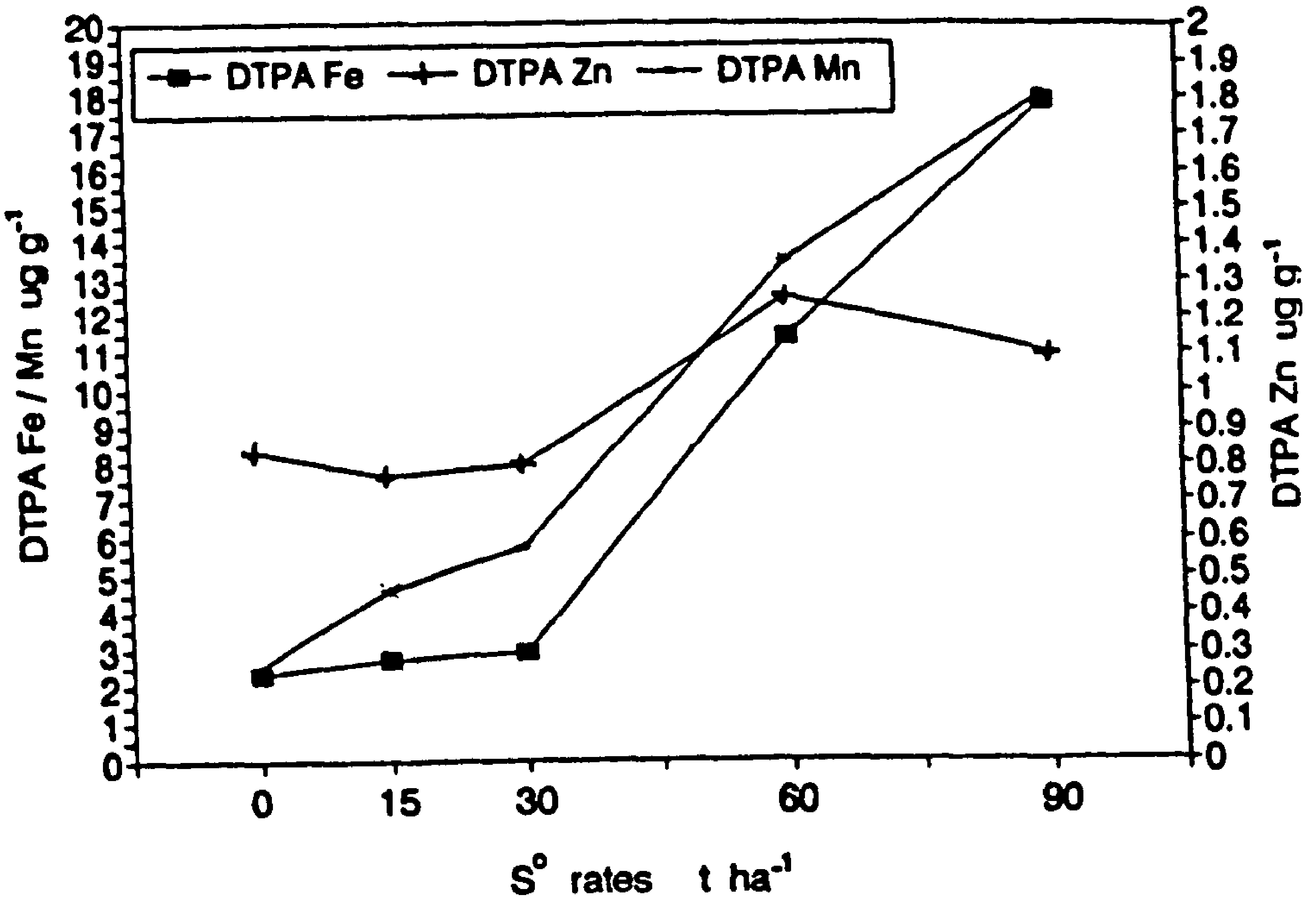


Fig.6.11 Effect of S° on some DTPA extractions from the field soil.

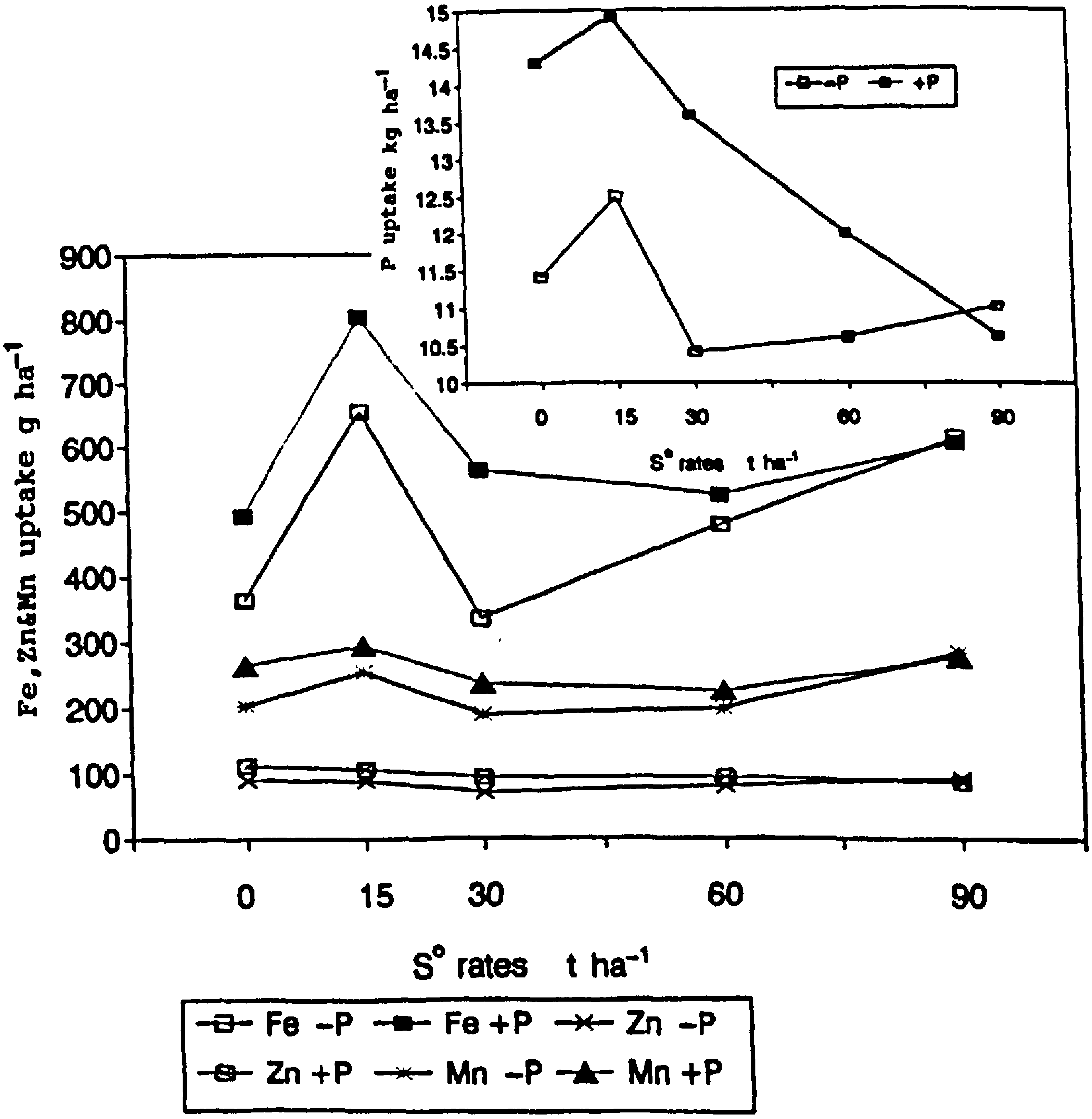


Fig.6.16 Elemental removal by whole wheat plants grown in S° treated field.

a greater effect on Fe. Nevertheless, these soils had already experienced appreciable S° oxidation when they were used in the glasshouse indicated from large drops in their soil pH and % equivalence of $CaCO_3$ as has been mentioned earlier. This however was achieved in a relatively short time of 10-11 weeks and may not have been long enough to generate changes on the soil Fe containing minerals. Long-term observation and more specific soil Fe extraction would be needed in the future to ascertain the changes to Fe mineralogy with respect to S° application.

Other similar reserach has shown increases of DTPA extractable Fe only with high rates of S° treatment (Abo-Rady *et al.*, 1988; Modaihsh *et al.*, 1989). It may be hypothesized that the action of S° oxidation on increasing soil extractable Fe may have been the result of a downward shift of soil pH. It has been reported that the solubility of Fe^{3+} increases by 1,000-fold for every unit decrease in pH (Lindsay, 1979). However, at the pH range of 7.4 to 8.5 maintained by the buffering characteristics of $CaCO_3$, the equilibrium concentration of total soluble Fe^{3+} would be the lowest at approximately $10^{-10.4}$M under well aerated soil conditions, considerably lower than the concentration required for optimum plant growth; $10^{-7.7}$M; (Lindsay and Schwab, 1982). Furthermore, this equilibrium solubility was controlled by $Fe(OH)_3$ frequently designated as soil-Fe. and this the most dissolvable form independently of all other crystalline Fe oxides dictated the Fe solubility (Lindsay and Schwab, 1982). Since the soil pH in this study, especially in the field experiment, did not drop below 7.5 (table 6.3.1.3.4), lower pH values could not account solely for the increased DTPA extractable Fe. It could be further hypothesized that in protected microsite environments such as those around oxidizing S° particles, pH would be much lower than in the bulk soil especially if $CaCO_3$ activity had been reduced, but perhaps more importantly, at these microsites increased micro-organism activity due to S° oxidation might create reducing conditions. Schwab and Lindsay (1983_a)

indicated that at low redox potentials (pe + pH), Fe^{2+} activity increased. However the controlling Fe-minerals were other than soil Fe. Siderite ($FeCO_3$) and ferrosic hydroxide ($Fe_3(OH)_8$) controlled Fe^{2+} activity at pe+pH below and above 8.5, respectively. Nevertheless, Fe solubility would not increase appreciably until pe+pH dropped below 12 (Lindsay and Schwab, 1982), and below 9.75 before Fe^{2+} solubility would be sufficient for plant requirements (Lindsay, 1984). Often these conditions would restrict plant root growth (aquatic plants would be an exception) and may lead to less Fe-adsorption thus accentuating Fe deficiency (Lindsay, 1984). Moreover, limited aeration and high micro-organism respiration proposed here to generate reducing conditions around S° particles also lead to a build-up of HCO_3^-, which has been associated with the induction of Fe chlorosis. Loeppert (1986) in a review paper attributed HCO_3^- induced Fe stress as a result of (i) reduction of Fe solubility in soil solution, (ii) interference with Fe metabolism and mobility within the plant and (iii) hindering Fe-stress plant responses in reducing their rhizosphere environment to increase Fe solubility. However, high Ca^{2+} activity would decrease HCO_3^- activity in soil solution (Loeppert, 1986). This would be expected with the dissolution of $CaCO_3$ as a result of S° oxidation and the subsequent increases in Ca^{2+} concentration. Therefore, lower pH and/or redox potential in soil microsites would be able to dissolve Fe. This soluble Fe would diffuse out with the concentration gradient to other parts of the soil. Its safe to suggest that this soluble Fe would then react with the other soil constituents. Soluble Fe was found to react readily with soil $CaCO_3$ in well aerated conditions and a precipitate of Fe oxides would form (Loeppert *et al.*, 1984$_a$). Ferrous (Fe^{2+}) and ferric (Fe^{3+}) would react differently with $CaCO_3$ consuming, respectively, 2 and 3 equivalents of $CaCO_3$ for each mol neutralized (Loeppert and Hossner, 1984; Loeppert and Clarke, 1984). Loeppert and Hossner (1984) suggested that with Fe^{2+} the product of this reaction was predominantly FeOOH (lepidocrocite) and FeOOH (geothite), depending on CO_2

content, deposited on the edges and corners of $CaCO_3$ crystals, while with Fe^{3+} the deposits formed a mosaic pattern on $CaCO_3$ surfaces. They further added that with Fe^{3+} the precipitation reaction was a product of hydrolysis of Fe polymers in suspension, forming ferrihydrite, $Fe(OH)_3$, an amorphous or partly crystalline Fe oxide. This Fe formation was the result of reaction with the dissolution product of $CaCO_3$ near its surface rather than directly on its surface, and these then precipitated on top of already deposited Fe-oxides. This concept would be important in that any reduction of $CaCO_3$ surface area as a result of S° oxidation, as discussed earlier, would favour the formation and deposition of ferrihydrite. This the most soluble of all Fe-oxide minerals in calcareous environments, would dictate the rate of Fe-oxide dissolution (Loeppert and Clarke, 1984). Moreover, ferrihydrite characterized by high surface reactivity due to its higher surface area would be more readily dissolved by any plant root reduction activity in the rhizosphere and would be thus more available for plant uptake (Loeppert *et al.*, 1984_b). Geiger and Loeppert (1986) in a correlation study had found that this amorphous Fe-oxide was the main contributor to the labile Fe pool extracted by DTPA. Also, clay and organic matter were found to indirectly influence plant-Fe availability and DTPA-Fe extractability (Geiger and Loeppert, 1986; Loeppert and Hallmark, 1985) in a positive way by their ability to stabilize the amorphous ferrihydrite. This may explain the indirect interaction between S° application and organic matter (compost manure) in maintaining higher DTPA-extractable Fe in the field soil (figure 6.11). To summarize, these indigenous soil factors controlling Fe availability in calcareous conditions such as $CaCO_3$ content and activity, Fe mineralogy and reactivity, clay and organic matter content coupled with environmental and biological activities (Loeppert *et al.*, 1988) would be transformed as a result of S° oxidation and contribute in the formation of a more stable Fe-available ferrihydrite phase.

Reports of changes of Zn solubility in response to S° or H_2SO_4 application to calcareous soils have not been consistent from one study to another. Significant increases in DTPA-extractable Zn were reported with low levels of S° application (Kalbasi *et al.*, 1988; Falatah and Schwab, 1990), while other studies indicated a lack of response in DTPA-Zn extractions with rates of S° from low to moderate levels (Abo-Rady *et al.*, 1988; Modaihsh *et al.*, 1989). Application of H_2SO_4 had to exceed 100% of the acid titratable basicity of the soils before Zn solubility was significantly increased (Ryan *et al*, 1974). However, at such rates of acid treatment, soil pH was extremely acid ($pH<2$). The mechanism that controls Zn solubility in soil still generates contrasting findings in the soil science community, where some describe this relationship as a precipitation-dissolution process and others depict it as adsorption-desorption reactions. Precipitation of Zn in the forms of zinc oxides, hydroxides, carbonates, phosphates and silicates have been dismissed as the mechanisms controlling soil Zn solubility due to their higher dissolution products than those usually found in soils (Lindsay, 1979). Adsorption-desorption reactions on the other hand were not fully understood, especially which specific ionic species are involved with which adsorbent and under which mechanisms they operate. It has been shown that Zn adsorption is influenced by soil pH and generally Zn solubility declined with increasing pH values (Saeed and Fox, 1977; Bar-Yosef, 1979). However, the presence of organic matter would further complicate the relationship. While some workers report increases in Zn solubility due to Zn-OM complexation, but only at high organic matter concentrations in alkaline environments (Bar-Tal *et al.*, 1988), other reports (Shuman, 1988_{a+b}) indicate that organic matter caused lowering of Zn solubility by increasing Zn adsorption by freshly released Fe and Mn oxides. Many soil minerals and constituents could adsorb Zn. Clay minerals and organic matter would react with soluble Zn in a physisorption (ion exchange) mechanism (Saeed and Fox, 1977; Wada and Abd.Elfattah, 1979; Shuman, 1979; Harter, 1983; Brummer *et al.*, 1983), while other studies suggested a chemisorption (covalently bonded) mechanism especially with hydrous oxides, particularly Fe-oxides (Kalbasi *et al.*, 1978; Schuman, 1976, 1977; Jahiruddin *et al.*, 1986). Elrashidi and O'Connor (1982) had described Zn adsorption by the Freundlich isotherm equation when Zn concentration was low, deviating from the equation at higher concentrations. They therefore suggested that there could be several adsorbent sites or more than one mechanism for Zn adsorption in soils. The reaction of Zn with soil $CaCO_3$ has been described as surface solution adsorption between $ZnCO_3$ and $CaCO_3$, however behaving in a less ideal manner by the formation of zinc hydroxides and/or hydroxycarbonate precipitates (Papadopoulos and Rowell, 1989). Furthermore, Madrid and Diaz-Barrientos (1992) suggested that Zn ions had precipitated as either Zn-oxide or carbonate through the substitution of Zn^{2+} for Ca^{2+} ions in the $CaCO_3$ structures. Although both precipitation or adsorption of Zn with $CaCO_3$ were plausible the relative importance of this reaction in comparison with other soil adsorbents was small. The great influence that metal oxides especially Fe, Al and Mn can contribute in binding Zn even in the presence of $CaCO_3$ (Brummer *et al.*, 1983) has been demonstrated. This complex Zn behaviour with various soil constituents may explain the irrational behaviour of Zn in response to the changes brought about by S° treatments (figures 6.9, 6.10 and 6.11). Freshly precipitated amorphous $Fe(OH)_3$, released by acidifying S°, could have lowered Zn solubility by providing additional sites for adsorption. The same could be said about Mn-oxides and possibly Al-oxides (DTPA-extractable Al was not measured). It has been shown that amorphous Fe has a greater ability in reducing Zn solubility than crystalline Fe-oxides (Lindsay, 1979). If high DTPA-extractable Fe can reflect a higher level of amorphous $Fe(OH)_3$ (Geiger and Loeppert, 1986), then this may be the reason for lowering DTPA-extractable Zn at high S° rates (figures 6.9, 6.10 and 6.11). However, the nature of the reaction of Zn with metal oxides was not clear, sometimes described as adsorption, other times as co-precipitation.

Lindsay (1979) suggested that franklinite ($ZnFe_2O_4$) could control Zn solubility in soils. Precipitation mechanisms involving Zn and Fe were also supported by Pulford (1986), Sajwan and Lindsay (1988) and Ma and Lindsay (1990). Brummer *et al.* (1983) concluded that adsorption-desorption operated in soil at pH below 7, whereas at higher pH precipitation-dissolution may take place. Pulford (1986), on the other hand, believed that both surface adsorption and precipitation were likely to occur and Fe-Zn precipitation operated independently of soil pH. In trying to explain the effect of S° oxidation on zinc solubility and subsequent plant availability, it is suggested that in soil microsites where active S° oxidation was able to appreciably reduce this micro environment pH, Zn solubility had increased from the existing soil-Zn minerals or the new Zn fertilizer. Furthermore, simultaneously Fe, Mn and possibly Al would also be released. As these ions diffused to other parts of the soil where higher pH conditions exist, Zn may have co-precipitated with Fe or other ions. It also could be that freshly precipitated Fe, Mn or Al-oxides had created additional sites for Zn adsorption. This may explain the initial small increases in DTPA-extractable Zn (figures 6.9, 6.10 and 6.11), but this did not increase further with the higher S° applications.

Manganese as mentioned earlier reacted most favourably to S° application. Its DTPA extraction had increased in semi linear fashion with increasing rates of S° application (figures 6.9, 6.10 and 6.11). The behaviour was similar to other findings that indicated S° had increased DTPA extractable Mn (Lindell and Sornsen, 1974; Soliman, 1987; Abo-Rady *et al.*, 1988; Modaihsh *et al.*, 1989). Furthermore, as in this study increased Mn-extraction was independent of soil pH, it is suggested that the release of Mn in response to S° oxidation can be attributed to the reduction effect of S and its partially oxidized intermediates rather than to the decrease in pH (Garey and Barber, 1952; Tisdale and Bertramson, 1949) caused by complete S° oxidation to H_2SO_4. Manganese occurs in nature in many oxidation states with many minerals contributing under various conditions to its solubility. In a broad introduction, Schwab and Lindsay (1983b) described the minerals controlling Mn solubility and how pH and redox potential can influence their direction. Its interesting to note, that in this study on Kuwait soils, the concern about soil Mn levels is not plant availability but rather direct toxicity or possible nutrient antagonisms. These topics will be further discussed in the effect of S° treatments on plant responses. There could be another explanation for the large increases in DTPA-extractable Mn with S° application. Soil salinity increased in direct resonse to increases in S° rates. This salinity could have increased soil Mn solubility by ionic strength effects coupled with complexation as has been suggested by Krishnamurti and Huang (1992). The higher salinity could also have reduced Mn(III, IV) into Mn(II) (Westermann *et al.*, 1971) which may have accumulated on the exchange sites only to be replaced by other cations such as Ca^{2+}, Mg^{2+} and Na^{+}. This has been hypothesized by Khattak and Jarrell (1988, 1989). However in another study (Khattak *et al.*, 1989) found no evidence for the Mn-salinity induced reduction. Probably poor soil structure caused by saline/sodic conditions had induced this reduction, but they supported the idea that increased Mn solubility was a result of displacement from the exchange sites, or through the formation of soluble Mn-ligand complexes.

6.4.3.3 Effect of S° on plant yield responses, some elemental tissue concentration and their plant uptake

Plant yield did not respond positively to the application of S°. As mentioned earlier in the results section, plant yield in fact declined with the amendments of S° both in the glasshouse trials and the field experiments, however only at high rates of S° corresponding to 100 and 200% of the theoretical $CaCO_3$ neutralization power. At lower rates (25 and 50%) there were no significant changes in the yield. On the other hand P, Fe, Zn and Mn plant availability as has been already discussed responded each in a unique way to the inclusion of S°.

$NaHCO_3$-P extractions increased significantly at the lower rates of S°, but declined again at higher rates, while DTPA-Fe levels only increased significantly with the higher S° treatments (S_4 and S_5). DTPA extractable-Zn, increased to some extent when S° was used, but this was not consistent, while DTPA-Mn extractions steadily increased beyond the levels required for plant growth.

Plant tissue concentrations of P for field plant parts (figure 6.12) and those for glasshouse corn (figure 6.13) indicated to a limited extent an initial increase in P concentration followed by a decline in relation to increasing rates of S° application. If the critical P tissue concentration is taken to be 2,500 and 3,000 µg/g for corn plants and whole wheat plants respectively (Melsted *et al.*, 1969), then these comments may be appropriate. Corn responded positively to increasing rates of S° by increasing its tissue concentration of P to above the critical level of 2,500 µg/g at S° rates of 15 t/ha and above for the field experiment (figure 6.12). With glasshouse trials however, only brackish water irrigated P fertilized corn at S° rate of 60 g/kg soil, achieved 2,500 µg P/g tissue concentration (figure 6.13). Perhaps the soil physical problems encountered in the distilled water set, with the inherently low P soil availability, hindered plant accumulation of P. Wheat tissue P concentration reported here are for the grain and the straw separately. Nevertheless neither had P concentrations exceeding the critical 3,000 µg/g level (Melsted *et al.*, 1969). Furthermore, the grain tissue concentration of P was maintained at about 2,500 µg/g regardless of the S° rate, while those for the straw portions steadily increased in response to the increasing S° rates. It has been suggested that wheat plants can only develop viable grains if they contain a minimum P concentration of about 2,500 µg/g and when P availability was restricted this would normally result in less grains being developed.

Fe tissue concentration for corn in the two glasshouse trials and those of the field increased in response to S° rates in similar fashion (figures 6.14 and 6.15

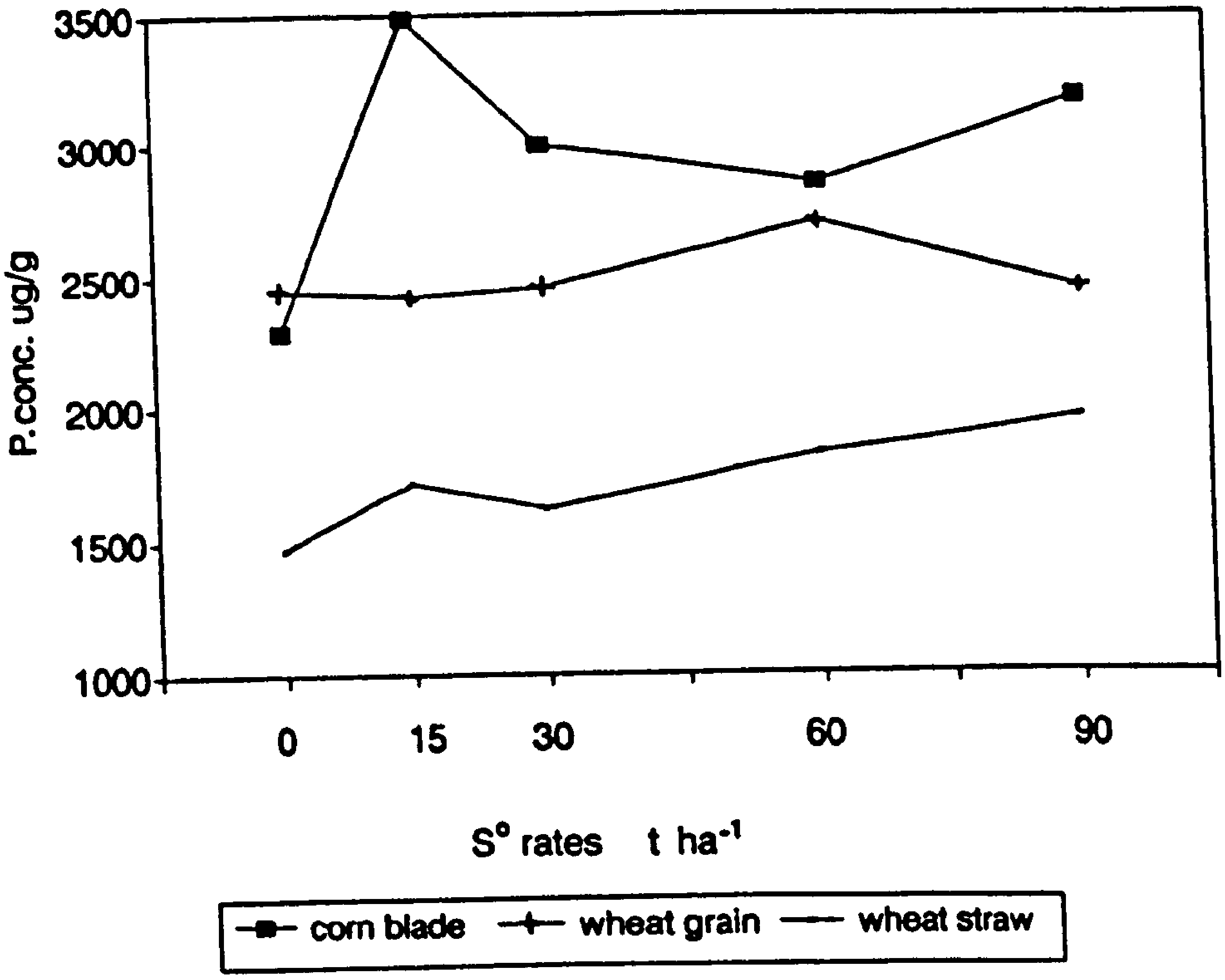


Fig.6.12 Effect of S° on various plant P tissue concentration grown in S° treated field.

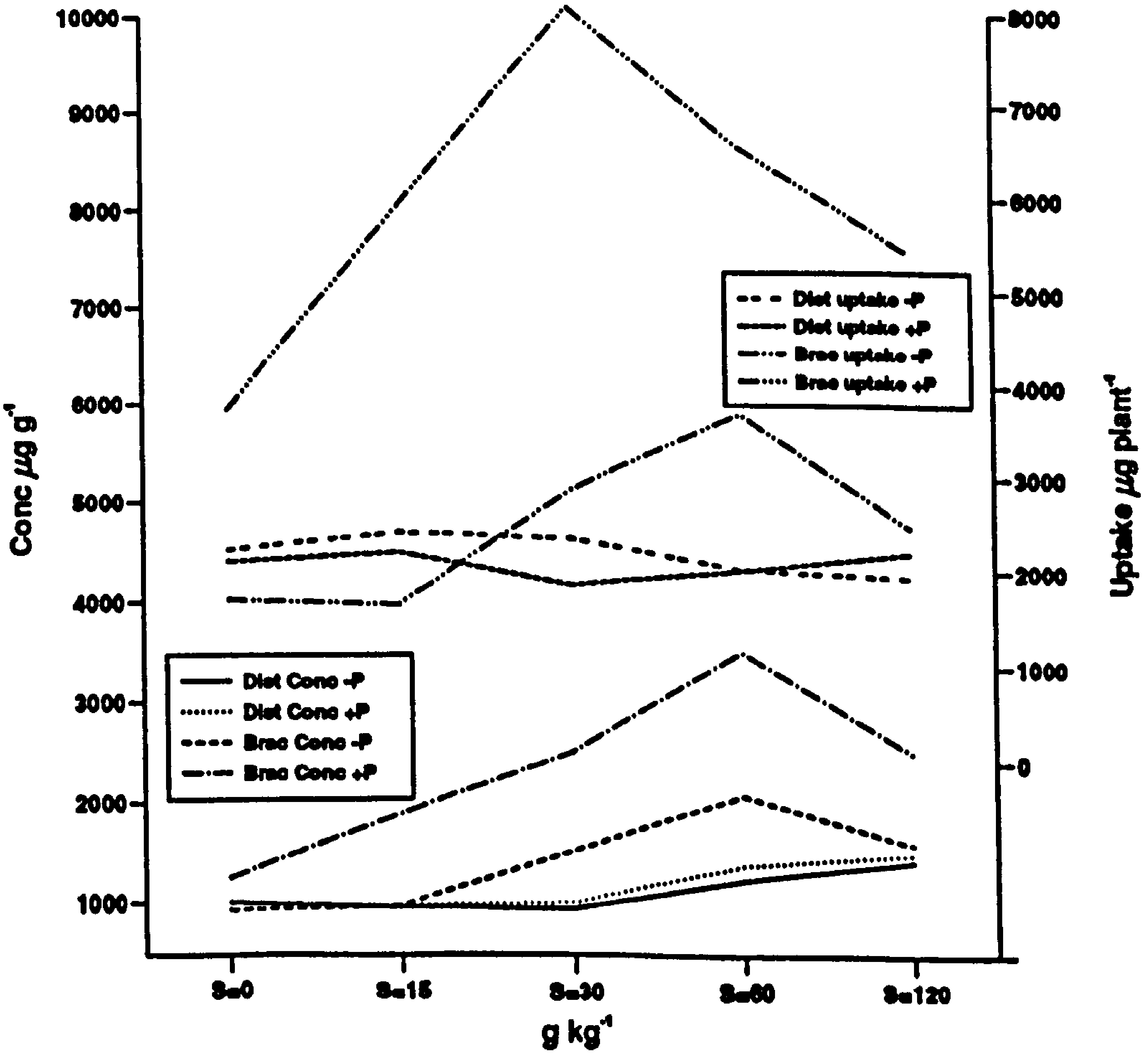


Fig.6.13 Effect of S° on maize plant P tissue concentration and uptake under distilled or brackish irrigation with or without P fertilizer.

respectively). Furthermore, none had its tissue concentration levels below the reported critical level of 25 µg/g (Melsted *et al.*, 1969) even for those not treated by S° or fertilized with $FeSO_4$. A possible explanation for the higher Fe tissue concentration while clear chlorosis was visible may be that this Fe was biologically inactive. Patel *et al.* (1977) reported a lack of any relationship between Fe tissue concentration and chlorosis symptoms. Chlorosis seems to be due to an inactivation of metabolic Fe possibly by biological and/or chemical means, however these conditions could result in greater Fe adsorption thus the higher Fe tissue accumulation (Singh, 1970). It is known that many factors such as other elemental concentrations, environmental conditions and plant enzymtic activity can affect Fe metabolism, mobility and absorption. However these plant physiological relationships are beyond the scope of this study.

Zinc tissue concentration for the various plant parts (figures 6.14 and 6.15) were consistently above the critical level of 15 µg/g (Melsted *et al.*, 1969), with the exception of wheat straw (figure 6.15). Moreover, these levels did not bear any relationship to the rate of S° treaments. It seems that, as had been observed in the DTPA-Zn extraction, plant Zn availability and absorption was not greatly affected by the S° treatments.

Plant tissue concntrations of Mn responded positively to S° treatments and their levels were well above the reported critical levels (15 and 30 µg/g for corn blades and whole wheat plants, respectively) (Melsted *et al.*, 1969). These increases, however were not as large as increases that were measured in DTPA-Mn extraction, in response to increasing rates of S°. The tissue Mn concentration levels about doubled (figures 6.14 and 6.15) whereas in the soil their DTPA-extraction levels increased by seven fold (figures 6.9, 6.10 and 6.11) in response to S° treatments. It could be that Mn was not a limiting nutrient and the plants absorbed little more than their requirement.

Statistical correlation between each element soil extraction and plant tissue

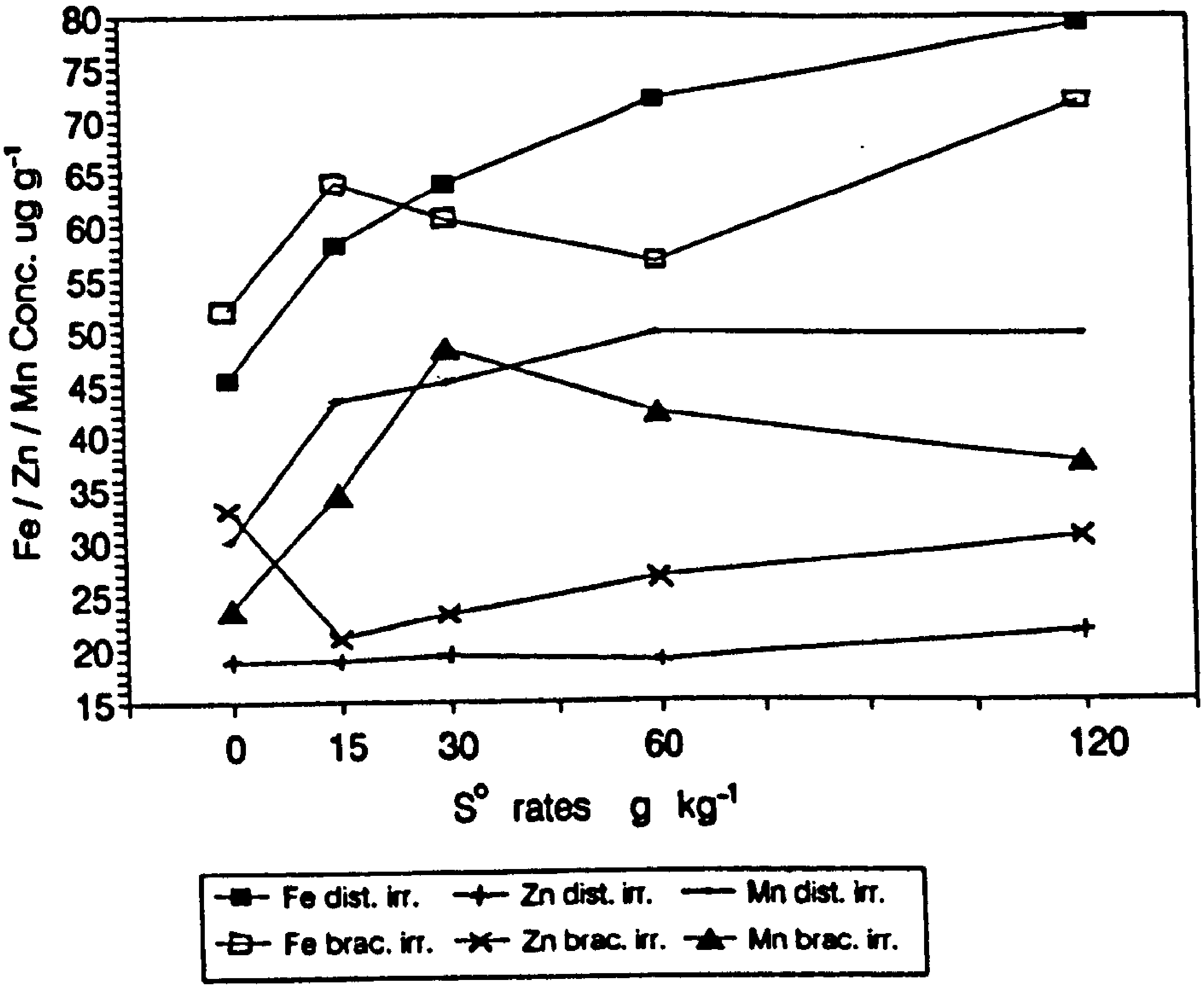


Fig.6.14 Effect of S° on Fe, Zn and Mn concentrations for maize irrigtaed with distilled or brackish water.

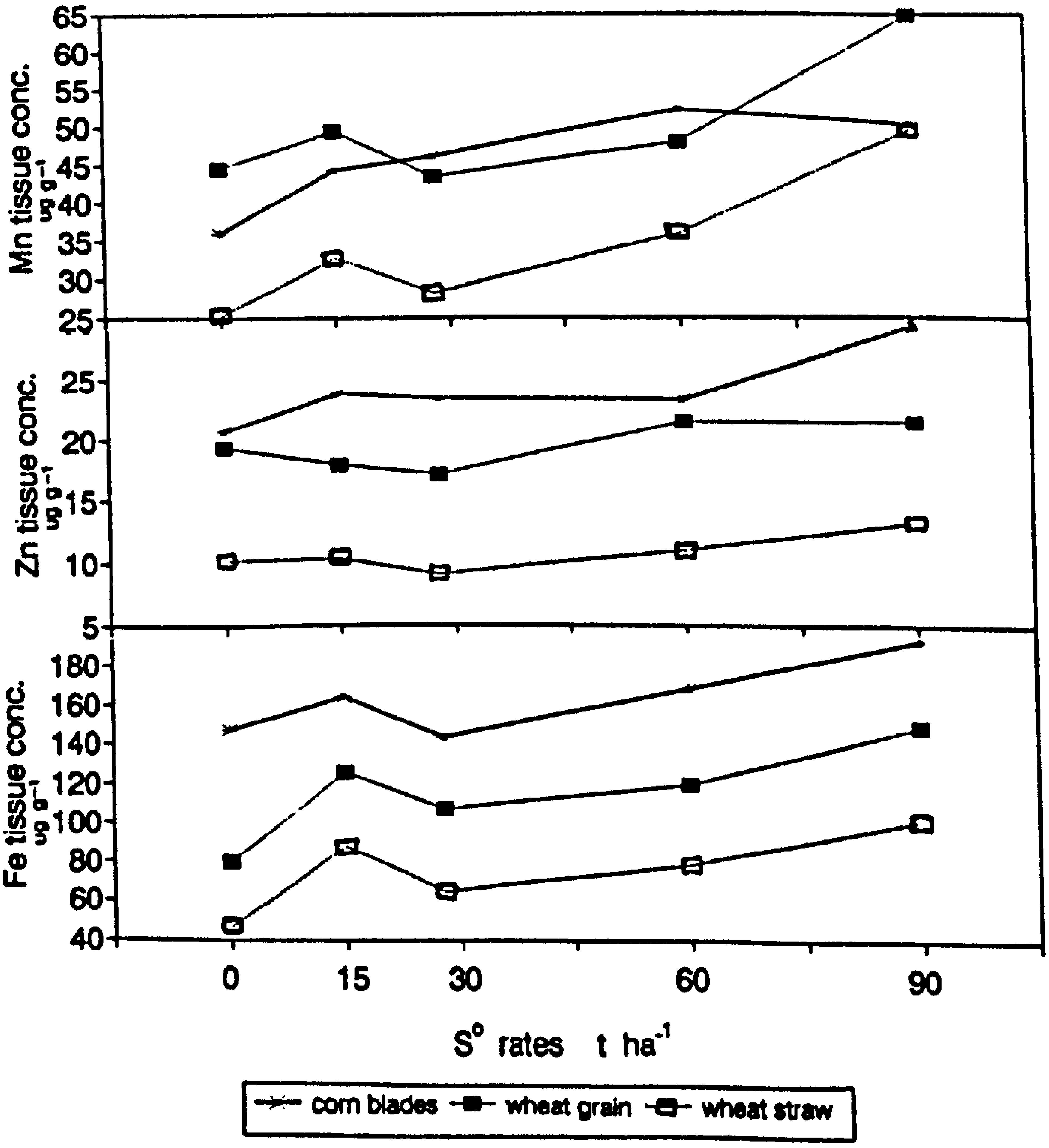


Fig.6.15 Effect of S° on Fe, Zn and Mn concentrations in various plant parts grown in the field.

concentration or plant uptake was quite poor and mostly insignificant. Positive correlation $p<0.05$ was found only for field corn tissue P concentration, wheat straw P and Mn concentration, and tissue Fe concentration for brackish water irrigated corn. These results, however, were not surprising, they were confounded on the one hand by improvements in some elemental plant availability, while on the other hand, plant yields were declining, i.e. as plant size decreases tissue elemental concentration may increase (Jarrell and Beverly, 1981). Therefore plant elemental tissue concentration might not be an appropriate indication of $S^{\bullet}$ treatment in this study. Plant uptake which combines elemental tissue concentration with plant yields was also difficult to assess because of the opposite direction of each component. Table 6.4.2 expresses plant yield as a percentage of the control for both glasshouse sets and for field grown wheat in the grain and straw portions. For most cases there was no significant decline in yield at treatments S_2 and S_3 corresponding to 25 and 50% of the theoretical $CaCO_3$ neutralization power. However the trends were downward. At the higher $S^{\bullet}$ rates (S_4 and S_5) the yield had declined by 25 to 35 percent of the control. On the other hand, when averaging all plant uptake of P, Fe, Zn and Mn as a percentage of the control (S_1) (table 6.4.2) each element responded in a different way. While P uptake steadily declined, Fe increased by 15 to 65%. Zinc uptake declines were moderate with the exception of the highest $S^{\bullet}$ treatment S_5. Mn uptake behaved as if independent of $S^{\bullet}$ treatment. Nevertheless, treatment S_2 (lowest $S^{\bullet}$ application rate) consistently resulted in the highest accumulation for all elements with the exception of Zn which declined by 5%. When considering whole wheat plant uptake of P, Fe, Zn and Mn (figure 6.16, p182), similar observations were possible. $S^{\bullet}$ application at a rate of 15 t/ha caused greater uptake of P and Fe, while Zn and Mn uptake levels did not vary much when compared with the other $S^{\bullet}$ application rates. Other published studies on elemental concentration or uptake are difficult to compare. Not only were the

Table 6.4.2 Plant yields expressed as a percentage of the control (S_1) for distilled and brackish water irrigated corn and field wheat, and P, Fe, Zn and Mn uptake of all plants averaged as a percentage of control treatment (S_1)

Treatment	Yield % of control				elemental uptake % of control			
	distilled	brackish	wheat (grain)	wheat (straw)	P	Fe	Zn	Mn
S_1	100	100	100	100	100	100	100	100
S_2	92	98	101	95	104	163	95	112
S_3	92	81	93	89	95	114	85	89
S_4	58	65	72	72	84	106	84	85
S_5	62	64	64	75	74	123	76	103

conditions different but often the S° application rates were not as high as those used in this study. However in the reports of relatively high S° treatment rates, responses were usually not consistent and did not always correspond to the findings in this study. In a study where the highest S° rates were equivalent to treatment S_3, crop (palm seedlings) yield decreases were similar to those in this project and palm leaf P concentration increased in a similar manner (Abo-Rady *et al.*, 1988) but at higher S° rates it did not decline. On the other hand while Fe tissue concentration levels in this study increased by 50 to 100%, in their study even though S° rates were lower they reported a massive 4-7 fold increase in tissue Fe concentration. Zn levels were in line with this study, whereas tissue Mn concentration in this study increased by a moderate 50-70% (figures 6.14 and 6.15) in their analysis and there were increases from about 15 to more than 200 and 350 μg/g for the two soils they studied. Procopiou *et al.* (1976) also used high S° rates comparable to those used in this study. However in their case there were increases in yield. Moreover elemental tissue concentration was more or less in line with the findings of this study with the exception of Mn, which was higher than the levels reported here. However, they used soybean as a test crop and it could be that this plant has a greater tolerance and/or requirement for tissue Mn.

One major observation was the consistent lack of yield improvement with S° treatment and a large decline in yield at higher S° rates. Explanations for these responses are mostly speculative but some of the most likely reasons are briefly discussed below.

1. Soil salinity; as has been already discussed the E.C. of the soils 1:2 extract as an indicator of their salinity status had increased from 5 to 10-12 dS/m (figure 6.6). This could be the reason for the yield decline. However, comparing salinity levels with those in the literature regarding crop yields was difficult since the E.C. values measured here were of 1:2, soil suspensions and were not saturation

extracts (tables 6.3.1.3.1-4). It may be that for this extremely sandy soil, saturation extract salinity would be higher. However, since the only added anions were those of SO_4^{2-} (product of S° oxidation), lower soil:water ratio as expected in saturation extracts would be most unlikely to contain higher concentrations of SO_4^{2-} due to the fact that this anion would be controlled by the solubility product of gypsum. It could be that sulphate salts other than $CaSO_4$ were formed i.e. Na_2SO_4 or K_2SO_4 but these salt cation inputs would be fixed in this experiment with the exception of those on the exchange sites. Hassan *et al.* (1970_{a+b}) reported decreased yield as EC_e increased above 12, they also indicated a negative effect of salinity on macro/micro-nutrient uptake. Nevertheless, future measurement of soil extract salinity components would be necessary to understand their equilibria especially with regard to soil management. Other studies had indicated as shown here that S° amendment could lead to increases in soil salinity (Bole, 1986; Abo-Rady *et al.*, 1988; Modaihsh *et al.*, 1989) and moreover it was suggested that this was the reason for lower palm seedling yields (Abo-Rady *et al.*,1988). It has been reported that excessive salinity could reduce plant absorption of some nutrients such as N and Fe and this could contribute to lower yields (Amer *et al.*, 1964; Dahiya and Singh, 1979).

2. Manganese toxicity; DTPA-Mn extraction had large increases in relation to S° application (figures 6.9, 6.10 and 6.11), and furthermore plant tissue concentration of Mn also increased (figures 6.14 and 6.15). Could this then be the reason for reduced plant yield? The answer is not clear. There are no generally accepted levels of tissue Mn concentration associated with known toxicity symptoms. In some of the literature there were reports of higher Mn tissue concentrations with no problems of lower yield (Procopion *et al.*, 1976), while others reported tissue concentrations in excess of 1,000 $\mu g\ Mn\ g^{-1}$ (Khattak and Jarrell, 1989), and they suggested potential toxic effects. Soil DTPA-Mn levels although higher than the critical plant required limits were not unusual for

agricultural soils (Sillanpaa, 1982). However, the possibility of direct Mn-toxicity or indirect antagonism reactions with other nutrients could not be ruled out. Attempts to find a correlation between plant yield and Mn soil or tissue concentrations were not statistically successful. Similarly comparing Fe/Mn ratios both in the soil extracts and plant tissue with yield indicated no significant relation to yield decline. Other studies have suggested a relationship between Mg/Mn ratio with respect to crop Mn toxicity tolerance (Goss *et al.*, 1992; Goss and Carralho, 1992) with a ratio great than 112 required to ensure that plant growth would not be affected by Mn-toxicity. In the future, such possible negative effects of increased Mn availability should be investigated, especially with the simultaneous changes to other soil ions.

3. Elemental sulphur and its oxidation products caused potential toxicity; S° on its own would be considered non-toxic to plants due to its inert nature, however S° would be rapidly transformed into various S-oxide products. Thiosulphate ($S_2O_3^{2-}$) and tetrathionate ($S_4O_6^{2-}$), which are intermediates in the oxidation of S°, have known phyto-toxicity characteristics (Nor and Tabatabai, 1972). Their presence in the soil would however be short-lived due to their rapid conversion into sulphate (SO_4^{2-}). As mentioned earlier, with the high rates of S° used in this study there could be a persistence of some of these intermediates and this may have contributed to yield reduction. Future studies should investigate this possibility.

High soil SO_4^{2-} levels may result in an accumulation of S in plant tissue. It has been suggested that there could be an interaction between N and S (Aulakh *et al.*, 1980; Randall *et al.*, 1981) and any imbalances may lead to yield reduction. An optimum ratio of available N to available S in the soil was estimated to be 7 to 1 (Janzen and Bettany, 1984). In the present study high dosage of NO_3^- or N type fertilizer was used. However no N:S ratio was measured in the soil solution. Furthermore, the soil was characterized by $CaSO_4$ saturation (gypsiferous) even prior to S° application, and coupled with the infusion of more SO_4^{2-} through the irrigation water (except in the distilled water irrigated glasshouse experiment) would maintain a constant level of SO_4 due to $CaSO_4$ precipitation. Provided that Ca and/or Mg ions were not limited additional SO_4^{2-} (from S° oxidation) would simply precipitate. Calcium would be expected to increase in the active dissolution of soil calcite in response to the acidification of the soil. Nevertheless, the concept of N:S ratio should be further investigated with emphasis on tissue concentrations of these elements and any trends in yield response.

4. Limitation of P availability; although P had low plant availability and recoverability in calcareous soils, the changes brought about by S° oxidation may have accentuated this problem. High microbial populations associated with S° oxidation may imobilize P due to greater competition for the limited P supply. This would be related to the rates of S° used and to time as substrate exhausted P would be released.

Another change that could reduce P availability might be the increases in Fe and Al oxides and Ca ions which may increase P adsorption/precipitation. These conditions were clearly found at higher rates of S° application and this may have decreased plant P availability thus causing a reduction in plant growth.

These negative effects of S° and perhaps others may have individually or collectively caused the yield reductions.

6.5 Conclusion

Soil amendment with S° was conducted with the anticipation that some of the problems presented in this calcareous soil would be reduced, especially the low plant availability of P and of micronutrients. S° had been applied at rates that could eliminate from 1/4 to all the $CaCO_3$ contained in the soil. These high rates of S° application resulted in mixed responses some were desirable, but others were not. The effect of S° on plant-P nutrition showed some benefit, but only at moderate rates of S°. At higher rates both P-"availability" extracts (Olsen test) and plant-P absorption declined. There seems to be some potential to improve soil-P status and plant-P nutrition by the use of S°. Rates however, have to be low so that changes in the Fe, Mn and Al oxide and in newly released Ca would be minimised. Therefore an application of about 10 t/ha to this soil should increase P availability and recoverability. Long term effects, however, could be problematic if repeated annual applications might give results similar to the negative impact that high rates of S° had on plant yield and P-nutrition. It could be speculated that Ca-ion solubility would increase since it would be controlled by gypsum instead of the calcite soil fraction, and therefore increases in P-Ca precipitation might occur. The influence of metal oxides on P-adsorption in the long term would be difficult to judge. It is not clear if low rates of S° could transform soil metal oxide/hydroxide minerals to forms that have higher P affinity, apart from Mn-oxides. Nevertheless, from the preliminary results of this study, application of S° in low amounts could be beneficial to crop quality since it had improved its P-content. Furthermore, although yield did not increase at these rates it did not however cause lower plant growth.

Effects of S° on Fe were the reverse of those on P. At the lower rates of S° application Fe availability (DTPA-extraction) was not responsive. Higher rates on the other hand did increase both soil Fe-extractability and plant tissue Fe concentration, but it reduced plant yields. The effect of S° on Fe might be indirect by creating conditions that can facilitate changes on Fe mineralogy. If acidic and/or reduced environment were the prerequisites for this Fe transformation, then high S°/soil ratios would be needed. Plant Fe requirements could be satisfied by part of the root system if Fe in the vicinity was adequately supplied and therefore increasing Fe availability in fractions of the entire rooting zone might be sufficient to meet plant needs. Using S° in localized zones at higher concentrations to facilitate Fe transformation could be the solution to Fe deficiency. This concept had been suggested by Wallace and Mueller (1978) and Razeto (1982), but it would only be applicable to perennial trees and shrubs, while for field crops especially small grains or forage legumes partial localised acidification probably would not be practical. Short crop season and field management practices such as discing and ploughing would dilute the desired effect of S° amendment in improving Fe availability. Nevertheless using S° in combination with Fe salts in drilled holes a short distance from the trunk of orchard or vine type crops grown on Fe deficient calcareous soils would from the findings of this study provide economical and practical solutions. Zinc reaction to S° application was not extensive and no clear benefit or harm to its plant availability could directly be attributed to the S°. Mn, on the other hand, had a clear response to S° even at the lower rates of application. Its improved availability, however, could be toxic or cause a number of nutritional imbalances. Its relation to other ions both in the soil and plant deserves further investigation. If as has been suggested Mg/Mn ratio plays an important role in reducing the potential toxic Mn effects at higher concentrations, the soil Mg status should be carefully assessed. Changes to Mg solubility, exchange and equilibrium with other soil constituents due to the acidification by S° were not monitored in this study. Since the calcite fraction of the soil was primarily $CaCO_3$, then increases in soluble Mg were unlikely. High Ca ion concentrations however, would affect the exchange equilibrium and this may have shifted additional Mg into soil solution.

The increased ionic strength of the soil solution directly and indirectly from S° oxidation would have had an adverse effect on plant growth. To reduce this salinity problem by means of leaching was not possible with the available water supply, since the irrigation water contained levels of SO_4^{2-} close to those of dissolved gypsum and this water could not dissolve and carry away any additional Ca or Mg ions. It might however remove soluble Na and K ions. Although the soil of this study had no particular problem with sodicity, the increased Ca ion concentration in response to S° oxidation could form a practical solution to sodic soils. Use of gypsum salts on sodic soil has been practised before, but S° could be preferable. It would be needed in less volume, and the generated acidity would be greatly beneficial in reducing the extreme alkaline conditions of sodic soils. This however, would require sodic soil that contained an appreciable amount of $CaCO_3$. The Ca ions released would help in improving the soil physical structure and provided that a good supply of quality water was available, increased salinity could be eliminated.

The incorporation of S° in this soil was assumed to shift its pH and $CaCO_3$ content downward in a linear fashion. However, the soil pH did not decline until the greater portion of the $CaCO_3$ had dissolved. Based on this, soil pH under calcareous conditions could not be used to judge soil acidification. Furthermore, the decline in $CaCO_3$ content did not reflect the extent of the decrease in its activity. The activity of $CaCO_3$ would be related to its surface area and therefore, the procedure developed in this study to measure effective $CaCO_3$ size fraction merits further improvement and assessment. Its simplicity, rapidity, low cost and the need for only basic laboratory instruments could make it a useful routine laboratory exercise., particularly for soils containing gypsum.

Oxidation of S° in the soil was quite rapid. Under a wide range of temperature and moisture levels it has been successfully oxidized. It also needs adequate oxygenation, but the micro-organisms responsible were not identified in this study. Furthermore, oxidation rates were measured indirectly, which imposed certain limitations. The newly developed procedure utilizing HPLC to measure the remaining unoxidized S° might add greater accuracy in assessing oxidation rates.

The changes that occurred to some of the physical and chemical characteristics of this soil when S° was incorporated were profound. Soil $CaCO_3$ content and activity were greatly reduced, and at this stage soil pH also declined. Salinity and soil gypsum contents had simultaneously increased. The elements that were studied showed various responses, and there may be other elements (eg Mg^{2+}) that had been affected but were not investigated and all must be examined as they can directly or indirectly affect plant growth potential.

7. GENERAL CONCLUSION AND RECOMMENDATIONS

The purpose for undertaking this work was to improve forage production to meet specific market requirements. As stated one of the constraints facing crop production was the calcareous nature of the available soil with its problems of limited nutrient availability. The two management practices utilised in these studies to alleviate the problem of some nutrient deficiencies have shown some strong possibilities for increasing their phyto-availability. The use of pyrophosphate additives with normal phosphorus fertilisation practices improved the element extractability ($NaHCO_3$-P), and more importantly crop uptake of this element. Plant growth increased in greater proportions when P was supplied in a way that incorporated small amounts of PP. In the field experiment, the soil had such a build up of P from previous applications, that the $NaHCO_3$-extraction P test indicated plant supplies were adequate. Therefore, it is reasonable to suggest that generous P fertilisation could satisfy crop requirements. Nevertheless, in the same field experiments, wheat grain yields were higher with additional P fertilisation, however, yield did not further increase with the incorporation of PP. If smaller amounts of PP could maintain higher P availability, then this could form the basis for more efficient P fertilisation regimes. In addition to the improved P-fertiliser recoverability, PP had clear advantages in improving soil zinc supplies. This element (Zn) is deficient in the soil. Application of $ZnSO_4$ as fertiliser did not improve Zn-soil status whereas, the presence of PP even in small amounts did change the DTPA-Zn extractability to "adequate" levels. This clearly was supported by higher plant Zn-uptake.

The second approach of incorporating elemental sulphur (S°) as soil acidulent has shown mixed results. In general, high rates corresponding to 100% or more of $CaCO_3$ neutralisation power induced lower plant growth, and therefore, could not be recommended on this soil, except possibly in the course of soil reclamation. Furthermore, with regard to P and Zn phyto-availability, the response to S° addition was too small with questionable benefits. On the other hand, S° had profound effects on soil iron (Fe) and manganese (Mn), but soil DTPA-Fe extractability increased to "adequate" levels only at high S°-soil ratios. This could be accomplished in localised portions of the whole soil, but would only be practical with perennial types of crop. This soil had a clear Fe-deficiency problem confirmed from soil extracts and plant symptoms. The choice of plants used (Fe-inefficient) in this study was deliberate so that soil treatments and subsequent plant responses could be identified. For improved forage production, the use of "Fe-efficient" cultivars or the use of soil applied chelates or foliar sprays should be evaluated. Soil-Mn levels as shown from DTPA-extraction indicate that this soil had no Mn-deficiency problems, but if with time there was depletion of this element, the use of S° could improved its plant availability. The use of S° in low rates alone or incorporating small amounts of Mn-salt could maintain adequate soil supply of this nutrient.

In addition to these specific recommendations for crop production on this soil, other areas of interest were identified from these studies and deserve further investigation:

1. What would be the ideal level of PP/OP mixture necessary for optimum crop growth for this and other soils that had P-fixation properties?
2. What should be the form and means of producing P-fertiliser so that it contains PP, that would give the best results in increasing fertiliser recoverability?
3. The nature of PP reaction in maintaining higher P and Zn recoverability under calcareous conditions needs more investigation, specifically mechanisms and durability.
4. If the active presence of PP is a prerequisite for its influence on soil P and Zn, then preventing its hydrolysis to OP through any inhibition processes would be greatly beneficial and needs to be studied.
5. The use of S° on this soil produced some specific problems. However, it did

reduce soil $CaCO_3$ activities and soil pH and therefore long term changes in some of the physical and chemical properties should be monitored.

6. Crystalline soil-Fe had been proposed to transform to an amorphous form as a result of S° oxidation. This area of Fe-mineralogy needs further investigation perhaps by I.R. techniques to indicate what parameters and what levels would be required for this transformation. This information could form the basis for S° recommendation where it is to be used to correct Fe-deficiency.

7. Where S° was used as soil acidulent or in S-deficient soil, more information on its rate of oxidation and which micro-organism sections were responsible need to be assessed especially with the recent advances in direct S° measurement.

8. Many possible nutrient antagonisms, such as P/Zn, P/Fe, Fe/Zn, Mn/Zn and Fe/Mn could have arisen from changes produced in response to the soil treatments utilised in these studies. Further work is needed at both soil and plant levels to understand the nature of these relationships.

9. The reduction in plant growth at higher S° application rates were suggested to have resulted from increased salinity levels, toxic build up of Mn and S-byproducts, or low P-availability. All these areas need further confirmation. In respect of soil salinity, if leaching could be successful and this allowed a recovery in plant growth, then the use of S°, even at higher rates could be beneficial at least with regard to Fe-deficiency. On the other hand Mn ratio(s) to other elements needs to be assessed. S° oxidation intermediates, which could be the reason for the plant growth decline should disappear when all applied S° had transformed. Higher SO_4^{2-} which was suggested to interfere with plant NO_3^- uptake, could be reduced by soil leaching providing low SO_4^{2-} water was available. As with low P availability through microbial immobilisation, or fixation with Fe, Mn or Al oxides/hydroxides this could be rectified by additional P application especially if it included PP.

10. In these studies only a few plant nutrients were investigated. It is conceivable

however, that the status of other soil elements both essential for plant growth or those elements that could be phytotoxic at higher concentration had changed.

All these possibilities could therefore affect crop productivities as a result of these soil treatments. In these studies, limited aspects were examined and further investigations are still needed for fuller explanations.

REFERENCES

Abo-Aquad A.G., Fareed M., Warood M., Hussan N., Al-Shorebgy M., Baiomy B. and Al-Wahshi A. (1984) "Present and future assessment of animal feed resources in the Arab World". *Arab Centre for the Study of Arid Land Development (A.C.S.A.D.) Regional report.*

Abo-Rady M., Duheash O., Khalil M. and Turjoman A.M. (1988) "Effect of elemental sulphur on some properties of calcareous soils and growth of date palm seedlings". *Arid Soil Research and Rehabilitation* **22** 121-130.

Agriculture and Fisheries Resources Authority (A.F.R.A.) "Public Authority for Agriculture and Fisheries Affairs". *Annual Report 1985.*

Al-Abdul-Razzak F.H. (1984) "Marine resources of Kuwait. Their role and development of non-oil resources". Pubs: University of Kuwait Press.

Al-Awadi E.A. (1988) "Stratigraphic study of Dammam Formation in Umm-Gudair area, Kuwait. A Thesis in Geology". *MSc University of Kuwait.*

Amer,F., ElGabaly,M. and Balba,A. (1964) "Cotton response to fertilization on two soils differing in salinity." *Agronomy Journal* **56** 208-211.

Amer F., Khalil M.A. and Diab G.S. (1982) "Agronomic effectiveness of pyrophosphate as an additive to monocalcium phosphate and diammonium phosphate in calcareous soils" *Soil Sci. Soc. Am. J.* **46** 579-583.

Amer F., Mahmoud A.A. and Sabet V. (1985) "Zeta potential and surface area of calcium carbonate as related to phosphate sorption." *Soil Sci. Soc. Am. J.* **49** 1137-1142.

Amer F. and Mostafa H.E. (1981) "Effect of pyrophosphate on orthophosphate reactions in calcareous soils" *Soil Sci. Soc. Am. J.* **45** 842-847.

Amer F. and Ramy A. (1971) "On the possibility of characterizing calicium phosphate in calcareous soils by isotopic exchange". *Journal of Soil Sci.* **22** 267-274.

Arslan A. and Dutt G.R. (1993) "Solubility of gypsum and its production in aqueous solutions of mixed electrolytes". *Soil Science* **155(1)** 37-47.

Asher L.E. and Bar-Yosef B. (1982) "Effects of pyrophosphate, EDTA and DTPA on zinc sorption by Montmorillonite". *Soil Sci. Soc. Am. J.* **46** 271-276.

Attoe O.J. and Olson A.R. (1966) "Factors affecting rate of oxidation of elemental sulphur and that added in rock phosphate-sulphur fusions". *Soil Science* **101** 317-324.

Aulakh M.S., Pasricha N.S. and Sahota N.S. (1980) "Yield, nutrient concentration and quality of mustard crops as influenced by nitrogen and sulphur fertilizers". *Journal of Agriculture Science* **94** 545-549.

Bar-Tal A., Bar-Yosef B. and Chen Y. (1988) "Effects of fulvic acid and pH on zinc sorption on Montmorillonite" *Soil Science* **146** 367-373.

Bar-Yosef B. (1979) "pH dependent zinc adsorption by soils" *Soil Science Society America Journal* **43** 1095-1099.

Bar-Yosef B. and Asher L.E. (1983) "Reactions of pyrophosphate in soils and its effects on zinc sorption at various pH levels". *Soil Science* **136**(2) 82-88.

Barrow N.J. (1987) "The effect of phosphate on zinc sorption by a soil". *Journal Soil Sci.* **38** 453-459.

Barrow N.J. and Shaw T.C. (1979) "Effects of ionic strength and nature of the cation on desorption of phosphate from soil". *J. Soil Sci.* **30** 53-65.

Bascomb C.L. (1961) "A calcimeter for routine use on soil samples". *Chemy Ind.* 1820-187.

Bascomb C.L. (1982) "Particle size analysis (p.15-18) in "Soil survey laboratory methods" (Avery B.W. and Bascombe C.L. eds) *Soil survey technical monograph no.6.*

Behbehani A.S.K. (1980) "Structural and Petrographic analysis of Mishrif member of the Magura Formation in Hout, Dorra and Khafji oil fields. Offshore Kuwait-Saudi Arabia divided neutral zone". *MSc Thesis, University of Toledo* p.44.

Bell L.C. and Black C.A. (1970) "Crystalline phosphates produced by interaction of orthophosphate fertilizers with slightly acid and alkaline soils." *Soil Sci. Soc. Am. Proc.* **34** 735-740.

Berner,R.A. and Morse,J.W. (1974) "Dissolution kinetics of calcium carbonate in sea water." *Am. J. Sci.*, **274**108-134.

Blanchar R.W. and Hossner L.R. (1969) "Hydrolysis, sorption and plant uptake of phosphorus from 32 corn belt soils treated with ortho, pyro, tripoly and trimetaphosphate". *Soil Sci. Soc. Am. Proc.* **33** 622-625.

Bole J.B. (1986) "Amelioration of a calcareous solonetzic soil by irrigation, deep ripping and acidification with elemental sulphur". *Can. J. Soil Sci.* **66** 347-356.

Borggaard O.K. (1983) "The influence of iron oxides on phosphate adsorption by soil". *J. Soil Sci.* **34** 333-341.

Borggaard O.K., Jorgensen S.S., Moberg J.P. and Raben-Lange B. (1990) "Influence of organic matter on phosphate adsorption by aluminium and iron oxides in sandy soils". *J. Soil Sci.* **41** 443-449.

Boswell F.C., Paker M.B. and Gains T.B. (1989) "Soil zinc and pH effect on Zn concentration of corn plants". *Commun. in Soil Sci. and Plant Anal.* **20** 1575-1600.

Bowen G.D. (1969) in Whittington W.J. (ed.) "Root Growth". Pubs: Butterworth, London.

Bromfield S.M. and David D.J. (1978) "Properties of biologically farmed manganese oxide in relation to soil manganese". *Aus. J. Soil Res.* **16** 79-89.

Brown J.L. (1981) "Calcium phosphate precipitation: Effects of common and foreign ions on hydroxyapatite crystal growth". *Soil Sci. Soc. Am. J.* **45** 482-486.

Brown A.L., Krantz B.A. and Eddings J.L. (1970) "Zinc on phosphorus interactions as measured by plant response and soil analysis". *Soil Science* **110**(6) 415-420.

Brummer G., Tiller K., Herms U. and Clayton P. (1983) "Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils". *Geoderma* **31** 337-354.

Bui E.N., Loeppert R.H. and Wilding L.P. (1990) "Carbonate phases in calcareous soils of western United States". *Soil Sci. Soc. Am. J.* **54** 39-45.

Burleson C.A., Dacus A.D. and Gerard C.J. (1961) "The effect of P fertilization on the Zn nutrition of several irrigated crops." *Soil Sci.Soc. Am. Proc.* **25** 365-368.

Burleson C.A. and Page N.R. (1967) "Phosphorus and zinc interactions in flax". *Soil Sci. Soc. Am. Proc.* **31** 510-513.

Chandhry F.M. and Loneragan J.F. (1972) "Zinc adsorption by wheat seedlings: I Inhibition by macronutrient ions in short-term experiments and its relevence to long-term zinc nutrition". *Soil Sci. Soc. Am. J.* **36** 323-327.

Chapman S.J. (1989) "Oxidation of micronized elemental sulphur in soil". *Plant and Soil* **116** 69-76.

Chen Y. and Barak P. (1982) "Iron nutrition of plants in calcareous soils". *Advances in Agronomy* **35** 217-240.

Cheniae G.M. (1970) "Photosystem II and O_2 evolution". *Ann. Rev. Plant Physiol.* **21** 467-498.

Christensen P.D. and Lyerly P.J. (1954) "Yield of cotton and other crops as affected by applications of sulphuric acid in irrigation water". *Soil Sci. Soc. Am. Proc.* **18** 433-436.

Clarke E.T., Loeppert R.H. and Ehrman J.M. (1985) "Crystallization of iron oxides on calcite surfaces in static systems". *Clays Clay Min.* **33** 152-158.

Clement L. (1978) "Sulphur increases availability of phosphorus in calcareous soils". *Sulphur in Agriculture* **2** 9-12.

Curtin D., Selles F. and Stepphuhn H. (1992) "Influence of salt concentration and sodicity on solubility of phosphate in soils". *Soil Science* **153(5)** 409-416.

Dahiya,S.S. and Singh,M. (1979) "Effect of salinity, alkalinity and iron sources on availability of iron." *Plant and Soil* **51** 13-18.

Dawood F.A. (1989) "Effect of high rates of sulphur on the $CaCO_3$ and $CaSO_4$ content of calcareous soils". *Plant and Soil* **120** 307-309.

Day P.R. (1965) "Particle fractionation and particle-size analysis ch.43 p.545-566 in "Methods of soil analysis" (Black C.A. ed). Pubs: Amer. Soc. Agron., Wisconsin.

DeLuca T.H., Skogley E.O. and Engels R.E. (1989) "Band-applied elemental sulphur to enhance the phytoavailability of phosphorus in alkaline calcareous soils". *Biology and Fertility of Soils* **7** 346-350.

Dewey III J.F., Pitman W.C., Ryan W.B.F. and Bonnin J. (1973) "Plate tectonics and evolution of alpine system" *Geol. Soc. Am. Bull.* **84** 3137-3180.

Dick R.P. and Tabatabai M.A. (1986) "Hydrolysis of polyphosphates in soils". *Soil Science* **142**(3) 132-140.

Dick R.P. and Tabatabai M.A. (1987) "Factors affecting hydrolysis of polyphosphates in soils". *Soil Science* **143**(2) 97-104.

Drouineau G. (1942) "Dosage rapide du calcaire actif de sols". *Ann. Agron.* **12** 441-450.

Eanes E.D., Gillessen I.H. and Posner A.S. (1965) "Intermediate states in the precipitation of hydroxyapatite". *Nature* **208** 365-367.

El-Mahi Y.E. and Mustafa M.A. (1980) "The effects of electrolyte concentration and sodium adsorption ratio on phosphate retention by soils". *Soil Science* **130** 321-325.

Elrashidi M.A. and O'Connor G.A. (1982) "Influence of solution composition on sorption of zinc by soils". *Soil Sci. Soc. Am. J.* **46** 1153-1158.

El-Zahaby E.M. and Chien S.H. (1982) "Effect of small amounts of pyrophosphate on orthophosphate sorption by calcium carbonate and calcareous soils". *Soil Sci. Am. J.* **46** 38-46.

El-Zahaby E.M., Chien S.H., Savant N.K., Vlek P.L.G. and Mokwunye A.U. (1982) "Effect of pyrophosphate on phosphate sorption and ammonia volatization by calcareous soils treated with ammonium phosphates". *Soil Sci. Soc. Am. J.* **46** 733-740.

Ellis R.Jr., Davis J.F. and Thurlow D.L. (1964) "Zinc availability in calcareous Michigan soils as influenced by phosphorus level and temperature." *Soil Sci. Soc. Am. Proc.* **28** 83-86.

Engelstad O.P. and Allen S.E. (1971) "Ammonium pyrophosphate and ammonium orthophosphate as phosphorus sources: Effects of soil temperature, placement and incubation". *Soil Sci. Soc. Am. Proc.* **35** 1002-1004.

Ergun H. (1969) "Reconnaissance soil survey". Report to the Government of Kuwait". *FAO/KU/TF17*, Mimeo, Rome.

Falatah A. and Schwab A.P. (1990) "Plant-available iron and zinc in a calcareous soil as affected by additions of sulphur and micronutrient fertilizer". *J. Fertilizer Issues* 7(2) 35-40.

Farnworth,J. and Ruxton,I.B. (1974a) "The effect of varying rates of phosphate application on the productivity and composition of Hasawei alfalfa grown in irrigated arid zone conditions." *U.C.N.W. and M.A.& W. S.A. Joint Ag. Res. & dev Proj.* **40** 1-16

Farnworth,J. and Ruxton,I.B. (1974b) "The effect of phosphate applications on yield and composition of forage barley and sorghum grown as reclamation crops in irrigated arid zone conditions." *U.C.N.W. and M.A. & W. S.A. Joint Ag. Res. & dev. Proj.* **46** 1-9.

Fleming A.L., Chaney R.L. and Coulombe B.A. (1984) "Bicarbonate inhibits Fe-stress-response and Fe uptake-translocation of chlorosis-susceptible soybean cultivars". *J. Plant Nutrition* 7 699-714.

Fourcassie F. and Gadet R. (1966) "Contribution à l'étude de l'efficacité des polyphosphates comme engrais phosphates". *Bull. Ass. Fr. Etude Sol* 8 2213-2237 cited in Singh Y. and Dartigues (1970) "Efficiency of polyphosphates and orthophosphates in zinc-deficient soils". *Plant and Soil* **32** 397-411.

Fox R.L., Atesalp H.M., Kampbell D.H. and Rhoades H.F. (1964) "Factors influencing the availability of sulphur fertilizers to alfalfa and corn". *Soil Sci. Soc. Am. Proc.* **28** 406-408.

Frank S.J. and Fehr W.R. (1983) "Band application of sulphuric acid or elemental sulphur for control of Fe-deficiency chlorosis of soybeans". *Agronomy Journal* **75** 451-454.

Freeman J.S. and Rowell D.L. (1981) "The adsorption and precipitation of phosphate onto calcite". *J. Soil Science* **32** 75-84.

Freese D., Van der Zee S.E. and Van Riemsdijk W.H. (1992) "Comparison of different models for phosphate sorption as a function of the iron and aluminium oxides of soils". *J. Soil Sci.* **43** 729-738.

Garcia M.E. and Carloni L. (1977) "The effect of sulphur on solubility and forms of phosphorus in soil". *Agrochemica* **21** 163-169.

Garey G.L. and Barber S.A. (1952) "Evaluation of certain factors involved in increasing Mn availability with sulphur" *Soil Sci. Soc. Am. Proc.* **16** 173-175.

Gaur B.L., Singh H.G. and Cahoon G.A. (1971) "Effect of sulphur in the prevention of incipient iron chlorosis in corn. *Comm. Soil Sci. Plant Anal.*2(4) 259-265 cited in Kalbasi *et al* (1988) "Effect of sulphur treatments on yield and uptake of Fe, Zn and Mn by corn, sorghum and soybeans". *J. Plant Nutrition* 11(6-11) 1353-1360.

Geiger S.C. and Loeppert R.H. (1986) "Correlation of DTPA extractable Fe with indigenous propoerties of selected calcareous soils". *J. Plant nutrition* 9(3-7) 229-240.

Gilliam J.W. and Sample E.C. (1968) "Hydrolysis of pyrophosphate in soils: pH and biological effects". *Soil Science* **106** 352-257.

Giordano P.M., Sample E.C. and Mortvedt J.J. (1971) "Effect of ammonium ortho and pyrophosphate on Zn and P in soil solution". *Soil Science* **111**(2) 101-106.

Goss M.J. and Carvalho M.J.G.P.R. (1992) "Manganese toxicity: the significance of magnesium for sensitivity of wheat plants". *Plant and Soil* **139** 91-98.

Goss M.J., Carvalho M.J.G.P.R., Cosimini V. and Fearnhead M.L. (1992) "An approach to the identification of potentially toxic concentrations of manganese in soils". *Soil Use and management* 8(1) 40-44.

Griffin R.A. and Jurinak J.J. (1973) "The interaction of phosphate with calcite". *Soil Sci. Soc. Am. Proc.* **37** 847-850.

Griffin R.A. and Jurinak J.J. (1974) "Kinetics of phosphate interaction with calcite." *Soil Sci. Soc. Am. Proc.* **38** 75-79.

Gupta V.K. and Mehla D.S. (1980) "Influence of sulphur on the yield and concentration of copper, manganese, iron and molybdenum in berseem (*Trifolium alexandrinum*) grown on two different soils". *Plant and Soil* **56** 229-234.

Hamad M.E., Rimmer D.L. and Syers J.K. (1992) "Effect of iron oxide on phosphate sorption by calcite and calcareous soils". *J. Soil Sci.* **43** 273-281.

Harter R.D. (1983) "Effect of soil pH on adsorption of lead, copper, zinc and nickel". *Soil Sci. Soc. Am. J.* **47** 47-51.

Hassett J.J. and Jurinak J.J. (1971) "Effect of Mg^{2+} ion on the solubility of solid carbonates". *Soil Sci. Am. Proc.* **35** 403-406.

Hassan N. and Olson R.A. (1966) "Influence of applied sulphur on availability of soil nutrients for corn (Zea Mays L.) nutrition". *Soil Sci. Soc. Am. Proc.* **30** 284-286.

Hassan N.A., Drew J.V., Knudson D. and Olsen R. (1970a) "Influence of soil salinity on production of dry matter and uptake and distribution of nutrients in barley and corn: I Barley (*Hordeum vulgare L.*)". *Agron. J.* **62** 43-45.

Hassan N.A., Drew J.V., Knudson D. and Olsen R. (1970b) "Influence of soil salinity on production of dry matter and uptake and distribution of nutrients in barley and corn: II Corn". *Agron. J.* **62** 43-45.

Helyar K.R., Munns D.N. and Burau R.G. (1976) "Adsorption of phosphate by Gibbsite: I. Effects of neutral chloride salts of calcium, magnesium, sodium and potassium". *J. Soil Sci.* **27** 307-314.

Hoeft R.G. and Sorensen R.C. (1969) "Micronutrient availability in three soil materials as affected by applications of zinc, lime and sulphur". *Soil Sci. Soc. Am. Proc.* 33 924-928.

Holford I.C.R. and Mattingly G.E.G. (1975$_a$) "The high and low energy phosphate adsorbing surfaces in calcareous soils". *J. Soil Sci.* 24(4) 407-417.

Holford I.C.R. and Mattingly G.E.G. (1975$_b$) "Phosphate sorption by Jurassic oolitic limestones". *Geoderma* 13 257-264.

Holford I.C.R. and Mattingly G.E.G. (1975$_c$) "Surface areas of calcium carbonate in soils". *Geoderma* 13 247-255.

Holford I.C.R., Wedderburn R.W. and mattingly G.E.G. (1974) "A langmuir two- surface equation as a model for phosphate adsorption in soils". *J. Soil Sci.* 25 242-255.

Hons F.M., Stewart W.M. and Hossner L.R. (1986) "Factor interactions and their influence on hydrolysis of condensed phosphates in soils". *Soil Science* 141(6) 408-416.

Hossner L.R. and Melton J.R. (1970) "Pyrophosphate hydrolysis of ammonium, calcium and calcium ammonium pyrophosphates in selected Texas soils". *Soil Sci. Soc. Am. Proc.* 34 801-805.

Hossner L.R. and Phillips D.P. (1971) "Pyrophosphate hydrolysis in flooded soil". *Soil Sci. Soc. Am. Proc.* 35 379-383.

Hughes J.D. and Hashimoto I. (1971) "Triammonium pyrophosphate as a source of phosphorus for plants". *Soil Sci. Soc. Am. Proc.* 35 643-647.

Inskeep W.P. and Bloom P.R. (1986) "Calcium carbonate supersaturation in soil solutions of calciaquolls". *Soil Sci. Soc. Am. J.* 50 1431-1437.

Iyengar S.S. Martens D.C. and Miller W.P. (1981) "Distribution and plant availability of soil zinc fractions". *Soil Sci. Soc. Am. J.* 45 735-739.

Jafarzadeh A.A. and Burnham C.P. (1992) "Gypsum crystals in soils". *J. of Soil Sci.* 43(3) 409-420.

Jahiruddin M., Chambers B.J., Livesey N.T. and Cresser M.S. (1986) "Effect of liming on extractable Zn, Cu, Fe and Mn in selected Scottish soils". *J. Soil Sci.* 37 603-615.

Jahiruddin M., Livesey N.T. and Gresser M.S. (1985) "Observations on the effects of soil pH upon zinc absorption by soils". *Commun. in Soil Sci. Plant Anal.* 16(3) 909-922.

Janzen H.H. and Bettany J.R. (1984) "Sulfur nutrition of rapeseed I. Influence of fertilizer nitrogen and sulfur rates". *Soil Sci. Soc. Am. J.* 48 100-107.

Janzen H.H. and Bettany J.R. (1987$_a$) "The effect of temperature and water potential on sulphur oxidation in soils". *Soil Science* 144(2) 81-89.

Janzen H.H. and Bettany J.R. (1987$_b$) "Measurement of sulphur oxidation in soils". *Soil Science* 144(6) 444-452.

Jarrel,W.M. and Barerly,R. (1981) "The dilution effect in plant nutrition studies." *Adv. Agron.* 34 197-224

Jauregui M.A. and Reisenauer H.M. (1982) "Calcium carbonate and manganese dioxide as regulators of available manganese and iron". *Soil Sci.* 134(2) 105-110.

Jurinak J.J. and Bauer N. (1956) "Thermodynamics of zinc adsorption on calcite , dolomite and magnesite-type minerals". *Soil Sci. Soc. Am. Proc.* 20 466-471.

Kadry L.T. (1973) "Distribution of calcareous soils in the near east region, their reclamation and land use measures and achievements" p. 17-27 in "Calcareous Soils", FAO Bulletin 21.

Kalbasi M., Filsoof F. and Rezai-Nejad Y. (1988) "Effect of sulphur treatments on yield and uptake of Fe, Zn and Mn by corn, sorghum and soybeans". *J. of Plant Nutrition* 11(6-11) 1353-1360.

Kalbasi M., Manuchehri N. and Filsoof F. (1986) "Local acidification of soil as a means to alleviate iron chlorosis in quince orchards". *J. of Plant Nutrition* 9(3-7) 1001-1007.

Kalbasi M., Racz G.J. and Loewen-Rudgers L.A. (1978) "Mechanism of zinc adsorption by iron and aluminium oxides". *Soil Science* 125 146-150.

Kamen-Kaye M. (1970) "Geology and productivity of the Persian Gulf Synclinorium". *AAPG Bull.* 54(12) 2391-2394.

Kashirad A. and Bazargani J. (1972) "Effect of sulphur on pH and availability of phosphorus in calcareous soils, influence of sulphur and nitrogen on yield and chemical composition of corn" *Ztchr. F. Pflanzenernährung U. Boden Kunde* 131 6-13.

Kassler P. (1973) "The structural and geomorphic evolution of the Persian Gulf"in "The Persian Gulf" Purser B.H. (ed). Pubs: Springer-Verlag, Berlin. p.11-32.

Kastner M. (1970) "An inclusion hourglass pattern in synthetic gypsum" *American Mineralogist* 55 2128-2130 cited in Jafarzadeh A.A. and Burnham C.P. (1992) "Gypsum Crystals in Soils". *J. Soil Sci.* 43(3) 409-420.

Keller P. (1969) "The effect of sodium chloride and sulphate on sulphur oxidation in soil". *Plant and Soil* 30(1) 15-22.

Khan A.A. and Zende G.K. (1977) "The site for Zn-P interactions in plants". *Plant and Soil* 46 259-262.

Khasawneh F.E., Hashimoto I. and Sample E.C. (1979) "reactions of ammonium ortho and polyphosphate fertilizers in soils: II hydrolysis and reactions with soil". *Soil Sci. Soc. Am. J.* 43 52-58.

Khasawneh F.E., Sample E.C. and Kamprath E.J. (1980) "The role of phosphorus in agriculture". *Soil Sci. Soc. Am. Inc.*, Madison, Wisconsin.

Khattak R.A. and Jarrel W.M. (1988) "Salt-induced manganese solubilization in California Soils". *Soil Sci. Soc. Am. J.* 52 1606-1611.

Khattak R.A. and Jarrel W.M. (1989) "Effect of saline irrigation waters on soil manganese leaching and bio-availability to sugar beet". *Soil Sci. Soc. Am. J.* 53 142-146.

Khattak R.A., Jarrel W.M. and Page A.L. (1989) "Mechanism of native manganese release in salt-treated soils". *Soil Sci. Soc. Am. J.* 53 701-705.

Kittams H.A. and Attoe O.J. (1965) "Availability of phosphorus in rock phosphate-sulphur fusions". *Agronomy Journal* 57 331-334.

Krishnamurti G.S.R. and Huang P.M. (1992) "Dynamics of potassium chloride induced manganese release in different soil orders". *Soil Sci. Soc. Am. J.* 56 1115-1123.

Kuo S. and Lotse E.G. (1972) "Kinetics of phosphate adsorption by calcium carbonate and Ca-kaolinite". *Soil Sci. Soc. Am. Proc.* 36 725-729.

Lajtha K. and Bloomer S. (1988) "Factors affecting phosphate sorption and phosphate retention in descent ecosystem". *Soil Science* 146(3) 160-167.

Langin E.S., Ward R.C., Olson R.A. and Rhoades H.F. (1962) "Factors responsible for poor response of corn and grain sorghum to phosphorus fertilization". *Soil Sci. Soc. Am. Proc.* 26 574-578.

Larsen S. (1967) "Soil Phosphorus". *Advances in Agronomy* 19 151-210.

Larsen S. and Widdowson A.E. (1966) "Influence of pyrophosphate on soil-fertilizer reaction products in a calcareous soil". *Chemical Ind. (London)* p. 1302.

Lathwell D.J., Cope J.T.Jr. and Webb J.R. (1960) "Liquid fertilizers as sources of phosphorus for field crops". *Agronomy J.* 52 251-254.

Lauren D.R. and Watkinson J.H. (1985) "Elemental sulphur analysis using HPLC on 10 µm rigid polymer particles". *Journal of Chromatography* 348 317-320.

Lawrence J.R. and Germida J.J. (1988) "Relationship between microbial biomass and elemental sulphur oxidation in agricultural soils". *Soil Sci. Soc. Am. J.* 52 672-677.

Lee A., Boswell C.C. and Watkinson J.H. (1988a) "Effect of particle size on the oxidation of elemental sulphur, *Thiobacilli* numbers, soil sulphate and its availability to pasture". *New Zealand J. Agric. Res.* 31 179-186.

Lee A., Watkinson J.H. and Lauren D.R. (1988b) "Factors affecting oxidation rates of elemental sulphur in a soil under a rye grass dominant sward". *Soil Biol. Biochem.* 20(6) 809-816.

Lehr J.R. and Brown W.E. (1958) "Calcium phosphate fertilizers: II A petrographic study of their alteration in soils" *Soil Sci. Soc. Am. Proc.* 22 29-32.

Lehr J.R., Engelstad O.P. and Brown E.H. (1964) "Evaluation of calcium ammonium and calcium potassium pyrophosphates as fertilizers". *Soil Sci. Soc. Am. Proc.* 28 396-400.

Li P. and Caldwell A.C. (1966) "The oxidation of elemental sulphur in soil". *Soil Sci. Soc. Am. Proc.* 30 370-372.

Lindell D.L. and Sornsen R.C. (1974) "Sulfur and manganese release from soils treated with prilled sulfur and sulfur bentonite". *Soil Sci. Soc. Am. Proc.* 38 368-372.

Lindemann W.C., Aburto J.J., Haffner W.M. and Bono A.A. (1991) "Effect of sulphur source on sulphur oxidation". *Soil Sci. Soc. Am. J.* 55(1) 85-90.

Lindsay W.L. (1974) "Role of chelation in micronutrients availability" in Carson E.W. (ed) "The plant root and its environment". Pubs: University Press of Virginia, Charlottesville.

Lindsay W.L. (1979) "Chemical equilibria in soils." *Wiley Interscience, New York.*

Lindsay W.L. (1984) "Soil and plant relationships associated with iron deficiency with emphasis on nutrient interactions". *J. Plant Nutrition* 7(1-5) 489-500.

Lindsay W.L. and Moreno E.C. (1960) "Phosphate phase equilibria in soils". *Soil Sci. Soc. Am. Proc.* 24 177-182.

Lindsay W.L. and Norvell W.A. (1969) "Development of a DPTA micronutrient soil test". *Agronomy Abstracts* 69 84.

Lindsay W.L. and Norvell W.A. (1978) "Development of DTPA soil test for zinc, iron, manganese and copper". *Soil Sci. Soc. Am. J.* **42** 421-428.

Lindsay W.L. and Schwab A.P. (1982) "The chemistry of iron in soils and its availability to plants". *J. Plant Nutrition* **5** 821-840.

Lindsay W.L., Frazier A.W. and Stephenson H.E. (1962) "Identification of reaction products from phosphate fertilizer in soil". *Soil Sci. Soc. Am. Proc.* **26** 446-452.

Loeppert R.H. (1986) "Reactions of iron and carbonate in calcareous soils". *J. Plant Nutrition* 9(3-7) 195-214.

Loeppert R.H. and Clarke E.T. (1984) "Reactions of Fe^{2+} and Fe^{3+} in calcareous soils". *J. Plant Nutrition* 7(1-5) 149-163.

Loeppert R.H. and Hallmark C.T. (1985) "Indigenous soil properties influencing the availability of iron in calcareous soils". *Soil Sci. Soc. Am. J.* **49** 597-603.

Loeppert R.H. and Hossner L.R. (1984) "Reactions of Fe^{2+} and Fe^{3+} with calcite". *Clays and Clay Minerals* **32**(3) 213-222.

Loeppert R.H., Geiger S.C., Hartwig R.C. and Morris D.R. (1988) "A comparison of indigenous soil factors influencing the Fe-deficiency chlorosis of sorghum and soybean in calcareous soils". *J. Plant Nutrition* 11(6-11) 1481-1492.

Loeppert R.H., Hossner L.R. and Amin P.K. (1984a) "Formation of ferric oxyhydroxides from ferrous and ferric perchlorate in stirred calcareous systems". *Soil Sci. Soc. Am. J.* **48** 677-683.

Loeppert R.H., Hossner L.R. and Chmielewski M.A. (1984b) "Indigenous soil properties influencing the availability of Fe in calcareous hot spots". *J. Plant Nutrition* 7(1-5) 135-147.

Loganathan P., Isirimah N.O. and Nwachuka D.A. (1987) "Phosphorus sorption by ultisols and inceptisols of the Nigerian delta in Southern Nigeria". *Soil Science* **144** 330-338.

Loutfi G.L.O. (1971) "Geologic studies on the middle and upper Cretaceous formations in the offshore Khafji oilfield, Kuwaiti Saudi Arabia neutral zone area". *MSc Thesis, University of Kuwait.*

Ma Qiying and Lindsay W.L. (1990) "Divalent zinc activity in arid-zone soils obtained by chelation". *Soil Sci. Soc. Am. J.* **54** 719-722.

Madrid L. and Diaz-Barrientos E. (1992) "Influence of carbonate on the reaction of heavy metals in soils". *J. Soil Science* **43** 709-721.

Marschner H. (1978) "Role of rhizosphere in iron nutrition of plants". *Iran J. Agric. Res.* **6**(2) 69-80.

Marschner H., Romheld V. and Kissel M. (1986) "Different strategies in higher plants in mobilization and uptake of iron". *J. Plant Nutrition* **9** 695-713.

Marshall R.W. and Nacollas G.H. (1969) "The kinetics of crystal growth of dicalcium phosphate dihydrate". *Journal of Physical Chemistry* **73** 3838-3844.

Mathers A.C. (1970) "Effect of ferrous sulphate and sulphuric acid on grain sorghum yields". *Agronomy Journal* **62**(5) 555-556.

Mattingly G.E.G. (1975) "Labile phosphate in soils". *Soil Science* **119**(5) 369-375.

McBride M.B. (1979) "Chemisorption and precipitation of Mn^{2+} at $CaCO_3$ surfaces". *Soil Sci. Soc. Am. J.* **43** 693-698.

McBride M.B. and Blasiak J.J. (1979) "Zinc and copper solubility as a function of pH in an acid soil". *Soil Sci. Soc. Am. J.* **43** 866-870.

McCaskill M.R. and Blair J. (1987) "Particle size and soil texture effects on elemental sulphur oxidation". *Agronomy Journal* **79** 1079-1083.

McCready R.G.L. and Krouse H.R. (1982) "Sulphur isotope fractionation during the oxidation of elemental sulphur by *Thiobacilli* in solonetzic soil". *Can. J. Soil Sci.* **62** 105-110.

Melsted S.W., Motto H.L. and Peck T.R. (1969) "Critical plant nutrition composition values useful in interpreting plant analysis data". *Agronomy J.* **61** 17-20.

M.E. & W. (Ministry of Electricity and Water) (1981) "Geology and ground water hydrology of the State of Kuwait".

M.E. & W. (1988-89) "Annual Report"

Miyamoto S. (1977) "Predicting effects of sulphuric acid on qualities of irrigation and drainage waters in calcareous soils". *J. of Environmental Quality* **6** 12-18.

MnKeni P.N.S. and MacKenzie A.F. (1985) "Retention of ortho and polyphosphates in some Quebec soils as affected by added organic residues and calcium carbonate". *Can. J. Soil Sci.* **65** 575-585.

MnKeni P.N.S. and MacKenzie A.F. (1988) "Ortho and polyphosphate P fertilizers as affected by added organic materials and calcium carbonate". *Can. J. Soil Sci.* **68** 243-250.

Moore D.P. (1972) "Mechanisms of micronutrient uptake by plants" in Mortvedt J.J. (ed) "Micronutrients in Agriculture". Pubs: Soil Sci. Soc. Am. INC. p. 171-198.

Mortvedt J.J. and Osborn G. (1977) "Micronutrient concentrations in soil solution after ammonium phosphate applications". *Soil Sci. Soc. Am. J.* **41** 1004-1009.

Modaihsh A.S., Al-Mustafa W.A. and Metwally A.I. (1989) "Effect of elemental sulphur on chemical changes and nutrient availability in calcareous soils". *Plant and Soil* **116** 95-101.

Moore,T.J., Hartwig,R.C. and Loeppert,R.H. (1990) "Steady state proceedure for determining the effective particle-size distribution of soil carbonates." *Soil Sci. Soc. Am. J.* **54** 55-59.

Mukeni,P.N.S and MacKenzie,A.F. (1987) "Effect of added organic residues and calcium carbonate on polyphosphate hydolysis in four Quebec soils." *Plant and Soil* **104** 163-167.

Murphy L.S. and Walsh L.M. (1972) "Correction of micronurient deficiencies with fertilisers" in Mortvedt J.J. (ed) "Micronutrients in Agriculture". Pubs: Soil Sci. Soc. Am. INC p.347-388.

Murris R.J. (1980) "Middle East: Stratigraphy evolution and oil habitat". *AAPG Bull.* **64(5)** 597-618.

Nor Y.M. and Tabatabai M.A. (1977) "Oxidation of elemental sulphur in soils". *Soil Sci. Soc. Am. J.* **41** 736-741.

Norvell W.A. and Lindsay W.L. (1982) "Estimation of concentration of Fe^{3+} and $(Fe^{3+})(OH^-)^3$ ion product from equilibria of EDTA in soil". *Soil Sci. Soc. Am. J.* **46** 710-715.

Olson R.V. (1950) "Effects of acidification, iron oxide addition and other soil treatments on sorghum chlorosis and iron absorption". *Soil Sci. Soc. Am. Proc.* **15** 97-101.

Olsen S.R. and Watanabe F.S. (1959) "Solubility of calcium carbonate in calcareous soils". *Soil Science* **88** 123-129.

Olsen S.R., Cole C.V., Watanabe F.S. and Dean L.A. (1954) "Estimation of available phosphorus in soils by extraction with sodium bicarbonate". *U.S.D.A.* 939

Omar S.S., Al-Yagubi A. and Senay Y. (1981) "Geology and ground water hydrology of the State of Kuwait" in Abulazz M.S. (ed) "First Symposium on the future development of water resources in the Gulf and Arabian Peninsula". *J. the Gulf and Arabian Peninsula Studies, Kuwait University* 1 5-67.

Omar S.A., Taha F.K. and Nassef A. (1990) "Ecological monitoring of vegetation in Kuwait's rangelands" in Helwagy R. (ed) "Proceedings of the First International Conference on Range Management in the Arabian Gulf".

Orabi A.A., Abdallah A., Mashadi H. and Barakat A.H. (1981) "Zinc-phosphorus relationship in the nutrition of corn plants (Zea Mays L.) grown on some calcareous soils". *Plant and Soil* 59 51-59.

Orabi A.A., Ismail A.S. and Mashadi H. (1982) "Zinc-phosphorus relationship in the nutrition of tomato plants as affected both by the soil and by the rate of applied zinc". *Plant and Soil* 69 67-72.

Owen R.M.S. and Nasr S.N. (1958) "Stratigraphy of Kuwait-Basra area" in "Habitat of Oil" *AAPG* 42 1252-1278.

Papadopoulos P. and Rowell D.L. (1989) "The reactions of copper and zinc with calcium carbonate surfaces". *J. Soil Science* 40 39-48.

Parent L.E., MacKenzie A.F. and Perron Y. (1985) "Influence of four levels of pyrophosphatase activity on the rate of pyrophosphate hydrolysis in organic soils". *Commun. in Soil Sci. Plant Anal.* 16(10) 1095-1105.

Patel G.J., Ramakrishnayya B.V. and Patel B.K. (1977) "Effect of soil and foliar application of ferrous sulphate and of acidulation of soil on iron-chlorosis of paddy seedlings in Goradu soil nurseries in India". *Plant and Soil* 46 209-219.

Pena F. and Torrent J. (1984) "Relationships between phosphate sorption and iron oxides in Alfisols from a river terrace sequence of mediterranean Spain". *Geoderma* 33 283-296.

Pepper I.L. and Miller R.H. (1978) "Comparison of oxidation of thiosulphate and elemental sulphur by two heterotrophic bacteria and *Thiobacillus thiooxidans*". *Soil Science* **126**(1) 9-14.

Pepper I.L., Miller R.H. and Ghonsikar C.P. (1976) "Microbial inorganic polyphosphates: Factors influencing their accumulation in soil". *Soil Sci. Soc. Am. J.* 40 872-875.

Philen O.D. and Lehr J.R. (1967) "Reactions of ammonium polyphosphates with soil minerals". *Soil Sci. Soc. Am. Proc.* 31 196-199.

Plummer,L.N., Wigley,T.M. and Parkhurst,D.L. (1978) "The kinetics of calcite dissolution in CO_2-water systems at 5 and 60°C and 0.0 and 1.0 atmospheres CO_2" *Am. J. Sci.* **278** 179-216.

Procopiou J., Wallace D. and Alexander G.V. (1976) "Microelement composition of plants grown with low to high levels of sulphur applied to calcareous soil in glasshouse". *Plant and Soil* 44 359-365.

Pulford I.D. (1986) "Mechanisms controlling zinc solubility in soils". *J. Soil Science* 37 427-438.

Randall P.J., Spencer K. and Freney J.R. (1981) "Sulfur and nitrogen fertilizer effects on wheat. I. concentrations of sulfur and nitrogen to sulfur ratio in grain, in relationship to yield response". *Australian J. Agric. Res.* 32 203-212.

Randhawa N.S. and Broadbent F.E. (1965) "Soil organic matter - metal complexes:6". *Soil Science* 99 362-366.

Razeto B. (1982) "Treatments for iron chlorosis in peach trees". *J. Plant Nutrition* 5(4-7) 917-922.

Rhoades J.D. (1984) "Soluble salts p. 167-197" in "Methods of soil analysis part 2 chemical and microbiological properties 2nd edition" Page A.L. (ed) Pubs: Soil Sci. Soc. Am. Inc. Madison, Wisconsin.

Richards L.A. (ed) (1954) "Diagnosis and improvement of saline and alkali soils". *U.S.D.A. Handbook 60* (Washington D.C.).

Rida M. and Modaihsh A.S. (1988) "Gypsum formation in sulphur treated calcareous soil". *Arab Gulf Journal of Scientific research* 11 3-24.

Rehm G.W. and Caldwell A.C. (1969) "Relationship of soil texture and sulphur oxidation". *Agronomy Journal* 61 333-334.

Romheld V., Marschner H. and Kramer (1982) "Responses to Fe deficiency in roots of "Fe-efficient" plant species". *J. Plant Nutrition* 5 488-498.

Ross D.S. and Barlett R.J. (1981) "Evidence for non-microbial oxidation of manganese in soil". *Soil Sci* 132 153-160.

Ruellan A. (1973) "Morphology and distribution of calcareous soils in mediterranean and desert regions" in "Calcareous Soils" *F.A.O. Soil Bulletin* 21 7-15.

Ryan J. and Stroehlein J.L. (1979) "Sulphuric acid treatment of calcareous soils: Effect on phosphorus solubility, inorganic phosphorus forms and plant growth". *Soil Sci. Soc. Am. Proc.* 43 731-735.

Ryan J., Curtin D. and Cheema M.A. (1985a) "Significance of iron oxides and calcium carbonate particle size in phosphate sorption by calcareous soils". *Soil Sci. Soc. Am. J.* 49 74-76.

Ryan J., Hasan H.M., Baasiri M. and Tabbara H.S. (1985b) "Availability and transformation of applied phosphorus in calcareous Lebanese soils". *Soil Sci. Soc. Am. J.* 49 1215-1220.

Ryan J., Miyamoto S. and Stroehlein J.L. (1974) "Solubility of manganese, iron and zinc as affected by application of sulphuric acid to calcareous soils". *Plant and Soil* 40 421-427.

Ryan J., Stroehlein J.L. and Miyamoto S. (1975a) "Sulphuric acid applications to calcareous soils: effects on growth and chlorophyll content of common Bermuda grass in the greenhouse". *Agronomy Journal* 67 633-637.

Ryan J., Stroehlein J.L. and Miyamoto (1975b) "Effect of surface applied sulphuric acid on growth and nutrient availability of five range grasses in calcareous soils". *J. Range Management* 28 411-414 cited in Hagstrom (1984) "Current management practices for correcting iron deficiency in plants with emphasis on soil management". *J. Plant Nutrition* 7 23-46

Ryden J.C. and Syers J.K. (1975) "Rationalization of ionic strength and cation effects on phosphate sorption by soils". *J. Soil Sci.* 26 395-406.

Ryden J.C. and Syers J.K. (1977) "Origin of labile phosphate pool in soils". *Soil Science* 123(6) 353-361.

Ryden J.C., Syers J.K. and McLaughlin R. (1977) "Effect of ionic strength on chemisorption and potential determining sorption of phosphate by soils". *J. Soil Sci.* **28** 62-71.

Saeed M. and Fox R.L. (1977) "Relations between suspension pH and zinc solubility in acid and calcareous soils". *Soil Science* 124(2) 199-204.

Saeed,M. and Fox,R.L. (1979) "Influence of phosphate fertilization on zinc adsorption by tropical soils." *Soil Sci. Soc. Am. J.* 43 683-686.

Sajwan K.S. and Lindsay W.L. (1988) "Effect of redox, zinc fertilization and incubation time on DTPA-extractable zinc, iron and manganese". *Commun. in Soil Science Plant Anal.* 19(1) 1-11.

Saroha M.S. and Singh H.G. (1980) "Interrelationship between iron and sulphur in the prevention of chlorosis in sugar cane on alkaline calcareous soils". *Indian J. Agricultural Sci.* **50**(1) 34-40.

Savant N.K. and Racz C.J. (1972) "Effect of added orthophosphate on pyrophosphate hydrolysis in soil". *Plant and Soil* **36** 719-721.

Savant,N.K. and Racz,C.J. (1973) "Reaction products of applied pyrophosphates in some Manitoba soils." *Can. J. Soil Sci.* 53 111-117.

Schinas S. and Rowell D.L. (1977) "Lime-induced chlorosis". *J. Soil Science* **28** 351-368.

Schwab A.P. and Lindsay W.L. (1983a) "Effect of redox on the solubility and availability of iron". *Soil Sci. Soc. Am. J.* 47 201-205.

Schwab A.P. and Lindsay W.L. (1983b) "The effect of redox on the solubility and availability of manganese in a calcareous soil". *Soil Sci. Soc. Am. J.* 47 217-220.

Schwertmann U. and Taylor R.M. (1977) "Iron oxides" in Dixon J.B. and Weed S.B. (eds) "Minerals in Soil Environments" p. 145-180 Pubs: Amer. Soc. Agronomy, Madison, Wisconsin,

Sen Gupta M.B. and Cornfield D.H. (1964) "Effect of four acidifying materials added to a calcareous soil on the availability of phosphorus to ryegrass". *Plant and Soil* **21** 388-390.

Shahid S.A. (1988) "Studies on the micromorphology of salt-affected soils in pakistan". *Thesis submitted to the Univ. of Wales, Bangor, UK.*

Shukla M.P., Shanker H. and Pathak R.K. (1983) "Sulphur, zinc and boron nutrition of Rai (*Brassica juncea*) *J. Indian Soc. Soil Sci.* **31** 517-520.

Shuman L.M. (1975) "The effect of soil properties on zinc adsorption by soils". *Soil Sci. Soc. Am. Proc.* **39** 454-458.

Shuman L.M. (1976) "Zinc adsorption isotherms for clays with and without iron oxides removed". *Soil Sci. Soc. Am. J.* **40** 349-352.

Shuman L.M. (1977) "Adsorption of Zn by Fe and Al hydrous oxides as influenced by ageing and pH". *Soil Sci. Soc. Am. J.* **41** 703-707.

Shuman L.M. (1979) "Zinc, manganese and copper in soil fractions". *Soil Sci.* **127** 10-17.

Shuman L.M. (1988$_a$) "Effect of organic matter on the distribution of manganese, copper, iron and zinc in soil fractions". *Soil Science* **146(3)** 192-198.

Shuman L.M. (1988$_b$) "Effect of removal of organic matter and iron or manganese oxides on zinc adsorption by soil". *Soil Science* **146(4)** 248-254.

Shuman L.M. (1988$_c$) "Effect of phosphate level on extractable micronutrients and their distribution among soil fractions". *Soil Sci. Soc. Am. J.* **52** 136-141.

Sillanpaa M. (1982) "Micronutrients and the nutrient status of soils: A Global study". *F.A.O. Soil Bull.* **48**

Sims J.T. (1986) "Soil pH effects on the distribution and plant availability of manganese, copper and zinc". *Soil Sci. Soc. Am. J.* **50** 367-373.

Sims J.L. and Patrick Jr. W.H. (1978) "The distribution of micronutrient cations in soil under conditions of varying redoc potential and pH". *Soil Sci. Soc. Am. J.* **42** 258-262.

Singh H.G. (1970) "Effect of sulphur in preventing the occurrence of chlorosis in peas". *Agronomy Journal* **62** 708-711.

Singh Y. and Dartigues A. (1970) "Efficiency of polyphoshates and orthophosphate in zinc-deficient soils". *Plant and Soil* **32** 397-411.

Skiba U. and Wainwright M. (1984) "Oxidation of elemental-S in coastal-dune sands and soils". *Plant and Soil* **77** 87-95.

Smith R.M. and Martell A.E. (1976) "Critical stability constants vol.4: Inorganic complexes. Plenum Press, New York. Cited in Bar-Yosef B. and Asher L.E. (1983) "Reactions of pyrophosphate in soils and its effect on zinc sorption at various pH levels". *Soil Science* **136(2)** 82-88.

Soliman M.F. (1987) "Effect of sulphur on enhancing manganese utilzation from various sources". *Agrochimica* **31(6)** 548-557.

Soliman M.F. (1989) "Effect of nitrogen and sulphur fertilizers on Fe, Mn and Zn uptake by corn plants grown in a coarse-textured calcareous soil". *Agrochimica* **33(4-5)** 219-229.

Spencer W.F. (1960) "Effects of heavy applications of phosphate and lime on nutrient uptake, growth, freeze injury and root distribution of grapefruit trees". *Soil Sci.* **89** 311-318.

Stevenson F.J. (ed) (1986) "Cycles of soil carbon, nitrogen, phosphorus, sulphur micronutrients". *John Wiley and sons, New York.*

Stochlein J.L., Sabet S.A. and Clementz D.M. (1968) "Response of plants to polyphosphate on calcareous soils". *Agronomy J.* **60** 576-577.

Stott D.E., Dick W.A. and Tabatabai M.A. (1985) "Inhibition of pyrophosphatase activity in soils by trace elements". *Soil Science* **139(2)** 112-117.

Stuckenhotz D.D., Olsen R.J., Gogan G. and Olsen R.A. (1966) "On the mechanism of P-Zn interaction in corn nutrition". *Soil Sci. Soc. Am. Proc.* **30** 759-763.

Suarez D.L. and Rhoades J.D. (1982) "The apparent solubility of calcium carbonate in soils". *Soil Sci. Soc. Am. J.* **46** 716-722.

Subbarao Y.V. and Ellis R.Jr. (1975) "Reaction products of polyphosphates and orthophosphates with soils and influence on uptake of phosphorus by plants". *Soil Sci. Soc. Am. Proc.* **39** 1085-1088.

Sutton C.D. and Larsen S. (1964) "Pyrophosphate as a source of phosphorus for plants". *Soil Science* 97 196-201.

Sutton C.D., Gurnary D. and Larsen S. (1966) "Pyrophosphate as a source of phosphorus for plants: II hydrolysis and initial uptake by a barley crop". *Soil Science* **101**(3) 199-204.

Tabatabai M.A. (1982) "Analytical methods for sulphur in soils". *Proc. of Int. Sulphur 1982 Conference* 1 391-407.

Tabatabai M.A. and Dick W.A. (1979) "Distribution and stability of pyrophosphatase in soils". *Soil Biology and Biochemistry* **11** 655-659.

Tisdale S.L. and Bertramson B.R. (1949) "Elemental sulphur and its relationship to manganese availability". *Soil Sci. Soc. Am. Proc.* **13** 131-137.

Torrent J. (1987) "Rapid and slow phosphate sorption by Mediterranean soils: Effect of iron oxides". *Soil Sci. Soc. Am. J.* **51** 78-82.

Udo E.J., Bohn H.L. and Tucker T.C. (1970) "Zinc adsorption by calcareous soils". *Soil Sci. Soc. Am. Proc.* **34** 405-407.

Uzu F.O., Udo E.J. and Juo S.R. (1983) "Pyrophosphate as a source of phosphorus for maize in some acid soils from southern Nigeria". *J. Agr. Sci. Camb* **100** 477-483.

Van Breemen N. and Wielemaker W.G. (1974) "Buffer intensities and equilibrium pH of minerals and soils: I. The contribution of minerals and aqueous carbonate to pH buffering". *Soil Sci. Soc. Am. Proc.* **38** 55-60.

Van Breeman N. and Wielemaker W.G. (1974) "Buffer intensities and equilibrium pH of minerals and soil: II Theoretical and actual pH of minerals and soils". *Soil Sci. Soc. Am. Proc.* **38** 61-66.

Van Wazer J.R., Griffith E.J. and McCullough J.F. (1955) "Structure and properties of the condensed phosphates". *Journal Am. Chem. Soc.* **77** 287-291.

Vempati R.K. and Loeppert R.H. (1986) "Synthetic ferrihydrate as a potential iron amendment in calcareous soils". *J. Plant Nutrition* **9**(3-7) 1039-1052.

Vempati R.K. and Loeppert R.H. (1988) "Chemistry and mineralogy of Fe-containing oxides and layer silicates in relation to plant available iron". *J. Plant Nutrition* **11(6-11)** 1557-1574

Vishniac W. and Santer M. (1957) *Bacteria Review* **21** 195 cited in Weir R.G. (1975) "The Oxidation of elemental sulphur and sulphides in soil" p.40-49 in McLachlan K.D. (ed) "Sulphur in Australasian Agriculture" *Sydney Univ. Press, Sydney, Australia.*

Vitolins M.I. and Swaby R.J. (1969) "Activity of sulphur-oxidising micro-organisms in some Australian soils". *Aus. J. Soil Res.* 7 171-183.

Von Tress,M., Loeppert,R.H. and Matis,J.H. (1985) "A calcite dissolution model for the estimation of particle size distribution." *Soil Sci. Soc. Am. J.* **49** 302-307.

Wada K. and Abd-Elfattah A. (1979) "Effect of cation exchange material on zinc adsorption by soils". *J. Soil Science* **30** 281-290.

Wainwright M. (1984) "Sulphur oxidation in soils". *Adv. Agron.* **37** 349-396.

Wainwright,M., Novell,W. and Graystone,S. (1988) "Effects of organic matter on sulphur oxidation in soil and influence of sulphur oxidation on soil nitrification." *Plant and Soil* **96** 369-376.

Wallace A. and Abou-Zamzan A.M. (1984) "Nitrogen and bicarbonate relationships with iron nutrition in plants". *J. Plant Nutrition* 7 587-594.

Wallace A. and Mueller R.T. (1978) "Complete neutralization of a portion of calcareous soil as a means of preventing iron chlorosis". *Agronomy Joruanl* **70** 888-890.

Wallace A., Romney E.M. and Alexander G.V. (1976) "Banding of sulphur and sulphuric acid in soil in which iron-inefficient plants were grown". *Comm. Soil Sci. Plant Anal.* **7** 7-13.

Ward R.C., Langin E.J., Olson R.A. and Stuckenholtz D.D. (1963) "Factors responsible for poor response of corn and grain sorghum to phosphorus fertilization." *Soil Sci. Soc. Am. Proc.* **27** 326-330.

Warnock R.E. (1970) "Micronutrient uptake and mobility within corn plants (Zea mays L.) in relation to phosphorus-induced zinc deficiency". *Soil Sci. Soc. Am. Proc.* **34** 765-769.

Watanabe F.S. and Olsen S.R. (1965) "Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soils". *Soil Sci. Soc. Am. Proc.* **29** 677-678.

Watkinson J.H. (1989) "Measurement of the oxidation rate of elemental sulphur in soil". *Aus. J. of Soil Res.* **27** 365-375.

Watkinson J.H., Lee A. and Lauren D.R. (1987) "Measurement of elemental sulphur in soil and sediments: Field sampling, sample storage, pretreatment extraction and analysis by high performance liquid chromatography". *Aus. J. of Soil Res.* **25** 167-178.

Webb B.B. (1970) "Field and growth chamber comparisons of ortho and polyphosphate". *PhD Thesis Kansas State University, Manhattan, Kans.* cited in MnKeni P.N.S. and Mackenzie A.F. (1988) "Ortho and polyphosphate P fertilizer as affected by added organic materials and calcium carbonate" *Can. J. Soil Sci.* **68** 243-250.

Wedepohl K.H. (ed) (1978) "Handbook of Geochemistry". Pubs: Springer-Verlag, New York.

Weir R.G. (1975) "The oxidation of elemental sulphur and sulphides in soil". P. 40-49 in McLachlan K.D. (ed) "Sulphur in Australasian Agriculture". *Sydney Univ. Press, Sydney, Australia.*

Westermann D.T., Jackson T.L. and Moore D.D. (1971) "Effect of potassium salts on extractable soil manganese". *Soil Sci. Soc. Am. Proc.* **35** 43-46.

Wiklander L., Hallgren G. and Johnson E. (1950) *Ann. R. Agric. Swed.* **17** 425-440 cited in Wainwright M. (1984) "Sulphur oxidation in soils". *Adv. Agron.* **37** 349-396.

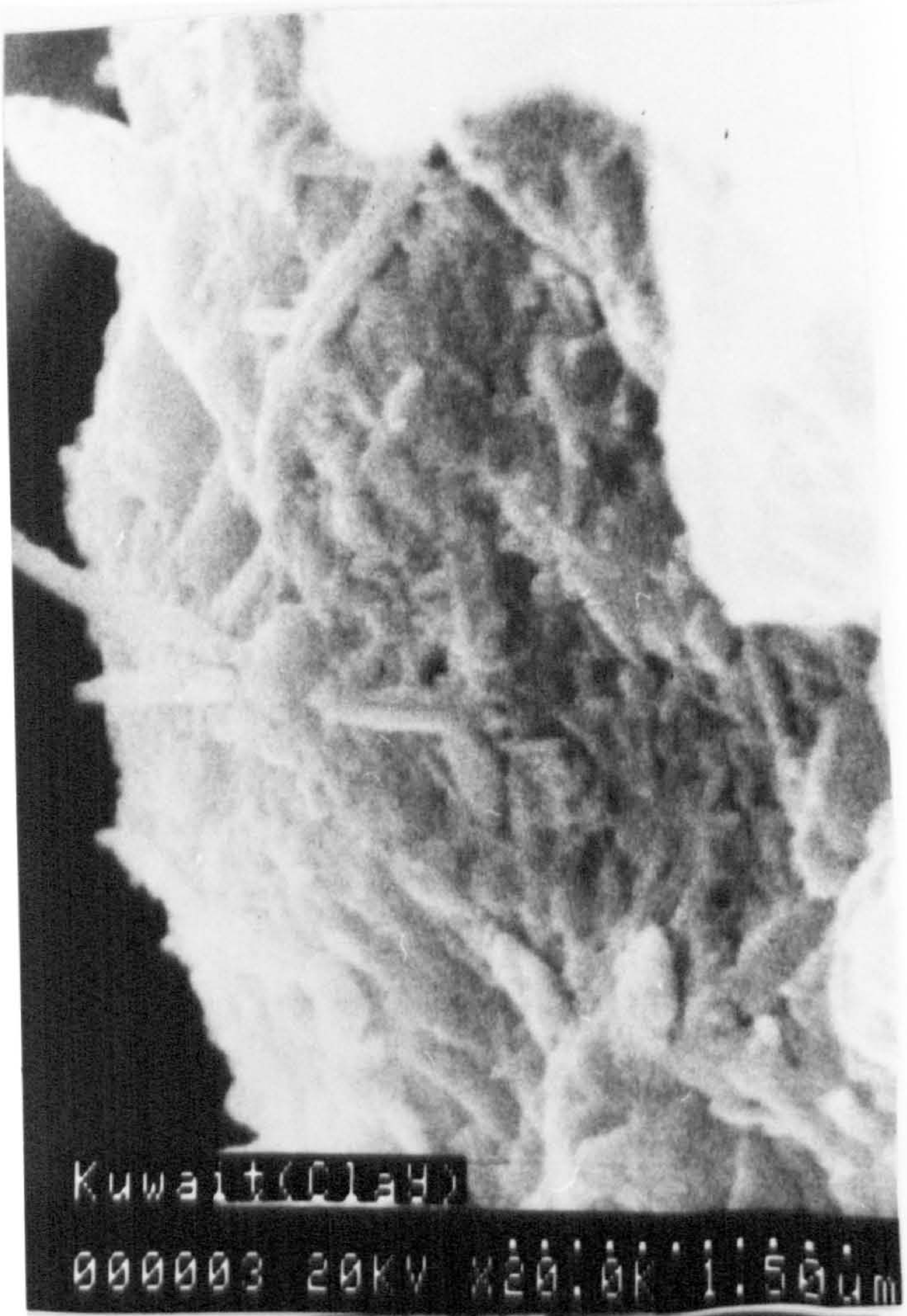
Xie R.J. and MacKenzie A.F. (1989) "The effect of pH on zinc treansformation in autoclaved soils treated with pyrophosphate". *Communication in Soil Sci. and Plant Analysis* **20**(9,10) 971-988.

Xie R.J. and MacKenzie A.F. (1990) "Zinc sorption, desorption and fractions in three autoclaved soils treated with pyrophosphate". *Soil Sci. Soc. Am. J.* **54** 71-77.

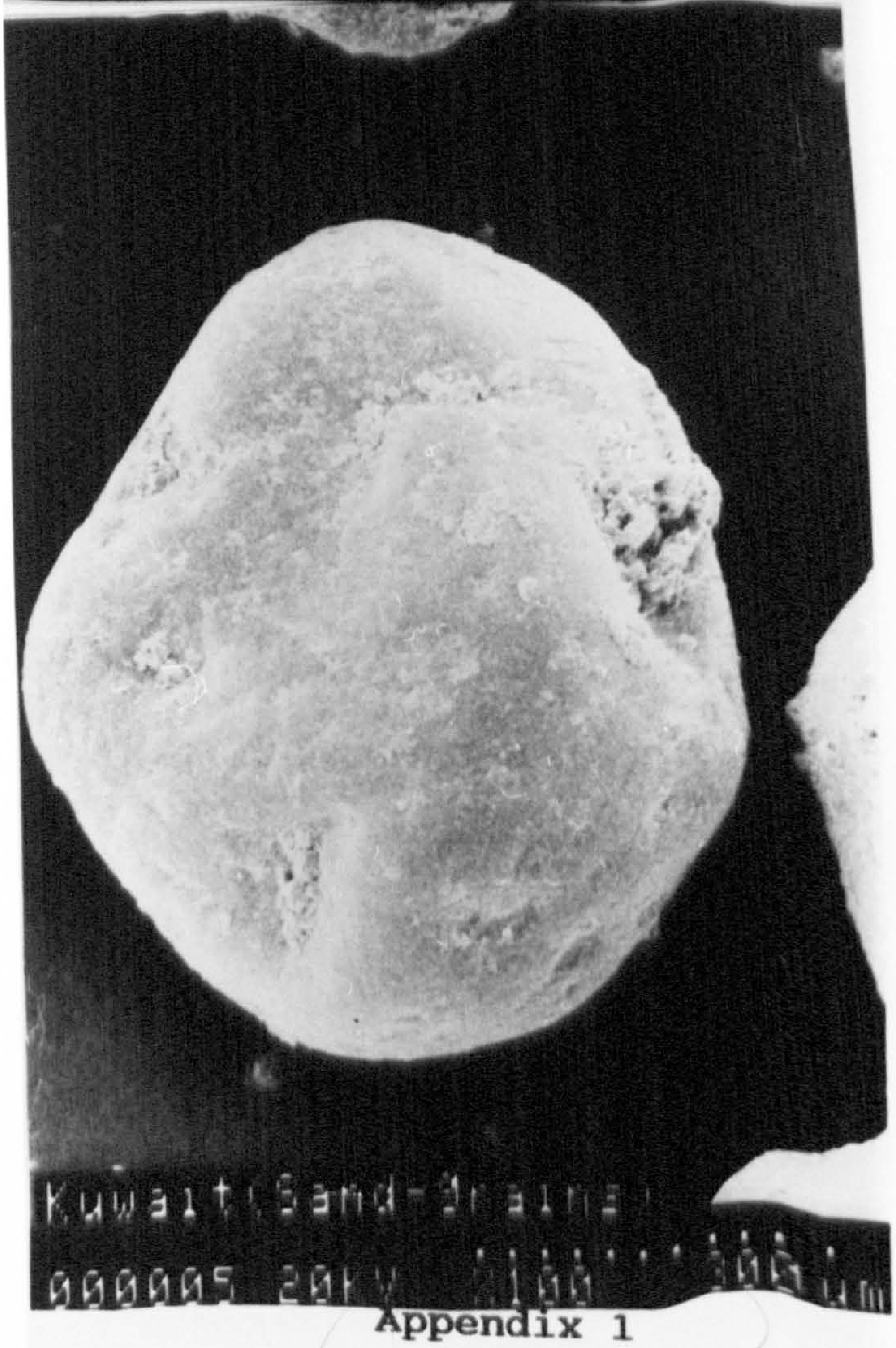
Yaalon D.H. (1957) "Problems of soil testing on calcareous soils". *Plant and Soil* **8**(3) 275-288.

APPENDIX I

SEM examination of some Kuwaiti soil particles

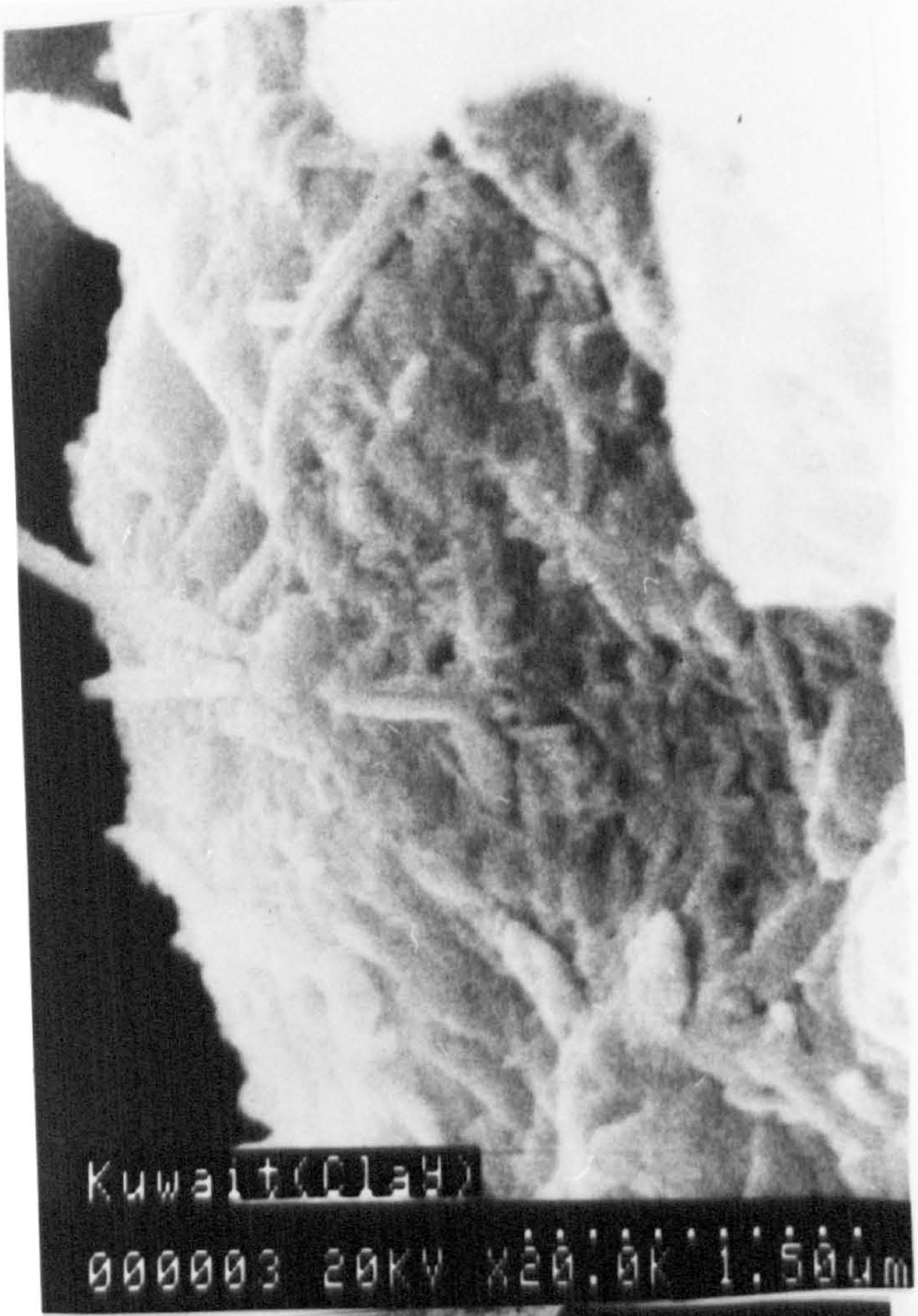


Palygorskite clay particles showing their fibrous nature.

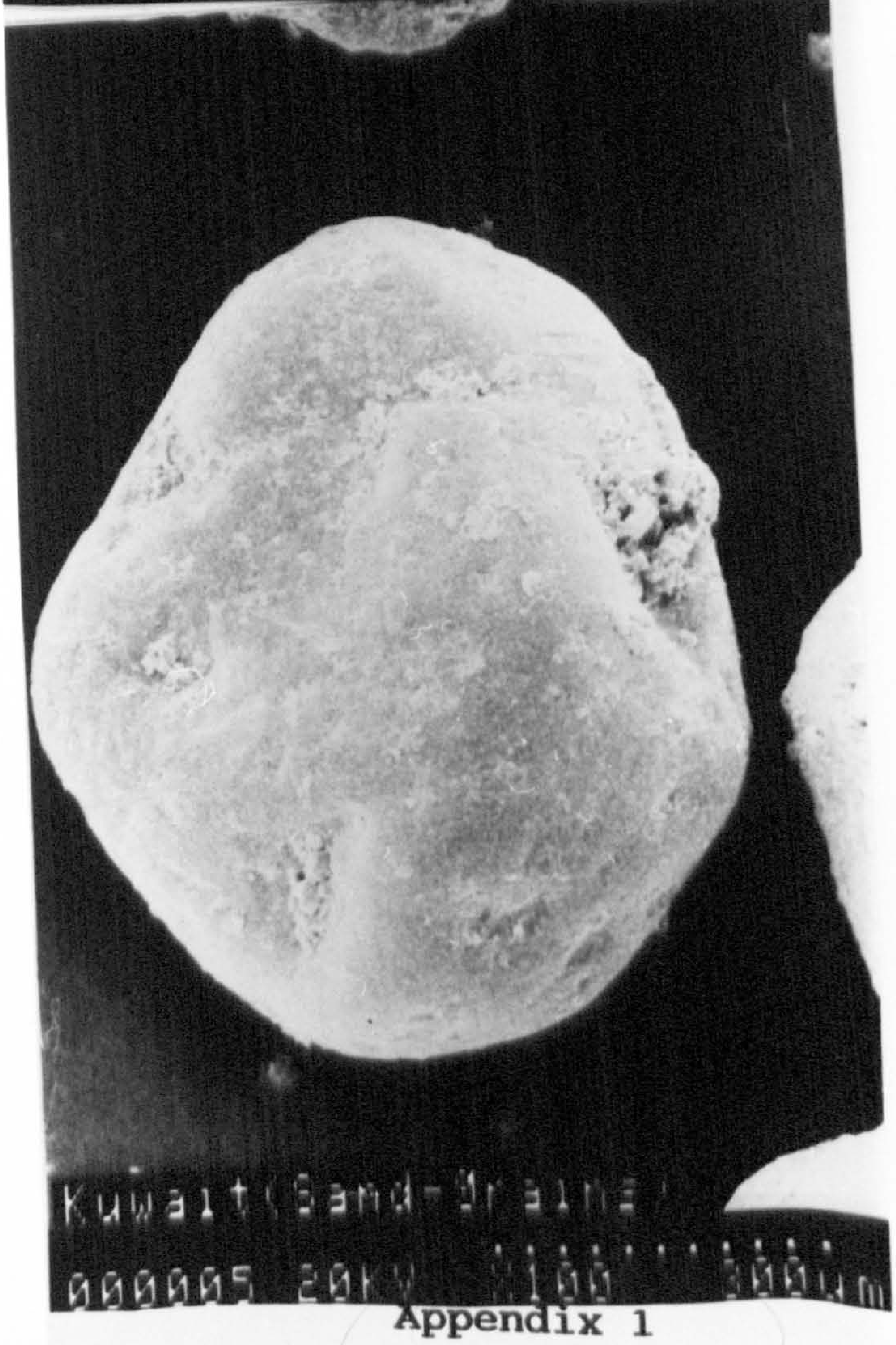


Around weathered quartz grain indicating wind deposition.

Appendix 1



Palygorskite clay particles showing their fibrous nature.



Around weathered quartz grain indicating wind deposition.

Appendix 1

APPENDIX II The Preliminary Field Experiment

This preliminary investigation was undertaken with the overall object of increasing plant growth and the availability of P and metallic trace elements. Soil acidulent S°, was incorporated at a rate of 60 tonnes per hectare. The purpose was to reduce $CaCO_3$ caused nutrient fixation and to lower soil pH to stimulate their higher solubility. The second treatment was that of farmyard manure applied at a rate of 60 m^3 per hectare. These high rates of organic amendments were used in an attempt to to create soil reducing conditions to increase plant nutrient solubility particularly those of Fe and Mn. For the same reason, the third treatment was of soil compaction, administered in the hope that reducing soil macropores would generate reducing conditions. This practice was investigated to increase metal ion solubility and possibly increase P availability by reducing P diffusion tortuosity. A control was included for the treatment.

Furthermore, to these main treatments sub-treatments of P and combinations of micronutrient salts were used as outlined in the methodology (section 2.1). Corn *Zea mays* was planted as a test crop. As mentioned before, some difficulties in timing/weather with this experiment prevented adequate crop response. Soil samples collected 100 days after plant establishment, however, were analysed for various parameters and the data statistically analysed. In table appendix II these results are reported.

In the analysis, each treatment is compared against the control. There were no changes in the soil pH or $CaCO_3$ content except with S° treatment, where there was a small decline, significant only with soil % $CaCO_3$ ($p<.05$) indicating a moderate level of S° oxidation. Soil nutrient extracts designed to reflect the plant nutrient availability had shown mixed responses. $NaHCO_3$-P extracts indicated no significant variation due to any of the treatments. However, control soil levels were more than 20 µg g^{-1} reflecting high P availability. This could be due to years of a high rate of fertilisation practised on this experimental plot.

APPENDIX II

Soil analysis from first season field experiment 100 days after treatment initiations (means of 12 replicates)

	pH 1:1	$CaCO_3$ % equi	$NaHCO_3$-P µg g^{-1}	DTPA-Fe µg g^{-1}	DTPA-Zn µg g^{-1}	DTPA-Mn µg g^{-1}	DTPA-Cu µg g^{-1}
S°	7.6	14.2	28.7	3.5	0.37	5.1	0.37
FYM	7.7	17.1	34.6	4.0	1.19	6.8	0.43
Compaction	7.9	17.4	23.1	3.2	0.39	3.8	0.41
Control	7.8	16.8	34.9	2.7	0.39	3.7	0.42
$LSD_{0.05}$	N.S	1.98	N.S	0.68	0.044	1.09	N.S
$LSD_{0.01}$		2.75		0.94	0.061	1.51	

There were very large variations in the $NaHCO_3$-P extraction levels. Moreover, this variation did not correspond to any of the treatments or fertilisation practices. It could be that the FYM which was added at a relatively high rate had leached into other treatment plots. Also this organic material had accumulated in greater amounts in between planting furrows, causing higher organic ratios in some of the random soil collections.

DTPA-Fe extracts were higher with the treatment of $S^{\bullet}$ and FYM, but not with soil compaction. This improved DTPA-Fe level in response to $S^{\bullet}$ application was significant at $p<0.05$, but still was at marginal levels (Lindsay and Norvell, 1978). It could be that more time was needed to have the full effect of $S^{\bullet}$ oxidation on Fe solubility. Similarly DTPA-Fe extractions were higher with FYM ($p<0.01$) but again still at marginal levels. DTPA-Zn extractions improved from deficient levels to adequate (Lindsay and Norvell, 1978) ($p<0.01$), however, only with FYM treatments. It could be that organic chelation or reducing conditions from FYM decomposition had increased Zn availability.

Treatments of $S^{\bullet}$ and FYM also increased soil DTPA-Mn extractions. These were significant at the $p<0.05$ and $p<0.01$ for the $S^{\bullet}$ and FYM respectively. However, DTPA-Mn levels for all treatments were higher than 1 $\mu g\ g^{-1}$ soil indicating that this nutrient is "adequate" in this soil (Lindsay and Norvell, 1978). Similarly, soil DTPA-Cu extraction was in the adequate range of plant availability, higher than 0.2 $\mu g\ g^{-1}$, even though it did not respond to any of the soil treatments. As already mentioned, plants were exposed to adverse weather conditions, but from plant tissue analysis, there was no variation in P, Fe, Zn, Mn and Cu concentrations except with FYM treatments, where Fe and Zn levels were lower (statistically not analysed), although plant growth was much greater than with the other treatments.

From this preliminary study the following points can be drawn:-

Organic amendments (FYM) had the greatest effect on DTPA-extraction of

Fe, Zn and Mn, and also resulted in better plant growth. However, corn plants still showed clear signs of Fe-chlorosis. This could be due to HCO_3^- generated from manure decomposition inducing Fe-chlorosis. Organic matter would also have great influence on soil physical characteristics especially in improving soil-water relations. therefore, this treatment was eliminated in the second season trials and instead all plots received FYM at one rate of 20 m^3 per hectare.

Soil compaction as a means of creating the more reducing conditions thought to increase nutrient availability levels failed to show any significant changes. All soil extraction levels and those of plant tissue concentration did not vary from the control. It could be that the coarse sandy texture of the soil did not compact enough to restrict air flow or that as time passed they reverted back to their natural condition. This treatment was eliminated from second season experimentation.

Soil treatment with $S^•$ had shown some positive effects in increasing soil DTPA-extraction of Fe and Mn. Furthermore, it had reduced soil $CaCO_3$ content. However, these results were inconclusive, since not enough time was allowed to show adequately the effect of $S^•$ oxidation on soil properties. In the second season $S^•$ amendments were studied in more depth.

APPENDIX III
Surface morphology map of Kuwait
After: W. Fuchs, T.E. Gattinger and H.F. Holzer,1968.

APPENDIX IV
General stratigraphy of Kuwait
After: H. Arisha, 1984 ; F.H. Abdulla, 1987.

A representative profile of Sulibiya series:

Profile No. 41

0-40	Cm	Pale brown (10YR 6/3) to brown (10YR 5/3, moist); gravelly sand; single grain; loose; strongly calcareous; a thin, whitish gravel layer on the surface.
40-90	Cm	Pale brown - very pale brown (10YR 6,5/3) to brown-greyish brown (10YR 6/3,5, moist); sand; single grain; loose strongly calcareous.
90-150	Cm	Light grey (2, 5Y 7/2) to light grey - pale yellow (2, 5Y 7/3, moist); gravelly sand; single grain; loose; strongly calcareous.

Range in characteristics:

Colour - Colour of topsoil, brown to light yellowish brown (10YR 5/3, moist) to light yellowish brown (10YR 6/4, moist).

Texture - Sand to sandy loam.

Relief - Undulating to level.

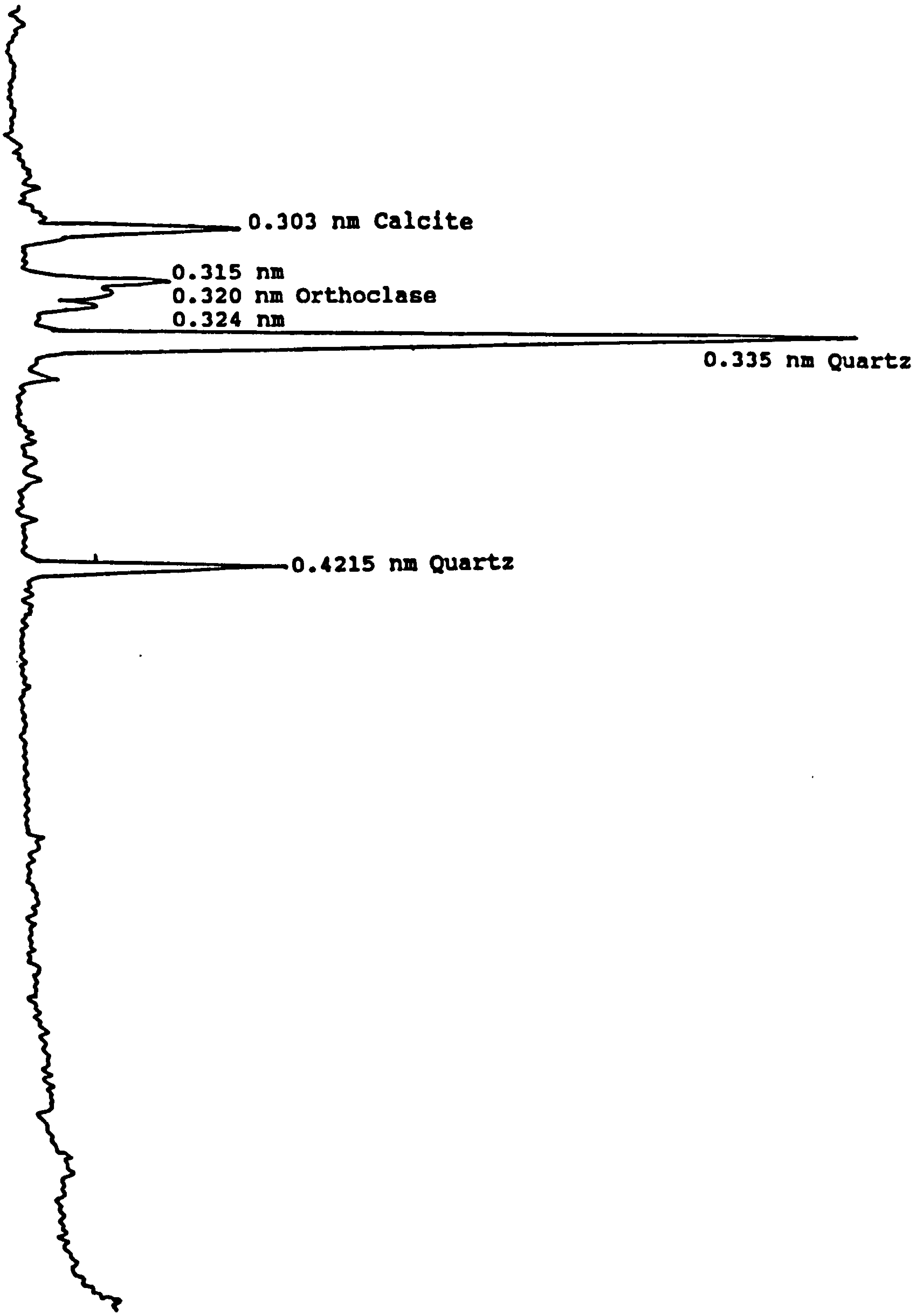
Drainage - Somewhat excessively to well.

Location of profile- South of Sulibiya.

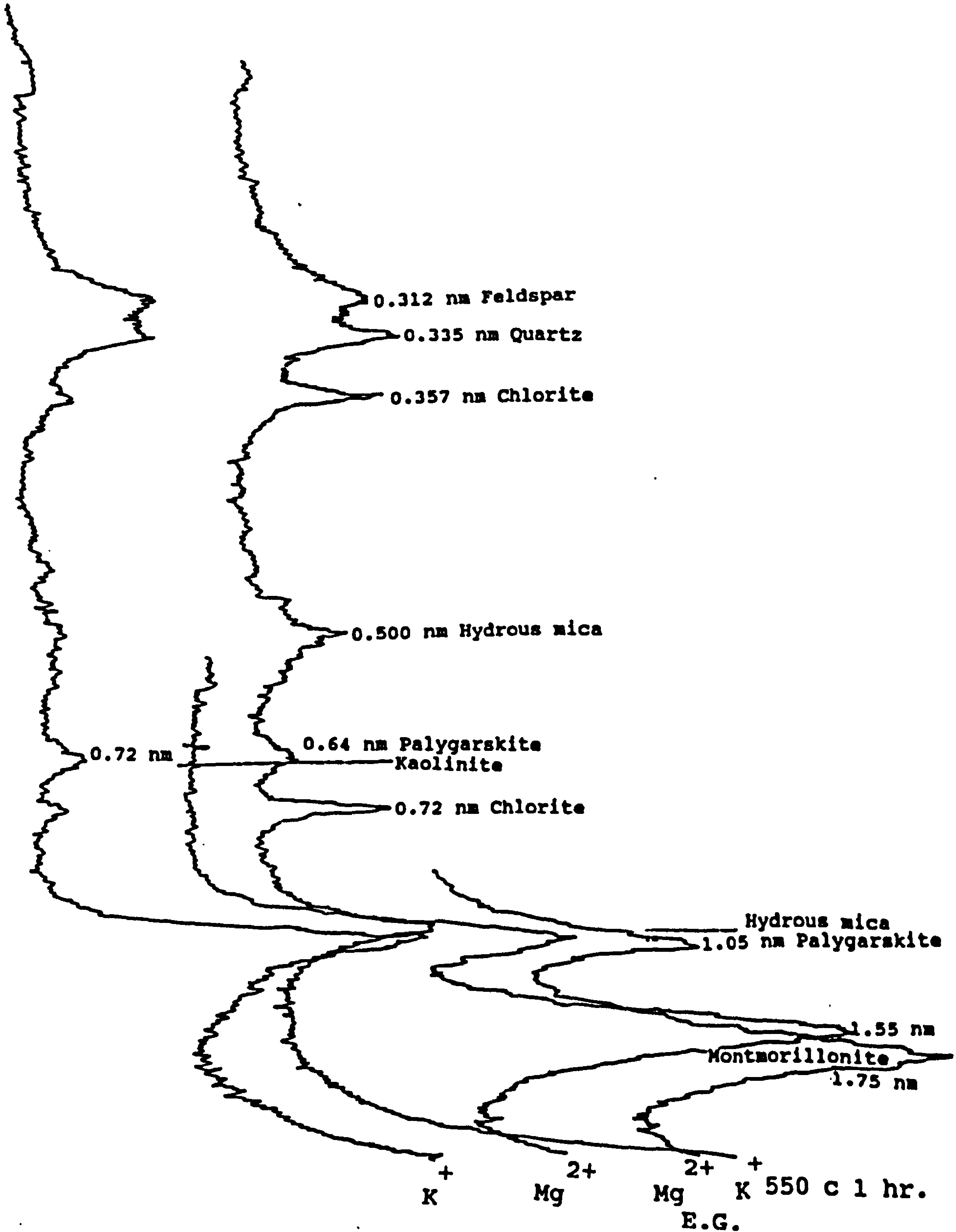
Use - Grazing

Date profile taken - 17-11-1965

APPENDIX V
Soil profile description (sulaibiya series)
After: H. Ergun, 1969. FAO/KU/TF17.

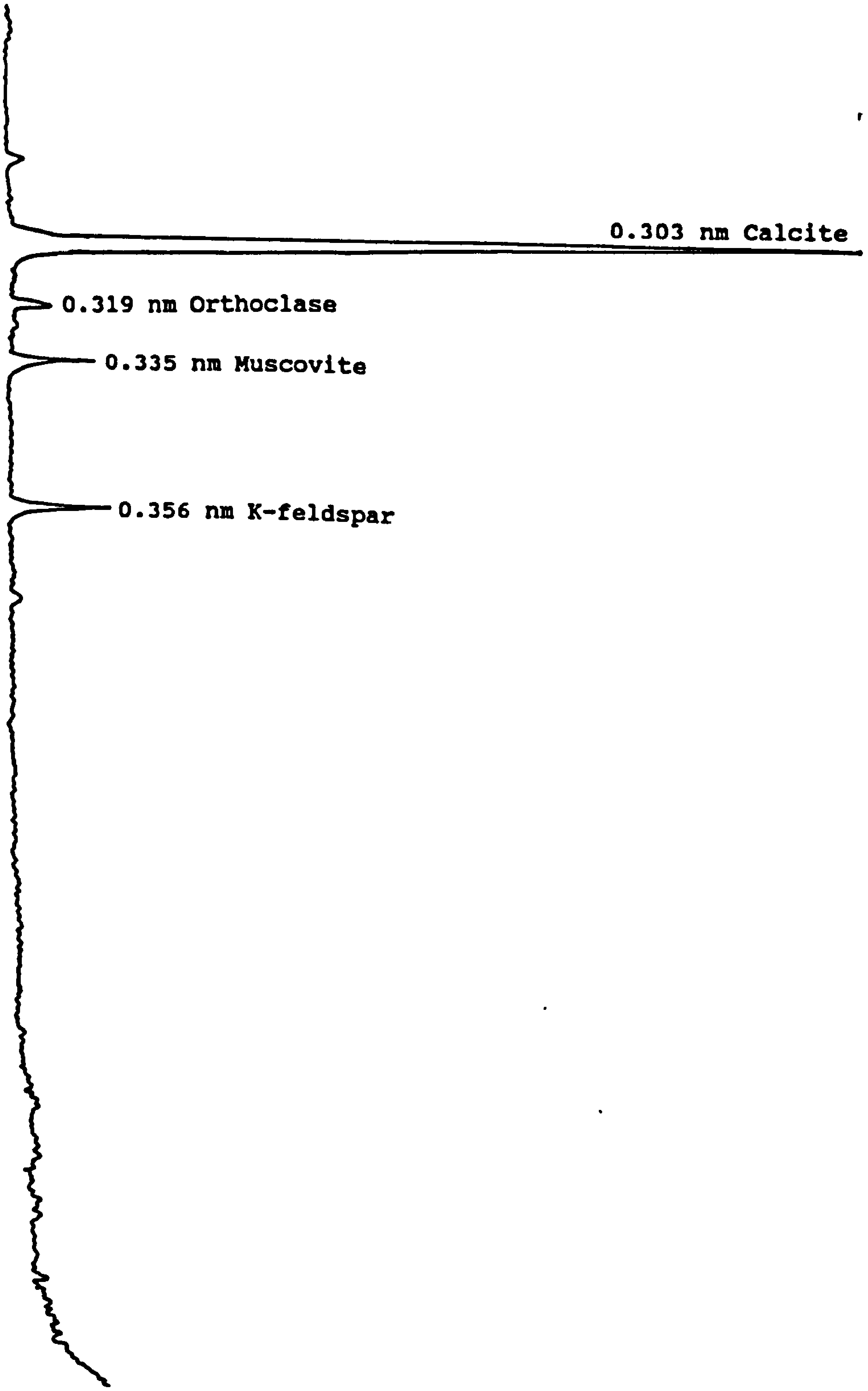


APPENDIX VI
XRDA trace: Sulaibiya soil.



APPENDIX VI

XRDA trace: Sulaibiya clay.



APPENDIX VI
XDRA trace: Sulaibiya gatch (caliche).