THE CORRECTION OF MANGANESE DEFICIENCY IN BARLEY CROPS GROWN ON THE WAROOKA CALCAREOUS SANDS

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STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except when due reference is made in the text of the thesis.

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SUMMARY

The research contained in this thesis was undertaken to establish the most satisfactory method to correct Mn deficiency in barley crops grown on the Warooka calcareous sands, (80 per cent $CaCO_3$), located on Southern Yorke Peninsula.

Seventy six per cent of added divalent Mn incubated with these soils was immobilised within 167 hours by chemical and biological processes. In this period 71 per cent of the total fixation was accomplished by chemical processes.

In field experiments conducted over seven years, manganese sulphate applications up to 16 kg Mn/ha drilled with the barley seed did not prevent Mn deficiency occurring in crops. However, the applications increased crop growth (tops and roots), delayed the appearance of plant symptoms characteristic of Mn deficiency, increased grain yield by an average of 61 per cent and improved grain quality. The optimum application of Mn at seeding for maximum grain yield was 6 kg Mn/ha (25 kg manganese sulphate/ha).

Increased vegetative growth and grain yield (from 14 to 23 per cent) and improved grain quality resulted where the fertiliser Mn was incorporated with the superphosphate carrier, (compound fertiliser), compared with fertilising with the conventional mixed fertiliser.

The incorporation of elemental S in compound fertilisers increased vegetative growth and grain yield by up to 10 per cent, particularly where S applications were high (63 - 126 kg S/ha) and where Mn and P fertiliser

applications were suboptimal for maximum crop yield. S applications do not obviate the necessity of applying P and Mn at seeding, and the small size of the crop response to S precludes its use as a fertilizer ingredient for these soils.

The application of up to three foliar sprays applied at 0.9 kg Mn/112 l/ha did not completely correct Mn deficiency in barley crops grown on these soils. The best results were obtained by applying 6 kg Mn/ha to the soil at seeding as a compound fertilizer and followed by up to three foliar sprays applied to the crop during the season.

I. INTRODUCTION

The first indication that Mn was necessary for satisfactory plant growth came at the turn of this century. Various reports, notably from Bertrand (1905) indicated that Mn salts applied to soils produced "catalytic" effects on plant growth. McHargue (1922) subsequently confirmed that Mn was an essential plant nutrient. Mn deficiency was the first recorded trace element deficiency in Australia (Samuel and Piper 1928), when "grey speck disease" in oats was remedied by the application of manganese sulphate to a volcanic rendzina soil at Mt. Gambier (S.A.) and to a ground water rendzina at Penola (S.A.). Subsequent work by Piper (1931) and Leeper (1935) showed that soil pH, soil water content, organic matter, redox potential and soil sterilisation influenced the availability of soil Mn.

Scott (1932), investigating crop failures on shallow grey mallee soils near Corny Point (S.A.), showed that large barley yield increases could be produced by applying manganese sulphate to these soils at seeding time. He further showed that the Mn applications were better added to the soil with the seed, than broadcast on the crop several weeks later. Cook and Angove (1942) reviewed the work undertaken on this soil during 1931 to 1941 and found that after 4 or 5 applications of manganese sulphate (32 kg/ha), the average barley grain yield response to Mn applications had decreased to a marginal level. They concluded that the quantity of manganese sulphate could be reduced at this stage. Higgs and Burton (1955) and Carter and Heard (1962) reported that barley crops grown on these soils responded to 22 - 24 kg/ha manganese sulphate applied at seeding. Pastures did not respond to applied Mn.

Within the last two decades, the more marginal highly calcareous aeolian sands within this region of Southern Yorke Peninsula have been developed for agricultural purposes. Higgs and Burton (1955) distinguished two soil types in this area on the basis of depth of sand (greater or less than 46 cm) over sheet limestone, although Carter and Heard (1962) and French et al. (1968) made no distinction between them.

Higgs and Burton (1955) showed that barley crops and pastures grown on both soil types responded to superphosphate, Mn, Cu and N applications in the year the land was brought into cultivation. They suggested 250 kg/ha superphosphate, 22 kg/ha manganese sulphate and 5.6 kg/ha copper sulphate could be profitably applied to the first crop. Carter and Heard (1962) suggested that barley crops grown on these soils required superphosphate (186 kg/ha) and manganese sulphate (24 kg/ha), but the first crop following land clearing should receive 314 kg/ha superphosphate and also 5 - 8 kg/ha copper sulphate. Despite these fertiliser applications widespread crop failures still occurred on these soils.

The research contained in this thesis, comprising field, laboratory and glasshouse experiments, formed the basis of work undertaken to correct nutritional disorders in barley crops grown on the Warooka calcareous soils. In some experiments, nutrients applications were less than that necessary to produce maximum grain yield, but the research was aimed to give practical solutions to farm problems in the area. The study examines the effectiveness of a range of experimental fertilisers in correcting Mn deficiency in barley crops grown on these calcareous sands. The crop response to Mn sprays, blended fertilisers, inclusion of elemental S in the soil applied fertilisers, together with the rates of application of Mn and superphosphate applied to these soils has been evaluated.

II. LITERATURE REVIEW

I. INTRODUCTION

Mn deficiency in crops is encountered on a wide range of soil types, but most commonly on soils with a pH greater than 6.5.

In Australia, Mn deficiency in crops has occurred on alkaline soils such as the rendzinas, groundwater rendzinas, calcareous sands, terra rossas and solodised solonetzic soils as well as on the acidic podsolic sands and Pliocene sediments. A variety of crops, including cereals, pastures and horticultural crops have been improved by Mn applications. More recently, low fertility in sheep in certain parts of South Australia, has been related to Mn deficiency in the pasture.

The valency form of Mn seems to be the major criterion that decides Mn availability to plants. Factors such as soil pH, redox potential, reactivity of the Mn bearing primary and secondary minerals and oxides, and the presence of organic matter influence the supply of soil Mn. The predominance of the biological oxidation of Mn, compared with chemical oxidation has attracted a great deal of attention.

The nature of the differences among species and varieties in sensitivity to Mn deficiency, as well as the fundamental mechanisms involved in the transfer of Mn ions to the root, and the subsequent uptake and translocation of Mn within the plant are subjects that need clarification.

A variety of methods have been used to correct Mn deficiency in crops, although much more needs to be known so that efficiency of the methods can be improved.

In the following pages, factors influencing the availability of Mn

in the soil and the absorption and distribution of Mn within the plant are briefly reviewed, with special reference to methods of correcting Mn deficiency in field crops.

2. THE FORMS OF MANGANESE IN THE SOIL

Swaine (1955) reported after a survey of the world literature, that total soil Mn concentrations in the surface horizons ranged from 200 - 3000 ppm. The total Mn content of seven Australian soils ranged from 130 - 2510 ppm in the A horizon, and 43 - 1600 ppm in the C horizon (Oertel 1961). Total soil Mn has been shown to be poorly correlated with Mn availability to plants (Neff and Nederski 1958, Page et al. 1962).

According to Goldschmidt (1958), the primary sources of soil Mn are the ferromagnesian minerals present in the igneous rocks. Mitchell (1964) reports that the Mn is relatively evenly distributed in these rocks. Redistribution of Mn during sedimentation is controlled by the state of oxidation, rather than by particle size segregation (Hodgson 1963). Consequently, under conditions of impeded drainage, soil Mn can be mobilised and leached to lower soil horizons (Mitchell 1964).

Mn incorporated into the insoluble hydrous oxides are trivalent or tetravalent, the macroscopic forms developing as stains or Mn nodules in the soil. Taylor et al. (1964) and Taylor (1968) have identified the occurrence of Mn in several secondary minerals such as birnessite, $(Ca, Mg, Na_2, K_2)\ x, Mn^{4+}\ Mn^{2+}, (O, OH_2)$, and lithophorite, $(Li_2\ Al_8\ (Mn^{2+}, Co, Ni)_2\ Mn^{4+}_{10}\ O_{35}.14H_2O)$, in several Australian and overseas soils. Weathering of the ferromagnesian and secondary soil minerals releases Mn mainly in a divalent form, which is then partly reoxidised but may

become associated with other soil fractions, notably the soil clay. The reactions of these fractions in the soil determine the supply of Mn available for plants.

Plants take up Mn almost certainly as divalent Mn (Page et al. 1962, Rivenbark 1961, Goering et al. 1969). Divalent Mn is present in soils as exchangeable Mn absorbed on organic or inorganic soil colloids or in the soil solution at concentrations usually less than 1 ppm (Viets 1962). It may also be present as insoluble carbonates and phosphates (Uren 1969).

The size of the water soluble Mn fraction at any given time, is influenced by soil pH (Page 1962), soil redox potential (Piper 1931) and the concentration of other ions in the soil solution (Viets 1962).

The quantative estimation of exchangeable Mn in the soil, depends on the soil/solution ratio, extraction time, pH, replacing ions and the pretreatment of the soil (Neff and Nederaki 1958, Boken 1958, Hannes and Berger 1960a,b, Page 1964). Increasing the soil pH by heavy applications of liming materials can greatly reduce the exchangeable and water soluble concentration of Mn (Heintze 1946, Christensen et al. 1950, Fujimoto and Sherman 1948, Jones 1957a). Soil acidification reverses this effect (Vavra and Frederick 1952). Soil redox potential is closely associated with soil aeration and the content of water held by these soils. These soil properties are in turn related to the soil drainage characteristics (Grable 1966). Steenbjerg (1934) and Wain et al. (1943), reported an increase in exchangeable soil Mn due to water logging. In contrast, drying the soil increases the concentration of exchangeable Mn (Fujimoto and Sherman 1945, Boken 1952, Zende 1954, Jones 1957a). The relevance of

of these observations and of soil pH and redox potential in relation to the size of the divalent soil Mn pool, is discussed in the following section.

3. FACTORS AFFECTING THE DIVALENT Mn STATUS OF SOILS.

(a) The Oxidation and Reduction of Divalent Mn.

Soil Mn is subject to valency transformations, depending on the oxidation - reduction status of the soil system. If oxidation and reduction are occurring simultaneously, the Mn concentration in the equilibrium solution will be governed by the relative velocities of the oxidation and reduction reactions.

Both chemical and biological oxidation of Mn occur in soils, particularly when they are neutral to alkaline in reaction. Several investigations have indicated that biological oxidation is more important than chemical oxidation (Mann and Quastel 1946, Mulder and Gerretsen 1952, Rivenbark 1961, Uren 1969). The rate of chemical oxidation increases as the pH increases (Dion and Mann 1946, Rivenbark 1961). In most soils, a large proportion of added divalent Mn is oxidised within several hours or days (Romney and Toth 1954, Lamm 1960, Rivenbark 1961, Weir and Miller 1962, Reid and Miller 1963, Uren 1969).

Biological immobilisation of divalent Mn may result from several causes;

(1) biological oxidation of divalent Mn according to the reaction (Bromfield, 1958a)

$$Mn^{2+} \xrightarrow[\text{Microbes}]{O_2} Mn\,O_{1.76}$$

Uren (1969) has also demonstrated that CO_2 is required by Mn-oxidising

microorganisms before they will oxidise divalent Mn. For maximum biological oxidation to take place, an optimum O_2/CO_2 ratio in the soil is required.

(ii) Plant roots and microbial colonies indirectly influencing the soil pH and redox potential, which affects the chemical solubility of soil Mn within the soil volume surrounding them (Hodgson 1963).

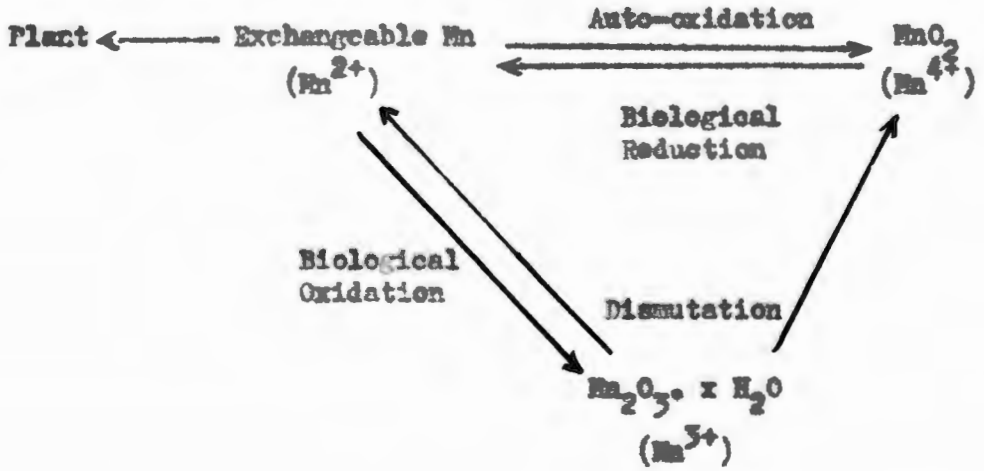
Prevention of microbial oxidation in sterilized soil, and reduction of microbial activity in air dry soil are known to increase water soluble and exchangeable Mn (Fujimoto and Sherman 1945, Mann and Quastel 1946, Timonin 1946, Boken 1952, Zende 1954, Jones 1957a). These increases are caused by Mn oxides being partially reduced to divalent Mn, even under aerobic conditions, which is not biologically re-oxidised due to the reduced microbial activity in the soil.

Rivenbark (1961) suggested that the chemical oxidation of Mn in the soils he investigated, was related to the oxidation state of the soil iron, and to a lesser extent aluminium. Soil pH exerted its effect by regulating the solubility and form of iron and aluminium which substituted for Mn in the higher oxides, thereby releasing divalent Mn. He also proposed that the primary products of Mn oxidation are compounds having the solubility characteristics of trivalent Mn oxides. Boken (1955, 1956a and b, 1960b) also showed that the addition of ferrous sulphate with and without pyrolusite (MnO_2) increased plant yield, Mn uptake and exchangeable soil Mn concentrations.

Schollenberger (1928) found that calcite crystals mixed with an acid sand became covered with a deposit of manganese dioxide. Ghuman and Whittig (1969) and Ghuman *et al.* (1968) postulated the formation of

a "mangocalcite", $((Ca, Mn)\ CO_3)$, in a calcareous soil that was flooded and then dried. Reduced Mn uptake by sorghum plants resulted. Heintze (1968) showed that Mn phosphates can form in solution, but are chemically precipitated in the pH range 6.5 to 9.0, suggesting that phosphate ions may chemically immobilise divalent Mn.

A comprehensive scheme illustrating the cycle of Mn in soils has been put forward by Dion and Mann (1946), as shown below.



This scheme has gained wide acceptance, but recent studies suggest it oversimplifies the actual processes involved. The essential features of the cycle are:

(i) water soluble and exchangeable soil Mn is available for plant absorption.

(ii) auto-oxidation (chemical oxidation of Mn^{2+} to Mn^{4+}) occurs at pH greater than 8.

(iii) biological oxidation of Mn^{2+} to Mn^{3+} is the first step in the Mn oxidation in less alkaline soils.

(iv) Mn^{3+} disproportionates to Mn^{2+} and Mn^{4+} according to the reaction:

$$2MnOOH + 2H^{+} \rightleftharpoons Mn^{2+} + MnO_2 + 2H_2O$$

The forward reaction proceeds more rapidly as the soil pH decreases.

(v) biological reduction of Mn^{4+} to Mn^{2+}.

The weakness of the cycle is found in the mechanisms of the last two reduction reactions, as applied to neutral and alkaline soils. According to Uren (1969), since the actual composition of the soil Mn oxides are unknown, the reduction reaction is probably better represented by:

$$MnO_x \xrightarrow[\text{electrons}]{H^{+}} Mn^{2+}$$

The rate of the reduction reaction is determined by the activity of the hydrogen ions, a supply of electrons from soil reducing processes, and the reactivity of the Mn oxides.

Wadsley and Walkley (1951) have shown the reductive reactivity of Mn oxides was related to the oxide composition (higher oxidation states being more reactive), oxide particle size (smaller particle sizes expose a larger surface area for reduction), and the degree of crystallinity of the oxide (amorphous forms are more reactive). Jones and Leeper (1951a, b) demonstrated that Mn oxides with these specific properties (e.g. manganous manganite) were capable of correcting Mn deficiency in oats and peas grown on Mn deficient soils. Other oxides (e.g. hausmannite) which did not possess these characteristics were inert soil amendments. The rate at which the Mn oxides were reduced by mild reducing agents, such as quinol, was a good index of their availability to plants. Jones and Leeper (1951b)

postulated the loss of reactivity of the Mn oxide with length of time in contact with soil was due to the reversion of the Mn oxide to a more ordered crystalline structure. Uren (1969) considered the reversion was a function of a decrease in the total reactive surface area (T.R.S.A.) of the Mn oxide, where,

T.R.S.A. = surface area x reactivity of the oxide.

The ability of growing roots to reduce Mn, by supplying electrons through root exudates, by altering the reducing capacity of the rhizosphere, or by contact reduction is widely recognised (Bromfield 1958a, b, Passioura and Leeper 1963a, Uren 1969). Electrons are also released from the decomposition of soil organic matter (Mann and Quastel 1946, Leeper 1947).

In the theory of "contact reduction" proposed by Leeper (1935, 1947), Passioura and Leeper (1963a), and Uren (1969), reduction of Mn oxides occurs at the root-soil interface, and the released divalent Mn is then directly absorbed by the root. Although difficult to substantiate experimentally, the theory has credibility, as the growing portions of the root system can reduce oxidised compounds (Schreiner et al. 1910, Uren 1969). The postulated process may also include "contact exchange" (Jenny 1939). The importance of the soil-root contact reduction theory cannot be overlooked, and it would appear that the amount of root contact reduction occurring in any one system depends on the plant root density.

In summary, the release of divalent Mn in neutral and alkaline soils to plant roots is a function of a complex dynamic oxidation - reduction system. Biological and chemical oxidation of divalent Mn decreases the concentration of Mn available to plant roots. Soil and

plant reduction processes (microbial, root, rhizosphere or root contact reduction) on the other hand increase the concentration. The importance of soil pH and redox potential exert a strong influence on the system through their effects on microbial populations and activities, the solubility of Mn and other compounds in the soil, and the ability of the plant roots to reduce Mn oxide and to absorb the divalent Mn released.

(b) Other Factors.

Other soil factors which influence the concentration of divalent Mn in soils include the soil organic matter, the role of which has been critically reviewed by Fassioura and Leeper (1963b), the adsorption of Mn onto inorganic colloids, and the occulsion of Mn in developing soil sesquioxides (Mg and Bloomfield 1961, 1962, Le Riche and Weir 1963). An analysis of the importance of these factors as they affect Mn supply to plants is beyond the scope of this review.

4. MANGANESE ABSORPTION BY PLANT ROOTS AND TRANSLOCATION TO THE FOLIAGE.

(a) Mn at the Root - Soil Interface.

Barber et al. (1966) and Barber (1968) have suggested there are three significant mechanisms in the uptake of Mn by plants; mass flow (convection), diffusion, and root interception. The quantitative evaluation of the relative contribution of each of these mechanisms towards Mn uptake does not appear very precise, but their role in the Mn nutrition of plants has been established.

Following Barber's approach, Halstead et al. (1968) suggested that diffusion was an important pathway in Mn deficient soils, whereas convection was important in soils well supplied with Mn. Differences in plant Mn

uptake between soils, were attributed to differences in the magnitude of root interception and/or diffusion. Pascicura and Loeper (1963a), favoured the root-Mn oxide contact reduction theory, to explain Mn uptake by plants in neutral and alkaline Mn deficient soils. In this theory the Mn oxide is reduced on "contact" with the plant root. Jenny (1966) suggested that the surface diffusion of Mn from clay through the mucilage may be important in the transfer of Fe and Mn in alkaline soils. Root exudates may also be important in supplying Mn to plants (Bromfield 1958a,b), although the exact mechanism is not well understood. However, the effect of the rhizosphere on Mn uptake into plants is being increasingly recognised (Ozanne and Barber 1970).

Gerretsen (1937) and Hasler (1951) have shown that Mn deficient plants have reduced root systems. According to Mulder and Gerretsen (1952) this may be in part due to decreased multiplication in the meristematic zone of the root tip. Page (1961) showed that more Mn is absorbed by the root tip than by the remainder of the root. These observations suggest that root morphology, root density and root growth may be important determinants of the amount of Mn absorbed from a soil by plants.

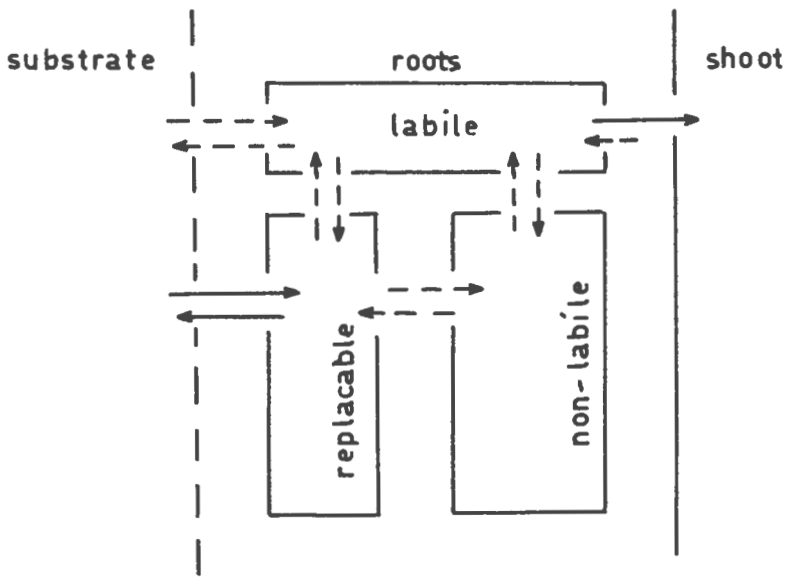
(b) Mn Entry into Roots.

Page and Dainty (1964) and Munns et al. (1963b) have apportioned the root absorption of Mn into two arbitrary phases;

(i) an initial rapid uptake which is completed in about 30 minutes, representing the rapid attainment of equilibrium in a process of ion exchange between the root cell wall (Donnan free space) and the external medium. This fraction of root Mn was called "exchangeable".

(ii) A slow uptake phase in which the equilibrium is not reached even after three hours. This phase is more likely to be associated with sites chemically or spatially different from those retaining the "exchangeable" Mn. However, the Mn taken up in this phase was not within the cytoplasm, as the uptake was not influenced by plant metabolic processes (Page and Dainty 1964).

Munns et al. (1963b) proposed the following model to explain root uptake and transport of Mn to leaves.



The proposed scheme involved three Mn fractions within the root, a replaceable fraction ("exchangeable Mn") and two non-replaceable fractions that were not exchangeable with the substrate. The first non-replaceable fraction was considered "labile" (i.e. Mn could be transferred from this fraction to the shoot). This Mn fraction accumulated more rapidly than the non-labile fraction and was concentrated towards the extemities of young roots. Mn translocation t the shoots was a function of the size and rate of turnover of this fraction in the root. The non-labile Mn pool was concentrated in the older regions

of the root, and was largely bypassed in the movement of Mn from the root to the shoot. It may be mobilised when Mn supply from the soil is low.

van Diest and Schuffelen (1961) proposed that the absorption of Mn was via two carriers; one specific for Mn and the other non-specific, depending on the chemical affinity of Mn or Ca for the binding site.

They concluded that Ca, in addition to lowering the solubility of Mn in soils, also competed with Mn for absorption sites within the plant. Quellette and Dessureaux (1958), and Barber (1968) have also shown that the supply of Ca in the substrate can affect Mn absorption and translocation to the shoots. The antagonistic effect of Ca, is likely to be important in crops grown on calcarecus soils, low in Mn supply.

Rivenbark (1961) showed that Ca, Fe and Al depressed Mn uptake in soybeans, whilst Bingham (1963) showed that heavy phosphate applications increased the concentration of Mn in the roots of four plant species. Nambiar and Cottenie (1971) showed that increases in soluble soil Mn by reduction does not necessarily lead to an increase in Mn uptake by the plant, if there is a concomitant increase in divalent iron in the soil solution. The antagonistic effect of Fe may be relevant in puddled soils.

(e) Translocation and Redistribution of Mn within the Plant.

Munns et al. (1963b) and Vose (1963) have suggested that the root Mn may act as a reservoir for Mn translocation to the foliage, which may be important during periods of Mn stress in the plant. However, Munns et al. (1963b) proposed that the primary pool of root Mn for translocation to the shoots was the "labile pool", and that the rate of Mn translocation from the root was determined by the size and rate of turnover of this pool. Single

and Bird (1958) showed that root Mn concentration was depleted to about 10 ppm, and then maintained at this concentration, despite severe Mn stress in the shoots.

Mn is preferentially translocated from the roots to the actively growing centres of the plant shoots (e.g. young leaves or the primary shoot apices), largely bypassing the older leaves (Williams and Vlamis 1957, Vose 1963).

Williams and Vlamis (1957) observed numerous "islands" in leaves suffering Mn toxicity. They demonstrated that the necrotic spots on the leaves were highly concentrated in Mn, suggesting immobilisation or precipitation of Mn had occurred. Similar "islands" were observed by Millikan (1951) and Romney and Toth (1954) in the older tissues of several species. These "islands" were not observed when soluble silicates were added to the nutrient solution, suggesting that silicates alter the distribution of Mn within leaves, thereby preventing accumulation (Williams and Vlamis 1957). Single and Bird (1958) suggested that when leaf Mn concentrations are high, Mn may be deposited as silicates, phosphates of molybdates. These depositions may control the concentration of Mn within the leaf, without interfering with Mn utilisation or redistribution.

Williams and Moore (1952) found that leaf Mn was not redistributed during the senescence of oat plants. Mn accumulated in the leaf up to the grain ripening period, but the rate of accumulation decreased after flowering. However, Mn redistribution from individual leaves may have occurred, which their method of sampling could not have detected. Part of the Mn in cereal stems is exported to the grain after flowering (Williams and Moore 1952, Heintze 1968). Single and Bird (1958) and Vose

(1963) demonstrated that Mn contained in old cereal leaves does redistribute to the new leaves probably via the phloem. The amount of Mn redistributed is however relatively small, but may have significant physiological effects. Vose (1963) concluded the extent of Mn redistribution was determined by the severity of the plant Mn stress.

Mn accumulated in pea plants before the flowering period is not redistributed during flowering (Lewis 1939, Heintze 1946, Quastel et al. 1948). If Mn supply to the plant is limiting during the period of seed formation, "marsh spot" deficiency symptoms develop.

5. AGRONOMIC TECHNIQUES FOR CORRECTING Mn DEFICIENCY IN PLANTS.

The correction of Mn deficiency in crops has been attempted by several methods; application of fertilisers to the soil, foliar application of Mn salts, the growing of tolerant species and cultivars, and soil sterilisation.

(a) Mn Fertiliser Applications to the Soil

Soluble or slightly soluble Mn salts, such as sulphates, chlorides, oxides and phosphates have been used in attempts to prevent or correct Mn deficiency in crops. Application rates have generally varied between 20 - 400 kg/ha manganese sulphate equivalent.

Divalent Mn salts have been shown to be superior to the insoluble manganic salts such as manganese dioxide (Piskel 1953, Higgs and Burton 1953), and potassium permanganate (Sherman and Harmer, 1941). In most instances where comparisons have been made, manganese sulphate has proved equally effective or superior to the other carriers. (Connor 1932, Sherman and Harmer 1941, Schropp 1949, Piskel 1953, Piskel and Mourkides

1955, Shepard et al. 1960, Beer et al. 1968, Smilde 1968). According to Tisdale and Cunningham (1963), manganese oxide (MnO), which is slightly soluble in weak acids compared favourably with manganese sulphate, and was at least four to five times more effective than manganese dioxide. Smilde (1968) observed that MnO and $MnSO_4 \cdot H_2O$ applications to a Mn deficient calcareous soil resulted in similar yield responses in oats. Jones and Leeper (1951, a,b) showed that plants grown on Mn deficient soils could extract Mn from several natural and synthetic Mn oxides. The extent of Mn dissolution depended on the total reactive surface area of the oxides to undergo reduction (a function of the surface area and degree of crystallinity). Oxides with small surface areas or high crystallinity (e.g. hausmannite) were inert, whereas manganous manganite (σ MnO_2) was equal or better than manganese sulphate in supplying Mn to plants.

Band placement of manganous Mn carriers has been shown to be more effective than surface broadcasting for the correction of Mn deficiency in a variety of plant species (Scott 1932, Leeper 1935, Quastel et al. 1948, Steckel et al. 1948, Shepard et al. 1960, Hannes and Berger 1960). The failure of surface applied Mn salts to correct Mn deficiency seems largely due to positional unavailability, related to the poor mobility of Mn in deficient soils.

Complete correction of Mn deficiency in crops by applying inorganic Mn salts to the soil has been recorded (Conner 1932, Wallace 1940, Harmer 1942). However, other studies have shown that although yield may be increased, the application of inorganic Mn salts to some soils results in only a temporary correction of Mn deficiency (McLachlan 1941, Barbier et al. 1950, Henkens

and Smilde 1967). Even when yield has been increased, low apparent recoveries, (less than 1 per cent) of the fertiliser Mn by plants have been observed (Piper 1931, Coic et al. 1950). This has been attributed to the progressive oxidation of divalent Mn in the fertiliser (Wain et al. 1943, Heintze 1946, Viets 1962).

The residual effect of manganese sulphate is usually low or non existent, particularly on severely deficient soils (Leeper 1939, 1947, McLachlan 1943, Wain et al. 1943). This again is partly due to the oxidation of the applied Mn. Jones and Leeper (1951b) suggested that the residual effect of reactive Mn oxides in soils was greater than that of manganese sulphate.

In conclusion the application of inorganic Mn carriers to deficient soils often results in only a short lived correction of plant Mn deficiency because of the progressive oxidation of the applied Mn to unavailable forms. The effectiveness of any one Mn application will depend on the severity of the deficiency, the method of fertiliser placement, the soil and the crop being grown.

(b) The Application of Acid Forming Fertilisers.

Localised or broad scale soil acidification increases the concentration of divalent Mn in the soil. It may also prolong the availability of applied fertiliser Mn.

(i) The role of elemental S and allied fertilisers in correcting Mn deficiency.

The addition of elemental S to soils has frequently been advocated to prevent or reduce Mn deficiency in crops (Boullanger 1912, Leeper 1939, Sherman and Harmer 1941, Harmer 1942, McLachlan 1943, Quastel et al. 1948,

Tisdale and Bertramson 1949, Johansson and Ekman 1956). Ludwick et al. (1968) suggested that sulphur fortified Mn carriers held promise for supplying Mn over extended periods, particularly to crops grown on marginally deficient soils.

The effectiveness of this technique for correcting Mn deficiency depends on the rate of S oxidation. Attoe and Olsen (1966) and Powrie (1967) have shown that the rate of S oxidation is determined by the presence, population size and activity of S oxidising micro-organisms. Particle size and porosity of the fertiliser granules were also considered important.

Oxidation of S by specific soil bacteria, results in the formation of sulphate and hydrogen ions, and the release of electrons. The hydrogen ions and electrons are then used to reduce MnO_2 according to the stoichiometric equations (Tisdale and Bertramson 1949).

$$S + 4H_2O \xrightarrow{\text{microbes}} SO_4^{2-} + 8H^+ + 6e$$

$$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$$

Increases in the amount of exchangeable Mn on the addition of large amounts of elemental S (314 - 1680 kgS/ha), particularly in the presence of applied MnO_2 has been reported (Tisdale and Bertramson 1949, Carey and Barber 1952, Vavra and Frederick 1952). However, the increase in exchangeable Mn was small in Mn deficient soils, regardless of the fall in soil pH. On the other hand, Vavra and Frederick (1952) showed that the addition of S and MnO_2 together, resulted in a large increase of

extractable soil Mn in a deficient soil, and only a small increase in a non deficient soil. The authors concluded the small increase in exchangeable Mn in the deficient soil, was limited by the amount of soil Mn available for reduction.

Ludwick (1964) evaluated Mn - S fusions as sources of manganese for plant growth, and showed that Mn uptake was directly related to the solubility of the Mn compound, and inversely related to the size of the fertilizer granule, and only slightly influenced by the ratio Mn/S in the granule within the range 1:1 to 1:4. Ludwick et al. (1968) subsequently showed that plant yield and Mn uptake from eight successive cuts of perennial ryegrass was greater where manganous carbonate - S fusions were applied compared with applications of manganese dioxide - S fusions.

In laboratory perfusion experiments, application of thiosulphates to soil, rapidly decreased soil pH and increased the content of soluble Mn (Vavra and Frederick 1952). In field experiments, Quastel et al. (1948) showed that thiosulphate applications up to 5022 kg/ha reduced plant Mn deficiency symptoms and increased the concentration of soluble Mn in leaves, but the effects were transient.

(ii) <u>The application of phosphatic fertilisers in relation to Mn availability</u>.

(a) <u>The effect of phosphatic fertilisers on the availability of native soil Mn</u>.

Lindsay and Stephenson (1959a,b,c) studied the relation between mono calcium phosphate (MCP) and its dissolution products in soil. They demonstrated that in the initial period of phosphate dissolution, the soil pH around the pellets was lowered to about one, and considerable quantities of soil Mn were dissolved by the acidic fertilizer solution.

As this concentrated solution moved slowly away from the fertilizer pellet into the adjacent soil some of the dissolved soil constituents moved with the fertilizer solution. As more soil was contacted, the pH of the solution rose and certain phosphate compounds slowly began to precipitate. Presumably, soil Mn released in this manner must be absorbed by plant roots before soil processes again render it insoluble.

Bingham and Garber (1960) showed that very heavy phosphate applications (900 kgP/ha) significantly increased leaf and root Mn concentrations in citrus grown in twenty soils ranging in pH from 4.3 to 8.2. Mn concentrations in soil saturation extracts were increased by the heavy P applications, but this increase was not always associated with changes in soil pH. Page et al. (1963) and Larsen (1964), showed that heavy superphosphate applications increased the availability of soil Mn to crops. Page attributed the effect to a decrease in soil pH. Larsen (1964) speculated on the possibility that P might also enhance translocation of Mn within the plant. Evidence of improved Mn supply on application of P has also come from Hossner and Richards (1968), who employed pure ammonium phosphate fertilizers. Finke (1966), with three different soils each brought to a range of pH values, studied the uptake of Mn, Fe and Al as affected by different sources of P fertilizer. The major conclusions were that Mn uptake was related to the pH of the fertilizer and the soil, and that superphosphate applications increased the Mn uptake in barley.

In contrast to the above mentioned reports, Steckel et al. (1948) found that plant yield and Mn concentration was not

significantly affected by application of 73 kgP/ha as superphosphate. Heintze (1968) showed the grain yield of oats was depressed by applying 840-1680 kg/ha superphosphate equivalent as an MCP solution to a Mn deficient alkaline fen soil, and concluded that the acidifying properties of phosphate fertilisers, and the resulting mobilisation of soluble Mn will operate only in soils of low buffering capacity.

In summary, the dissolution of phosphatic fertilizers applied in large quantities in most cases has caused the production of an acidic fertilizer solution which decreases the soil pH around the fertilizer granule and dissolves native soil Mn. The Mn so released either as divalent Mn or as a complex manganese phosphate increases the amount of soil Mn available to the plant. The amount of Mn released and its availability with time is likely to be determined by the soil properties.

(b) <u>The effect of phosphatic fertiliser on fertiliser Mn availability</u>.

(i) <u>Mn and P applied as separate entities</u>.

Steckel <u>et al</u>. (1948) in a pot experiment showed that plant Mn concentrations were increased by mixing superphosphate and manganese sulphate together in a band compared with applying the fertilisers separately. One increment of banded manganese sulphate and superphosphate was more effective than two increments of banded manganese sulphate alone. The authors attributed this increased efficiency to both limited soil - Mn fertiliser contact, and the precipitation of Mn phosphates, which in the vicinity of increased acidity, provided a small but continual supply of Mn to the plants. Hammes and Berger (1960) reported yield increases

in oats where manganese sulphate had been mixed and banded with an acid forming fertiliser, compared with applying Mn in a band.

Heintze (1968) demonstrated by electrometric titration and chemical analysis of an aqueous $MnSO_4$-H_3PO_4 system, that Mn phosphates are formed, but are completely precipitated between pH 6.5 - 9. In a glasshouse experiment she showed that manganese sulphate and MCP solution additions to a Mn deficient alkaline fen soil, resulted in depressed oat grain yields (except at the higher Mn application rates). Straw weights however were increased. Grain Mn concentration was decreased and stem and leaf Mn concentrations were increased, particularly where the Mn and MCP solutions were applied together, suggesting the P effect exerts its influence within the plant itself. Similar conclusions were drawn by Larsen (1964). The apparent conflict between Heintze's results and the other investigations cited could be in the form of the fertiliser materials (solution compared with solid fertilisers) which may have influenced the rate of fixation of the applied Mn. Differences in soil properties may have also affected the results.

(ii) Granulated compound fertilisers containing P and Mn

Walsh and McDonnell (1957) reported greater cereal yields were produced where a compound N-P-K fertiliser containing Mn was drilled with the seed, than where manganese sulphate was broadcast or sprayed onto the crops. Hosmer and Richards (1968) tested the behaviour of a range of compound Mn fertilisers prepared by blending $MnSO_4.H_2O$ with MCP, mono ammonium phosphate (MAP), diammonium phosphate (DAP) and ammonium poly phosphate (APP) in the ratio of Mn:P of 1:2. Greater

plant Mn uptake was measured in soybean plants fertilised with these compound fertilisers, compared with plants fertilised solely with Mn. Although a growth response to Mn application was not obtained in this experiment, the relative value of the phosphate carriers for increasing Mn uptake into soybean after thirty days growth was -

$$MAP = APP >> MCP = DAP$$

Plant Mn uptake was greater where the saturated pH of the phosphate carrier was between pH 2 and 4. Mn movement into the surrounding soils, depended on the phosphate carrier and was not detected at pH > 5.8. Mitikin (1954) also showed that fertiliser Mn is more strongly held in N-P-K fertilisers, as the fertiliser pH increases.

Hosmer and Blanchard (1968) studied the reactions of seventeen compound Mn ammonium polyphosphates (Mn concentration 5 - 5.8 percent total product) in a Mn deficient soil. The period of reaction was 14 days. X-ray analysis of the fertiliser residues identified the insoluble reaction product, $Mn_2(NH_4)_2(P_2O_7)_2.2H_2O$ in thirteen samples. The remaining four fertilisers all had saturated fertiliser pH > 2.5, and following reaction with the soil only 10 percent of the fertiliser Mn was retained in the pellet. There was a direct relation between the amount of Mn retained in the pellet after reaction with the soil and the saturated fertiliser pH, ($r^2 = 0.92$). Giordano and Mortvedt (1969) also showed that manganese sulphate (10 percent Mn in the final product) incorporated with APP or triammonium pyrophosphate (TPP) reduced the solubility of both the fertiliser Mn and P, due to the formation of a relatively insoluble fertiliser reaction product identified as $Mn(NH_4)_2P_2O_7.2H_2O$. Granulating

Mn with MAP slightly affected the fertilizer ingredient solubilities. They concluded that Mn polyphosphates would be poor carriers of Mn.

(c) The Application of Mn Frits and Chelates

Frits are high temperature fused glasses of very low solubility, containing trace metals. Their application aims to supply small quantities of micronutrients continually to the developing crop. Shepard et al. (1960), Holden et al. (1962), Middleburg and Baren (1965), and Henkens and Smilde (1967) showed that Mn frits were inferior to other Mn carriers in supplying Mn to plants. The rate of release of Mn from the frits was apparently insufficient to meet the crop requirements during development.

Mn chelates have been applied to the soil, or as foliar sprays, but their use has been limited to high value crops and ornamentals because of their cost (Nelson 1965). Their effectiveness depends on the stability of the Mn-ligand complexes. They are known to retain Mn in a soluble form for a longer period of time than carriers which do not form complexes. However, the Mn in the complexes can be displaced by several cations, depending on the affinity of the competing ion for the complexing ligand, the equilibrium pH and other cations present (Lindsay et al. 1966, Boxma and De Groot 1971).

Perkins and Purvis (1954) showed that Fe replaced Mn from MnEDTA applied to a Mn deficient soil. Tomato yields did not respond to an application of 5.6 kg Mn/ha in the chelated form and higher rate of application reduced yields. More recently, Boxma and De Groot (1971) showed that the stability of Mn-EDTA was too low to supply plants with adequate Mn, due to alkaline hydrolysis and substitution of Mn by Ca in the chelate.

Mn-DTPA on the other hand not only corrected Mn deficiency but also Fe deficiency due to the partial replacement of Mn in the chelate by Fe.

In general, the soil application of Mn chelates for the correction of Mn deficiency has had only limited success, primarily due to the cost and the low stability constant of commercially available Mn chelates. However, in the future these carriers may provide useful sources of trace metals to crops, as newer products such as MnDTPA are evaluated.

(d) Foliar Application of Manganese

The application of nutrients to plant foliage has gained the wide attention of many workers as a means of correcting nutrient deficiencies in field crops (Caldwell 1955, Thorne 1955, Wittwer et al. 1963). Micronutrients are often efficiently supplied to crops by foliar sprays, partly because of the low mobility of the metal ions in soils and partly because the micronutrients are required by the plant in such small quantities. Foliar sprays also enable nutrients to be supplied at specified periods in crop development.

(i) Mn compounds used in foliar sprays.

McLean and Gilbert (1925) and McLean (1927) were the first to report that dilute manganese sulphate sprays could be used to correct Mn deficiency in crops. Table 1 summarises the quantities of Mn, spray concentrations, and spray volumes used by some investigators to correct Mn deficiency in a range of crops. Correction of Mn deficiency can be achieved by foliar applications of manganese sulphate covering a reasonably wide range of spray concentrations and spray volumes. In

TABLE 1

Details of some investigations in which Mn foliar sprays have been used to correct Mn deficiency in crops.

Reference	Crop	Manganese sulphate applied (kg/ha)	Manganese sulphate solution conc. (%)	Solution volume (l/ha)
Lewis[+] (1939)	Peas	5.6–22.4	0.5–2.0	1122
Steckel (1946)	Soybeans	11.2	0.8	1403
Nicholas (1951)	Oats	2.8–14.0	0.1–0.5	2805
Osaki (1955)	Peas, beans	3.4	0.3	1122
Henkens (1958)	General	12–15	1.5	1122
Greenall (1960)	Wheat	22.4	0.6	3590
McLeod (1961)	Wheat	5.6–22.4	3.3–13.3	168
Rose and Dermott (1962)	Cereals, peas	5.6	0.5	1122
Henkens and Jorgman (1965)	Cereals, beet, peas	9–15	1.5–2.5	600–1000
Elliot (1969)	Oats, tobacco	3–9	0.7–2.1	450

[+] Mn applied as manganous chloride.

general, 1 - 2 percent manganese sulphate solutions have been used on most crops, however higher concentrations have been employed in spraying fruit trees before bud development (Henkens 1958).

Lewis (1939) applied manganous chloride and efficiently corrected "marsh spot" in peas. According to Tisdale and Cunningham (1963), finely pulverised manganous oxide compared favourably with manganese sulphate. MnO forms an alkaline solution which does not burn foliage. Mn chelates have been used as foliar sprays with some success, but their use is restricted by their high costs (Wallace 1962).

(ii) Uptake and redistribution of foliar applied Mn.

Relatively large amounts of foliar applied Mn can be absorbed by leaves of many plant species (Bukovac and Wittwer 1957, Mederski and Neff 1958, Singl 1958, Vose 1963, Wittwer et al. 1963). For example, Bukovac and Wittwer (1957) indicated that within 24 - 28 hours fifty percent of the applied Mn had been absorbed into bean leaves. Mederski and Neff (1958) showed that sixty percent of the Mn absorbed by soybean leaves was taken up during the first two hours following dipping the leaves in Mn solution. They further showed that Mn penetration into the leaves increased at lower vapour pressure gradients between the leaf and the atmosphere, and at higher solution temperatures (20.6°C versus 2.2°C). Young leaves were more efficient absorbers of foliar applied Mn than older leaves. Single (1958) demonstrated that rewetting the sprayed wheat leaves did not significantly increase Mn absorption.

Foliar applied Mn is poorly redistributed within the plant, the translocation being largely, but not entirely, restricted to small movements in the immediate vicinity of the appli ation site.

However, small amounts of Mn are translocated to young developing tissues (Bukovac and Wittwer 1957, Singl 1958, Henkens and Jorgman 1965, Vose 1963). Single (1958) showed that healthy wheat leaves that were sprayed with Mn remained healthy, despite a shortage of Mn in new forming leaves. He suggested the immobility within the phloem was not the only factor and that possibly Mn may tend to accumulate at reaction centres remote from the phloem (e.g. mitochondria or chloroplasts).

Henkens and Jorgman (1965) showed that the redistribution of foliar applied Mn in barley and beet depended on the site of application of the Mn. Treatment of the basal part of leaves resulted in a more pronounced movement towards the leaf tip, than vice versa. The underside of leaves absorbed more Mn than the upper side. This may have resulted from differences in stomate number and cuticle structure between the two sides of the leaf. Transport from the left side of the leaf to the right side was comparatively small. Romney and Toth (1954) showed that Mn could be absorbed through the stem and petiole and that the redistribution of the absorbed Mn was again towards the younger tissues.

Foliar applied Mn is also redistributed to the roots in small quantities (Boken 1960, Henkens and Jorgman 1965 and Romney and Toth 1954). However Single (1958) did not find an increase in root Mn content twenty days after a foliar application of Mn to wheat plants. Mn may have been redistributed from the root during this period.

(iii) Timing the foliar applications of Mn.

Henkens (1958) and Henkens and Jorgman (1965) showed in field experiments with cereals, beet and potatoes conducted on Mn deficient soils, that manganese sulphate sprays were best applied as

soon as the deficiency symptoms appeared. Crop yield and quality was improved by further foliar sprays, as Mn deficiency symptoms reappeared in newly formed leaves, following the initial spray application.

Additional yield response to more than one foliar spray have been reported in other crops, (Steckel 1946, Nicholas 1951, Heard and Reuter 1965, Cox 1968). van Alphen (1956) in his review concluded that repeated dilute Mn sprays resulted in greater plant responses than did a single more concentrated spray. Several Mn foliar sprays applied during the flowering period of pea crops has resulted in negligible loss of pea quality due to "marsh spot" (Lewis 1939, Rose and Dermott 1962, Henkens and Jorgman 1965). In contrast, other workers have suggested that a single Mn spray can counteract Mn deficiency in their situations (McLachlan 1941, 1943; Walsh and Cullinan 1945; Greenall 1960; Hammes and Berger 1960; McLeod 1961). However, in some of these studies the spray was applied on only one occasion, and it is possible that plant yields may have been increased by additional sprays.

The number of sprays required and their timing to effect maximum correction of Mn deficiency in crops will depend on the amount of new foliage that develops, the severity of the plant stress, the time the plant stress appears in relation to plant harvest and finally on the restoration of more favourable soil conditions.

To summarise, manganese foliar sprays have proved a useful method for correcting Mn deficiency in crops. The Mn is rapidly absorbed into the leaf and improvements in crop growth and colour can often be observed within a few days. These improvements may only be temporary, because of the low mobility of Mn within the plant. In some

situations repeated foliar sprays may be required to "completely" correct plant Mn deficiency. Foliar sprays are still inefficient methods for correcting Mn deficiency, since the quantity of Mn applied in a single spray far exceeds the plant's requirements for its complete growth. Available evidence suggests the initial spray should be applied when the first plant deficiency symptoms are visible. In severely deficient situations, soil applications of Mn, followed by foliar sprays are necessary (Heard and Reuter 1965).

(e) Use of Tolerant Species and Cultivars

Differences in tolerance of plant species to Mn deficiency have been reported (Samuel and Piper 1929, Mulder and Gerretsen 1952, Walsh and McDonnell 1956, Gerloff 1963, Labanauskus 1963). For example, Walsh and McDonnell (1956) list wheat, oats, sugar beet, mangels, potatoes, peas, raspberries, black currants and apples as being the most susceptible crops in Ireland to Mn deficiency.

Bromfield (1958b) compared the growth of oats (susceptible) and vetch (tolerant) on a Mn deficient soil. The two species differed in root morphology (root density and surface area) and hence in their ability to contact Mn ions, as well as the nature and amounts of root exudates capable of dissolving manganic oxides in the soil. He postulated that the species tolerance difference to Mn deficiency was due to the vetch having a higher concentration of Mn dissolving root exudates along its roots, than oats. Recently, Nambiar and Cottenie (1971) compared the Mn uptake of maize and beans under different soil water regimes, and postulated that the higher reductive capacity of bean plants, coupled with their higher

rate of transpiration are the two major plant factors responsible for differences in Mn uptake between the two species. It is also interesting to note that the bean plants were shown to have a smaller root system than the maize plants.

Differential varietal tolerance to Mn deficiency has also been widely reported (Gallagher and Walsh 1941, 1943, Mulder and Gerretsen 1952, Puckridge 1958, Toms 1958, 1959, Munns et al. 1963a). The tolerance mechanisms are complex. Walsh and Cullinan (1945) suggested the difference in varietal tolerance of peas was probably one of actual Mn requirements, as varietal differences were not accompanied by corresponding differences in plant Mn content. Steenbjerg (1944) drew similar conclusions when comparing oat varieties. Vose and Griffiths (1961) showed that resistant pea varieties had less leaf Mn but higher root Mn contents. Munns et al. (1963) reported differences of 30 to 50 percent in the Mn content of the shoots of different oat varieties. From the results of solution culture experiments, they postulated that the varietal differences could be explained by the size and rate of turn-over of a labile fraction of Mn in the root. Varietal differences in root Mn concentration were due to a non-labile fraction, the size of which was pH and temperature dependent.

Ouellette and Beaureaux (1958) suggested that differential resistance to Mn toxity in lucerne clones was in part due to differences in Mn translocation between the roots and the shoots; the tolerant cultivars had more Mn in the roots and less in the shoots. The differences were related to the active Ca in the root. Timonin (1946) showed that the rhizosphere of a susceptible oat variety contained a large population

of Mn oxidising bacteria, casein hydrolysing bacteria, and denitrifying organisms than a more resistant variety.

In a comprehensive study of oat variety susceptibility to Mn deficiency, Boken (1966) made the following observations, which emphasises that experimental technique is most important in assessing differential varietal tolerance.

> "... the effect of Mn on dry matter yield must constitute the decisive criterion of the suitability of a method, the varietal differences, independant of Mn application should not affect the results, and finally it is necessary to study the importance of the Mn level to the mutual susceptibility of the varieties."

In conclusion, it is apparent that growing resistant species or cultivars on marginally deficient soils may be a useful method for overcoming Mn deficiency. In severely deficient soils Mn fertilization will still be necessary, regardless of plant tolerance to Mn deficiency. The mechanisms contributing to the tolerance of plant Mn stress are complex, but plant differences in Mn requirements, differential Mn uptake by the root due to differences in the root itself or the effect that the root has on the soil, the rate of Mn translocation from the root to the shoot, and the efficiency of Mn utilisation by the plant would seem important.

(f) The Use of Soil Sterilants

It has already been noted that soil sterilisation prevents biological oxidation of divalent Mn in soils. Chemical reduction of Mn oxides to divalent Mn take place even under sterile conditions, leading to an increase in exchangeable Mn concentration in the soil.

Timonin (1946) and Timonin and Giles (1952) showed that sterilising

soil with calcium cyanide (560 kg/ha) significantly reduced or eliminated the rhizosphere populations of certain micro-organisms, including Mn oxiders, for up to 101 days. Cynagas, chloropicrin, and formaldehyde were also partially successful. An oat crop sown 125 days after the CaCN application did not develop "grey speck" symptoms, but the symptoms appeared on plants grown in unsterilised soil fertilised with manganese sulphate. The exchangeable soil Mn concentration was increased by the sterilisation, but the water soluble and easily reducible Mn concentrations were not affected.

The use of soil sterilants to reduce or eliminate Mn deficiency in field crops, offers possibilities provided economic returns are achieved, and are comparable with more conventional techniques of Mn fertilisation. There is little available field data comparing types and application rates of sterilants, nor has their residual value for subsequent crops been assessed. The use of complete sterilants may also have harmful consequences if the beneficial microflora and fauna in the soil are destroyed.

III. THE ENVIRONMENT OF THE REGION

1. GENERAL REGIONAL FEATURES

Figure 1, illustrates the region in which the experiments were conducted, and the approximate location of the experimental sites. The calcareous sands are situated on Southern Yorke Peninsula, South and West of the Warooka township. The total land area involved is approximately 100,000 ha.

2. REGIONAL CLIMATIC DATA.

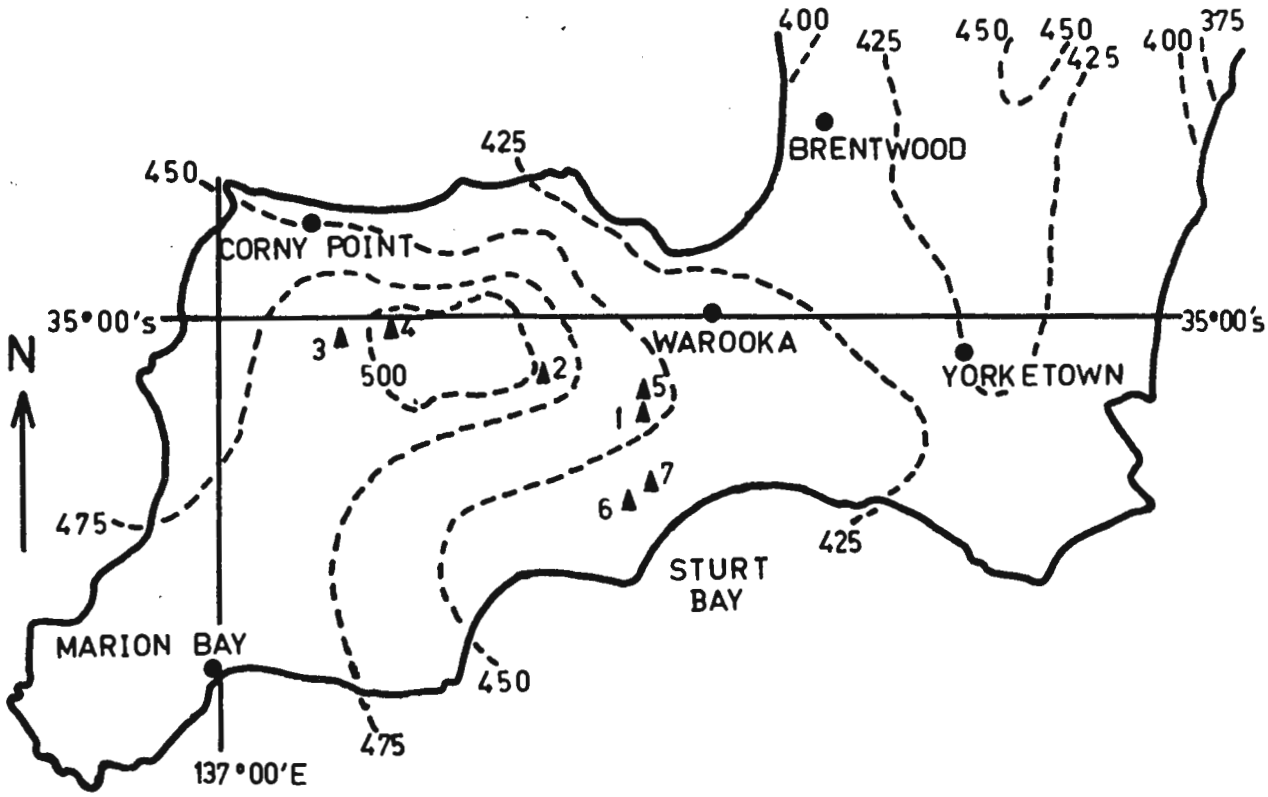
The close proximity to the coast results in a general maritime climate within the region. Summer and spring temperatures are usually lower and less extreme than other areas of comparable rainfall in South Australia, winter temperatures are slightly higher, and frosts are rare (Trumble 1948). Climatic data for the region is given in Appendix 1.

Mean annual rainfall in the region lies between 432 mm (17 in.) and 508 mm (20 in.). The annual rainfall isohyets are shown in Figure 1. The mean growing season rainfalls[+] (April-October) at the Warooka and Corny Point townships are 364 and 359 mm respectively, of which an average of 81 and 75 mm respectively falls in the September-October period. Appendix 2 summarises the recorded rainfall received at the Experimental sites or in the Warooka or Corny Point townships.

[+] Compiled from the Bureau of Meteorology, South Australia.

FIGURE 1

The location of field experiments undertaken between 1963-1969 on the Warooka calcareous sands situated on Southern Yorke Peninsula, and the annual rainfall isobeyts for the region.



● TOWNSHIPS

▲ LOCATION OF EXPERIMENTAL SITES

1. 1963
2. 1964
3. 1965
4. 1966
5. 1967
6. 1968
7. 1969

– – – – MEAN ANNUAL RAINFALL ISOHEYTS(mm)

3. TOPOGRAPHY.

The area is gently undulating (see Plate 1), comprising calcareous flats interspersed with calcareous dunes. Most of the area is between 15 to 110 m above sea level.

4. THE SOILS AND THEIR CHARACTERISTICS.

Two calcareous sands principal profile forms (Uc 2.11 and Uc 1.11 (Northcote 1965)), can be distinguished within the area. They are associated with isolated tongues of shallow grey mallee soils (Gc 1.11). The Uc 2.11 soil usually occurs in the flats, but can be encountered on rising land, whilst the Uc 1.11 soil is generally confined to the dune rises (see Plate 2). Both profile forms often occur together and gradations from one type to another occur over short distances. The two forms show little profile development, and are similar to at least 30 cm. The main difference between the two profile forms is depth of lime sand. Profile descriptions are given below:

Uc 2.11.

0 - 8 cm: grey calcareous sand with an accumulation of organic matter and abundant free lime.

8 - 30/45 cm: light pinkish calcareous sand, grading to white with depth.

45 cm + : white fragmented calcrete, grading to a more rubbly limestone with depth.

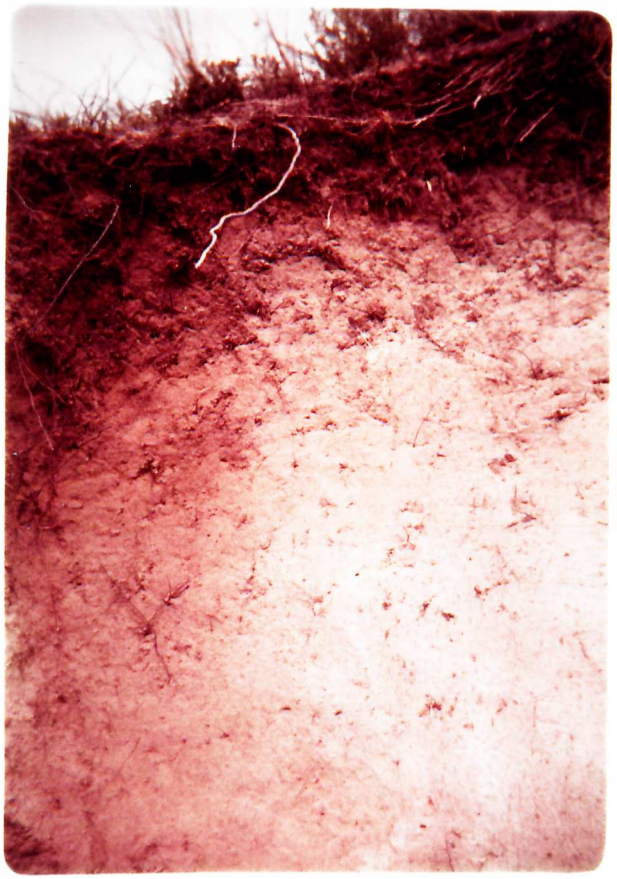
PLATE 1 and 2

Above: Typical virgin scrub existing on the Arrooka calcareous soils before land clearing.

Below: Gently undulating topography following land clearing.

PLATE 3

Profile of the Warooka calcareous soil (Wc 1.11)



Ec 1a11.

0 - [illegible] cm: Grey calcareous sand with an accumulation of organic matter and abundant fine lime.

[illegible] - 30 cm: Light pinkish calcareous sand, grading to white with depth.

30 cm +: White calcareous sand.

Table 2 lists some properties of the two profiles. The surface (0-10 cm) layers of both soils have high lime contents and this increases with depth. The water holding capacity of the soils is high for a sand, and the bulk density of the surface soil is very low. This is because the soil particles are very porous.

The total soil nitrogen and phosphorus concentrations in the surface soils, when expressed on a weight basis are above average compared with other South Australian cereal belt soils (Russell 1968, Rudd (priv. comm.)). Appendix 3 indicates the total trace element concentrations for each profile form. The concentration of Mn, Cu, Zn, Fe decreases with depth, but the Uc 2.11 soil appears to have a slightly higher trace element content in the surface horizon than the Uc 1.11.

5. LAND USE.

Agricultural enterprises undertaken within the region include barley, wheat and oats cropping, sheep and cattle raising. A three year rotation (crop-pasture-pasture) is generally practised, and barley is the principle crop grown. In some instances, two year rotations have recently been introduced. Pastures are frequently poor in production and legume composition, although occasional first class

TABLE 2.

Properties of the two Warooka calcareous profile forms (Uc 1.11; 1968 experimental site and Uc 2.11 1969 experimental site.)

Soil Property	Soil Profile Form.	Soil depth (cm)				
		0-10	10-20	20-30	30-45	45-60
Soil colour Dry	Uc 1.11	10YR 6/2	10YR 7/1	10YR 8/1	10YR 8/1	10YR 8/1
Soil colour Moist		10YR 4/2	10YR 5/3	10YR 6/3	10YR 6/3	10YR 6/3
Soil colour Dry	Uc 2.11	10YR 5/1	10YR 7/1	10YR 7/1	10YR 7/1	10YR 7/1
Soil colour Moist		10YR 3/1	10YR 5/3	10YR 5/3	10YR 5/3	10YR 5/3
Soil pH	Uc 1.11	8.5	8.6	8.5	8.7	8.9
	Uc 2.11	8.5	8.6	8.6	8.8	8.9
% Lime	Uc 1.11	81.5	85.0	88.5	93.0	96.0
	Uc 2.11	80.0	84.5	85.0	89.0	89.0
% Sand	Uc 2.11	84	89	91	89	92
% Silt		4	2	2	3	4
% Clay		12	9	7	8	4
Wilting Point (%)	Uc 1.11	21.6	24.8	27.1	20.3	N.D.+++
	Uc 2.11	31.3	31.5	27.3	26.0	22.9
Field Capacity (%)	Uc 1.11	34.0	38.1	42.5	43.1	35.8
	Uc 2.11	50.4	48.3	42.7	39.6	33.4
Total Soil N (%)	Uc 1.11	0.135	0.150	0.100	0.065	0.055
	Uc 2.11	0.265	0.128	0.085	0.042	0.038
C/N ratio	Uc 1.11	15.2	12.2	15.1	15.1	19.7
	Uc 2.11	15.0	17.1	17.6	27.1	23.7
Total Soil P (ppm)	Uc 1.11	385	268	235	223	240
	Uc 2.11	400	273	275	260	280
$NaHCO_3$ soluble P (ppm)	Uc 1.11	46	22	16	16	18
	Uc 2.11	31	8	5	3	1
Bulk density (g/cc)	Uc 1.11	0.66+		N.D.		
	Uc 2.11	0.54++		N.D.		

\+ sampled at harvest time.

++ sampled 6 weeks after sowing a crop.

+++ N.D. = Not determined.

pastures have been grown on these soils. The principle annual medic species include: Medicago truncatula (Gaerta), M. polymorpha (L.) M. minima (L.) (Bart). Lucerne, M. sativa (L.) produces well on these soils. Wimmera rye grass, Lolium rigidum (Gaud), Bromus mollis (L.) and Stipa species form the main grass species of the leys. Perennial weeds, mignonette (Reseda lutea(L.)), Lincoln weed (Diplotaxis teniofolia (L.) D.C.), and the annual Wimmera rye grass generally requires control during the cropping phase of the rotation.

IV. EXPERIMENTAL METHODS

1. FIELD EXPERIMENTS.

(a) Experimental Details.

Table 3 lists details of the barley field experiments undertaken in this study. The experimental aims of each individual experiment are given in Table 4.

(b) Preparation of Experimental Fertilisers.

"Mixed" fertilisers[+] were prepared by thoroughly mixing commercial grade components. "Compound" fertilisers[+] were made in a small scale production plant by blending the Mn and Cu sulphate and/or elemental sulphur with the "denfresh superphosphate" at approximately 90°C during the fertiliser granulation process. The desired granule sizes were obtained by seiving the material following curing. The different particle size fractions obtained by the seiving had similar chemical composition (see Table 13).

(c) Seeding Operations.

Land preparation consisted of three to five cultivations undertaken within four to five months of seeding. Seed and fertiliser were applied to prepared land using 9 or 10 hoe farm machinery. The fertiliser was banded with the seed. Barley seeding rates ranged from 56 to 83 kg/ha.

[+] Mixed fertilisers, are fertilisers in which the ingredients are physically mixed, and are designated in the text as P + Mn or P + Mn + Cu etc.

Compound fertilisers are designated in the text as (P, Mn), (P,Mn,Cu) or (P, Cu, Mn, S) etc.

TABLE 3

Field Experiments on the Warooka calcareous sands during 1963-1969.

Expt. No.	Year	Barley Variety	Expt. design	Soil Type	No. Reps	Plot Area (ha)	Sowing date	Harvest date	Barley Seeding rate (kg/ha)	Basal fertilizer (kg/ha)		
										N	P	Cu
1	1963	Prior	R.B.D.+	Uc.2.11	4	0.036	Jun. 13	Nov. 26	75	0	19	2
2							Jul. 16	Dec. 19				
3	1964		B.I.B.++	Uc.1.11	5	0.032	Jun. 18	Dec. 7	75	0	19	2
4	1965		B.I.B.	Uc.2.11	7	0.006	Jun. 22	Dec. 1	56	0	19	1
5			R.B.D.		2	0.006	Jun. 25	Dec. 2				
6	1966		B.I.B.	Uc.2.11	6	0.006	Jul. 29	Dec. 20	85	0	19	1
7			B.I.B.		6	0.006	Jul. 29	Dec. 20				
8	1967		R.B.D.	Uc.2.11	4	0.006	Jul. 12	Nov. 24	78	26	19	1
9	1968	Clipper	R.B.D.	Uc.1.11	4	0.006	Jun. 6	Dec. 5	81	39	19	2
10			R.B.D.		4	0.009	Jun. 4	Dec. 5			19	
11			L.S.++		5	0.009	Jun. 5	Dec. 4			19 & 39	
12			Factorial		5	0.009	Jun. 5	Dec. 4			19	

TABLE 3 (Contd.)

Expt. No.	Year	Barley Variety	Expt. design	Soil Type	No. Reps	Plot Area (ha)	Sowing date	Harvest date	Barley Seeding rate (kg/ha)	Basal fertilizer (kg/ha)		
										N	P	Cu
13	1969	Clipper	B.L.S.P.++++	Uc.1.11	5	0.005	Jun. 11	Nov. 27	77	37	28	2
14			Factorial	Uc.2.11	4	0.009	Jun. 10	Nov. 26				
15			R.B.D.	Uc.2.11	2	0.009	Jun. 6	-				
16			R.B.D.	Uc.2.11	4	0.009	Jun. 11	Nov. 25				

+ R.B.D. = randomised block design

++ B.I.B. = balanced incomplete block design

+++ B.L.S. = balanced lattice square design

++++ B.L.S.P.= balanced lattice split plot design

TABLE 4

The aims of Field Experiments conducted on the Varocka calcareous sands.

Expt. No.	Experimental Aims
1 & 2	The effect of soil applied Mn application (0, 6 kg Mn/ha) and number of Mn foliar sprays (0, 1, 2) on barley production.
3 & 4	The effect of soil applied Mn application (0, 2, 4 kg Mn/ha), the number of Mn foliar sprays, and their time of application on barley production.
5	The effect of soil applied Mn application (0, 6 kg Mn/ha) and sprays (2) on barley production.
6	The effect of soil applied Mn (4, 6, 8, 16 kg Mn/ha) and S (0, 12, 24, 28, 63 kg S/ha) application in compound fertilisers on barley production.
7	The effect of soil applied Mn application (4, 6, 8, 16 kg Mn/ha) and Mn foliar sprays on barley production.
8	The effect of soil applied Mn application (0, 4, 6, 12, 16 kg Mn/ha) the ratio of Mn/S in compound fertilisers, and the influence of Mn foliar sprays on barley production.
9	The effect of fertiliser Mn and S placement in compound and mixed fertiliser on barley production.

TABLE 4 (Contd.)

Expt. No.	Experimental Aims
10	The effect of soil applied Mn application (0, 6, 12, 16 kg Mn/ha) and elemental S (126 kg S/ha) and two Mn foliar sprays on barley yield.
11	The interaction of P (19, 39 kg P/ha), Mn (6, 16 kg Mn/ha) and S (0, 24, 63, 126 kg S/ha) applied as compound fertilisers on barley production.
12	The interaction of S application rate (4) and S particle size (5) applied in compound fertilisers on barley production.
13	The effect of Mn fertiliser carrier (9) and up to 3 successive Mn foliar sprays on barley production.
14	The effect of Mn application rate and solution concentration applied in foliar sprays on barley production.
15	The effect of soil applied Mn fertiliser (0, 6 kg Mn/ha) on the root growth and top growth of barley crops.
16	The effect of Mn carrier (3) and Mn foliar sprays on barley production.

A basal application of nitrogen fertilizer was drilled at seeding depth on all experimental sites sown between 1967 - 1969. Technical lindane (0.28 kg/ha) was applied to control Heteronyx electus (Blackb.) (Fam. Scarabaeidae) by thoroughly mixing with the basal N fertilizer applied to all 1969 experiments. All experiments between 1967 and 1969 received a pre-emergence Avadex[R] application (0.85 l Avadex/112 l water/ha) to control Wimmera ryegrass. The weedicide was applied to the soil surface within three days of seeding and incorporated by light harrowing. Control of this weed resulted at all sites. A post-emergence application of LV-57[R] (1.75 l/ha) was applied to all experiments sown in 1968 to control mignonette and lincoln weed. Satisfactory control resulted.

(d) Nutrient Spraying Operations.

In experiments where Mn was applied as a basal foliar spray, applications were achieved by a 6m boom spray fitted with flat fan jets, which delivered 112 l/ha at 427 kg/cm^2 pressure. The sprays were applied at right angles to the row direction and the spray boom height adjusted to give double spray overlap between adjacent jets.

Where Mn was applied to individual plots, a modified Drake and Fletcher mistifier knapsack unit was used. A 1.8m aluminium boom, with six double flat fan jets was constructed (2-60-690067), and attached to a hand lance which incorporated a pressure gauge. Lance pressure was easily manipulated by a pressure regulator, fitted between the lance and the spray tank. The rate of delivery was measured at pressures between

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R: Avadex = 2, 3, 3 - trichloro allyl di iso propyl thiocarbamate.

LV - 57 = the butoxy ethanol ester of 2, 4 dichloro phenoxy acetic acid.

356 and 427 kg/cm^2, and the sprays were applied by walking down each plot at the appropriate speed. Spray drift onto adjacent plots was prevented by screening with a hessian sheet carried by a second person.

With the exception of Field Experiments 1 and 2, all experiments were sprayed with a refined manganese sulphate product, "Soluble Manganese Sulphate"^{R} (32% Mn). The 1963 experiments were sprayed with a solution prepared from commercial manganese sulphate (25.5% Mn; 90% $MnSO_4$). Application rate and spray concentrations varied as shown in Table 5. A surfactant, Agral^R 60 (110-605 ppm) was added to all spray solutions used in the 1966-1969 experiments.

Spraying was conducted when practicable during early morning, however some sprays were applied during the afternoon. Prevailing weather and crop leaf surface conditions were noted on each occasion foliar sprays were applied, and are tabulated in Appendix 4.

TABLE 5a

Rates of Mn applied in foliar sprays

Year	Rate of Mn application (kg/ha)	Spray Volume (l/ha)	Mn conc. in spray (%)
1963	1.45	168	0.85
1964	1.43	112	1.28
1965	1.43	112	1.28
1966	1.43	112	1.28
1967	1.79	168	1.07
1968	1.43	168	0.85
1969	1.26	112	1.13

R = Soluble Manganese Sulphate (Trade Name)
R = Agral 60 (Trade Name)

(e) The Plant Sampling and Preparation.

Plant tops were harvested at approximately two weekly intervals during the season from quadrats (3.5 to 6.9m of drill row) in Field Experiments 3, 4, 8, 9, 11, 12 and 15. The plants were cut at ground level, placed in paper bags, and dried in a forced draught oven at 90°C. The samples were weighed, ground in a stainless steel mill to < 2mm, and stored in cardboard cannisters. In some experiments, barley heads were separated from the leaf and stem material and weighed following oven drying.

(f) Root Sampling.

Root growth was measured in Experiment 18 at two weekly intervals. Eight core samples per plot were randomly taken in the crop row with a 4.4cm diameter tube sampler. Sampling depths were 0 - 7.5cm, 7.5 - 15cm and 15 - 30cm. Each sample was washed with tap water in a slowly oscillating root washing machine, similar to that described by Fehrenbacher and Alexander (1955).

The roots and stones retained on a 1mm screen were dried in a forced draught oven at 50°C and the roots subsequently separated by hand. Root length was measured by the intercept method of Newman (1966).

(g) Barley Quality Assessment.

Barley grain quality was assessed by the visual appraisal of grain sample characteristics (endosperm vitreousness, grain shape and hull thickness) together with measurement of:

(i) Percent screenings - 100 g sample shaken for 30 seconds on a 2.25mm screen, and percent foreign material then calculated.

(ii) 1000 grain weight - the number of grains in a 15 g sample counted by an electronic counter. 1000 grain weight was then calculated.

Samples were classified into the four commercial barley grades used by the Australian Barley Board - M (malting), 3, 4, and 5 (feed barley).

Percentage malt extract is considered the best method of evaluating barley malting quality (Meredith et al. 1962). However, experienced quality assessors can reliably estimate malting potential of known barley varieties grown in known agricultural regions by commercial "hand" evaluation methods (Meredith et al. 1962, Doolette (priv. comm.)).

(h) Soil Sampling and Preparation.

Soil samples were collected from several experimental sites with a 10cm diameter Jarrett soil auger from six randomly selected sites. Samples were taken from the 0-10cm, 10-20cm, 20-30cm, 30-45cm and 45-60cm profile depths. The soil samples from each depth interval were bulked, thoroughly mixed and subsampled. The subsamples were air dried and the < 2mm fraction stored for analysis.

2. GLASSHOUSE EXPERIMENT

(a) Experimental Aim and Design

A glasshouse experiment was undertaken to determine whether barley plants grown on the Warooka soil (Uc 2.11) would respond to sulphate-S applications. The experimental design was thirty increasing application rates of sulphate-S, up to the equivalent of 126 kg S/ha. One replicate was used.

(b) Glasshouse Procedures

The experiment was conducted in an enclosed glasshouse, using polythene pots, measuring 23cm diameter x 23 cm tall. 3.8 kg airdry soil was added to each pot and the fertilisers, in solid analytical grade form, were applied to this surface. The basal fertiliser per pot consisted of 1.5g monocalcium phosphate (equivalent to 95 kg P/ha), 114 mg manganous chloride (equivalent to 6 kg Mn/ha), and 22 mg cuprous chloride (equivalent to 2 kg Cu/ha). The sulphur was added as calcium sulphate. A further 0.35 kg of soil was added, and nine barley seeds (cv. Clipper) per pot sown. More soil was added to give a total of 5 kg soil/pot. A basal application of N (13ml 0.5M ammonium nitrate solution per pot) was added to the soil surface, and the pots brought to 6.25 kg with distilled water.

The pots were watered to weight with distilled water, usually twice weekly, and weeds were pulled out when they appeared. The experiment began on April 9, 1970, and was harvested when the barley heads

were "in the boot", on June 17, 1970. The plant tops were weighed and prepared for analysis using the techniques described in Section 1e.

3. INCUBATION EXPERIMENTS

(a) Incubation Experiment 1.

(i) Experimental aims and design

This experiment was conducted to investigate the oxidation of elemental S in the Waroona soil (Ue 1.11), and the effect of the S oxidation on the availability of fertiliser and indigenous soil Mn and P. The experiment was a 5 x 2 x 6 factorial with 2 replicates. The treatments were:

Fertilisers:

Treatment	Composition	Amount added to soil (ppm soil)
Control	-	-
S	Elemental S	2000 ppm S
(P, S)	Superphosphate Elemental S	456 ppm P 2125 ppm S+
(P, Mn, S)	Superphosphate Elemental S $MnSO_4$ $4H_2O$	456 ppm P 2310 ppm S+ 88 ppm Mn
(Mn, S)	Elemental S $MnSO_4$ $4H_2O$ Mg stearate (adhesive)	88 ppm Mn 2000 ppm S 0.01 mg/g soil

All fertilisers were ground < 1mm.

+All treatments aimed to supply 2000 ppm S. The elemental S composition above is based on chemical analysis of each fertiliser material.

Inoculation:

One series was inoculated with Thiobacillus thiooxidans and T. thioparus, and the other series was uninoculated.

Incubation:

Samples were taken for analysis after incubating for; 0, 2, 4, 6, 12 and 52 weeks.

(ii) Experimental Methods

The fertiliser was thoroughly mixed with 20g sieved (<2mm) airdry soil in 7.6cm tall x 3.8cm diameter plastic incubation vials. The inoculated series received 10 ml of diluted inoculum (composed of 4 ml inoculum[+] per litre double distilled water). The uninoculated vials received 10 ml double distilled water, which brought the soil to a water potential of 0.33 atmosphere.

The open vials were incubated in closed aluminium containers at 25°C. Water was added to the containers at intervals to give a humid atmosphere within the containers, in an attempt to maintain the water content of the soil. However, it was still necessary to add 1.0 ml of distilled water to the vials after 9 and 41 weeks incubation.

At the end of the incubation period, the incubated soil was extracted for determination of elemental S, $NaHCO_3$-soluble P, CaNaEDTA-soluble Mn, and quinol plus CaNaEDTA-soluble Mn. Details of the extraction procedures are given in Section 5.

[+] Dr. R.J. Swaby, C.S.I.R.O. Division of Soils, kindly provided the Thiobacillus inoculum.

(b) Incubation Experiment 2.

This experiment was undertaken to examine the effect of soil sterilization on the concentration of divalent Mn in Warooka soil (Uc 1.11), to which various Mn fertilizers had been added. The experiment was a 4 x 2 x 5 factorial with 2 replicates. The treatments were:

Fertilizers:

Treatment	Composition	Amount added to soil (ppm soil)
Control	-	-
Mn^{2+}	$MnSO_4 \cdot 4H_2O$ (A.R.)	450 ppm Mn
(P, Cu, Mn)	Superphosphate Copper sulphate Manganese sulphate	2250 ppm P 151 ppm Cu 500 ppm Mn
P + Mn + Cu	Superphosphate Copper sulphate Manganese sulphate	2215 ppm P 160 ppm Cu 390 ppm Mn

Soil Sterilization:

Two series of vials were used, one of which received 10 ml 0.1% $HgCl_2$ per vial (sterilized soil), and the other series received 10 ml distilled water (unsterilized soil).

Incubation:

Samples were taken for analysis after incubating for 0, 2, 24, 72 and 167 hours.

At the end of each incubation period, the whole soil sample in each vial was extracted for 2 hours with acetate buffered CaNaEDTA extractant, and the filtrate analysed for Mn. Details of the experimental procedures are given in Section 5.ii.c.

4. FERTILIZER ANALYSIS

(a) Nutrient Composition of Fertilizers.

The fertilizers were analysed for total and water soluble P, total Mn, and Cu concentration by the methods recommended by the A.O.A.C. (Horwitz, 1970).

The nutrient content of different particle size fractions of a compound and a mixed fertilizer was determined. 1420 g of each fertilizer was sieved on a sieving machine for two minutes through a series of sieves with 4.8, 2.0, 1.0, 0.5, 0.25 and < 0.25mm apertures. The weight of fertilizer remaining on each sieve was recorded and the fertilizer subsequently analysed chemically.

(b) Uniformity of Nutrient Delivery from Seeding Equipment.

A mixed fertilizer containing superphosphate, manganese sulphate and copper sulphate was hand mixed and a Connor-Shea seeder was calibrated to deliver the fertilizer at 237 kg/ha. Traverses were made over a concrete floor, and the fertilizer output collected in aluminium trays (28 x 18 cm). Two such longitudinal runs were undertaken using different outlets from the fertilizer box. The fertilizer collected in each tray was placed in

a plastic bag, weighed, and the whole sample analysed for nutrient composition. Results were expressed on an airdry basis, and the absolute nutrient content in each collection tray related to the total fertilizer weight delivered from the seeder, by linear regression analysis.

(c) Chemical Analysis of Mixed and Compound Fertilizers.

(i) X-ray diffraction analysis.

A compound and a mixed fertilizer were prepared using analytical grade copper and manganese sulphates and commercial grade superphosphate. The fertilizers were of the following composition:

Fertilizer	Nutrient Composition (%) oven dry basis			
	Mn	Cu	P_T	P_{WS}
Compound	2.11	0.56	9.47	7.77
Mixed	1.64	0.47	9.27	8.45

P_{WS} = Water Soluble P.

P_T = Total P.

The products were ground and subjected to X-ray diffraction analysis[+], using cobalt radiation, to determine if reaction products were formed in the compound fertilizer during manufacture.

(ii) Extraction of Mn from fertilizers.

The compound fertilizer was extracted for various periods in different solvents to determine the rate and amount of Mn release

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[+] Analysis undertaken by the Australian Mineral Development Laboratories

from the fertilizer. 1.0g (airdry) of each fertilizer was extracted in 100ml of either distilled water or 0.01M Na_2EDTA solution in an end over end shaker (22 revs/min) for periods of up to two hours. The resulting extracts were filtered and anlysed for total Mn content and pH. Both the mixed and compound fertilizer was also extracted in the acetate buffered CaNaEDTA solvent for 120 and 180 minutes and the filtrates subsequently analysed for total Mn content and pH.

5. ANALYTICAL METHODS

(a) Plant Analysis.

(i) Plant digestion procedures.

For Mn and Cu analyses, approximately 1g sample of ground plant material was oven dried, reweighed, and then digested in nitric and perchloric acids (10ml HNO_3: 1ml 60% $HClO_4$). The samples were predigested before heating, and following digestion were filtered and diluted to 25ml.

For P analyses, 0.2g of ground plant material was digested in 4ml concentrated sulphuric acid. Approximately 5ml H_2O_2 was added and the digestion continued until the solution was colourless. The digests were diluted to 100ml.

Duplicate analyses were usually made on all samples. Deviations greater than $\pm$ 5% between sample duplicates were rejected and the analysis repeated. Blank digests were frequently done. Normal stringent glass cleaning routines were employed in all laboratory work.

(ii) Analytical procedures.

Mn and Cu concentrations in plant digests were determined by atomic absorption spectrophometric procedures (Allan 1959, 1961a) using standards containing 1.2% perchloric acid. Low Cu concentrations were measured using the method of Allan (1961b).

The P concentrations of plant digest were determined by the molybdenum blue automatic colorimetric technique developed by Williams and Twine (1967). S analyses were carried out by the Australian Mineral Development Laboratories using the modified slow combustion-titration method of the British Standards Institute (1958).

(b) Soil Analysis.

(i) General soil properties.

The following analyses were done on the Warooka soils:

pH - 1:5 soil water suspension.

Organic C - by the method of Walkley and Black (1934).

Total soil N - Digestion by the Kjeldahl procedure with concentrated sulphuric acid and a Se catalyst, and the ammonium in the digest determined by the automatic procedure of Williams and Twine (1967).

Total soil P - by the method of Beckwith and Little (1963).

Percentage Lime - by the rapid titration method of Piper (1947).

Particle size analysis - by a modification of the method of Hutton (1955), using a Plumett balance. Lime was not removed by HCl pretreatment, and the soils were dispersed with an ultrasonic vibrator according to the method of Edwards

and Brenner (1967).

Water potential - Soil water content was determined at 0.33 and 15 atmospheres by the method of Richards (1947).

(ii) Extractable soil nutrients.

(a) $NaHCO_3$ soluble P.

Duplicate 1.0g airdry soil samples were extracted with 100ml 0.5N $NaHCO_3$ at pH 8.4 for 16 hours on an end over end shaker at 25°C. The P concentration of the filtrates were determined by the automatic colorimetric molybdenum blue method of Colwell (1965). Acceptable deviations between laboratory duplicates was ± 5%. In incubation Experiment 1 20.0g of soil was extracted in 500ml of the solvent.

(b) Exchangeable and easily reducible Mn.

20.0g of soil was extracted for 25 minutes with 100ml 0.05% quinol in 50% ethanol. The mixture was centrifuged for 5 minutes at 2500 revs/min., and the supernatant removed by a suction pipette. A further 85 ml 50% ethanol was added to the extracting bottle which was vigorously shaken, centrifuged and the supernatant again discarded. The soil slurry was extracted for 2 hours with 100ml of the acetate buffered CaNaEDTA solvent. This solution was prepared by mixing equal volumes of:

2% calcium saturated sodium ethylene diamine tetraacetate (CaNaEDTA) - 22g calcium carbonate was shaken overnight with 2% Na_2EDTA and the suspension filtered.

and,

A filtered buffer solution consisting of equal

volumes of 0.5M calcium acetate and 1.0N ammonium acetate. The pH of this solution was adjusted to 8.4 by the addition of liquid ammonia.

The samples were centrifuged for 5 mimutes at 2500 revs/min., filtered, and the Mn concentration of the filtrate determined by atomic absorption spectrophotometry, using standards made in the acetate buffered CaNaEDTA.

(c) Exchangeable and water soluble Mn.

The incubated soil from Incubation Experiments 1 and 2 were extracted with 100ml of the acetate buffered CaNaEDTA for 2 hours. The resulting soil filtrate was usually concentrated five times and the Mn concentrated determined.

(d) Elemental S.

(i) Extraction procedure.

The soil was oven dried at 45°C for 48-72 hours, transferred to 33 x 80mm soxhlet thimbles, and extracted for three hours with approximately 200ml A.R. benzene in soxhlet apparatus. The resulting benzene extract was diluted to 200ml. (Swaby (pers. comm.)).

(ii) Analytical procedure.

The analytical procedure to that developed by Bartlett and Skoog (1954). It is based on the reaction of elemental S with cyanide forming thiocyanate which is then determined colorimetrically

by the formation of the ferric-thiocyanate complex.

A 1.0ml aliquot of the benzene extract was added to 3.0ml of an aqueous acetone solution of potassium cyanide (KCN) - 0.1g KCN dissolved in 100ml aqueous acetone (95% A.R. acetone). The solution was diluted to 25ml with aqueous acetone. A 5.0ml aliquot was then added to a stoppered test tube containing 5.0ml ferric chloride - aqueous acetone solution (0.4g $FeCl_3.6\ H_2O$ per 100ml aqueous acetone mixed for 24 hours and filtered). The solutions were mixed and immediately the solution colour intensity was read on a spectrophotometer at 465nm using 1 cm cells against blanks containing 5 ml aqueous acetone and ferric chloride. S standards dissolved in benzene were treated in a similar manner.

V. RESULTS AND DISCUSSION

A. APPLICATION OF MANGANESE SULPHATE AT SEEDING

A. APPLICATION OF MANGANESE SULPHATE AT SEEDING

1. VISUAL OBSERVATIONS DURING CROP DEVELOPMENT

The primary symptom of Mn deficiency was a general plant chlorosis, particularly in the younger leaves. As the leaves matured, brown specks developed, which eventually became necrotic. Severely deficient plants were retarded in development and sparsely tillered. Plant and tiller mortality became severe, from stem extension to maturity, resulting in increased competition from weeds.

The time of appearance and intensity of the symptoms were related to the quantity of Mn applied at seeding, as shown in Table 6 and Plates 4 and 5. Crop colour and growth was consistently affected within approximately 40 days from seeding, (at the beginning of plant tillering), where no fertilizer Mn had been applied at seeding. Increasing the quantity of Mn, up to 6 kg Mn/ha, progressively delayed the appearance of the syndrome. However, as the crops reached the stem extension stage, Mn deficiency symptoms in plants were evident in all experiments, even where applications of 16 kg Mn/ha had been applied.

In some experiments, it was observed that barley plants temporarily recovered from Mn stress, often, immediately after heavy rains. Similar observations were made by Piper and Walkley (1943). Restoration of crop colour and growth was observed when Mn foliar sprays were applied, at the time that plant Mn deficiency symptoms were first seen.

The two barley cultivars used, (Prior and Clipper), were not compared for sensitivity to Mn deficeincy in any experiment, but visual

TABLE 6

The initial appearance of Mn deficiency symptoms in barley crops grown on the Warooka soil, as influenced by the rate of Mn applied at seeding.

Year	Field Expt. Number	Mn applied (kg/ha)	Initial appearance of the syndrome		
			Days from seeding	Feekes'+ scale	Visible symptoms recorded
1963	1	0	42	2	Chlorosis
		6	78	N.R.++	Chlorosis and reduced growth
	2	0	45	2	Chlorosis
		6	72	N.R.	Chlorosis and reduced growth
1964	3	0	39	2	Chlorosis
		2	54	2 (3tillers)	Chlorosis and reduced growth
		4	68 - 81	4 - 5	Chlorosis and reduced growth
1965	4 & 5	0	42	2 (1-3 tillers)	Chlorosis and reduced growth
		4	42-56	2 - 4	Chlorosis and reduced growth
		6	70-86	5 - 6	Reduced growth
1967	8	0	48	2 (3tillers)	Chlorosis and reduced growth
		4	48	2	Chlorosis and reduced growth (?)
		6	68	4 - 5	Reduced growth
		12	>68	N.R.	N.R.
		16	>68	N.R.	N.R.
1968	10	0	44	2 (4-5 leaves)	Chlorosis and reduced growth
		6	58	3	Chlorosis and reduced growth
		12	>58	3 - 4	N.R.
		16	>58	3 - 4	N.R.
1969	13	0	43	2	Chlorosis and reduced growth
		6	62	5	Chlorosis and new leaves

+Feekes' scale of cereal plant growth (Large 1954) as illustrated in Figure 2.

++ N.R. = not recorded.

1963-1967, Prior barley, 1968-1969, Clipper barley.

Stage

1	One shoot (number of leaves can be added) = "brairding"	Tillering
2	Beginning of tillering	
3	Tillers formed, leaves often twisted spirally. In some varieties of winter wheats, plants may be "creeping" or prostrate	
4	Beginning of the erection of the pseudo-stem, leaf sheaths beginning to lengthen	
5	Pseudo-stem (formed by sheath of leaves) strongly erected	
6	First node of stem visible at base of shoot	Stem Extension
7	Second node of stem formed, next-to-last leaf just visible	
8	Last leaf visible, but still rolled up, ear beginning to swell	
9	Ligule of last leaf just visible	
10	Sheath of last leaf completely grown out, ear swollen but not yet visible	
10.1	First ears just visible (awns just showing in barley, ear escaping through split of sheath in wheat or oats)	Heading
10.2	Quarter of heading process completed	
10.3	Half of heading process completed	
10.4	Three-quarters of heading process completed	
10.5	All ears out of sheath	
10.5.1	Beginning of flowering (wheat)	Flowering (Wheat)
10.5.2	Flowering complete to top of ear	
10.5.3	Flowering over at base of ear	
10.5.4	Flowering over, kernel watery ripe	
11.1	Milky ripe	Ripening
11.2	Mealy ripe, contents of kernel soft but dry	
11.3	Kernel hard (difficult to divide by thumb-nail)	
11.4	Ripe for cutting. Straw dead	

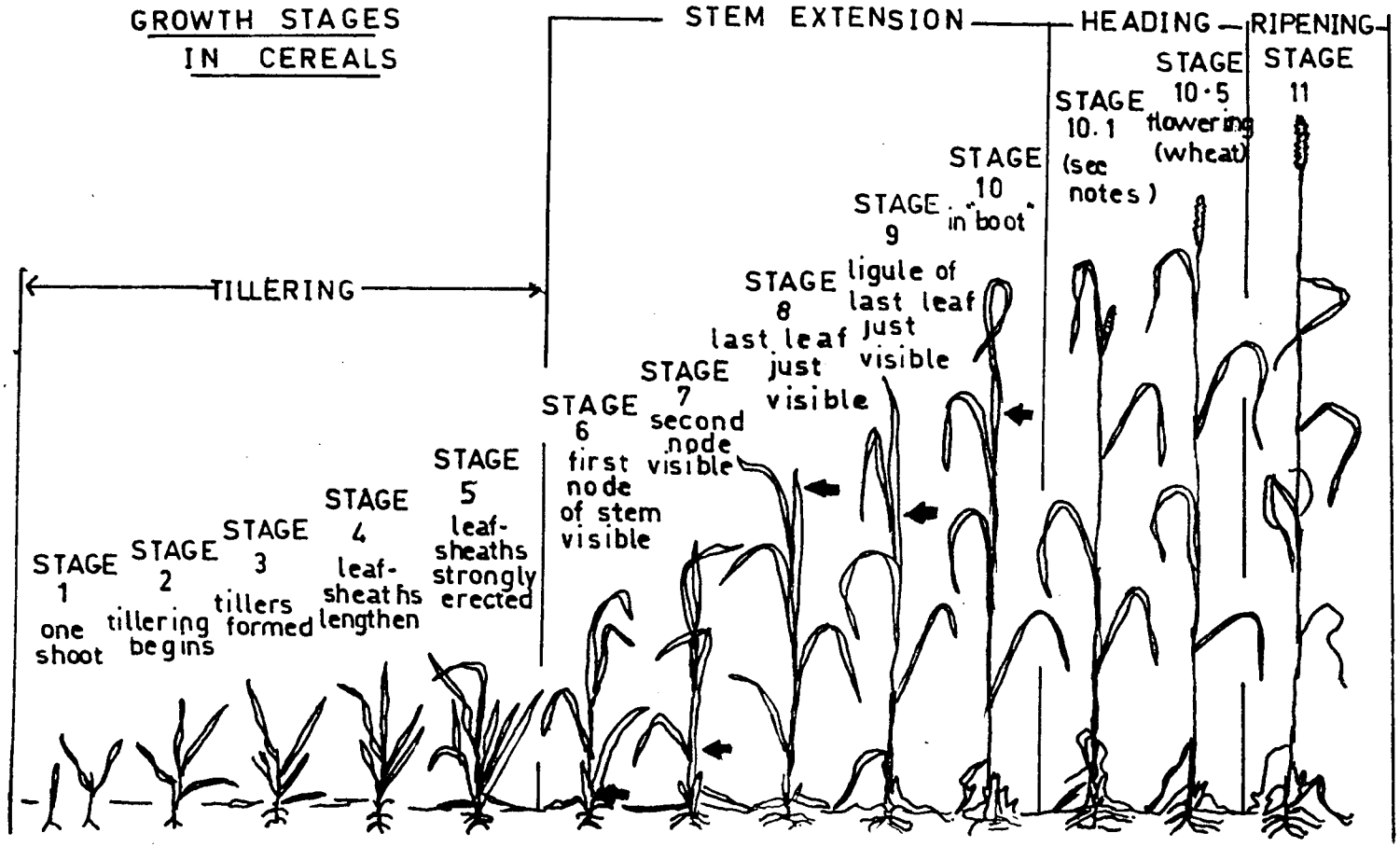

GROWTH STAGES IN CEREALS
STEM EXTENSION
HEADING
RIPENING
TILLERING
STAGE 1 one shoot
STAGE 2 tillering begins
STAGE 3 tillers formed
STAGE 4 leaf-sheaths lengthen
STAGE 5 leaf-sheaths strongly erected
STAGE 6 first node of stem visible
STAGE 7 second node visible
STAGE 8 last leaf just visible
STAGE 9 ligule of last leaf just visible
STAGE 10 in "boot"
STAGE 10.1 (see notes)
STAGE 10.5 flowering (wheat)
STAGE 11

FIGURE 2.

Plates 4 and 5

Above: Symptoms of Mn deficiency in Prior barley, evident in early crop development where no Mn fertilizer was applied at seeding (centre plot), compared with crops which received Mn fertilizer at seeding (plots either side).

Below: The effect of Mn deficiency in Clipper barley at grain maturity: the crop which received no Mn (left) is sparsely tillering, and ears are mainly sterile, compared with crop on right, which was fertilized with Mn.

observations suggested that their tolerance to Mn stress was similar. Mn deficiency in crops grown on these soils is so severe, that it is unlikely that the sowing of tolerant cultivars will overcome the problem.

2. PLANT GROWTH AND Mn ACCUMULATION IN BARLEY FOLIAGE DURING CROP DEVELOPMENT.

The results in Table 7, show that in Field Experiment 3 (1964), plant dry weight was not significantly influenced by Mn application at seeding of up to 4 kg Mn/ha, until the mid tillering stage (54 days from seeding). Mn accumulation in plant tops was significantly affected by the quantity of Mn applied at seeding, even after 4 weeks of growth.

Table 8, (Field Experiment 8, 1967), compares the crop dry weight and Mn accumulation during the intermediate and later stages of plant development, of crops which received greater quantities of Mn at seeding than those applied in Field Experiment 3. The results show that crop dry weight was increased during the early tillering phase, (48 days after seeding) by the quantity of Mn applied at seeding, but the increases were not significant until the 68 day sampling (late tillering). Increasing the rate of Mn application from 6 to 16 kg Mn/ha resulted in no further increases in crop dry weight at this stage, although the crop which received 6 kg Mn/ha was showing symptoms characteristic of Mn deficiency. Similar results were obtained in Field Experiment 4 (1965), details of which are given in Appendix 5.

TABLE 7

Plant dry weight (kg/ha) Mn concentration (ppm) and Mn uptake (g/ha) during Prior barley crop growth

(Field Experiment 3, 1964)

Applied Mn (kg Mn/ha)	28 days[+++] 2-3 leaves/plant			42 days Commencing tillering			54 days 3 tillers/plant			68 days Tillering			81 days Late tillering			112 days Awns just visible		
	Dry Weight	Mn Conc	Mn Uptake	Dry Weight	Mn Conc	Mn Uptake	Dry Weight	Mn Conc	Mn Uptake	Dry Weight	Mn Conc	Mn Uptake	Dry Weight	Mn Conc	Mn Uptake	Dry Weight	Mn Conc	Mn Uptake
0	20	16.8	0.33	49	17.0[+]	0.83	74	33.3	2.58	111	22.0	2.45	[++]					
2	23	21.8	0.50	52	22.3	1.16	85	29.5[+]	2.51	142	22.3	3.14	[++]					
4	23	27.5	0.64	56	29.8	1.69	105	35.5	3.77	187	17.8	3.44	293	17.5[+]	5.21	663	10.3	6.67
L.S.D. P = 0.05	4	4.5	0.10	10	10.6	0.83	19	10.8	1.26	28	5.9	0.71						

[+] denotes when crop became visibly deficient in Mn.

[++] Further measurements not detailed, as these plots received Mn sprays. The effect of the foliar sprays is discussed in Section D.

[+++] harvest, in days after seeding.

TABLE 8

Plant dry weight (kg/ha) Mn concentration (ppm) and Mn uptake (g/ha) during Prior barley crop growth

(Field Experiment 8, 1967)

Applied Mn (kg Mn/ha)	48 days+++			68 days			78 days			92 days			110 days		
	2 tillers/plant			Leaf sheath erecting			Stem extension started			25-50% ears emerged			Grain milky ripe		
	Dry Weight	Mn Conc	Mn Uptake	Dry Weight	Mn Conc	Mn Uptake	Dry Weight	Mn Conc	Mn Uptake	Dry Weight	Mn Conc	Mn Uptake	Dry Weight	Mn Conc	Mn Uptake
0	90+	20.0	1.68	221	11.7	2.63	536	12.1	6.58	842	9.6	8.30	1454	5.8	8.65
4	95+	28.8	2.73	++											
6	92	33.9	3.28	306+	16.0	4.82	++								
12	96	42.6	4.07	341	20.7	7.02	856+	16.8	14.66	1363	12.9	17.26	2217	8.3	18.37
16	109	41.4	4.51	333	17.2	5.86	801+	15.9	12.76	1419	12.2	17.43	1860	8.6	16.27
L.S.D. P = 0.05	24	13.7	2.62	83	4.9	1.85	191	4.3	5.14	308	2.4	3.75	432	1.0	5.41

+ denotes when crop became visibly deficient in Mn.

++ Further measurements not detailed, as these plots received Mn sprays
The effect of the foliar sprays is discussed in Section D.

+++ harvest, in days after seeding.

In Figure 3, plant dry weights of crop which received 0, 12 and 16 kg Mn/ha at seeding, are shown for five harvests between the mid tillering and grain ripening stages of crop development. The significant difference in crop dry weight, measured 68 days after seeding, between the control and the crops fertilized with Mn at seeding, widens with subsequent growth, particularly during the period of rapid crop growth (between late tillering and ear emergence). The crops which received 12 and 16 kg Mn/ha did not significantly differ in top growth at any sampling time, and were both showing symptoms of Mn deficiency at the beginning of stem extension (78 days from seeding).

The results in Table 8 and Figure 4 shows that Mn accumulated by crops which received 12 and 16 kg Mn/ha was consistently greater than that accumulated by the control crop. Differences occurred early in crop development and increased further during the phase of rapid crop growth (late tillering to ear emergence). The rate of Mn accumulation in the tops decreased after ear emergence. The crops which received 12 and 16 kg Mn/ha accumulated similar amounts of Mn in their tops at all stages of growth. At the 110 day harvest, the plant tops had accumulated Mn equivalent[+] to 0.081 per cent and 0.048 per cent of the fertilizer applied to these crops respectively.

3. ROOT GROWTH.

The data presented in Table 9, (Field Experiment 15, 1969) are highly variable, but two observations are worthy of comment;

[+] Calculated by $\frac{\text{Mn uptake/ha (Fertilized crop - Control crop)}}{\text{Mn applied/ha}} \times 100$

FIGURE 3

Dry matter production (kg/ha) during crop development as influenced by the quantity of Mn applied to the Warooka soil at seeding (Field Experiment 8, 1967).

I = L.S.D., P = 0.05.

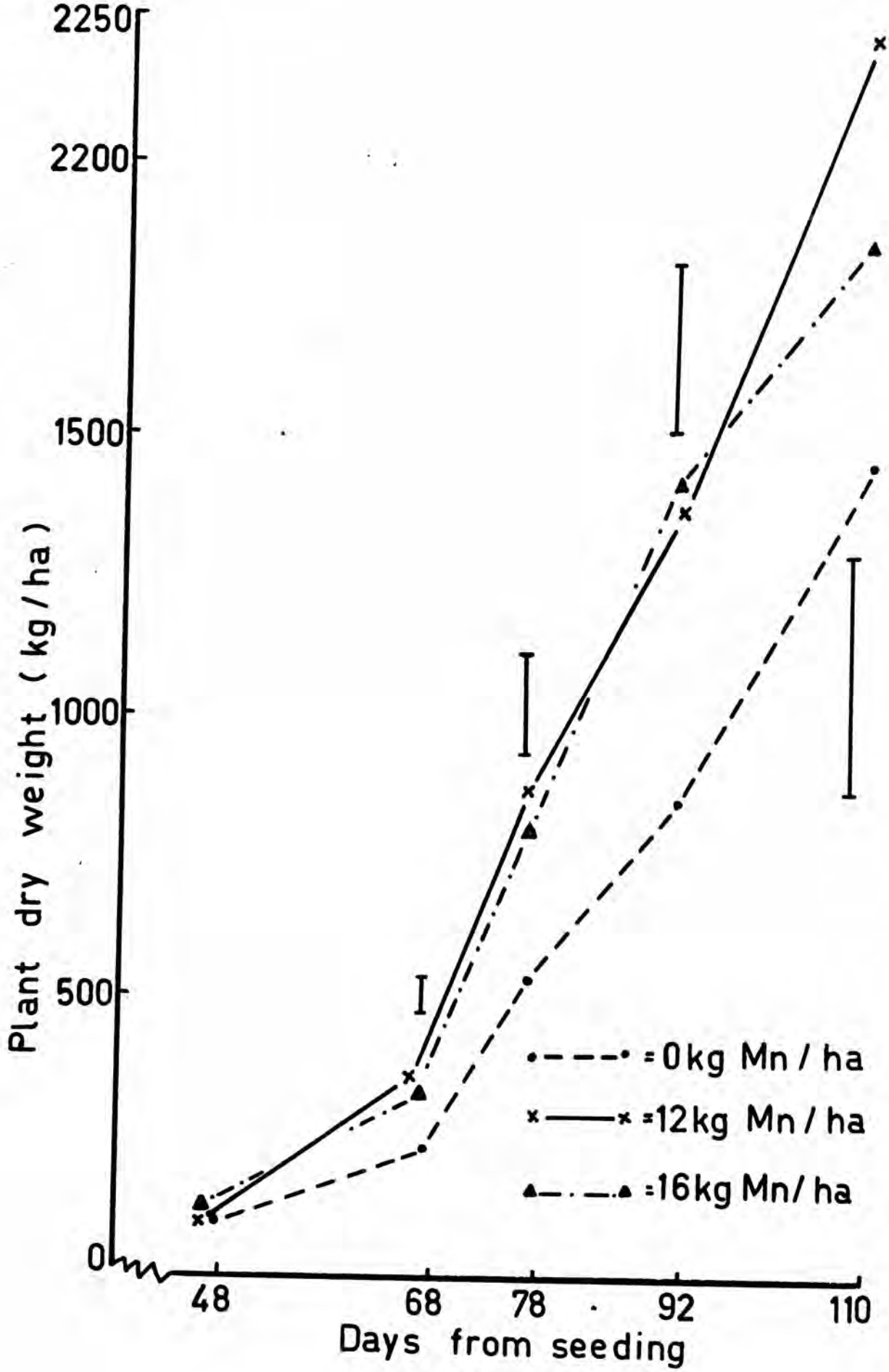

2250
2200
1500
1000
500
0
Plant dry weight (kg / ha)
48
68
78
92
110
Days from seeding
= 0 kg Mn / ha
= 12 kg Mn / ha
= 16 kg Mn / ha

FIGURE 4

The amount of Mn accumulated in the tops (g/ha) during crop development as influenced by the quantity of Mn applied to the Warooka soil at seeding (Field Experiment 8, 1967).

I = L.S.D., P = 0.05.

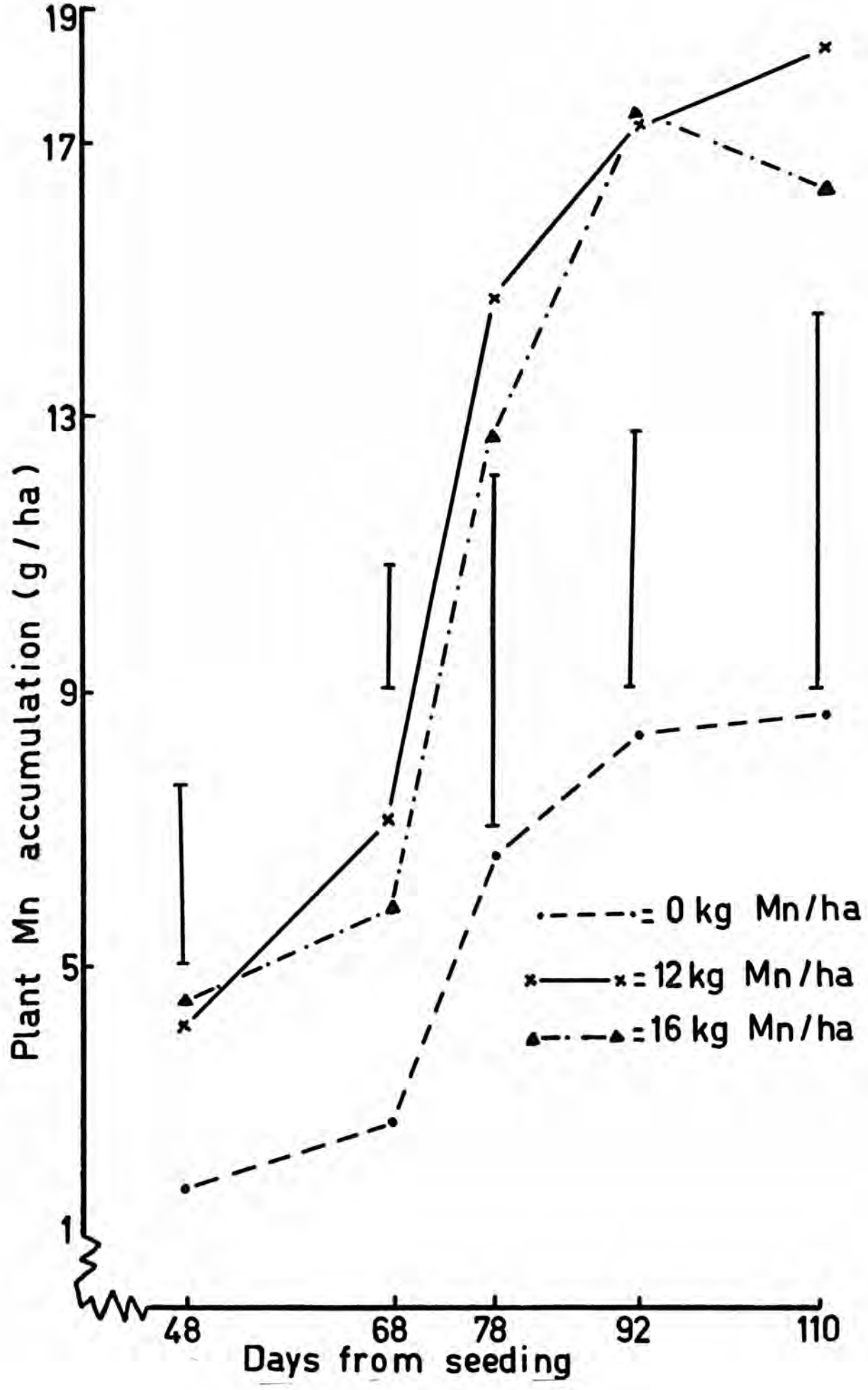

19
17
13
9
5
1
Plant Mn accumulation (g / ha)
48
68
78
92
110
Days from seeding
= 0 kg Mn/ha
= 12 kg Mn/ha
= 16 kg Mn/ha

TABLE 9

The effect of Mn fertilizer applications on plant dry weight and root growth (Field Experiment 15, 1969)

	56 days++		71 days		83 days	
	Tillering		Stem extension beginning		Stem extension	
	Mn application (kg/ha)					
	0	6	0	6	0	6
Plant dry weight (kg/ha)	166 ± 40+	353 ± 84	325 ± 76	1010 ± 213	381 ± 143	1321 ± 338
Root length (cm/cc soil)						
Depth 0 – 7.5 cm	2.54 ± 1.93	3.49 ± 2.20	3.30 ± 1.58	11.57 ± 5.05	3.12 ± 1.81	10.12 ± 6.82
7.5 – 15 cm	3.28 ± 1.66	2.18 ± 1.73	2.23 ± 0.98	2.62 ± 1.12	1.69 ± 1.09	2.17 ± 1.82
15 – 30 cm	1.32 ± 0.95	1.22 ± 0.80	1.16 ± 0.41	1.72 ± 0.67	0.87 ± 0.78	1.68 ± 0.62

+ mean ± standard error

++ sampling date, in days after seeding

(a) There was little change in root density from tillering to stem extension, where no Mn was applied at seeding.

(b) Applications of Mn at seeding increased the density of roots in the surface 0 - 7.5cm by the beginning of stem extension (71 days from seeding). During the same period (56 to 71 days after seeding) there was a large increase in plant dry weight.

The increased rate of root growth was not sustained during stem extension. During this period, the growth rate of both crops decreased, and the plants were showing symptoms of Mn deficiency, which may account for the cessation of root growth. However, it is also possible that root proliferation at this stage of crop development, was beyond the sampling depth used, or between the drill rows. Root growth was only measured directly below the actual drill row, to a depth of 30cm.

4. GRAIN YIELD AND QUALITY DATA FROM FIELD EXPERIMENTS

Table 10 shows the barley grain yield responses to different quantities of manganese sulphate, (25.5% Mn), applied at seeding, as mixed fertilizers containing basal applications of superphosphate and copper sulphate. The response of up to three Mn foliar sprays is also shown. In all experiments, manganese sulphate applied at seeding consistently increased grain yield. The maximum response to soil applications was obtained with 6 kg Mn/ha (25 kg manganese sulphate/ha).

Soil applications up to 16 kg Mn/ha alone did not completely correct Mn deficiency in crops grown on these soils, as indicated by the additional yield increase obtained in some experiments from Mn

TABLE 10

The effect of soil and foliar applications of Mn (as manganese sulphate) on barley grain yield (kg/ha)

Year	Barley grain yield (kg/ha)																						
	1963				1964	1965			1966			1967			1968			1969				
Expt. Number	1		2		3	4	5		7			8			9	10		13				
Number Mn / Mn soil applic.(kg/ha)	0	2	0	2	2	2	0	2	0	1	2	0	1	2	0	0	2	0	1	2	3		
0	719	1613	392	971	611		0	802				482			1059	1334	1435	1216	1407	1883	2214		
2					846																		
4					964	925		964			1026			807									
6	1181	1724	900	1188		1222	779		930	1026	1104		785	790		1698	1760	2236	2696	2915	3172		
8									835	1015													
12												830	846			1788	1833						
16									998	1037		852	835		1390	1710	1771						
L.S.D. P = 0.05	327		256		163	168	117		112			112			67	106		370					
Cultivar	PRIOR														CLIPPER								

foliar sprays applied later in crop development. When crops were sprayed with Mn, there was a decrease in yield differences obtained from applying different quantities of Mn at seeding. In some experiments these differences were eliminated. However, in the majority of cases, barley which received Mn at seeding together with up to three Mn sprays produced significantly higher yields, than crops which received the spray treatments only. The evidence indicates that to achieve maximum yields on these soils, it is essential to apply Mn both at seeding and in subsequent foliar sprays.

The results in Table 11, show that in all experiments, barley malting grade was improved by applying Mn at seeding. 1000 grain weights were sometimes increased and percent screenings decreased by the Mn applications. In Field Experiment 10 (1968), Mn applications greater than 6 kg Mn/ha did not measurably affect malting grade.

5. THE EFFECT OF SOIL STERILISATION ON EXTRACTABLE SOIL Mn

Figure 5 illustrates the effect of soil sterilisation on the amount of Mn extracted by acetate buffered CaNaEDTA from incubated surface soil (Incubation Experiment 2). In the unsterilised soil, no significant changes in extractable Mn occurred throughout the experimental period. In contrast, after 2 hours incubation the concentration of extractable Mn in the sterilised soil had significantly increased. The Mn concentration continued to increase throughout the incubation period, although the rate of increase gradually declined.

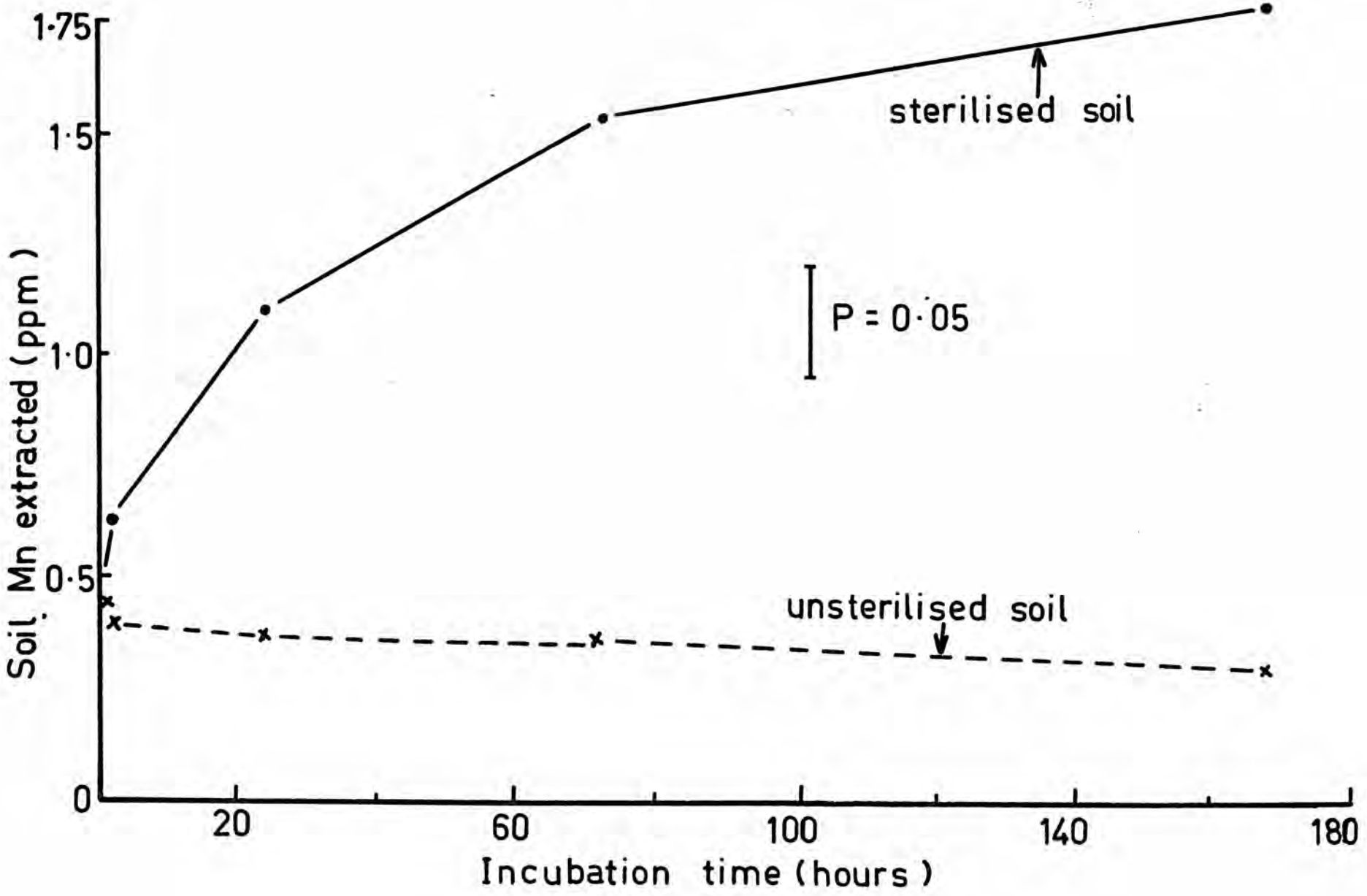
TABLE 11

The influence of Mn applications at seeding on malting grade (MG), percent screenings (PS), and 1000 grain weight (GW).

Applied Mn (kg Mn/ha)	1963						1967			1968			1969		
	Expt. 1			Expt. 2			Expt. 8			Expt. 10			Expt. 13		
	MG	PS	GW (g)	MG	PS	GW (g)	MG	PS	GW (g)	MG	PS	GW (g)	MG	PS	GW (g)
0	3-4	9.6	38.3	4-5	9.4	37.7	4	20.3	34.9	4	11.4	36.6	3-4	8.2	37.4
6	M-3	9.6	38.6	3	10.1	40.6				3-4	9.6	38.7	M-3	8.0	39.7
12							3-4	10.4	38.6	3	9.3	38.6			
16							3-4	9.5	40.9	3-4	10.2	37.6			
L.S.D. P = 0.05		0.6	2.6		0.5	2.2		4.0	1.3		1.6	1.8		2.4	2.3
Cultivar	Prior									Clipper					

FIGURE 5

The effect of soil sterilization on the concentration of divalent Mn in incubated Warooka soil. (Incubation Experiment 2).


1·75
1·5
1·0
0·5
0
Soil Mn extracted (ppm)
sterilised soil
P = 0·05
unsterilised soil
20
60
100
140
180
Incubation time (hours)

At the end of the incubation period, soil aliquots[+] were plated on nutrient agar media. After seven days incubation, there was no microbial growth in the sterilised soil, whereas the unsterilised soil had a profuse microflora population of fungii, bacteria and actinomycetes[+]. The adopted sterilisation procedure had therefore been successful.

The effect of sterilisation on the amount of Mn extracted by acetate buffered CaNaEDTA from incubated surface soil to which Mn fertilizer had been added is shown in Figure 6. The results are expressed as ppm soil Mn or as the percentage recovery of Mn added i.e.

$$\text{Apparent recovery of fertilizer Mn} = \frac{\text{Extracted Mn (soil + fertilizer)} - \text{Extracted Mn (soil)}}{\text{Fertilizer Mn}} \times 100$$

With no incubation (extracted immediately after the addition of the fertilizer), one extraction with the solvent removed almost all (94 per cent) of the added divalent Mn. Beckwith (1955) also showed that this extractant was capable of removing divalent Mn from soils.

After two hours incubation, the concentration of extractable Mn in both the sterilised and unsterilised soil had significantly decreased, and further declined with longer periods of incubation. After 167 hours incubation, the concentration of divalent Mn in the unsterilised soil had

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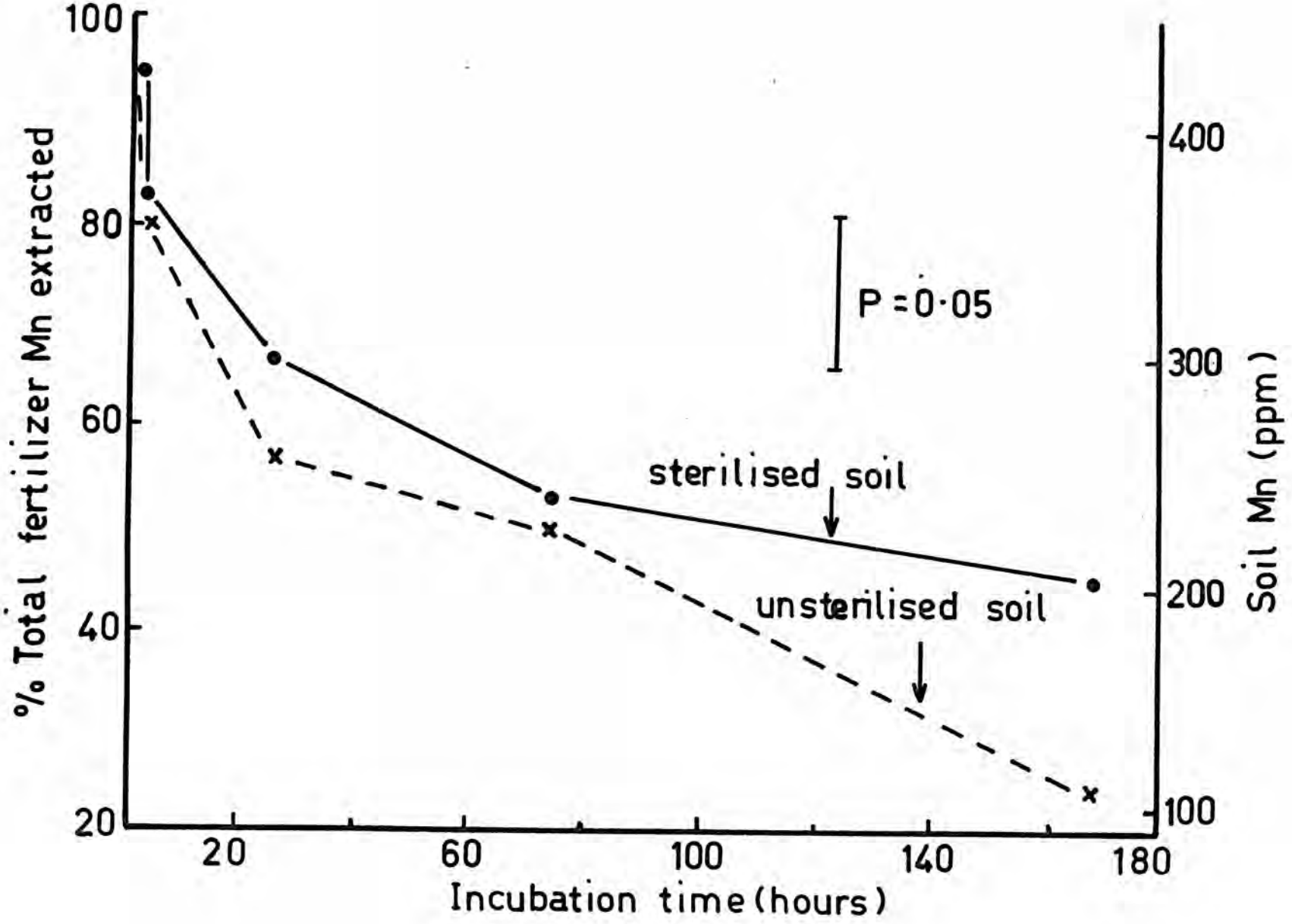
[+] Soil aliquots were plated and microflora populations kindly assessed by Dr. A.D. Rovira, C.S.I.R.O. Division of Soils, Adelaide.

FIGURE 6

The influence on soil sterilisation and time of incubation on the rate of immobilisation of divalent Mn added to the Warocka soil (Incubation Experiment 2).


100
80
60
40
20
% Total fertilizer Mn extracted
400
300
200
100
Soil Mn (ppm)
P = 0·05
sterilised soil
unsterilised soil
20
60
100
140
180
Incubation time (hours)

been reduced to 24 per cent of the initial quantity of Mn added to the soil (representing chemical and microbiological immobilisation), whereas the concentration in the sterilised soil had only been reduced to 45 per cent (representing chemical immobilisation). The results indicate that in the initial period of fertilizer Mn reaction with the Warooka soil, chemical fixation of Mn is more important than biological immobilisation. At least part of the Mn was converted to a more oxidised, but still readily reducible form. This is discussed more fully in Section C. (Table 22).

6. DISCUSSION

The results presented in this section have shown that barley crops grown on the Warooka calcareous soils suffered acute Mn deficiency within 40 days of seeding unless the soils were supplemented with fertilizers containing Mn. The crops responded markedly to soil applied Mn.

The availability of soil applied Mn for crop growth was short lived, since plants became deficient in Mn during stem extension, irrespective of the quantity of Mn applied at seeding. Applications of at least 6 kg Mn/ha delayed the appearance of Mn deficiency symptoms until the late tillering - stem extension period, but "complete" correction of Mn deficiency in the crop was not achieved by soil applications alone. In this respect, the results of this study confirm previously published work on other Mn deficient soils, (McLachlan 1941, Wain et al. 1943, Barbier et al. 1950, Henkens and Smilde 1967), that applications of Mn to the soil result in only temporary correction of the deficiency.

The evidence in Figure 4 indicated that during the period when crops have the potential to make rapid growth (late tillering to ear emergence), the rate of Mn accumulation per hectare in plant tops was greatest, and was influenced by the quantity of Mn applied at seeding, and yet crop dry matter production in this period was restricted by a shortage of Mn (Crop Mn deficiency symptoms). It is therefore likely that during this period the crop requirement for Mn is greater than at any other phenological stage.

The increased uptake of Mn into the plant tops during the period of rapid crop growth is probably associated with rapid root proliferation occurring during this period (Table 9). A direct result of this would be an increased uptake of native or applied Mn. However, redistribution of Mn stored in the root may also be implicated. (Munns et al. 1963a, Vose 1963). Emphasis in the past has been given to the role that root exudates (Bromfield 1958a), root contact reduction (Passioura and Leeper 1963b, Uren 1969) and root rhizospheres (Bromfield 1958b) play in solubilising soil Mn for uptake by plant roots. The evidence in this study has shown that Mn deficient crops have restricted root systems, which suggests that a major limitation of Mn uptake from Mn deficient soils is the ability of plant roots to encounter available pools of Mn within the soil. Further experimentation is needed in this area to isolate the major factors responsible.

The apparent recovery of fertilizer Mn by the plants was also very low. These results confirm previously published studies on other Mn deficient neutral to alkaline soils, (Piper 1931, Coic et al. 1950),

which suggests that the applied divalent Mn was rapidly converted in these soils to forms unavailable for plant growth. However, it is also likely that on calcareous soils such as these, the high activity of Ca in the soil solution or in the plant itself may determine the efficiency of soil applied Mn (Ouellette and Dessureaux 1958, Rivenbark 1961, van Diest and Schuffelen 1966, Barber 1968).

The results of the incubation study indicated that both chemical and biological fixation of applied divalent Mn takes place in the Warooka soil. However, in the initial period of fertilizer reaction with the soil, chemical fixation was more important. In contrast, biological immobilisation of applied divalent Mn in the initial period has been considered more important than chemical fixation on other soils, some of which were calcareous (Mann and Quastel 1946, Mulder and Cerretsen 1952, Rivenbark 1961, Uren 1969). Reid and Miller (1963) have shown that both slow and fast reactions operated when divalent Mn was added to an alkaline loam. Although the nature of the reaction products is basically unknown, it is possible that the products of the slower reactions may have important long term effects on Mn availability to plants.

The concentration of divalent Mn in the Warooka soils is very low, (0.4 ppm Mn), when compared with concentrations measured in other soils by Beckwith (1955), using acetate buffered CaNaEDTA (4 to 150 ppm Mn). The small increase in the concentration of divalent Mn following soil sterilisation confirms the results of previous studies by Mann and Quastel (1946) Fujimoto and Sherman (1948), Timonin and Giles (1952). This increase is probably caused by changes in soil redox potential following

wetting of the soil which converts manganic Mn to divalent Mn, which in the absence of a microbial population is not biologically refixed. As there is only a small increase in divalent Mn following sterilisation, it is unlikely that soil sterilisation will prove to be a satisfactory method of supplying sufficient Mn to crops throughout their development. In addition, soil sterilisation may also seriously affect the physical, chemical and biological processes in the soil. (Warcup 1957).

B. APPLICATION OF COMPOUND FERTILIZERS CONTAINING MANGANESE

B. APPLICATION OF COMPOUND FERTILIZERS CONTAINING MANGANESE

1. NUTRIENT COMPOSITION OF COMPOUND AND MIXED FERTILIZERS AND VARIABILITY IN THEIR DELIVERY FROM APPLICATION EQUIPMENT.

Table 12 shows the nutrient composition of various particle size fractions of a compound and mixed fertilizer with similar total nutrient content. The compound fertilizer was coarser than the mixed fertilizer, and variations in nutrient composition between the various particle size fractions were less than in the mixed fertilizer. For example, 94.5 per cent of the Mn occurred in 98 per cent of the compound fertilizer granules which had diameters > 1mm. In contrast 57 per cent of the mixed fertilizer occurred in the same size fraction and this contained only 28.5 per cent of the fertilizer Mn.

The data in Table 13 and Figure 7 show the variability that occurs in delivery of mixed fertilizers from application equipment with star feeding mechanisms.

TABLE 13

Variability in delivery (g/m) of a mixed fertilizer from application equipment.

Hoe Outlet	Total fertilizer		Total P			Total Mn			Total Cu		
	Mean	C.V. (%)	Mean	C.V. (%)	$100R^2$	Mean	C.V. (%)	$100R^2$	Mean	C.V. (%)	$100R^2$
4	3.69	52.3	0.33	62.6	96.3	0.078	89.7	84.1	0.011	86.4	76.9
7	4.77	33.8	0.42	39.6	99.8	0.134	44.2	86.7	0.026	45.8	77.3

C.V. = coefficient of variation

TABLE 12

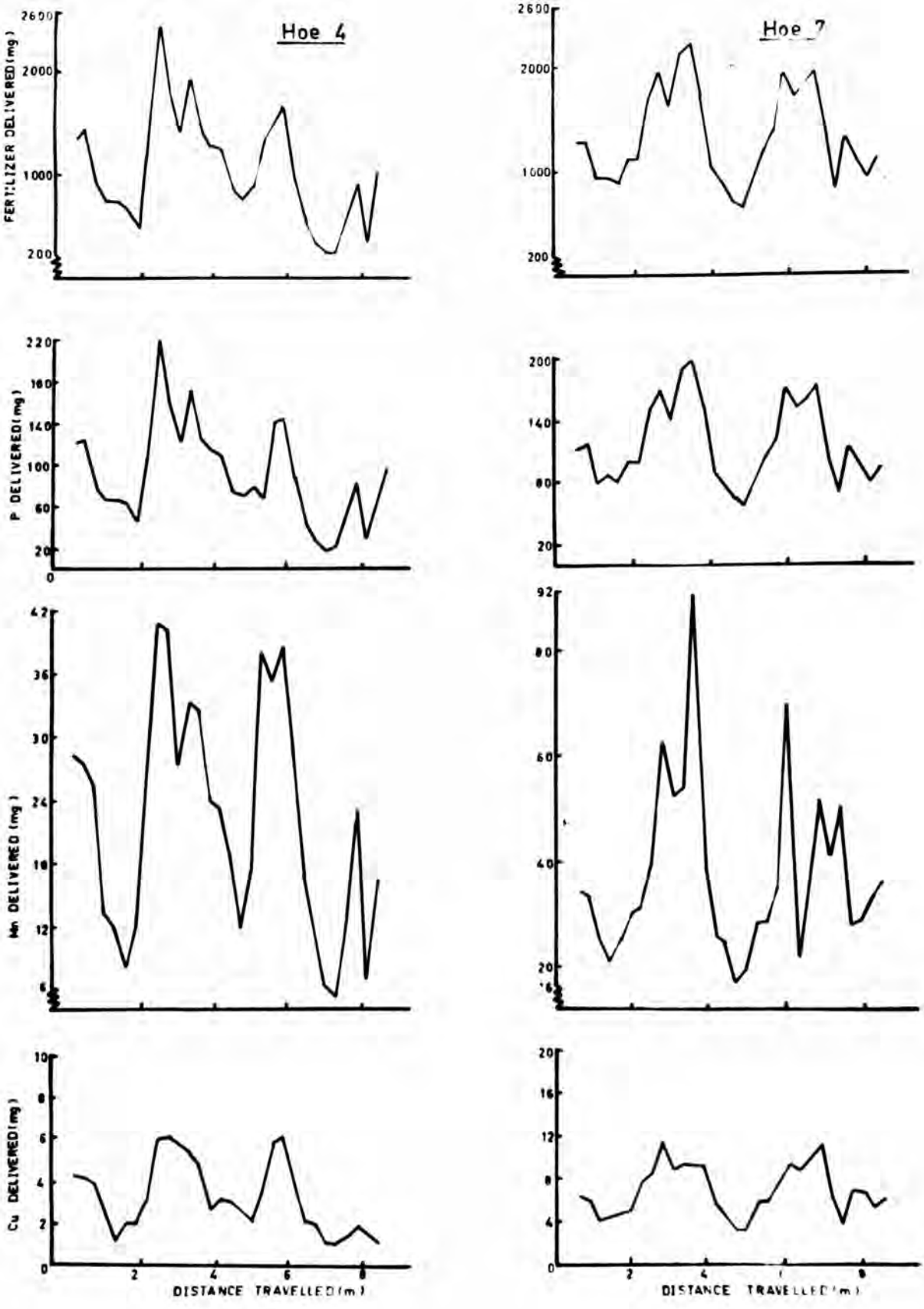
The relationship between particle size and the nutrient content of a compound and mixed fertilizer

Fertilizer	Granule Size (mm)	Granule Size distribution (%)	Nutrient concentration				Nutrient distribution expressed as % of total nutrient in fertilizer			
			Cu (%)	Mn (%)	P (%)	Pws+ (%)	Cu (%)	Mn (%)	P (%)	Pws+ (%)
	> 4.8	15.3	0.55	2.59	10.2	8.2	17.9	11.2	15.1	16.0
Compound	4.8 - 2.0	61.7	0.45	3.61	10.2	7.6	59.3	63.0	60.7	59.9
Total Cu = 0.46%	2.0 - 1.0	20.3	0.42	3.53	10.1	7.6	18.3	20.3	19.8	19.7
Total Mn = 3.46%	1.0 - 0.5	3.0	0.43	3.77	9.6	7.2	3.0	3.2	2.8	2.8
Total P = 10.2%	0.5 - 0.25	1.0	0.44	4.17	10.2	7.1	0.9	1.2	1.0	0.9
Pws = 7.7%	< 0.25	0.7	0.41	5.61	10.4	8.1	0.4	1.1	0.7	0.7
	> 4.8	1.0	0.005	0.05	11.8	8.7	0.01	.02	1.2	1.2
Mixed	4.8 - 2.0	27.0	0.01	0.31	11.0	8.6	0.53	3.04	30.3	30.9
Total Cu = 0.50%	2.0 - 1.0	29.0	0.06	2.42	10.3	7.9	3.38	25.46	30.5	30.5
Total Mn = 3.09%	1.0 - 0.5	19.0	0.38	4.53	9.5	7.2	14.05	31.22	18.4	18.2
Total P = 9.8%	0.5 - 0.25	13.0	2.22	5.24	8.9	6.5	56.14	24.71	11.8	11.2
Pws = 7.5%	< 0.25	11.0	1.21	6.90	6.9	5.5	25.89	15.56	7.8	8.1

+Pws = water soluble phosphorus

FIGURE 7

The longitudinal distribution of a mixed fertilizer and its ingredients from two fertilizer box outlets of a star-feeder operated seeding drill.


Hoe 4
Hoe 7
FERTILIZER DELIVERED(mg)
P DELIVERED(mg)
Mn DELIVERED (mg)
Cu DELIVERED(mg)
DISTANCE TRAVELLED(m)
DISTANCE TRAVELLED(m)

Much of the variability is associated with the passage of the star point up to and over the fertilizer box outlet (Penman 1933, Hutchinson 1961, Reuter (unpub. data)) and this would also occur with application of compound fertilizers. However, part of the variability was due to segregation of the fertilizer ingredients following mixing. For example, the coefficient of determination of the linear regression of fertilizer delivered against fertilizer P delivered approximates to 100. In contrast, the $100R^2$ for fertilizer delivered against fertilizer Mn or Cu delivered had a much poorer degree of correlation (See Table 13). If no segregation of the fertilizer ingredients occurred, then the $100R^2$ for each nutrient could be expected to equal 100.

2. THE NATURE OF Mn IN COMPOUND FERTILIZERS

The results in Table 14 indicate that although almost all the Mn in the compound fertilizer can be recovered by extraction with distilled water and Na_2EDTA solutions, (the resulting filtrates being acidic), only about 60 per cent is recovered in the alkaline acetate buffered CaNaEDTA.

The high apparent recovery of fertilizer Mn from $MnSO_4.4H_2O$ by the acetate buffered CaNaEDTA indicates that this extraction procedure is capable of removing divalent Mn in the presence of soil. However, using the same extractant, the apparent recovery of the fertilizer Mn from the compound and mixed fertilizers was only 21 and 57 per cent respectively, indicating the presence of superphosphate lowered the concentration of divalent Mn during the initial period of fertilizer reaction with the soil.

TABLE 14

The apparent and absolute recovery of fertilizer Mn, in the presence or absence of Warooka surface soil, by various chemical extraction procedures.

Fertilizer added	Extraction Procedure[+]	Apparent or absolute recovery of fertilizer Mn (%)	Filtrate pH
	Extracted in the absence of soil:		
	Distilled water	94.5	2.9
Compound	0.01M Na_2EDTA	95.6	2.9
	Acetate buffered CaNaEDTA (pH 8.5)	62.8 ± 5.4	8.2
	Extracted in the presence of soil:[++]		
	Acetate buffered CaNaEDTA (pH 8.5)	20.8	N.D.
Mixed	Acetate buffered CaNaEDTA (pH 8.5)	57.4	N.D.
$MnSO_4 \cdot 4H_2O$	Acetate buffered CaNaEDTA (pH 8.5)	93.2	N.D.

[+] Extraction period=2 hours.

[++] Apparent recovery calculated as

$$\frac{\text{Extracted Mn (soil + fertilizer)} - \text{Extracted Mn (soil)}}{\text{Mn applied in fertilizer}} \times 100$$

Untreated soil Mn concentration = 0.44 ppm Mn.

The low apparent and absolute recovery of Mn in the compound fertilizer suggests that part of the fertilizer Mn was not in a divalent form, implying the formation of reaction products, such as manganese phosphates, either during manufacture or following fertilizer dissolution in the soil. The high solubility of the fertilizer Mn in distilled water and Na_2EDTA does not preclude the formation of fertilizer reaction products during manufacture, as the dibasic ($MnHPO_4 \cdot 3H_2O$), tribasic ($Mn_3(PO_4)_2 \cdot 7H_2O$) and pyro ($Mn_2P_2O_7$) manganese phosphates are soluble in acidic solutions (Lange 1961). Further, because of the high apparent recovery of added divalent Mn from the $MnSO_4 \cdot 4H_2O$, by the acetate buffered CaNaEDTA extractant, it is unlikely that divalent Mn released from the fertilizer is chemically precipitated in the alkaline extracting solution.

If reaction products are formed in the compound fertilizer during manufacture, the concentration of $MnSO_4 \cdot 4H_2O$ will be lower than in the mixed fertilizer. X-ray diffraction techniques failed to detect $MnSO_4 \cdot 4H_2O$ lines in the compound fertilizer material, but weak lines were present in the mixed fertilizer. This provides qualitative evidence for the presence of Mn in some form other than the sulphate in the compound fertilizer. The concentrations of $MnSO_4 \cdot 4H_2O$ in the fertilizer were so low, as to preclude quantitative estimation of the $MnSO_4 \cdot 4H_2O$ remaining, or of the reaction products.

3. THE EFFECT OF SOIL STERILISATION ON THE RELEASE OF Mn FROM COMPOUND AND MIXED FERTILIZERS.

The results in Table 15 (Incubation Experiment 2) show that only 21 and 57 per cent of the added Mn in the compound and mixed fertilizers respectively was extracted in the presence of unsterilised soil with no incubation. The lower apparent recovery of the Mn contained in the

TABLE 15

The effect of soil sterilisation on the apparent percentage recovery of Mn from mixed and compound fertilizers incubated with Warooka soil (Incubation Experiment 2).

Fertilizer	Soil sterilisation	Apparent recovery of fertiliser Mn (%)					L.S.D. P=0.05
		Incubation period (hours)					
		0	2	24	72	167	
Compound	-	21	54	35	31	31	8
	+	30	48	44	33	30	
Mixed	-	57	55	52	30	23	12
	+	53	54	49	38	43	

L.S.D. for comparing fertilizers = 9 per cent.

compound fertiliser compared with the mixed fertiliser may have been due to the formation of less soluble reaction product in the compound fertilizer or to a slower rate of Mn dissolution due to the larger particle size, since after 2 hours incubation Mn recovered from the soil fertilised with the compound fertiliser increased by about 34 per cent.

After 24 hours incubation, the extractable Mn concentration of the soil fertilized with the mixed fertilizer slowly decreased. In contrast, during the same period, the Mn concentration of the soil which received the compound fertilizer remained at a relatively constant level. This suggests that the Mn is either steadily released from this fertilizer, or the released fertilizer Mn is not so readily immobilised.

Soil sterilisation had only a minor overall effect on the apparent recovery of the fertilizer Mn. However, after 167 hours incubation, the apparent recovery of the Mn from the mixed fertiliser applied to sterilised soil was significantly greater than the recovery in the unsterilised soil. This is analogous to the sterilisation effect measured in soil fertilized with $MnSO_4.4H_2O$ (Figure 6).

4. FIELD COMPARISONS OF COMPOUND AND MIXED FERTILIZERS

The results in Tables 16, 17 and 18 (Field Experiment 9, 1968) show that plant top growth was restricted within 57 days, and Mn and P accumulation in the foliage was depressed within 43 days from seeding, where no Mn fertilizer was applied. These early differences in crop growth and nutrient uptake between the control crop and the crops which received Mn fertilizer were maintained throughout the season.

Although differences in the dry weight of crops which received the compound or the mixed fertilizers were evident early in crop development, (Table 16) the differences were not significant until the late tillering stage, (71 days from seeding), and favoured the use of the compound fertilizer. At this stage, significant differences in Mn accumulation

TABLE 16

The effect of Mn carrier on plant top dry weight (Field Experiment 9, 1968).

Fertilizer[+++]	PLANT DRY WEIGHT (kg/ha)						
	43[+] 2[++]	57 3	71 3	85 4	99 6	112 N.D.	125 10.4-10.5
Nil, P	63	82	142	300	559	1116	2169
Mixed, P + Mn	63	117	235	439	703	1538	3123
Compound, (P, Mn)	74	140	312	563	1061	1960	3546
L.S.D. P = 0.05	16	27	60	92	119	276	710

[+] Harvest, in days after seeding

[++] Feekes' scale of cereal growth

[+++] All fertilizers contained a basal application of Cu

TABLE 17

The effect of Mn carrier on plant Mn accumulation (Field Experiment 9, 1968).

Fertiliser +++	PLANT Mn ACCUMULATION (g/ha)						
	43+ 2++	57 3	71 3	85 4	99 6	112 N.D.	125 10.4–10.5
Nil, P	0.77	1.18	2.24	3.90	7.03	10.07	9.41
Mixed, P + Mn	2.88	4.27	5.72	9.56	13.84	18.85	23.77
Compound, (P, Mn)	2.85	4.22	8.49	12.07	16.69	23.77	28.49
L.S.D. P = 0.05	0.68	1.14	1.76	1.82	2.91	3.90	7.89

+ Harvest, in days after seeding

++ Feekes' scale of cereal growth

+++ All fertilisers contained a basal application of Cu

TABLE 18

The effect of Mn carrier on plant P accumulation (Field Experiment 9, 1968).

Fertilizer[+++]	PLANT P ACCUMULATION (g/ha)						
	43[+] 2[++]	57 3	71 3	85 4	99 6	112 N.D.	125 10.4-10.5
Nil, P	164	244	387	691	1458	2016	3323
Mixed, P + Mn	166	359	574	984	1673	2557	4477
Compound, (P, Mn)	223	445	783	1268	2421	3254	5478
L.S.D. P = 0.05	50	96	148	232	340	520	1020

[+] Harvest, days after seeding

[++] Feekes' scale of cereal growth

[+++] All fertilizers contained a basal application of Cu

in the plant tops also occurred. (Table 17). Between the 57 and 71 day harvests, the rate of Mn accumulation in the crop which received the compound fertilizer (0.305g/ha/day) was nearly three times that accumulated by the crop fertilized with the mixed fertilizer (0.103g/ha/day). In later harvests, the rate of Mn accumulation was similar, and independant of the Mn carrier applied. The crop fertilized with the compound fertilizer was visibly showing Mn deficiency symptoms 99 days after seeding. Differences between treatments in Mn accumulation by crop is illustrated in Figure 8.

The resulting improvement in Mn supply to crop from applying the compound fertilizer originates in the mid to late tillering phase of plant development. At the 125 day harvest, the top growth contained Mn equivalent to 0.12 per cent and 0.09 per cent of the fertilizer Mn applied in the compound and mixed fertilizers respectively.

The tops of the crop fertilized with the compound fertilizer accumulated greater amounts of P throughout crop development, than the crop which received the mixed fertilizer.

The results in Table 19 indicate that in Field Experiment 9 (1968)and 13 (1969) barley grain yield and quality were improved by applying compound fertilizers at seeding compared with applying mixed fertilizers. In addition, the initial appearance of Mn deficiency symptoms were observed later in both seasons where crops were fertilized with the compound fertilizer, which suggests prolonged activity of the Mn supplied in the compound fertilizers.

FIGURE 8

The amount of Mn accumulated in the tops ([redacted] g/ha) during crop development as influenced by the type of Mn carrier applied to the Warooka soil at seeding. (Field Experiment 9, 1968).

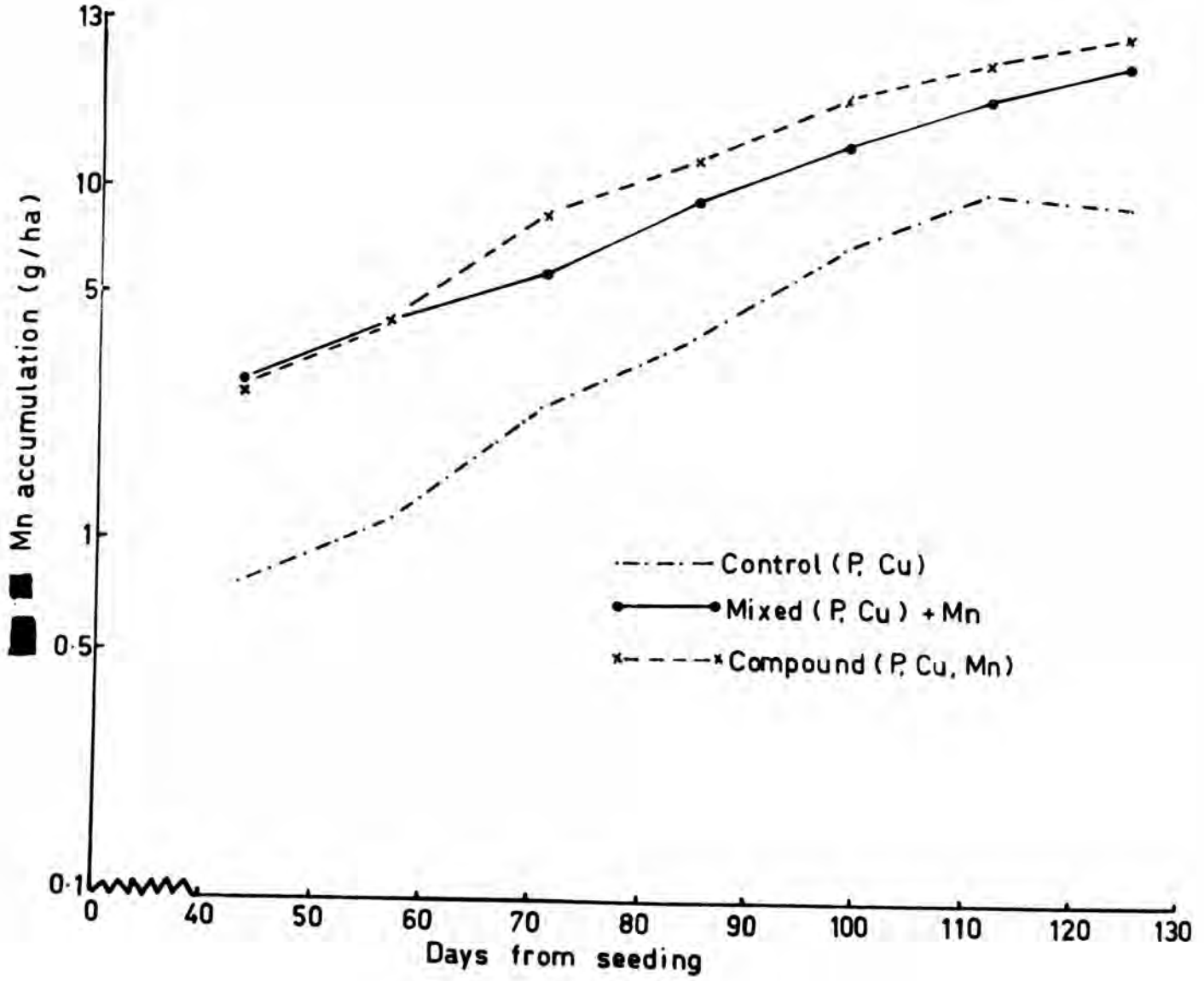

13
10
5
1
0·5
0·1
Mn accumulation (g/ha)
0
40
50
60
70
80
90
100
110
120
130
Days from seeding
Control (P, Cu)
Mixed (P, Cu) + Mn
Compound (P, Cu, Mn)

TABLE 19

The effect of Mn carrier on barley grain yield and quality (Field Experiment 9, (1968) and 13 (1969))

Fertilizer	1968					1969				
	Grain Yield (kg/ha)	Screenings (%)	1000 grain weight (g)	Malting grade	Mn symptoms observed (days from seeding)	Grain Yield (kg/ha)	Screenings (%)	1000 grain weight (g)	Malting grade	Mn symptoms observed (days from seeding)
Nil,+ P	1059	11.5	36.7	4	43	1351	7.0	38.5	3	43
Mixed P + Mn	1390	9.0	36.4	3-4	57	2309	5.9	39.2	M-3	62
Compound,(P,Mn)	1581	7.5	37.3	3	71	2847	3.8	40.6	M	76
L.S.D. P = 0.05	67	1.0	0.9			370	2.5	2.3		

+ All fertilizers contained a basal application of Cu

5. DISCUSSION AND CONCLUSIONS

The results presented in this Section have shown that definite agronomic benefits can be obtained from applying compound fertilizers to the Warooka soils, compared with the application of mixed fertilizers of the same nutrient content. The compound fertilizers have a more uniform nutrient composition than mixed fertilizers, and delivery from appli ation machinery is also more uniform because the fertilizer in redients do not segregate as a result of differences in particle size.

In a Field Experiment conducted in 1968, greater plant dry weight and Mn accumulation in plant tops were measured in the mid to late tillering phase of plant growth, in crops fertilized with the compound fertilizer, compared with the mixed fertilizer. Differences in plant P accumulation were also measured earlier.

The greater crop response to the compound fertilizer may result from a number of factors.

(a) The formation of fertilizer reaction products during the manufacture of the compound fertilizer, which may prolong the availability of the applied nutrients, by decreasing their rate of release into the soil. The evidence presented, suggested but did not conclusively prove the formation of such compounds. The actual identification of the compounds was also not pursued, since the main objective of the study was agronomic. However, it is worth noting that reaction products have been resolved in ammoniated phosphate carriers containing up to 10 per cent Mn by Hossner and Richards (1968) and Giordano and Mortvedt (1969).

(b) The incorporation of Mn with the superphosphate carrier, will increase the probability that the fertiliser Mn will diffuse from the fertilizer granule into an acidified soil volume surrounding the granule. This will delay the fixation of the applied Mn by the soil, which is supported by the results presented in Table 15. The incubation data also suggested that within this zone, the fertiliser Mn may react with other fertiliser products, (e.g. forming Mn phosphates), which may also resist soil fixation processes. Heintze (1968) has demonstrated that Mn phosphates can form but are chemical precipitated at pH >6.5. However, the acidity of the soil volume surrounding the granules may delay or counter chemical precipitation of these compounds.

(c) Mn applied in mixed fertilisers is finely divided, and its rate of fixation by the soil would be more rapid than "protected" Mn contained in the compound fertilizer granule, because of its larger surface area. Similar conclusions were reached by Millington and Powrie (1968) when describing sulphate removal from varying particle sizes of gypsum.

(d) Improved fertilizer efficiency of all applied nutrients, by the placement of the nutrients within a locally acidified soil zone surrounding the fertilizer granule. Lindsay and Stephenson (1959a,b,c) have shown that following the dissolution of mono calcium phosphate, the pH of the soil in the volume surrounding the fertilizer becomes extremely acidic and indigenous soil Mn is dissolved. This increased acidity may serve to prolong the availability of all applied nutrients in this calcareous soil. Plant roots penetrating into this soil volume will contact the applied nutrients, and possibly some dissolved indigenous soil Mn.

C. APPLICATION OF ELEMENTAL SULPHUR TO CORRECT MANGANESE DEFICIENCY

C. APPLICATION OF ELEMENTAL SULPHUR TO CORRECT MANGANESE DEFICIENCY

1. INCUBATION EXPERIMENTS

(a) Oxidation of Elemental S

The results of Incubation Experiment 1, shown in Table 20, indicate that about 20 to 50 per cent (42-114 mg S/100g soil) of the added elemental S was oxidised after 52 weeks incubation with Warooka surface soil (Uc.1.11). The rate of S oxidation was greater where the S was incorporated with superphosphate, but the incorporation of Mn had little effect. Inoculation of the soil with Thiobacillus had no significant effect on the rate of S oxidation. Attempts to isolate Thiobacillus microorganisms in the untreated

TABLE 20

Rate of elemental S oxidation in Warooka soil (per cent of S added)

Fertilizer	S added (mg)	Percent S oxidised				
		Incubation Period (weeks)				
		2	4	6	12	52
0	0	0	0	0	0	0
S	40	9.2	5.3	3.4	5.6	28.7
(P, S)	42.5	-0.5	13.8	11.6	16.8	42.2
(Mn, S)	40	14.7	9.4	0.9	0.2	20.1
(P, Mn, S)	46.2	4.9	7.9	2.7	8.5	49.4
L.S.D.	P=0.05	13.8	7.7	5.9	8.3	8.1

Warooka soil failed, due to the calcareous nature of the soil (Swaby (priv. comm.)).

(b) Elemental S Oxidation and its Effect on Extractable Soil Mn

The results presented in Table 21 show that elemental S had no effect on the amount of divalent Mn extracted from the soil by the acetate buffered CaNaEDTA solvent. The fluctuations in Mn concentration during

TABLE 21

The effect of elemental S on the concentration of Mn (ppm) extracted from incubated Warooka soil by acetate buffered CaNaEDTA

Fertilizer	Mn added (ppm)	Divalent Mn (ppm)					
		Incubation Period (weeks)					
		0	2	4	6	12	52
0	0	0.6	0.08	0.10	0.03	0.06	0.45
S	0	N.D.[++]	0.08	0.13	0.03	0.08	0.45
(P, S)	0	N.D.	0.08	0.15	0.03	0.08	0.45
(Mn, S)	88	68.8	0.08	0.19	0.02	0.08	0.45
(P, Mn, S)	88	53.2	1.57	0.26	0.04	0.16	0.45
L.S.D.[+] P = 0.05		0.5	0.76	0.30	0.02	0.05	

[+] L.S.D. for comparing (Mn, S) and (P, Mn, S)

[++] N.D. = not determined

the experiment were possibly caused by changes in soil water content in the incubation vials.

The data also show that fertilizer Mn was rapidly fixed on incubation with the soil. The presence of superphosphate in the fertilizer granule, slightly reduced the rate of fixation, possibly as a result of the acidity produced by the dissolution of the superphosphate granules. However, after 52 weeks incubation the amount of divalent Mn extracted was the same, in all treatments. The "apparent recovery" of fertilizer Mn in the presence of soil from the (P, Mn, S) and (Mn, S) fertilizer using the acetate buffered CaNaEDTA extractant was 57.1 and 95.2 per cent respectively. These recoveries are analogous to those discussed in section B.2.

Pretreatment of the soil with alcoholic quinol before the extraction with acetate buffered CaNaEDTA greatly increased the amount of Mn extracted, (Table 22), which indicates that part of the indigenous soil Mn was in easily reducible forms. The addition of Mn fertilizers to the soil, significantly increased the amount of extractable Mn at all incubation periods. The apparent recovery of the fertilizer Mn in the (P, Mn, S) and (Mn, S) fertilizers, using this extraction procedure was 65.0 and 93.6 per cent respectively.

The addition of elemental S alone to the soil slightly increased the concentrations of extractable soil Mn, (Table 22), between the 4 and 12 weeks incubation, although the difference was not significant after 52 weeks. The presence of superphosphate in the carrier, (P, S) significantly reduced the amount of Mn extracted from the soil to which no Mn fertilizer had been added. This effect of superphosphate was also observed in soils which received fertilizer Mn, (P, Mn, S) but the difference

TABLE 22

The effect of elemental S on the concentration of divalent and easily reducible Mn (ppm) extracted from incubated Warooka soil

Fertilizer	Mn added (ppm)	Divalent and easily reducible Mn (ppm)					
		Incubation Period (weeks)					
		0	2	4	6	12	52
0	0	20.5	15.6	17.6	15.8	21.6	19.1
S	0	N.D.[+]	16.4	19.2	17.3	23.1	18.7
(P, S)	0	N.D.	15.8	15.6	13.0	18.9	12.5
(Mn, S)	88	87.5	56.4	62.5	57.0	71.3	78.5
(P, Mn, S)	88	80.3	43.4	58.2	50.4	65.7	66.9
L.S.D. P=0.05 for comparing treatments which received no Mn		18.8	2.0	1.1	1.8	1.4	0.7
L.S.D. P=0.05 for comparing treatments which received Mn		18.8	8.7	12.9	11.5	17.4	17.1

[+] N.D. = not determined

was significant only during the first 2 weeks of incubation.

(c) Elemental S oxidation and its effect on extractable soil P

The results presented in Table 23 indicate that where superphosphate was not added to the soil, the rate of S oxidation had a variable effect on $NaHCO_3$-soluble P concentration, but the small changes that did occur, would probably have little practical significance.

TABLE 23

The effect of elemental S on the concentration of $NaHCO_3$-soluble P (ppm) extracted from incubated Warooka soil.

Fertilizer	P added (ppm)	$NaHCO_3$-soluble P (ppm)					
		Incubation Period (weeks)					
		0	2	4	6	12	52
0	0	29.2	23.2	22.9	20.8	28.2	23.8
S	0	28.4	19.8	22.6	20.6	29.2	26.0
(Mn, S)	0	28.8	28.9	27.3	20.5	27.4	29.1
(P, S)	456	406.3*	373.1	391.8	362.5	381.9	338.5
(P, Mn, S)	456	418.8**	336.9	336.0	335.3	337.5	300.1
L.S.D. P=0.05 for comparing treatments which received no P		5.2	1.8	4.1	0.9	1.4	1.6
L.S.D. P=0.05 for comparing treatments which received P		159	39.9	36	22	15.2	24

* Represents 83.3 per cent of total fertilizer P added, and 92.3 per cent of the water soluble fraction of the fertilizer

** Represents 85.3 per cent of the total fertilizer P added, and 92.7 per cent of the water soluble fraction of the fertilizer.

The amount of P extracted by $NaHCO_3$ from soil incubated with fertilizer containing superphosphate, showed a decrease during the first 2 weeks of incubation, which would coincide with dissolution of the fertilizer P and its reaction with the soil (Table 23). Subsequently, the P concentration in the soil decreased more gradually. The presence of Mn in the

compound fertilizer reduced the amount of P that was extracted by $NaHCO_3$.

The apparent recovery of fertilizer P in the (P, Mn, S) and (P, S) fertilizers by the $NaHCO_3$ extraction indicates that this procedure in the presence of Warooka soil, with no incubation, extracts more than 92 per cent of the water soluble fertilizer P fraction.

(d) The Effect of Thiobacillus Inoculation

Inoculation of the soil with Thiobacillus did not affect the rate S oxidation, or the amounts of divalent and easily reducible Mn in the soil and had an inconsistent effect on extractable soil P (Appendix 6).

2. GLASSHOUSE EXPERIMENT

The results of the Glasshouse Experiment which are summarised in Table 24, show that the dry matter yield of plants was not affected by applications of sulphate-S at rates up to the equivalent of 126 kg S/ha.

TABLE 24

Linear regression analysis[+] of plant data harvested from the Glasshouse Experiment grown on the Warooka calcareous sand (Uc. 2.11).

Plant property	Linear regression of plant property against sulphur rate (S)	Statistical significance of regression
Plant dry weight (g/pot)	D.W. = 19.3 - 0.009 S	N.S.
Total number tillers/pot	Number = 44.9 - 0.029 S	N.S.
Total number head bearing tillers/pot	Number = 27.4 - 0.016 S	N.S.
Plant S concentration (%)	S conc. = 0.314 + 0.001 S	***
Plant S uptake (mg/pot)	S uptake = 60.88 + 0.16 S	***

[+]Quadratic fits were not significant

The absence of a plant dry matter yield response to S under experimental conditions of adequate supply of all other plant nutrients indicates that S as a plant nutrient per se does not limit plant growth on this soil. This confirms field observations.

3. FIELD EXPERIMENTS

(a) The effect of elemental S application on barley grain yield

The data in Table 25, which summarises the results of six field experiments, indicates that in two years out of four, a grain yield increase to elemental S application was obtained (Field Experiments 8 (1967), 9 and 10 (1968)). In these two seasons, which contrasted greatly in rainfall, the response was evident at high application rates of S (viz. 126 kg S/ha), and where no fertiliser Mn was applied at seeding. The results in Table 26 (Field Experiment 9, 1968) indicate that yield increases and grain quality improvements are greater in crops which received fertilisers, in which the S was incorporated within the fertiliser granule.

In 1966 and 1969, (Table 25) grain yield increases to S were not obtained (Field Experiments 6, 7 and 13). In the 1966 experiments, barley yields were limited by late sowing (July 29th), and N deficiency. In 1969, the lack of response to S applications can probably be associated with the small quantity of S applied (24 kg S/ha).

The results presented in Table 27 (Field Experiment 12, 1968) show that variations in the particle size of S incorporated into compound fertilisers did not affect grain yield or quality, although increasing the quantity of S applied, did increase vegetative growth and grain yield and improved grain quality.

TABLE 25

The barley grain yield response to elemental S applications applied in mixed and compound fertilizers.

TREATMENT			BARLEY GRAIN YIELD (kg/ha)					
			Year					
S applied (kg/ha)	Mn applied (kg/ha)	Type of fertilizer+	1966		1967	1968		1969
			Field Experiment Number					
			6	7	8	9	10	13
0	0	C	701	930	482	1059	1334	1351
	6	M					1698	2309
		C						2847
	8	M		837			1788	
	12	M			830		1710	
	16	M		998	852	1390	1710	
		C				1581		
12	6	C	661					
16	8	C	802					
24	0	C						1379
	6	C	628	902	970			2741
31	8	C	835				2012	
	16	C	947					
47	6	C			958			
	12	C			1076			
63	16	C	947		975			
94	12	C			975			
126	0	C			617	1351	1631	
	6	C					1990	
	12	C					2012	
	16	C			1121	1732	2046	
							2046	
L.S.D., P = 0.05			84	112	112	67	106	370
Barley Cultivar			Prior			Clipper		

+ M = mixed fertilizer; C = compound fertilizer

TABLE 26

The effect of fertilizer S and Mn placement relative to the superphosphate carrier on barley grain yield and quality (Field Experiment 9, 1968).

Treatment[+]	Grain Yield (kg/ha)	Screenings (%)	1000 grain weight (g)	Malting grade
P	1059	11.5	36.7	4
P + S	1244	11.0	36.5	4
(P, S)	1351	10.1	36.9	4
P + Mn	1390	9.0	36.4	3-4
P + Mn + S	1401	8.7	36.8	3-4
(P, S) + Mn	1547	8.4	38.2	3
(P, Mn)	1581	7.5	37.3	3-4
(P, Mn) + S	1665	7.2	37.3	3
(P, Mn, S)	1732	7.8	38.1	3
L.S.D. P = 0.05	67	1.0	0.9	

[+]All fertilizer contained 1 kg Cu/ha blended with the Superphosphate carrier.

TABLE 27

The effect of varying S particle size and the quantity of S applied in S fortified compound fertilizers on barley grain yield, quality and vegetative growth (Field Experiment 12, 1968)

S applied (kg/ha)	S particle size (mm)	Mean Grain Yield (kg/ha)	Screenings (%)	1000 Grain Weight (g)	Malting grade	Dry Weight (kg/ha)	
						100 days+	156 days
0		1805	6.5	39.3	3	849	3473
24	0.7 - 1.0	1928	5.4	39.2	3	871	3631
	0.25 - 0.5	1855	6.3	38.9		810	3643
	0.15 - 0.25	1967	5.8	39.7		851	3845
	0.10 - 0.15	1984	5.6	39.4		900	3610
	< 0.076	2007	5.1	38.8		928	3960
63	0.7 - 1.0	1934	5.6	38.6	3	808	3513
	0.25 - 0.5	1923	5.6	38.8		886	4042
	0.15 - 0.25	1900	5.8	39.5		798	3660
	0.10 - 0.15	1967	5.6	39.4		822	3936
	< 0.076	1945	5.9	38.2		901	4018
126	0.7 - 1.0	1911	5.4	39.6	3	840	3562
	0.25 - 0.5	1872	5.8	38.7		950	3612
	0.15 - 0.25	2001	5.3	39.4		932	4061
	0.10 - 0.15	1923	5.8	39.6		900	3554
	< 0.076	1923	5.2	40.0		929	3437
L.S.D. P = 0.05		101	0.7	1.8		113	521

+ harvest; days after seeding

(b) The effect of elemental S placement on plant growth and nutrient accumulation.

The data from Field Experiment 9 (1968) summarised in Tables 28, 29 and 30, indicate that the application of elemental S increased crop dry weight, Mn and P accumulation in plant tops, only where S was incorporated with the superphosphate carrier. The response to S was again most pronounced where no Mn was applied at seeding.

S fortification of the mixed fertilizer ((P, S) + Mn) resulted in a consistent increase in plant P accumulation throughout crop development, increased crop dry matter yield within 85 days of seeding and increased plant Mn accumulation during the early stages of crop development. In contrast, S fortification of compound fertilizers ((P, Mn, S)) resulted in only small effects on crop growth and nutrient accumulation; dry weight was increased at late tillering, Mn accumulation was increased 57 days after seeding and plant P accumulation was not affected.

The results in Table 29 further indicate that during early crop development, the crop which received the mixed fertilizer (P + Mn) accumulated more Mn than the crop fertilized with the (P, S) fertilizer. After 99 days growth the amount of Mn accumulated by these crops were the same, which indicates that the part of the S response was to improve Mn supply to crops grown on these soils. In contrast, the crop fertilized with the S fortified compound fertilizer, (P, Mn, S), produced greater growth and accumulated more Mn and P throughout crop development compared with the crop which received the (P, S) fertilizer. These results indicate that S applications will not overcome the necessity of applying fertilizer Mn at seeding to crops grown on these soils.

TABLE 28

The effect of fertilizer S and Mn placement relative to the superphosphate carrier on plant dry weight, (Field Experiment 9, 1968).

Tr.	Fertilizer[+]	PLANT DRY WEIGHT (kg/ha)								
		43[++]	57	71	85	99	112	125		
								Total	Straw	Heads
1	P	63	82	142	300	559	1116	2169	1844	327
2	P + S	66	93	143	320	559	1150	2250	1878	377
3	(P, S)	67	119	238	458	885	1514	2961	2498	464
4	P + Mn	63	117	235	439	703	1538	3123	2661	462
5	P + Mn + S	60	109	199	363	708	1554	3141	2676	465
6	(P, S) + Mn	78	143	275	561	990	1761	3515	2970	545
7	(P, Mn)	74	140	312	563	1061	1960	3546	3021	525
8	(P, Mn) + S	69	160	279	567	951	1766	3618	3065	554
9	(P, Mn, S)	77	163	334	656	1163	2081	3735	3152	584
L.S.D. P = 0.05		16	27	60	92	119	276	710	641	98

[+] 2 kg Cu/ha applied in all fertilizers in the superphosphate carrier.

++ Harvest, in days after seeding.

TABLE 29

The effect of fertilizer S and Mn placement relative to the superphosphate carrier on plant Mn uptake in tops (Field Experiment 9, 1968).

Tr.	Fertilizer[+]	PLANT Mn ACCUMULATION (g/ha)								
		43[++]	57	71	85	99	112	125		
								Total	Straw	Heads
1	P	0.77	1.18	2.44	3.90	7.03	10.07	9.41	7.79	1.63
2	P + S	0.88	1.45	2.05	5.00	9.05	11.60	12.73	10.56	2.17
3	(P, S)	0.88	1.72	3.73	5.35	13.12	15.51	15.76	12.94	2.82
4	P + Mn	2.88	4.27	5.72	9.56	13.84	18.85	23.77	20.67	3.10
5	P + Mn + S	2.93	4.88	6.05	8.71	14.90	21.11	26.85	23.75	3.10
6	(P, S) + Mn	4.05	5.46	7.00	10.33	19.62	22.54	30.95	27.46	3.50
7	(P, Mn)	2.85	4.22	8.49	12.07	16.69	23.78	28.48	25.02	3.47
8	(P, Mn) + S	2.68	5.57	7.14	10.75	18.98	22.86	31.93	28.13	3.80
9	(P, Mn, S)	3.17	5.56	8.52	11.60	18.66	27.80	28.10	24.15	3.96
L.S.D. P = 0.05		0.68	1.14	1.76	1.82	2.91	3.90	7.89	7.38	0.84

[+] 2 kg Cu/ha blended with the superphosphate in all fertilisers

[++] Harvest, in days after seeding

TABLE 30

The effect of fertilizer S and Mn placement relative to the superphosphate carrier, on plant P uptake in tops (Field Experiment 9, 1968).

Tr.	Fertilizer[+]	PLANT P ACCUMULATION (g/ha)								
		43[++]	57	71	85	99	112	125		
								Total	Straw	Heads
1	P	164	244	387	691	1458	2016	3323	2307	1016
2	P + S	172	278	361	748	1327	2038	3068	2280	968
3	(P, S)	210	422	623	1056	2052	2507	4503	3147	1352
4	P + Mn	166	359	574	984	1673	2557	4477	3126	1353
5	P + Mn + S	143	299	523	902	1741	2631	5058	3701	1358
6	(P, S) + Mn	227	480	664	1278	2361	2940	5060	3449	1611
7	(P, Mn)	223	445	783	1268	2421	3254	5478	3743	1736
8	(P, Mn) + S	209	528	687	1279	2350	2783	5513	3771	1743
9	(P, Mn, S)	247	532	805	1494	2753	3370	5842	3945	1896
L.S.D. P = 0.05		50	96	148	232	340	520	1020	822	273

[+] 2 kg Cu/ha blended with the superphosphate in all fertilizers.

[++] Harvest, in days after seeding.

(c) The interaction of fertilizer P, Mn and S.

The results presented in Table 31 (Field Experiment 11, 1968) indicate that plant growth and grain yield were significantly increased by applications of P, Mn and S, to the soil at seeding.

The responses to S and to some extent Mn, were greater, where only 19 kg P/ha was applied. The vegetative growth response to Mn was not affected by S application, but grain yield responses to Mn were evident only where no S or low S rates had been applied.

Uptake of Mn, S and P in the plant tops was increased by the larger application of P (39 kg P/ha). S applications increased Mn uptake, but had a variable effect on P uptake; the increased Mn uptake due to S was smaller at the high rate of P application. Increasing the quantity of fertilizer Mn applied, increased Mn uptake, particularly at the low P application. In some instances, crops which received the high Mn application accumulated similar amounts of Mn in their tops to crops fertilized with S and the low application rate of Mn. S uptake was not affected by S application.

Barley quality was not influenced by treatment; all samples were graded 3.

4. DISCUSSION

(a) Factors influencing the rate of S oxidation

The rate of S oxidation in the Warooka soil, is comparable to the rates reported for other soils, (Table 32), although as shown by some of these authors the amount of S oxidised depends on the incubation conditions, (temperature, soil water content), S particle size, amount of

TABLE 31

The interaction of P, Mn and S on barley grain yield, dry weight and nutrient accumulation

(Field Experiment 11, 1968)

Fertilizer			Grain Yield	100 day harvest				156 Day harvest			
P rate (kg/ha)	Mn rate (kg/ha)	S rate (kg/ha)	(kg/ha)	Dry weight (kg/ha)	P uptake (g/ha)	Mn uptake (g/ha) x10	S uptake (g/ha)	Dry weight (kg/ha)	P uptake (g/ha)	Mn uptake (g/ha) x10	S uptake (g/ha)
19	6	0	1591	886	2260	126.6	2710	3130	3250	200.3	4030
		24	1652	836	2250	137.5	2540	3850	4170	245.3	5210
		63	1667	872	2210	150.3	2670	3800	5170	258.1	5040
		126	1746	990	2630	160.5	2920	3730	3950	277.8	4720
19	16	0	1633	912	2520	187.4	2650	3580	3740	210.7	4600
		24	1697	1049	2650	197.0	3040	4060	4600	310.9	4830
		63	1739	1099	2780	210.8	3030	3700	5210	284.4	4930
		126	1732	1117	2800	211.4	3140	3730	3890	280.9	4860
39	6	0	1817	1208	3170	206.8	3550	3950	4290	267.0	5150
		24	1820	1260	3400	203.8	3490	4140	5030	274.7	5290
		63+	1848	1231	3270	208.2	3300	3960	5850	295.7	5060
39	16	0	1866	1306	3290	231.2	3430	4260	5370	320.1	5490
		24	1899	1271	3270	231.2	3420	3970	4820	307.4	4880
		63	1881	1370	3630	243.8	3730	4040	6310	334.1	5030
		126	1879	1259	3370	253.6	3360	4190	5010	345.0	5150
L.S.D. P = 0.05			50	182	510	37.7	540	550	1560	64.2	779

+ (P_{39}, Mn_6, S_{126}) sown at incorrect application rate

TABLE 32

Rate of oxidation of Elemental S in soils

Reference	S added (mg/100g soil)	S particle size (mm)	Incubation period (weeks)	Percent S oxidation	S oxidised (mg/100g soil)
Joffe and McLean (1922) (8 soils)	100	Not given	4.5	30-63	30-63
Rudolfs (1922) (3 soils)	5 - 175	Not given	12	31-100	3-119
Moser and Olsen (1953) (4 soils)	200	< 0.15	3	20-65	40-135
Fenster (1965) (1 soil)	100	0.84-2.00 0.84-0.42 0.42-0.18	48	20 47 80	20 47 80
		0.088-0.125	8	100	100
Li and Caldwell (1966) (1 soil)	50	0.25-0.18	26	26	13
Bloomfield (1967) (1 soil)	100	< 0.50	20	24	24
Swaby and Vitolins (1968) (275 soils) High[+] Moderate Low None	1000	Not given	10	13-62 4-13 0.5- 4 0-0.4	13-61 4-13 0.5- 4 0-0.5
This study	200	Mostly >0.25	12 52	5.6 28.7	11 57

[+]Classified by authors, as soils in which elemental S is oxidised to a high, moderate or low degree.

S added, as well as soil properties. Where optimum conditions were present, all of the applied S was oxidised in some soils within a few weeks.

According to the classification scheme of Swaby and Vitolins (1968), the Warooka soil has a moderate capacity to oxidise S. These authors suggested that the slow rate of S oxidation measured in many Australian alkaline soils (pH > 7.5) was caused in part by the low pH requirements for optimum Thiobacillus growth. They further showed that the primary S oxidisers in many of these soils consisted of a wide range of heterotrophic organisms which produced little sulphuric acid during oxidation. The chemistry of S oxidation by these microorganisms is unknown. (Swaby (priv. comm.)). Secondary oxidisers are the autotrophs, Thiobacillus thioparus and T. thiooxidans but their presence in the Warooka soil was not confirmed due to the calcareous nature of the soil.

The pH of the Warooka soils is too high for optimum autotrophic S oxidising microorganisms growth (as indicated by the lack of response in S oxidation rate to soil inoculation with Thiobacillus), which would limit the rate of elemental S oxidation. It may also be restricted by a low population of primary oxidisers in these soils.

The rate of S oxidation is also determined by S particle size. Fox et al. (1964) and Attoe and Olsen (1966) have shown that S oxidation in soils is very slow where particle sizes are greater than 0.3mm. About 96 per cent of the elemental S particles (S), and 94 per cent of the compound fertilizer granules, (P, Mn, S) used in Incubation Experiment 1 had diameters greater than 0.25mm. The rate of oxidation of the S would therefore be limited by the surface area of the S exposed in both

types of fertilizers for microbial oxidation. This would explain the lack of crop response to variations in S particle size in S fortified compound fertilizers (Field Experiment 12) and the greater crop response to high elemental S applications (Field Experiments 8, 9 and 10). Attoe and Olsen (1966) and Ludwick et al. (1968) have also reported that the rate of elemental S oxidation in S fortified fertilizers is inversely related to fertilizer granule diameter.

Other factors are important in describing the rate of S oxidation and its effect on nutrient availability in the Warooka soil. In Field Experiment 9 (1968) it was shown that the plant response to S was obtained only when the S was incorporated with the superphosphate carrier, and the results from Incubation Experiment 1 showed that the rate of oxidation of the S applied in fertilizers containing superphosphate was increased. This is in spite of the smaller surface area of S exposed in these fertilizer granules for microbial oxidation compared with S applied separately but not blended with a carrier. Broomfield (1967) also showed that the oxidation of S, particularly in a calcareous soil was promoted by the addition of phosphate carriers.

The increased rate of S oxidation in S fortified superphosphate is likely to be associated with the localised acidity surrounding the fertilizer granule, which would favour the oxider's pH requirements for optimum growth (Starkey 1966, Swaby and Vitolins 1968). The activity of the oxidisers may also be stimulated by the ready supply of nutrients contained in the superphosphate (e.g. P, Zn, Ca) which are required for microbial growth (Burns 1967). However, this is only likely to be important in very deficient soils.

The incorporation of Mn had little effect on the rate of S oxidation, which confirms previous studies by Ludwick et al. (1968).

(b) The influence of S oxidation on Mn and P availability

Applying elemental S as a component of compound fertilizers, ensures that the applied fertilizer nutrients are in intimate contact with the sites of S oxidation. The products of S oxidation are able to influence the availability of both the native soil and fertilizer nutrients, thereby affecting an overall improvement in plant nutrition.

S applications had no effect on the concentration of extractable divalent Mn (Table 21), but when added alone, did slightly increase the concentration of easily reducible soil Mn (Table 22). The small effect of S oxidation on soil Mn availability, as assessed by empirical chemical methods contrasts with the large increases in exchangeable soil Mn measured in other soils following S applications, (Tisdale and Bertramson 1949, Vavra and Frederick 1952). The effect is probably related to the instability of the released divalent Mn in the Warooka soil; soil Mn reduced following S oxidation may be rapidly reoxidised by the soil, however no information is available on the rate at which Mn is reoxidised. It is also likely that the quantity and the forms of soil Mn available for reduction in the Warooka soils are too small or unsuitable (see footnote[+]). Similar conclusions were reached by Vavra and Frederick (1952), to explain small

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[+] Footnote:

According to Tisdale and Bertramson (1949) the reaction involves the release of six electrons for each S atom oxidised, and the use of two electrons for each Mn atom reduced. i.e. for each S atom oxidised, theoretically three Mn atoms can be reduced. Since 600 ppm S were oxidised after 52 weeks incubation in the S fertilized soil, theoretically 3100 ppm Mn could be released. However, in Table 22 it is seen that the Warooka soil contained only 20 ppm in an easily reducible form, which may preclude the realisation of the full effect of the S oxidation on Mn availability.

increases in exchangeable soil Mn, following S oxidation in another Mn deficient soil.

The extent of the crop Mn response to S applications on these soils is likely to be determined by the proximity of the potentially reducible Mn to the oxidising S. The plant roots must then rapidly absorb the released Mn, before it is reoxidised by the soil.

The results from Incubation Experiment 1 (Table 23) indicated that greater amounts of $NaHCO_3$-soluble P were extracted from soil fertilized with the (P, S) fertilizer compared with the (P, Mn, S) fertilizer. The effect of S oxidation in prolonging the availability of the fertilizer P however was not evaluated in this study. The results from Field Experiment 9 (Table 30) indicated that crop P uptake was increased by S fortification, particularly where no fertilizer Mn was applied (e.g. P, S). Evidence in Table 31 also showed that the crop response to S occurred only at the low superphosphate rate of application. Collectively, the evidence suggests that the crop response to S is also in part linked to enhanced P supply to the plant roots. On other soils, elemental S applications have also been shown to increase the availability of soil and fertilizer P to plants (Ashby et al. 1966, Hassan and Olsen 1966, and Kacar and Akgul 1967). Its effect has been associated with the fall in soil pH, following the oxidation of the S. Tisdale and Rucker (1969) have also suggested that the sulphate ion itself may increase P uptake by plants.

Another explanation for the S response seems plausible, but was not evaluated in this study. The application of S increases the quantity

of fertilizer sown. Assuming constant granule diameter, the number of fertilizer granules sown per unit length of planting distance will increase, thereby increasing the probability of plant roots encountering nutrient supplies. For example, increasing the quantity of fertilizer sown by 126 kg/ha, increases the number of granules delivered by 52 per cent compared with the normal application of 236 kg/ha (P_{19}-Cu_1-Mn_6). Similarly, by doubling the superphosphate application, the number of granules delivered approximately doubles (e.g. P_{39}-Cu_1-Mn_6), which may explain the lack of S response at the high application rate of P in Field Experiment 11. In this regard, it is interesting to note that Halstead *et al.* (1968) have suggested that root interception of soil Mn may be an important mechanism in the supply of Mn to plants in Mn deficient soils.

In conclusion, it has been shown that barley crops grown on the Warooka soils respond to elemental S applied in compound fertilizers. This is not a direct plant response to S, and was only evident when P and Mn supply to plants was sub optimal. Applications of S do not substitute for the use of P and Mn in fertilizers applied at seeding to these soils. The crop response to S is smaller than those recorded in other studies in which S applications have been used to correct Mn deficiency (Tisdale and Bertramson 1949, Carey and Barber 1952, Ludwick *et al.* 1968). On the Warooka soils it would be more realistic to use higher application rates of P and/or Mn fertilizer than applying S fortified compound fertilizers.

D. APPLICATION OF MANGANESE IN FOLIAR SPRAYS

D. APPLICATION OF MANGANESE IN FOLIAR SPRAYS

Mn deficiency in barley crops grown on the soils of the Warooka area was only temporarily corrected by applying Mn fertiliser to the soil at seeding. For a more complete correction of the deficiency, Mn foliar sprays were necessary in addition to the soil application (Table 10).

In most experiments, the grain yield response per unit of Mn applied was greater from foliar sprays than from soil applied Mn (Table 33). This is associated with the high Mn fixation capacity of the Warooka soil.

The success of foliar sprays in correcting Mn deficiency in crops, appears to depend on three factors; the severity of the plant Mn deficiency, adequate leaf area to intercept the spray, and suitable environmental conditions to facilitate absorption of sufficient Mn through the leaf cuticle to effect a crop response.

1. THE SEVERITY OF Mn DEFICIENCY

During the period of rapid cereal growth, (late tillering to ear emergence), the rate and amount of top growth was greatly reduced in Mn deficient crops (Table 8 and Figure 3). The Warooka soils are unable to supply the amount of Mn required by the crop during this period. At this time it is possible that the crop requirement for Mn is greatest due to the increased rate of dry matter production. If the soil cannot supply the crop requirement, Mn foliar spray applications at this time should result in rapid plant growth improvements.

(a) Timing of the initial spray.

The results in Table 34 (Field Experiment 3, 1964), indicate

TABLE 33

Grain yield response per unit of Mn applied either as foliar sprays or as Mn fertilizer at seeding.

Year	Expt. No.	Treatment[++]		Total Mn applied (kg/ha)	Grain yield response to Mn per kg Mn applied (kg/ha)
		Soil application	Number foliar sprays		
1963	1	0	-	0	-
		0	1	1.43	322
		0	2	2.86	314
		P + Mn	-	5.36	87
		P + Mn	1	6.79	137
		P + Mn	2	8.21	123
	2	0	-	0	-
		0	1	1.43	263
		0	2	2.86	202
		P + Mn	-	5.36	95
		P + Mn	1	6.79	111
		P + Mn	2	8.21	97
1964	4[+]	0	2	2.86	52
		P + Mn	-	4.0	95
		P + Mn	1	5.43	156
		P + Mn	2	6.86	208
1967	8	0	-	0	-
		P + Mn	-	4.0	219
		P + Mn	2	6.86	156
1968	10	0	-	0	-
		0	2	3.59	12
		P + Mn	-	16.0	9.7
		P + Mn	2	19.59	9.2
1969	13	0	-	0	-
		0	1	1.36	95
		0	2	2.72	299
		0	3	3.98	236
		(P, Mn)	-	5.72	262
		(P, Mn)	2	8.44	216
		(P, Mn)	3	9.80	206
	16	0	-	0	-
		(P, Mn)	-	5.72	343
		(P, Mn)	2	8.44	276

[+] Expressed as grain yield per kg Mn applied.

[++] For details, see text.

TABLE 34

The effect of soil and foliar applied Mn on dry matter yield and grain yield of barley (Field Experiment 3, 1964)

Mn applied at seeding (kg Mn/ha)	Spray time (days from seeding)	PLANT DRY WEIGHT (kg/ha)						Grain Yield (kg/ha)
		28 days+	42 days	54 days	68 days	81 days	112 days	
		2-3 leaves per plant	2++	3	4	4-5	Poor 8-9 Others 10-10.2	
0	68, 98	20	49	74	111	193	712	594
	42, 68, 98			93	176	297	1086	886
2	68, 98	23	52	85	142	260	908	930
	42, 68, 98			112	181	353	1336	1009
4	No spray	23	56	105	187	293	663	207
	42			109	182	299	896	443
	54, 98				178	282	995	964
	68					301	957	516
	42, 68, 98			96	197	315	1217	970
L.S.D. P = 0.05		4	10	19	28	49	219	163
Crop symptoms		None	control chlorotic	2kg Mn/ha (unsprayed) slightly chlorotic		4kg Mn/ha (unsprayed) slightly chlorotic		

+ Harvests, in days after seeding

++ Feekes' scale of cereal crop growth stages

that within 42 days of seeding although plant dry weight was not significantly affected by Mn applications at seeding, the crop which received no Mn was showing symptoms characteristic of Mn deficiency. Foliar sprays applied at this stage, resulted in significant plant dry weight increases, 12 and 26 days later in the crops that received 0 and 2 kg Mn/ha at seeding. During this period the latter crop (without spray) showed symptoms of Mn deficiency.

The crop fertilized with 4 kg Mn/ha at seeding did not respond in dry weight to the 42 day spray until 112 days after seeding, and did not show Mn deficiency symptoms until 81 days after seeding. This indicates that Mn sprays applied to crops not showing Mn deficiency symptoms are not necessarily wasteful if the crop is likely to suffer Mn stress at a later stage.

The data also indicate that Mn sprays applied immediately following the first appearance of Mn deficiency symptoms, restore crop growth to approximately that measured in non-deficient crops. Plants that suffer deficiency for protracted periods, and are then sprayed, never completely recover their full growth potential. Similar evidence from Field Experiment 4 (1965) is given in Appendix 5.

(b) Number of foliar sprays

The results in Table 35, from several field experiments show that grain yields were increased by increasing the number of Mn sprays applied to the crop. This was most obvious where only small quantities of manganese sulphate were drilled with the seed.

TABLE 35

The effect of the number of Mn foliar sprays, and the quantity of Mn applied at seeding on barley grain yield.

Mn applied at seeding[+] (kg/ha)	Number of Mn sprays applied	Barley grain yield (kg/ha)				
		1963		1964	1965	
		Expt. 1	Expt. 2	Expt. 3	Expt. 4	Expt. 5
0	0	717	392			
	1	1177	768			
	2	1614	970	376		
	3			886		
2	2			628		
	3			1009		
4	0			207		
	1			443	961	
	2			628	1041	
	3			970	1140	
6	0	1183	902			1003
	1	1648	1143		1248	
	2	1726	1188		1363	1373
L.S.D. P = 0.05		327	256	163	168	168

[+] All fertilizers applied as mixed fertilizers.

Table 36 shows the effect on grain yield of increasing the number of Mn sprays, applied to crops which received different types of Mn fertilizer at seeding (Field Experiment 13, 1969).

TABLE 36

The effect of number of Mn foliar sprays on barley grain yield

(Field Experiment 13, 1969)

Fertilizer at seeding	Grain Yield (kg/ha)			
	Number of Mn sprays			
	0	1	2	3
(P, Cu)	1351	1480	2164	2292
(P, Cu) + Mn	2309	2898	3116	2937
(P, Cu, Mn)	2847	3144	3178	3374

L.S.D. P= 0.05; 359 kg/ha

First spray applied: 57 days after seeding; Feeke scale = 3

Second spray applied: 84 days after seeding; Feeke scale = 5 to 6

Third spray applied: 112 days after seeding; Feeke scale = 10 to 10.4

Where no Mn was applied at seeding, one spray, 57 days after seeding, improved crop colour, but did not significantly increase grain yield. The crop had been acutely deficient for at least two weeks before the spray was applied. A second spray, applied 27 days later, produced a large increase in grain yield ($P < 0.001$), but the yield was inferior to that of the crops which received Mn at seeding and two foliar sprays. A third spray, 28 days after the second spray, did not increase grain yield further.

The application of a single spray, during plant tillering to crops that received the mixed fertilizer at seeding, resulted in a large grain yield increase (25.5 per cent), although the crop was not showing Mn deficiency symptoms at the time of spraying. The yield response to such a spray, applied to the crop fertilized with the compound fertilizer at seeding, was not significant. However, three sprays applied to this crop did produce a yield increase.

The yield response to the foliar applied Mn may have been limited by the dry seasonal conditions experienced, particularly after the third spray had been applied. However, it is important to note that the responses to foliar sprays in this experiment were obtained when the applications were made before or during the period of rapid crop growth, when all treatments were visibly deficient in Mn. Grain quality was also improved by increasing the number of sprays applied to the crop which received no Mn fertilizer at seeding (Appendix 7).

Figure 9 illustrates the amount of foliage Mn in unwashed plant samples collected in successive harvests following the application of Mn sprays. (Field Experiment 3, 1964). Large increases in the quantity of Mn, either on or in the leaves were observed two weeks after the sprays had been applied. This increase persisted for at least another two weeks, although the percentage increase had been reduced. Similar increases (Table 37) in plant Mn content were observed in Field Experiment 8 (1967), in plants harvested 14 and 32 days after a manganese sulphate spray had been applied.

The above evidence suggests that under field conditions following a Mn spray, the Mn in or on the leaf surface persists for at least four

FIGURE 9

The effect of Mn foliar sprays applied at three stages during crop development on the amount of Mn within or on the foliage per unit ground area.
Figures within histograms are the mean plant Mn concentrations (ppm).

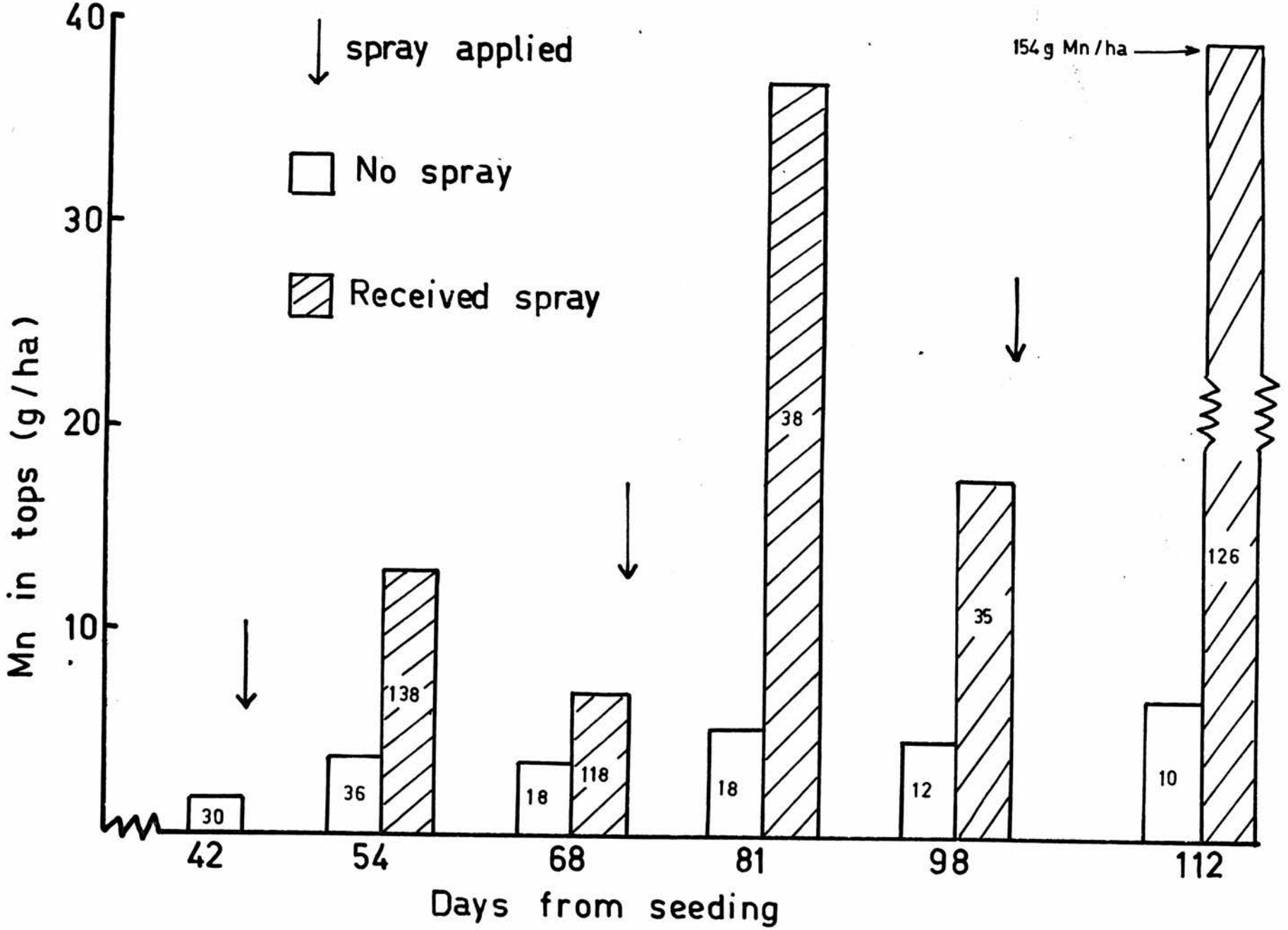
40
30
20
10
spray applied
No spray
Received spray
154 g Mn / ha
Mn in tops (g / ha)
30
36
138
18
118
18
38
12
35
10
126
42
54
68
81
98
112
Days from seeding

TABLE 37

Plant concentration and the absolute amount of Mn detected in unwashed plant tops harvested after a Mn Foliar spray had been applied 78 days after seeding (Field Experiment 8, 1967).

	78 days (sampled before spray applied)		92 days		110 days	
	Mn conc. (ppm)	Mn uptake (g/ha)	Mn conc. (ppm)	Mn uptake (g/ha)	Mn conc. (ppm)	Mn uptake (g/ha)
No spray+	16.8	14.7	12.9	17.3	8.2	18.4
Spray+	15.5	13.6	54.3	73.3	18.0	37.5
L.S.D., P = 0.05	6.3	3.3	16.6	26.0	9.8	31.7

+ 12 kg Mn/ha applied at seeding as a mixed fertilizer

weeks. The Mn content per unit ground area decreases with time following the foliar spray, which must represent the removal of spray residues from the foliage by subsequent rains or dew.

The evidence presented in Tables 35 and 36 indicate that on these soils, where the supply of Mn is so low, one Mn spray has only a temporary effect in correcting Mn deficiency. This has been attributed to the poor mobility of foliar applied Mn within the plant (Bukovac and Wittwer 1957, Single 1958, Vose 1963, Henkens and Jorgman 1965). Repeated Mn foliar sprays have been suggested to achieve maximal correction of Mn deficiency in crops grown on other soils (van Alphen 1956, Henkens and Jorgman 1965). The evidence from this study on the Warooka soils supports these previously published conclusions.

2. INTERCEPTION OF THE SPRAY BY THE CROP

On the Warooka soils where no fertilizer Mn is applied at seeding. Mn deficiency symptoms occur within 40 days of sowing. At this stage in crop development, (2 to 3 leaves/plant), crop leaf area per unit ground area will be low, and foliar spray interception by the crop must be correspondingly poor, compared with sprays applied later in crop growth. However, the crops do respond to Mn sprays applied during this period (Table 34). Figure 9 also shows that the later Mn sprays are applied in plant development, the greater is the amount of Mn present within or on the foliage per unit ground area. This can be associated with an increase in leaf area index with time and hence there is greater interception of the spray by the crop.

Barley sown at normal seeding rates (62 kg/ha), approaches maximum leaf area from stem extension onwards (Puckridge and Donald 1967), and

improved interception of the spray by the crop could therefore be expected during this period. Crops which received between 6 to 16 kg Mn/ha at seeding had characteristic Mn deficiency symptoms at or near stem extension. This also coincides with the period of maximum uptake of Mn by the plant (Figure 4). It is therefore logical in this situation to apply sufficient fertilizer Mn at seeding (viz. 6 kg Mn/ha) to enable the crop to reach stem extension without suffering Mn deficiency, at which time foliar sprays can be applied to coincide with maximum crop demand for Mn and near maximal spray interception.

The amount of crop surface area that will receive the Mn spray is also influenced by the spray volume used. Other studies (Table 1) have used higher solution volumes than those employed in this investigation. The results of Field Experiment 14 (1969), shown in Table 38, indicate that although Mn application rate and spray volumes varied together, the grain yield response to Mn sprays in this experiment was not influenced by spray volumes varying from 56 to 225 l/ha, or by Mn concentration, or by application rate. The two sprays in this experiment were not applied early in crop growth, at the time where responses to spray volume (or leaf interception of the spray) might be expected.

3. SUITABLE ENVIRONMENTAL CONDITIONS FOR FOLIAR Mn ABSORPTION AND CROP RESPONSE

Durkee (1967) suggested that to maximise the response to foliar nutritional sprays, they should be applied under high humidity conditions, and to crops not suffering water stress (stomatal closure). Early morning sprayings fulfil such conditions. Further Nederski and Hoff (1958) reported that the rate of Mn absorption by soybean leaves from Mn foliar

TABLE 38

The influence of Mn spray rate, solution concentration and spray volume on barley grain yield (Field Experiment 14, 1969).

Mn spray treatment		Spray Volume (l/ha)	Grain Yield (kg/ha)
Mn spray conc. (%)	Mn applied (kg/ha)		
No spray applied		-	2965
1.6	1.8	112	3559
	1.3	84	3610
	0.9	56	3632
1.2	1.8	152	3626
	1.3	112	3509
	0.9	76	3570
0.8	1.8	225	3677
	1.3	169	3604
	0.9	112	3598
L.S.D., P = 0.05			101

Sprays applied at Feekes' scale 3 and 5 to 6

sprays was very rapid during the first two hours following application. Moderately high temperatures (21°C), and environmental conditions that prevent drying of the spray deposit, (i.e. high relative humidity) favours a high rate of Mn absorption into the leaves.

Crop responses to foliar sprays were obtained to early morning sprays in Experiments conducted in 1963, 1964, 1965 and 1969, as shown in Table 33. Appendix 4 lists the environmental conditions during and after the application at some of these sites, and it can be seen that conditions were satisfactory for Mn foliar absorption.

However, in Field Experiment 8 (1967), foliar sprays were usually applied in the late morning - early afternoon to dry leaf surfaces, and crop responses to the sprays were not obtained. In Field Experiment 4 (1965), Mn sprays applied later than 99 days after seeding also did not respond (Appendix 5). Perhaps this lack of response can largely be attributed to the low rainfall and high air temperatures recorded during this period of growth (Table 39).

TABLE 39

Rainfall and air temperatures recorded at Warooka township during the period when Mn sprays were applied in 1965.

Days from seeding	Rainfall (mm)	Air temperature (°C)		
		Mean Maximum	Mean Minimum	Extremes
56-70	33	16	8	6-21
71-86	20	18	8	6-23
87-99	7	22	9	6-23
100-113	6	24	11	5-34+
114-127	1	23	11	5-28++
128-harvest	15	24	12	4-33+++

\+ 34°C recorded 9 days after the 99 day spray
++ 28°C recorded 1 day after the 113 day spray
+++ 33°C recorded 4 and 6 days after the 127 day spray.

Other factors in the field can also limit the crop response to foliar sprays. For example it is likely that the drought conditions experienced in 1967 (Field Experiment 8) limited most treatment responses; only 14mm of rain fell between the time the majority of the sprays were applied and grain harvest, and during this period, the crop developed from stem extension to maturity. Also in Field Experiment 10, (1968), although sprays were applied under near ideal conditions, it is probable that the crop response was limited by nitrogen deficiency caused by above average rainfall (April-October rainfall was 53 per cent greater than average). This was in spite of a basal dressing of 42 kg N/ha.

These observations are necessarily circumstantial, but are included since they partly explain the variation in crop response to Mn foliar applications, observed in this study. They serve to indicate that seasonal environmental conditions and conditions during and after the foliar applications are important, and are likely to determine the crop response to foliar sprays. Further experiments need to be undertaken to evaluate optimal conditions for rapid Mn uptake into foliage and to determine the factors which limit this process in the field.

4. OTHER CONSIDERATIONS

The need to respray crops with Mn, because of the reappearance of deficiency symptoms must be evaluated in terms of the Mn requirement of the crop. (Figures 3 and 4), environmental conditions as they influence Mn availability and crop growth, and proximity to harvest. This last consideration requires qualification. Sprays applied late in crop development by ground operated spray equipment can cause irrepairable

damage to the crop (Holmes and Lang 1963). In this study, such damage was observed, but not evaluated.

In most field experiments, Mn sprays applied late in crop development, usually did not significantly affect grain weight (Appendix 7), which was probably related to the low rainfall received in the grain ripening period. In more favourable seasons, grain yield and quality may be improved by late Mn spray applications, which may offset losses in grain yield from tractor wheel damage.

VI. GENERAL CONCLUSIONS

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Divalent Mn concentrations in the Warooka calcareous surface soil are low (0.4-0.6 ppm). Both chemical and biological fixation of applied manganous sulphate occurs on these soils. The fate of the immobilised Mn was not investigated, but at least some exists in higher valency forms since the added Mn can be partially recovered by a mild reducing agent. The rate of fixation, (341 ppm Mn or 77 per cent of the added Mn was immobilised after 167 hours) is similar to the rates measured in other soils (Mann and Quastel 1946, Uren 1969), but the rate of chemical fixation on the Warooka soils in the initial period of soil-fertilizer Mn reaction, (247 ppm Mn, or 55 per cent in 167 hours), is more rapid than occurs in other soils investigated, some of which were calcareous. (Mann and Quastel 1946, Mulder and Gerretsen 1952, Rivenbark 1961, Uren 1969).

Soil sterilisation delays the fixation of applied divalent Mn and increases the concentration of native soil Mn, but the rate of increase is too small (1.40 ppm Mn in 167 hours) for soil sterilisation to be a practical method for correcting Mn deficiency in crops grown on these soils.

Applications of Mn drilled with the seed as high as 16 kg Mn/ha as manganous sulphate in field experiments delayed the initial appearance of Mn deficiency symptoms, increased vegetative growth, root growth, and grain yield and improved grain quality. However, the applications alone did not prevent Mn deficiency occurring in crops grown on these soils. Investigations on other soils have also shown that soil applied Mn only results in a temporary correction of Mn deficiency (McLachlan 1941, Wain *et al.* 1943, Barbier *et al.* 1950, Henkens and Smilde 1967).

Barley grain yields were increased by 14 to 23 per cent and grain quality improved by sowing compound fertilizers in which the Mn was incorporated with the superphosphate carrier compared with the application of conventional mixed fertilizers. These improvements were attributed to the formation of fertilizer reaction products during the manufacture of the compound fertilizer and a delay in the fixation of the applied nutrients following their movement from the fertilizer into an acidified zone surrounding the granule, caused by acidity of the superphosphate. Other studies have also demonstrated that the application of phosphate carriers increases the availability of soil and fertilizer Mn to plants (Steckel et al. 1948, Lindsay and Stephenson 1959a,b,c, Bingham and Garber 1960, Bingham 1963, Page et al. 1963, Larsen 1964, Finke 1966, Hossner and Richards 1968). In addition, the Mn contained in the compound fertilizer is "protected" from soil fixation processes in the initial period of dissolution, by its incorporation in fertilizer granules of larger surface area than the Mn contained in the mixed fertilizer.

Elemental S fortification of compound fertilizers resulted in small grain yield increases of up to 10 per cent. The crop responses were only evident where high applications of S were applied (63-126 kg S/ha) and where Mn and P applications were suboptimal for maximum crop yield. The responses to S were attributed partly to increased Mn and P availability to plant roots. The magnitude of the crop response to S was smaller than those recorded in other studies, (Tisdale and Bertramson 1949, Garey and Barber 1952, Ludwick et al. 1968), and would not justify the use of S fortified compound fertilizers for correcting nutritional disorders on the Warooka soils.

Mn foliar sprays applied to crops grown on these soils, increased vegetative growth and grain yield and improved grain quality. The spray

response was particularly evident where the sprays were applied near to when Mn deficiency symptoms appeared, which supports the evidence reported by Henkens and Jorgman (1965). The grain yield response per kg Mn applied was greater from foliar sprays than from Mn applied to the soil, which agrees with previously published investigations on other soils (Lewis 1939, Mulder and Gerretsen 1952, Nicholas 1951, Nicholas and Fisher 1952, Wittwer et al. 1963, Smilde 1967). The correction of crop Mn deficiency by a single foliar spray however is only temporary, as symptoms of Mn deficiency reappear in the crop with subsequent growth. This has been attributed to the poor mobility of foliar applied Mn (Bukovac and Wittwer 1957, Single 1958, Vose 1963, Henkens and Jorgman 1965).

The practical conclusions to be drawn from this study, is that at the present time the best method for correcting Mn deficiency in barley crops grown on the Warooka soils is to apply 6 kg Mn/ha as a compound fertilizer at seeding. This application enables the crop to reach the late tillering phase before Mn deficiency occurs. At this stage in crop development, Mn foliar sprays (0.9 kg Mn/112 l/ha) can be more efficiently applied to crops, than at earlier stages of growth, because the crop requirement for Mn is high due to greater plant dry matter production and leaf area is maximal, for interception of the spray by the crop foliage.

VII. APPENDICES

APPENDIX 1.

Climatic data from Warooka township compiled from Bureau of Meteorology records.

Climatic Variable	Months											
	J	F	M	A	M	J	J	A	S	O	N	D
Mean Number rainy days (1861-1964)	3	4	4	9	13	14	17	16	13	10	7	5
Mean Max. air temp.(°C) (Calc. 30 yr. average)	28	29	26	23	19	16	15	16	18	22	24	27
Mean Min. air temp.(°C) (Calc. 30 yr. average)	15	16	14	14	9	7	7	7	8	9	12	14
Mean % relative humidity, 9 a.m. reading (Calc. 30 yr. average)	50	54	59	69	83	86	85	78	68	61	54	49

APPENDIX 2.

Monthly rainfall (mm) recorded at experimental sites, Warooka or Corny Point, together with average monthly rainfall at Warooka (1861 - 1961) and Corny Point (1888 - 1969).

Year	Recorded at:	Months (mm)												Yearly Total
		J	F	M	A	M	J	J	A	S	O	N	D	
1963	Warooka	33.5	11.2	2.8	55.4	107.7	91.7	114.3	72.1	31.2	29.5	2.8	4.3	556.5
1964	Warooka	7.6	30.2	3.6	60.2	51.8	86.9	121.9	29.0	65.3	74.4	65.0	18.3	614.2
1965	Corny Point	0	1.3	4.6	16.0	89.2	45.0	57.9	65.3	27.4	6.6	19.6	6.1	339.3
1966	Corny Point	2.3	5.8	29.5	6.1	42.9	60.5	101.9	38.4	63.0	25.9	11.4	57.7	442.0
1967	Site	7.1	86.6	2.8	7.6	18.0	10.7	65.8	41.1	24.4	13.5	0.8	6.6	285.0
1968	Site	N.D.	N.D.	42.4	171.2	99.0	69.6	72.1	67.8	40.6	39.4	23.6	8.9	
		3.6	8.1	38.9	104.9	93.7	89.2	59.7	70.4	26.9	49.3	19.8	15.0	599.2
1969	Site	12.7	74.2	5.3	39.1	49.0	29.0	54.6	30.0	28.2	2.5	13.2	5.1	342.9
Warooka average		13.4	18.1	15.0	34.5	56.6	65.7	66.4	59.2	45.0	36.4	22.8	16.3	449.4
Corny Point average		12.3	18.6	15.0	36.3	55.1	67.5	66.3	58.3	41.9	33.5	23.4	17.8	446.1

N.D. = not determined.

APPENDIX 3.

Trace Element content of Warooka calcareous sands.[+]

Trace Element	Soil profile form		Horizon depth (cm)		
			0–10	10–20	20–30
Manganese (ppm)	Uc 2.11	Range	125–151	66–80	44–54
		Mean	136	74	49
	Uc 1.11	Range	109–124	63–81	51–69
		Mean	116	70	60
Copper (ppm)	Uc 2.11	Range	15–18	10–14	10
		Mean	17	12	10
	Uc 1.11	Range	11–12	9	9–10
		Mean	12	9	10
Zinc (ppm)	Uc 2.11	Range	16–23	12–18	12–13
		Mean	19	14	12.5
	Uc 1.11	Range	15–20	12–19	12–13
		Mean	17	16	12
Iron (%)	Uc 2.11	Range	0.54–0.66	0.44–0.46	0.34–0.36
		Mean	0.58	0.45	0.35
	Uc 1.11	Range	0.40–0.44	0.38–0.42	0.39–0.42
		Mean	0.42	0.40	0.41

[+] Samples collected in 1967.

APPENDIX 4

Conditions recorded in the field during spraying operations undertaken in the 1965-69 Field Experiments, and the 9.00a.m. weather conditions determined at the Warooka weather station on the day and the day after the foliar sprays were applied.

Year	Spray Date	Weather recordings Warooka 9.00am.					Site rainfall concerning spray		Field observations at spraying time					
		Cloud+	R.H. (%)	R.H.++ next day %	Max Air Temp. (°C)	Min Air Temp. (°C)	Rain on day (mm)	In period before and after spray (mm)	Spray Time (am)	Weather conditions				Plant Surface
										Humidity	Cloud	Wind	Other	
1969	Aug. 7	0	71	60	14	6	0	2.5 - previous day	9.15-10.45	High	Overcast	Calm	Dew	Wet
	Sept. 3	8	48	75	17	9	0	3.8 - over next 3 days	6.45- 8.15	High	Overcast	Calm	Dew	Wet
	Oct. 1	0	34	5	22	11	0	No rain for 27 days	7.00- 8.30	Low	Cool	Moderate	Dew	Wet
1968	Aug. 15	8	52	45	14	6	0	10.4 - over next 6 days) 2.0 - previous day)	6.45- 8.15	High	Overcast	Slight	Light drizzle	Wet
	Sept.13	5	75	64	16	7	0	3.3 - previous day) 1.3 - over next 6 days)	6.45- 7.30	High	Sl.Overcast	Slight		Wet
1967	Aug. 30	0	12	20	16	6	3.1	4.1 - 4 days later	noon	Low	Clear	Slight	Warm	Dry
	Sept.19	8	20	51	16	8	1.2	0.3 - next day	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.
	Sept.29	8	49	60	21	9	1.2	0.3 - next day) 3.3 - three days later)	9.30-11.00	Moderate	Clearing	Slight	Warm	Drying
1966	Sept.15	8	86	72	15	8	0	5.3 - during next 3 days	NOT RECORDED					
	Sept.27	3	10	0	23	11	0	10.2 - during next 4 days						
	Oct. 6	8	100	40	16	5	0	7.9 - 8 days later						
	Oct. 18	6	52	41	19	10	4.1	1.5 - 2 days later						
	Nov. 1	4	64	22	18	7	1.3	No rain for 10 days						
1965	Aug. 16	8	61	87	13	8	2.3	23.1 - previous day) 25.4 - next day)	NOT RECORDED					
	Aug. 30	8	54	32	22	10	0	1.3 - two days later						
	Sept.15	5	61	60	14	6	0	No rain for 7 days						
	Sept.28	8	53	51	19	11	0	3.3 - during next 2 days						
	Oct. 12	3	44	36	26	15	0	1.3 - 5 days later						
	Oct. 26	6	72	44	23	111	0	1.3 - 5 days later						

+ Cloud cover as determined by Bureau of Meteorology Handbook.

++ R.H. = air relative humidity.

APPENDIX 5

The influence of quantity of Mn applied at seeding, and subsequent Mn foliar sprays on plant dry weight and grain yield (Field Experiment 4, 1965).

Mn applied at seeding (kg/ha)	Mn sprays applied (days after seeding)	MEAN PLANT DRY WEIGHT (kg/ha)							Grain Yield (kg/ha)
		42 days+	56 days	70 days	86 days	99 days	112 days	127 days	
4	56, 99	66	97	259	613	1128	1992	2537	1148
	70	66	109	250	544	1092	2052	2657	961
	70, 99	65	103	230	532	1152	1932	2647	1041
	70, 99, 127	62	90	253	548	1200	1824	2972	1140
	70, 112	62	110	236	566	1176	2064	2725	1039
	86	73	100	265	542	1272	2124	2664	1064
	86, 112	63	113	230	484	1128	1656	2616	924
	86, 127	67	108	248	475	948	1920	1908	1010
	99	73	112	229	437	960	1632	2263	808
	99, 127	67	110	245	551	996	1680	2089	957
6	86	74	132	308	728	1548	2100	2820	1248
	86, 112	72	116	298	691	1296	2196	2617	1222
	86, 127	73	128	331	666	1248	2172	2800	1363
	99	70	120	294	617	1272	2148	2732	1112
	99, 127	78	131	316	652	1152	1980	2688	1220
L.S.D. P= 0.05		N.S.	23	44	156	345	576	483	168

+ harvest, in days after seeding

APPENDIX 6

The effect of *Thiobacillus* inoculation on the concentration of $NaHCO_3$-soluble soil P in incubated Warooka Soil (Incubation Experiment 1).

Fertilizer applied	Inoculation	$NaHCO_3$-soluble P (ppm)					
		Incubation Time (weeks)					
		0	2	4	6	12	52
Nil	-	29.2	26.4	25.0	20.9	29.7	23.5
	+	N.D.	20.0	20.8	20.7	26.8	24.1
S	-	28.4	16.3	21.3	19.4	27.4	25.0
	+	N.D.	23.3	23.8	21.8	31.0	27.0
(Mn, S)	-	28.8	25.1	26.3	20.1	27.3	31.3
	+	N.D.	32.8	28.3	21.0	27.5	27.0
L.S.D. P = 0.05		5.2	2.6	5.8	1.3	2.0	2.3

N.D. = not determined.

APPENDIX 7

The effect of number of Mn foliar sprays on 1000 grain weight (g) and modal commercial malting grade (Field Experiment 13, 1969).

Fertilizer at seeding	Number of Mn sprays			
	None	One	Two	Three
(P, Cu)	38.5 (3)	38.9 (3)	41.9 (M)	41.4 (M)
(P, Cu) + Mn	39.2 (3)	42.0 (M)	41.9 (M)	41.4 (M)
(P, Cu, Mn)	40.6 (M)	42.0 (M)	43.1 (M)	42.6 (M)
Overall spray response	39.5	40.5	41.8	41.9

( ) = modal commercial malting grade.

L.S.D. P = 0.05 overall spray effect on gram weight = 0.8g.

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ACKNOWLEDGEMENTS

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