FORMS AND TRANSFORMATIONS OF SOIL MANGANESE AS AFFECTED BY LIME ADDITIONS TO A CENTRAL YELLOW-BROWN EARTH IN THE WAIRARAPA DISTRICT, NEW ZEALAND.

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I. INTRODUCTION

The application of liming materials to New Zealand agricultural soils for the purpose of increasing the productivity of pastures is an important soil ameliorative treatment. Specific benefits accruing from lime additions are thought to include the improvement of soil structure and moisture retention characteristics, increased supply of essential plant nutrients, and increased activity of desirable soil microorganisms. Much attention in New Zealand has focussed on the relationship between lime addition and the resultant increased plant availability of soil Mo. The lime and/or Mo requirement of New Zealand Soils have been reviewed by During (1972).

Recently, however, it has been suggested (N.D. Grace, pers. comm.) that pastures on certain Wairarapa hill country soils can contain a sufficiently high cohtent of the trace element Mn to impair the health and performance of grazing animals, particularly sheep. Such observations have been reinforced as a result of preliminary field trials indicating improved ewe fertility and growth rates of lambs following the application of lime to these soils. Further, the controlled feeding of supplemental dietary Mn to young sheep has been shown to depress their growth rate.

It is well known that the addition of lime to acid soil generally results in decreased availability of soil Mn for plant uptake. However, there is very little information for New Zealand soils on the amounts and forms of native soil Mn and the types of transformations resulting from lime application. The present field experiment was initiated to investigate the chemical forms of soil Mn in a typical unlimed Wairarapa hill country soil (Purimu silt loam) and to follow any changes in these forms, for a period of one year, following broadcast application of several rates of lime addition. When possible, bulk herbage samples were collected and analysed in order to assess changes in Mn content resulting from lime application.

II. REVIEW OF LITERATURE

A. FORMS OF MANGANESE IN SOILS

Manganese exists in a wide variety of forms in soil. There are several ionic species, and many compounds of differing degree of crystallinity and chemical composition. So far no satisfactory scheme has been proposed for the chemical fractionation or identification of these forms, although several empirical schemes have been proposed (Page, 1964).

In general, Mn in soils is thought to exist as water-soluble, exchangeable, organic and higher valence oxide forms.

1. Water-soluble Mn

Although divalent Mn^{2+} has been thought to be the major form of water-soluble Mn (Leeper, 1947; Fujimoto and Sherman, 1948; Weir and Miller, 1962), Hem (1964) has suggested that ion pairs such as $MnHCO^{+}_{3}$ of $MnSO_4$ are likely soluble species in natural waters. Analytical procedures rarely distinguish between these soluble Mn species.

Geering et al (1969) have reported that 84-99% of Mn in soil solution existed in an organic complexed form.

Morgan and Stumm (1964) suggest that other higher valence forms of soluble Mn, e.g. Mn^{4+}, would be expected to be very low over the pH range 3-10.

2. Exchangeable Mn

Ellis and Knezek (1972) reported that under acid conditions Mn^{2+} would be expected to exist as an exchangeable cation on both organic and inorganic colloid surfaces.

Page (1964 confirmed that exchangeable Mn behaved as a typical divalent ion and should obey laws governing Donnan equilibria, provided that selectivity effects were taken into account. Clark (1970) suggested that Wyoming bentonite had approximately the same affinity for Mn as for Ca and that it would be reasonable to assume that Ca and Mn were equivalent cations in most mineral soils.

3. Chelated Mn

Evidence for chelated Mn is obtained from reports by Hemstock and Low (1953), Beckwith (1955), Himes and Barber (1957) and Russel (1961) who showed that more Mn was extracted from soils using Cu salts than could be removed using other inorganic salts. Heintz and Mann (1947, 1949), found that extraction of Mn from soil was enhanced by the use of various inorganic salts, including $CuSO_4$, $CoCl_2$ and $ZnCl_2$. Cupraamonium ions ($Cu(NH_3)_4^{2+}$) were particularly effective in the recovery of Mn^{2+} from organic matter. Proteins, lignins, and polyuronides are believed to be responsible for chelation of Mn in soil. These compounds are thought to possess the necessary functional groups and configurations for chelation. Main and Schmidt (1935) pointed out that Mn^{2+} would form complexes with alpha hydroxy and dicarboxylic acids.

Schnitzer and Skinner (1967) stated that the fate of any particular metal ion in the soil, including whether it would be translocated or deposited in soil and available or unavailable to plant roots and other biological systems, would depend upon the relative stability of the combination or complex that was formed with organic matter. Stability constants are numerical expressions of the stabilities of such complexes. Results from their research (1966, 1967) indicated the following order of stabilities of complexes formed between a soil fulvic acid and nine divalent metal ions at pH 3.5 : Cu > Fe > Ni > Pb > Co > Ca > Zn > Mn > Mg. At pH 5.0 the order changed to : Cu > Pb > Fe > Ni > Mn ≈ Co > Ca > Zn > Mg.

Norvell (1972) showed that for a range of synthetic chelating agents Mn^{2+} had much less ability to complex with chelating ligands in soil solution than did Zn^{2+} or Cu^{2+}. Below approximately pH 6.3 none of the chelating agents tested raised the ratio of chelated-Mn to non-chelated Mn^{2+} above 1.0. However, Geering <u>et al</u> (1969) suggest that natural complexes in soil solution were able to maintain ratios of chelated to non-chelated Mn of about 10^1 or 10^2 in acid, neutral or calcareous soils.

4. Higher valence oxide forms

Ponnamperuma et al (1969) stated that the chemistry of Mn oxides is very complex. These complexities arise as a result of several features of Mn chemistry in soils and solutions :

(i) Mn can exist in several oxidation states.

Although Mn can exist in the oxidation states, $_{+}1$, $_{+}2$, $_{+}3$, $_{+}4$, $_{+}5$, $_{+}6$, $_{+}7$, only $_{+}2$, $_{+}3$, and $_{+}4$ states are found in nature.

(ii) Mn forms non-stoichiometric oxides with the metal in mixed valence states; for example Dubois (1936) reported that more than 150 oxides of Mn are known to exist with compositions ranging from $MnO_{1.2}$ to $MnO_{2.0}$. Morgan and Stumm (1964) observed that the oxidation products of Mn^2 in aqueous systems had compositions varying from $MnO_{1.3}$ to $MnO_{1.9}$, depending on pH, partial pressure of O_2, and temperature.

(iii) The higher oxides exist in several crystalline or pseudocrystalline states; for example the following higher oxides have been prepared and characterized crystallographically : Mn_3O_4; α , β , and γ-Mn_2O_3; α , β , and γ-MnOOH; and α , β , γ , and δ-MnO_2 (Wells, 1962; Bricker, 1965).

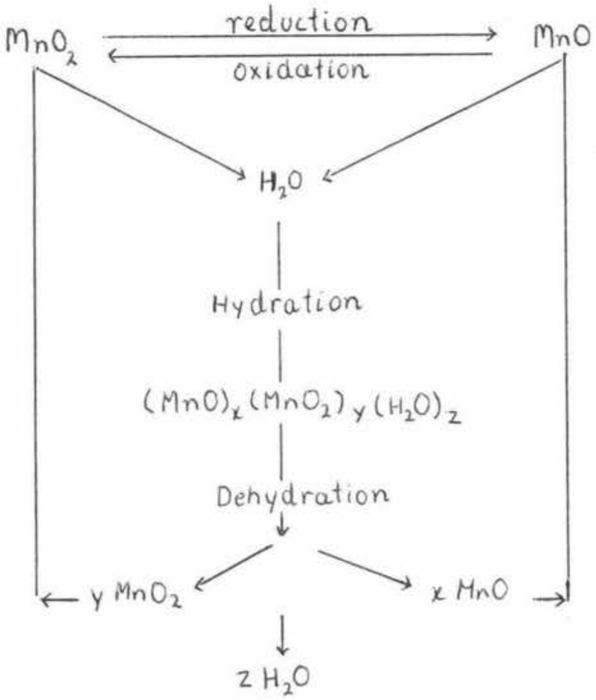
(iv) The oxides form co-precipitates, solid solutions, and perhaps superstructures, with Fe oxides. This phenomenon which may be ascribed to (a) similarities in some chemical properties of the higher oxides of Fe and Mn, including reversible oxidation-reduction, insolubility, and the presence of pH-dependent charges; (b) the closeness of the ionic radii of Mn^{++} ($0.80 A^o$) and Mn^{+++} ($0.66 A^o$) to those of Fe^{++} ($0.76 A^o$) and Fe^{+++} ($0.64 A^o$) respectively; and (c) perhaps crystal-lattice-induced valence changes.

Manganese nodules, concretions, and stains in soils, stream and lake sediments, and ocean floors are usually associated with substantial amounts of Fe and small amounts of Zn, Cu, Ni, and Co and other metals (Goldberg and Arrhenius, 1958; Taylor et al, 1964; Jenne, 1967; Morgan, 1967). The formation of Mn-Fe concretions is considered to be the result of sorption of Mn, Fe, and other polyvalent ions on to fine particles of MnO_2 and $Fe(OH)_3$, followed by coagulations of the MnO_2 and $Fe(OH)_3$, if these are in suspension (Goldberg and Arrhenius, 1958; Hem, 1964; Morgan and Stumm, 1964). The sorption of cations is due to the presence of a pH-dependent charge : above the isoelectric point, these hydroxides are negatively charged and sorb cations. The structure of the sorption products is not clearly understood. Such coprecipitations are thought to be more stable than MnO_2 alone (Hem, 1964).

Information on the mineralogy of Mn oxides in soils was reported by Taylor et al (1964) from a study of Mn nodules, concretions, and stains, in some Australian soils. Specific Mn minerals identified included lithiophorite $Li_2Al_8 (Mn^{++}, Co, Ni)_2 Mn_{10}O_{35} \cdot 14 H_2O$; birnessite, $(Ca,Mg,Na_2, K_2)x Mn^{4+} Mn^{2+} (O,OH)_2$; hollandite, $Ba (Mn^{4+}, Fe^{3+})_8O_{16}$; todorokite $(Mn^{2+}, Mg, Ca) Mn_6O_{13} \cdot 3\text{-}4H_2O$; and pyrolusite MnO_2. Lithiophorite occurred mainly in neutral to acid subsurface horizons whereas birnessite was more common in alkaline surface horizons. The Mn and Fe contents of the nodules varied widely. They also stated that pure Mn oxides and hydroxides appeared to be quite rare as secondary soil minerals. The intermediate oxides products such as bixbyite $(MnFe)_2O_3$, braunite $3 (MnFe)_2O_3 \cdot MnSiO_3$, jacobsite $(Mn^{2+} Fe) (Mn^{3+}Fe)_2O_4$ and vrendenburgite $Mn_3O_4 \cdot Fe_3O_4$ and perhaps manganite -MnOOH and Mn_3O_4 may be present in flooded soils (Ponnamperuma, et al, 1969).

Taylor et al (1964) considered that lithiophorite, birnessite and hollandite were the most common soil Mn minerals. For birnessite and lithiophorite the direction of mineralization was partly controlled by the ionic environment, which in turn was influenced by pH. The small crystalline size of these minerals, and especially of the birnessite, makes their surface reactions important, and Mn released during exchange reactions could arise from these minerals dispersed throughout the soil. Wadsley and Walkley (1951) suggested that the presence of foreign ions in soil Mn minerals would increase their surface reactivity. Ponnamperuma et al (1969) confirmed that the Mn oxides involved in redox equilibria in soils that undergo seasonal oxidation-reduction were complex non-stoichiometric oxides of variable composition.

A relationship between the various inorganic forms of Mn in soil has been proposed by Fujimoto and Sherman (1948) in the form of the Mn cycle.



In this cycle $(MnO)_x\,(MnO_2)_y$ represents Mn_3O_4, Mn_2O_3, and other oxides whose state of oxidation is intermediate between divalent and tetravalent forms of Mn. Of these manganic oxides a certain portion is potentially reducible and the remainder is chemically inert (Leeper, 1947). To explain the Mn cycle, Fujimoto and Sherman (1948) pointed out that in the soil there are two systems, viz. oxidation/reduction and hydration/dehydration, that influence the availability of soil Mn. The oxidation/reduction determines the relative amounts of manganous oxide and manganese dioxide, i.e. the equilibrium between the manganous Mn, the easily reducible as proposed by Leeper (1947). When free manganous oxide, manganese dioxide, and water are present in the soil, a complex hydrated Mn oxide is formed. This form of oxide is thought to be stable when moisture is present and the temperatures are low. When the soil becomes dry and the soil temperature rises, this form of oxide breaks up into its component parts. The component parts can then come under the influence of either one of the two processes, i.e. oxidation/reduction or hydration/dehydration, or one of the components (manganous oxide) may be taken up by plants. In this way the Mn cycle in the soil is realized.

B. FACTORS AFFECTING Mn AVAILABILITY IN SOILS

Mn availability and hence toxicity or deficiency in certain soils appears to be controlled by biological activity, organic amendments, pH and soil physical properties. Any factor which influences the oxidation/reduction potential of soil is found to have a corresponding effect on the valence and activity of Mn (Cheng and Quellette, 1971). Some of the factors known to influence the availability of Mn include :

1. Seasonal variation

Seasonal variation has been reported to affect the form of Mn in soil. Sherman and Harmer (1942) and Jackson and Sherman (1953) claimed that winter favoured manganous, and summer manganic, forms of Mn in alkaline soils. Cheng and Quellette (1971) reported that multiple freezing and thawing treatments under flooded conditions caused considerable release of exchangeable Mn. Decreasing the soil water content below 60% of its field capacity reduced the effect of soil temperature on the release of Mn. Grasmanis and Leeper (1966), on the other hand, reported Mn toxicity to pineapples and pear trees during hot dry weather. Mederski and Wilson (1955) reported that high Mn uptake was associated with high soil temperature and low moisture.

2. Redox potential

Leeper (1935) proposed an hypothesis involving the existence of soil Mn in a dynamic oxidation/reduction equilibrium, which he expressed as follows : Water-soluble Mn $\rightleftharpoons$ exchangeable Mn $\rightleftharpoons$ easily reducible MnO_2 $\rightleftharpoons$ relatively inert manganic oxides. Changes in oxidation-reduction status of soils resulted in interconversions between various oxidation states of Mn with a consequent effect on availability of soil Mn supply. Alkalinity and aeration favoured oxidation of Mn to higher valence forms, whereas acidity and anaerobic conditions tended to increase amounts of divalent available Mn^{2+}. Soil organisms are capable of effecting the oxidation of soil Mn, being most effective when the soil pH is around neutrality (Sauchelli, 1969). Patrick and Turner (1968) stated that Mn reduction from relatively insoluble oxidized forms to more soluble reduced forms occurred readily when an aerated soil was waterlogged. Together with the disappearance of oxygen and nitrate, an increase in the manganous ion (Mn^{++}) in the soil solution and on the cation exchange complex was one of the first measurable effects of reducing conditions resulting from waterlogging. These authors showed that the most striking effect of waterlogging on Mn transformation was the conversion of easily reducible manganic forms to the exchangeable manganous form. The transformation of Mn from easily reducible to exchangeable form was greatest over the redox range +400 to +300 mV and was essentially complete at +200 mV. Soluble Mn also increased in concentration below a potential of +400 mV.

Ponnamperuma (1969) pointed out that problems in the application of thermodynamics to the Mn system in flooded soils included (a) the large number and variety of Mn oxide species that may be involved; (b) the identification of the dominant solid species; (c) complications caused by non-stoichiometry of the oxides; (d) ignorance of the solid state of the complex oxides; (e) the uncertainty of the oxidation state of the metal before, during, and after reduction; (f) slow reaction rates; and (g) the limited pH range over which some equilibria operate.

It appears that a major problem in the application of thermodynamics to the Mn oxide systems in nature is the uncertainty of values for the standard free energies of formation of the solid species involved. This means that stability diagrams based on the pure oxides, which have been used successfully in geochemistry to explain broad mineral associations, may not apply in soil systems. The complex oxides of Mn likely to be present in soils may have standard free energies of formation which are considerably lower than those of their ideal counterparts. (Ponnamperuma, 1969)

Geering _et al_ (1969) suggested that if MnO_2 occurred in a soil and was in equilibrium with Mn^{2+} in soil solution, the activity of the Mn^{2+} should be predictable from measurements of soil pH, Eh, and the Mn^{2+}/MnO_2 half-cell reaction according to the reaction :

$$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$$

The equation derived from this half-cell reaction relating pH and Eh to Mn^{2+} activity is

$$\log (Mn^{2+}) = \frac{E^o}{0.0295} - 33.9 \text{ Eh} - 4\text{pH}$$

Measured values of the standard potential, E^o, range from 1.208 to 1.300 volts. Calculations showed however, that the predicted activity of Mn^{2+} was considerably higher than the measured Mn^{2+} activity. Explanations for this discrepancy included :

1. the absence of MnO_2 in the soil,
2. the uncertainty or inapplicability of Eh measurements in soils and soil solutions, and/or
3. the localised chemical reactions of Mn^{2+} in soil, as affected by the presence of certain soil microbes and plant roots.

Bohn (1970) showed that calculated Mn^{2+} concentrations based on Eh/pH data were usually too high, often by as much as 10^6, for soil suspensions. He concluded that solution Mn^2 was more related to the equilibrium solubility of the Mn oxides, expressed by the term pH - $\frac{1}{2}$pMn.

In general, the reducing properties of a soil increase with water saturation, with reducing soil microorganisms and their decomposition products, and with the reducing soil microorganisms of soil organic matter (Sauchelli, 1969). Leeper (1970) pointed out the compaction bear no relation to waterlogging; rather, the effect operating through the roots. The roots in the compacted soil were shorter and stubbier than normal and pressed tightly against the soil, thereby increasing the uptake of Mn as a result of interaction between the root and any MnO_2 that was in close proximity.

The lower the redox potential, the more marked is the reducing power of the soil, with the result that the manganic oxides (Mn^{3+} and Mn^{4+}) may be converted into the soluble oxide (Mn^{2+}) which are available to plants.

3. Organic matter levels

Leeper (1970) stated that the organic fraction of soil contained sufficient reducing capacity to liberate Mn^{2+} as the soil pH was decreased. This effect is illustrated by the following equation :

$$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$$

The electrons being supplied from the organic matter of soil or from biological processes.

In highly acid soils, plowing under crop residues may release large quantities of exchangeable Mn (from the soil and the crop residues) which can remain in an available form for comparatively long periods (Christensen et al, 1950). This could account for the presence of toxic concentrations of Mn in some acid soils. In addition, under similar conditions, leaching losses of Mn by percolating waters may be relatively high. On the other hand, in soils limed to near neutrality, the effect of organic matter additions on the Mn status would be relatively short-lived, because of the more rapid decomposition of the organic matter and the immediate fixation of released Mn. Consequently the Mn status would be altered for only short periods, and the release of Mn to crops much less. This may explain the occurrence of the Mn deficiencies on limed acid soils and on naturally calcareous soils (Thorne and Wann, 1950). Christensen et al (1950) found that the influence of organic matter on the Mn status in the limed soils was limited to the period of its decomposition. The release of Mn by organic matter decomposition was probably due to reducing conditions at the site of decomposition, to direct reduction of the Mn by organic compounds produced in the process, and to a reduction in pH due to organic acids production. (Bromfield and Sherman, 1950).

4. pH and liming

One of the most important soil factors governing Mn availability to plants is the degree of soil acidity. Decreasing the degree of soil acidity reduces the danger of Mn toxicity which usually occurs in soils of pH 4-5 (Leeper, 1947). Mulder and Gerretsen (1952) stated that soils with a pH of 5.5 contained much of their Mn in the water-soluble and/or exchangeable form. As the pH of the soil was increased, the Mn^{2+} was converted to the less available manganic oxides (Mn^{3+} and Mn^{4+}), resulting in reduced availability such that in some cases Mn deficiency occurred. This conversion presumably depended either directly or indirectly on the activity of microorganisms. Reduction of higher manganic oxides by organic matter is more important at lower pH's, since the reducing power of these compounds increases with acidity. The production of strong inorganic acids especially sulfuric acid by the sulfur-oxidizing bacterial and nitric acid would also increase the supply of available Mn to plants.

Liming of acid soils has often been reported to result in decreased amounts of water-soluble and exchangeable fractions of Mn at the same time increasing the amount of the easily reducible fraction (Christensen et al, 1950; Sanchez and Kamprath, 1959; Messing, 1965; Truong et al, 1971). Little is known about the specific nature of the fixation of Mn consequent to liming, Possibilities include the precipitation as Mn carbonate or hydroxide (Leeper and Swayby, 1940), oxidation to higher-valence forms, or gradual oxidation following precipitation (Leeper, 1947). Truong et al (1971) pointed out that the effect of liming on soil Mn was marked at low rates of lime application. These authors found that the addition of as little as 154.48 kg/ha lime markedly reduced the exchangeable Mn content of soils and increased the easily reducible component. The effect of lime on exchangeable Mn was attributed to local effects around dissolving lime particles. Fujimoto and Sherman (1948) also reported that the first light application (141 kg/ha) of either lime or dolomite produced a disproportionate reduction in plant uptake of Mn. With further lime application, Mn uptake was reduced gradually.

5. Air drying

Boken (1958) reported substantial increases in the exchangeable Mn when samples were stored in an air dry condition. In alkaline soils storage under dry conditions for six weeks caused a twofold increase from 0.5 to 1.0 ugMn/g. For acid soils Leeper (1970) found increases from 5 to 20 ugMn/g during storage. The effect was often analogous to that of sterilizing soils. Leeper (1970) suggested that of the two opposing reactions :

$$Mn^{2+} + 2OH^{+} + (O) = MnO_2 + H_2O \;......... (1)$$

$$MnO_2 + 4H^{+} + 2e = Mn^{2+} + 2H_2O \;......... (2)$$

bacterial oxidation (1) was impossible in the air-dry state, but that reduction of MnO_2 (2) by the organic components could still function. Perhaps the responsible molecules were slightly volatile, and could move through the soil thereby working over a long time period.

6. Steam sterilization

Steam sterilization has been found to increase water soluble and exchangeable Mn in very acid soils and subsequent uptake of Mn by plant. Easily-reducible from of Mn in the soil generally decreased (Fujimoto and Sherman, 1948; Cheng and Quellette, 1970b). Sterilization retarded plant growth on high Mn soil and improved it on low Mn soil.

7. Microorganisms and root exudates

Workers have shown that soil organisms can induce Mn deficiencies by oxidizing Mn^{2+} to Mn^{4+} (Timonin, 1946; Mulder and Gerretsen, 1952) Timonin (1946) provided evidence that Mn-oxidizing microflora in the root rhizosphere were associated with Mn deficiency of oats. Fumigants such as chloropicrin, formaldehyde, and dichloropropenes reduced or eliminated the symptoms of Mn-deficiency. These fumigants also markedly suppressed the Mn-oxidizing microorganisms. On the other hand addition of a straw mulch intensified the Mn deficiency condition and produced a large amount of Mn^{2+} oxidizing organisms. Microorganisms play an important role in the oxidation of Mn when the soil reaction is near or above neutrality (Tiller, 1963; Meek et al, 1968). Leeper (1970) reported that these species included both fungi and bacterial and hyphomicrobium, which have clogged the pipes of city and hydro-electric water supplies as a result of deposition of MnO_2. The importance of these organisms in soil is unknown.

Microbial metabolism can also increase the level of Mn^2 by reduction, processes, removal of O_2, or the formation of acid products. Thus the addition of carbohydrates or plant residues to soil result in production of Mn^{2+}, especially if the soil is waterlogged (Sauchelli, 1969).

Bromfield (1958) demonstrated that plant roots released substances that readily dissolve MnO_2 and that the acidic solutions greatly increased the availability of indigenous Mn. In his study plants were grown under sterile conditions on agar slopes.

C. FACTORS AFFECTING PLANT UPTAKE OF SOIL Mn

Manganese is thought to be absorbed by plants as the manganous form, but other forms of Mn, e.g. oxides of valency greater than 2, can affect the supply of Mn to plants. Leeper (1947) introduced the concept of an "easily reducible" fraction of Mn which would become available to plants when reduced to the manganous state. Leeper (1970) pointed out that synthetic Mn oxides such as manganite, pyrolusite (β-MnO_2), and δ-MnO_2 may provide plants with ample Mn when mixed with deficient soils. The availability of these forms was dependent on the method of preparation and on the specific surface of the oxides.

1. Effect of plant species and stage of maturity

Fleming (1963) analysed the Mn content of plant parts for 4 common grass and one clover species. The magnitude of species and plant part variation are summarised below :

	Content of Mn (ug/g) on oven-dry basis:		
Species:	Head:	Leaf:	Stem:
Cocksfoot	37	105	103
Meadow fescue	16	29	40
Perennial ryegrass	18	41	56
Timothy	42	38	28
Red clover	60	134*	24

*leaf + petiole

The concentration of Mn in grasses and legumes has been found to vary with respect to stage of growth of the plant by several workers. Macdonald (1951) found that the Mn content of Timothy, Birdsfoot trefoil, and Ladino clover increased slightly as these plants matured. Thomas et al (1952) found the Mn decreased in perennial ryegrass as the plant matured. In Bromegrass, on the other hand, Loper and Smith (1961) reported that the Mn content decreased to the heading stage, but increased from this stage to maturity.

2. Effect of Ca-salts

The influence of Ca on the Mn nutrition of plants is not clear cut. Some investigators have observed a suppressive effect of Ca on the absorption of Mn from nutrient solutions (Swanback, 1939; Taper and Leach, 1957), others have observed no influence (Morris and Pierre, 1947), and occasionally Ca has been reported to stimulate Mn uptake even to toxic levels (Chapman, 1931). Lohnis (1960) working with different plant species in one experiment, found a strong suppressive influence of Ca on uptake of Mn by beans, rape seed and alfalfa, no influence with mangolds, and stimulation with flax. Kannan (1969) showed that Ca alone markedly inhibited Mn uptake by isolated tobacco leaf cells.

In soils, the effect of Ca is usually considered to be an indirect one, in that addition of lime to an acid soil will raise the pH which, in turn, will result in reduced solubility of Mn (Jones, 1957). McNaught and During (1970) reported decreased Mn uptake, following liming, for both white clover and perennial ryegrass on a gley podzol in Westland. During and Rolt (1967) reported similar species responses to liming on Marton silt loam. However, there appears to be little information on the responsiveness to liming of low-fertility pasture species, such as browntop, sweet vernal and danthonia.

Van Diest and Schuffelen (1967) pointed out that Ca, in addition to reducing the solubility of Mn in soils, also competed with Mn for absorption sites within the plant. From their studies on the interaction between Ca and Mn uptake in nutrient solution culture, it was concluded, that for both oats and sunflower, Mn was absorbed via two carrier systems. Ca and Mn competed for sites on one of these carriers, whereas Mn uptake by the second carrier system was little affected by the presence of Ca. For oats, the presence of small quantities of Ca in the nutrient medium enhanced the net uptake of Mn. This apparent stimulation effect was not observed for sunflower.

3. Effect of other elements

(a) Nitrogen

Ammonium sulfate has been reported to increase, and sodium nitrate to decrease the availability of soil Mn to plants. These effects are thought to be indirect and associated with changes in pH resulting from the uptake of NH_4^+ and NO_3^- by the plants. Optimal Mn absorption from soil occurred around pH 6 to 7. Ammonium sulfate created an acidic condition in the soil, whereas sodium nitrate tends to produce an alkaline condition (Sauchelli, 1969).

(b) Phosphorus

Phosphorus is thought to affect Mn uptake in at least two ways.

(i) by altering the availability of soil Mn to the plant.

Phosphate fertilizers have been reported to exert variable effects on Mn availability (Hossner and Blanchar, 1970); whereas pyrophosphate cause a reduction in Mn uptake, $NH_4H_2PO_4$ improved availability.

Lindsay and Stepphenson (1959) showed that the solution diffusing from Ca $(H_2PO_4)_2$ pellets placed in a soil was extramely acid and dissolved large amounts of Mn as well as Fe and Al. Giordano and Mortvedt (1969) on the other hand reported that the solubility of Mn in corn fields was reduced appreciably when $NH_4H_2PO_4$ was applied. They postulated the formation of Mn $(NH_4)_2P_2O_7.2H_2O$; a compound of very low solubility which precipitated at pH's between 4 and 8.

(ii) by increasing uptake of Mn by plant.

Vlamis and Williams (1962) postulated a direct competition between Fe and Mn ions for absorption and suggested that high P levels in solution could increase Mn absorption as a result of reduced Fe availability. This explanation implies that high P in solution would reduce Fe concentration in the plant.

(c) Iron

Evidence of an Fe/Mn antagonism has been reported (Morris and Pierre, 1947; Bolle-Jones, 1955; Kirsch <u>et al</u>, 1960; Vlamis and Williams, 1962; Hiatt and Ragland, 1965). Chlorotic plants have been observed in acidic soils which contained large amounts of available Mn (Somers and Shive, 1942). Chlorosis was cured by the application of Fe sprays.

In nutrient solutions soybeans were grown with typical chlorosis symptoms due to Fe deficiency on substrates with high Mn concentrations. Results indicated that Fe and Mn were interrelated in their metabolic functions, with the effectiveness of one determined by the proportionate presence of the other. Hanger (1965) observed a similar effect of high Mn concentrations on red clover. Stunted growth and apical chlorosis were prevented by increasing the Fe concentration of the substrate. Grasmanis and Leeper (1966) reduced toxic Mn levels in apple leaf from 100 to 35 μg/g Mn by injecting Fe citrate into the tree or by applying FeEDTA to the soil. Further evidence for Fe/Mn antagonism was obtained by Wallihan and Miller (1968) who induced symptoms of Mn deficiency in avocado trees following application of FeEDTA. Weinstein and Robbins (1955) explained Mn induced Fe deficiency as the result of competition between Mn and Fe for a position in the haeme nucleus of Fe-containing enzymes.

Although the relationship of Fe to Mn is often used as good example of antagonism, in several studies on metals Cu has been found to be more effective than Mn in causing Fe chlorosis (Hewitt, 1951; Hunter and Vergnano, 1953; DeKock, 1956). Nason and McElroy (1963) are of the opinion that there is little effect of Fe on Mn uptake, because each has an independent role in plant nutrition. Furthermore, simultaneous deficiency symptoms of both elements have been reported, and clear distinction between Mn toxicity and Fe deficiency symptoms has been described in a number of plants.

(d). Molybdenum

Mn toxicity in flax has been alleviated by the addition of Mo fertilizer (Millikan, 1947, 1948). A marked reduction in the severity of the injury was observed when a relatively high concentration of Mo was added to the nutrient solution. From the similarity in visual symptoms of Mn excess and Mo deficiency, Millikan concluded that a close relationship existed between both disorders. Similar results were reported for flax (Andersen and Spencer, 1950), swedes (Walsh and Neenan, 1956) and apples (Fernandez, 1959). Others have suggested that Mn-induced, Fe-chlorosis is accentuated by additional supply of Mo to flax and tomatoes (Henny and Street, 1954; Hewitt, 1958; Gerlof et al, 1959).

D. ANALYTICAL METHODS FOR ESTIMATION OF SOIL Mn

Estimation of soil Mn has followed two main lines

(i) measurement of specific fractions of soil Mn content including water soluble, exchangeable and easily reducible and chelated forms;

(ii) indices of availability of Mn to plants.

(i) Soil Mn fractions

(a) Water-soluble Mn

Water is used as an extractant for soil Mn, especially for soils of low pH (Adams, 1965). The measured concentration of water-soluble Mn varies within the range 0 to 25 µgMn/g soil (Morris, 1948; Randhawa et al, 1961; Siman et al, 1971).

(b) Exchangeable Mn

Exchangeable Mn has been extracted using 1N solutions of NH_4OAc, $Ca(NO_3)_2$, or $Mg(NO_3)_2$ (Adams, 1965). This fraction of soil Mn is often related directly to Mn uptake (Piper, 1931; Heintz, 1938) and has generally correlated well with evidence of Mn deficiency in plants (Sherman and Harmer, 1943; Dion et al, 1947; Boken, 1958). Hoff and Mederski (1958) concluded that soil containing less than 20 µg/g of NH_4OAc extractable Mn expected to show Mn-deficiency symptoms for soybeans.

(c) Easily reducible Mn

This fraction of soil Mn includes higher oxides of Mn that are reduced by easily oxidizable organic substances, for example quinol or hydroquinone, which are considered to be potentially available to plants (Leeper, 1947). This author considered the quantity of easily reducible Mn dioxide to be of major importance to plants and suggested that below 5 µg/g would likely be critical for plant growth.

A common reducing agent used to extract this fraction of soil Mn is 0.2% hydroquinone in 1N NH_4OAc (Sherman _et al_, 1942; Leeper, 1947). A refinement of this method has been the use of

0.05% alcoholic hydroquinone followed by extraction with 0.5M-Ca $(NO_3)_2$ (Jones and Leeper, 1951a;) Hoff and Mederski, 1958).

Estimation of easily reducible Mn is considered to be dependent on the pH of extraction, the type of the salt solution, the choice of reducing agent and time of contact, and form of higher oxides of Mn present (Dion et al, 1947).

(d). Active Mn

This fraction of soil Mn is considered to be the sum of water-soluble, exchangeable and easily reducible forms of Mn (Messing, 1965).

(e). Chelated Mn

Insoluble chelated Mn has been estimated as that Mn removed from the soil by $Zn(NO_3)_2$ after prior extraction of the same sample with NH_4OAc. Soil Mn extractable by divalent salts such as Cu or Zn, has been shown to be chelated Mn (Bremner et al 1946; Heintz and Mann, 1949; Hemstock and Low, 1953; Beckwith, 1955; Himes and Barber, 1957). Ammonium acetate removes exchangeable and soluble chelated Mn with possible traces of insoluble chelated Mn in any NH_4OAc-extractable organic matter.

Walker and Barber (1960) extracted 12 Indiana soils with neutral 1N NH_4OAc followed by 0.03N $Zn(NO_3)_2$. Amounts of chelated Mn and exchangeable Mn were found to be highly correlated. Hammes and Berger found EDTA to be a good extractant for chelated Mn in one study (1960b) but of no value in another (1960a).

(ii) Available soil Mn

Many workers have attempted to estimate amounts of plant available soil Mn. Leeper (1935) pointed out that the easily reducible oxides of Mn, as determined with 0.2% hydroquinone, could be employed as an index of Mn availability. Hoff and Mederski (1958) compared nine Mn-extraction methods and reported that Mn extracted by alcoholic hydroquinone, 3N $NH_4H_2PO_4$, and 0.1N H_3PO_4 gave the highest correlation coefficients with Mn in soybean plants (Glycine Max L.). Hammes and Berger (1960) reported that Mn extracted by the 0.1N H_3PO_4 method correlated better with Mn in oats (Avena sativa L.) grown in the greenhouse than did Mn extracted by the other two methods used, viz., 1.5M $NH_4H_2PO_4$ and 1N H_3PO_4. Most measurements of plant available Mn have been directed towards the prediction of Mn deficiencies in neutral and alkaline soils.

In acid soils, Hoyt et al (1971) showed that a 16 hour extraction with 0.01M $CaCl_2$ gave the best estimate of plant available Mn for barley, rape and alfalfa. Another form of soluble Mn, that extracted by 0.1N HOAc, gave the next best estimate of plant available Mn. The other five extraction methods, consisting of 0.1N H_3PO_4 or 0.002N HCl for soluble Mn, 1N KCl or 1N NH_4OAc (pH 3) for exchangeable Mn, and 0.2% hydroquinone in 1N NH_4OAc (pH 7) for easily reducible Mn, gave fair to poor estimates of available Mn.

Browman et al (1969) concluded that for a wide variety of soil samples, the best prediction of Mn uptake was provided by a combination of NH_4OAc-extractable Mn and soil pH as independent variables, followed closely by 0.1N H_3PO_4 and 0.01M-EDTA in M$(NH_4)_2CO_3$. The combination of pH and NH_4OAc has the advantage that it can be performed on a routine basis for making fertilizer recommendations. Baser and Saxena (1971) reported that 3N $NH_4H_2PO_4$ can be best used for estimating plant available Mn. The high values of Mn extracted by this solution was thought to be the result of the reaction

$$Mn^{2+} + NH_4H_2PO_4 = NH_4MnPO_4 + 2H^+.$$

III. MATERIALS AND METHODS

A. MATERIALS

1. General locality and experimental area

The experimental area was on a hill country property located 2.5 km from Tiraumea, to the south-west of Puketoi Range, in the Wairarapa district of Wellington province (see Fig. 1).

The topography is moderately steep to steep with some rolling areas upon which the experimental sites were located.

The parent material of the soil is derived from a massive, calcareous, blue-grey siltstone, forming the Tongaporutuon stage of the Taranaki Series, dating from the late Miocene. The mean annual rainfall recorded for the experimental area over the period 1960-1971 was 1183 mm, with a range of 1638-950 mm.

The original vegetation of the area was dense podocarp-broadleaf forest. Following clearing in the years 1860-1910, much of the land reverted to manuka and gorse, especially in gullies and less accessible places. From 1960 onwards, all the cultivated land on the property was cleared of scrub, cultivated, and sown to new grass.

The soil, Purimu silt loam, hill soil (Soil Bureau Bulletin n.s. No. 5, 1954), is currently classified as a moderately weathered, moderately leached, yellow brown earth (Fulvic soil). At the experimental sites the profile consists of :

Site A.

A1H 0-3cm	dark greyish brown, silt loam; strongly developed fine granular structure; numerous roots; sharp boundary
A2h 3-13cm	very dark grey brown silt loam; loose; strongly developed nutty and granular structure; many roots; sharp boundary

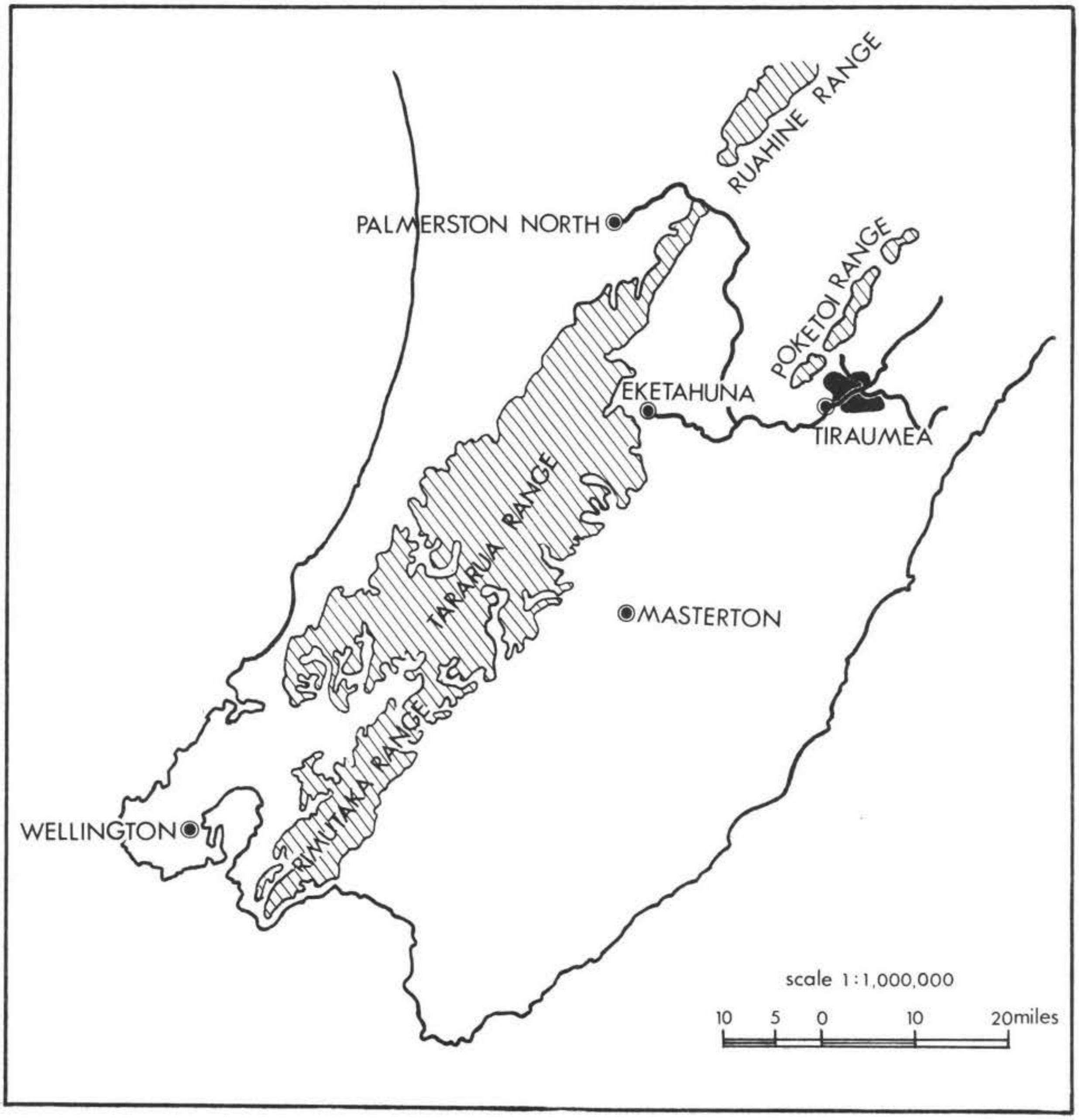


FIGURE 1. MAP SHOWING LOCATION AT TIRAUMEA IN THE WAIRARAPA DISTRICT.

B 13-18cm	brown silt loam; loose; moderately developed medium nutty structure; some roots; diffuse boundary
C on	yellowish brown silty clay loam; friable; massive structure; few roots; weathering mudstone

Site B.

A 1h 0-3cm	dark grey brown silt loam; strongly developed fine granular structure; numerous roots; sharp boundary
A2h 3-15 cm	brown to dark brown silt loam; friable; strongly developed fine nutty and granular structure; many roots; sharp boundary
B 15-19cm	dark yellowish brown silt loam; friable; moderately developed nutty structure; moderate number of roots; diffuse boundary
C on	yellowish brown silty clay loam; friable; massive structure; few roots; weathering mudstone

The soil is regarded as being of low to medium natural fertility. The experimental sites had received 102 kg of superphosphate annually for the previous 13 years and had been grazed with a stock density of approximately 4-5 ewe equivalents per acre.

2. Choice of experimental sites

Initially five areas each of approximately $14m^2$ were chosen as potential experimental sites. Three of these areas, designated sites A, C, and D were situated with a southerly aspect, and two, B and E, with a northerly aspect.

In order to assess homogeneity of Mn status at each site, duplicate 10cm soil cores were taken at close proximity from 5 random positions within each site. Each sample was separately analysed for total and easily-reducible Mn using methods described in section B.3. Results for Mn analyses are summarised in Table I. As a result of the statistical analyses, sites A and B were chosen for this experiment, by reason of their relative uniformity in Mn indices, and representation of different aspects. The grid references for these sites are M.E.M.E.1, N 154 (1957) 528022 and 523071.

TABLE I : Summary of statistical results for variability in Mn status of five potential experimental sites.

Site:	Aspect:	Total Mn:			Easily-reducible Mn:		
		error M.S.	†F value	Result	error M.S.	†F value	Result
A	south	4440.25	4.26	N.S.	3232	1.83	N.S.
B	north	8962.75	8.81	*	2821.4	3.08	N.S.
C	south	11385.15	5.22	*	2702.9	2.03	N.S.
D	south	59512.78	4.43	N.S.	30768.6	6.31	*
E	north	258090.35	17.07	* *	60949.5	96	* *

† F value for test of within site variability

* results statistically significant at the 5% level

* * results statistically significant at the 1% level

N.S. results not statistically significant

3. Estimation of required treatment replication

Since there was no significant difference between sites A, B and C, results of analyses of variance were combined to give an estimate of variance between positions for total and easily-reducible soil Mn.

(a) Average of position within site error M.S. for total Mn for sites A, B, C (Table I)

$$= \frac{4440.25 + 8962.75 + 11385.15}{3} = 8263$$

Required S.E. of a treatment mean to be about 5%, or 40 ugMn/g

$$\text{thus S.E.} = \sqrt{\frac{8263}{n}} = 40$$

$$\text{solving}, \quad n \simeq 5$$

where n = number of replications required. Average of position within site error M.S. for easily-reducible Mn for sites A, B, C (Table I) $= \frac{3232 + 2821.4 + 2702.9}{3} = 2918.66$

Required S.E. of a test mean to be about 5%, or 10 μg/Mn/g

$$\text{Thus S.E.} = \sqrt{\frac{2918.66}{n}} = 10 \text{ or } n \doteqdot 3$$

Although it can be seen that the number of replicates required for easily-reducible Mn would be 3, in this experiment 5 replicates were chosen, in accordance with the number of replicates required for total soil Mn.

4. Experimental design

A randomized block design was used for this experiment. Twenty plots, each of 1.82 x 2.74 m^2 were staked out at each site as shown in Fig. 2. To minimize overlapping of liming treatments at borders of adjacent plots a buffer strip distance of 0.46m was left between each plot. The design provided for the use of four liming rates (treatments) with 5 replications (blocks) at each site. In the absence of grazing stock during peak periods of pasture growth, the experimental area was trimmed to approximately 2-3 cm, using a motor mower to remove excess herbage.

5. Lime application

The liming material used was a finely-ground commercial lime (95% $CaCO_3$).

Four rates of lime addition corresponding to 0, 1270, 2540 and 5080 kg/ha were used in this experiment.

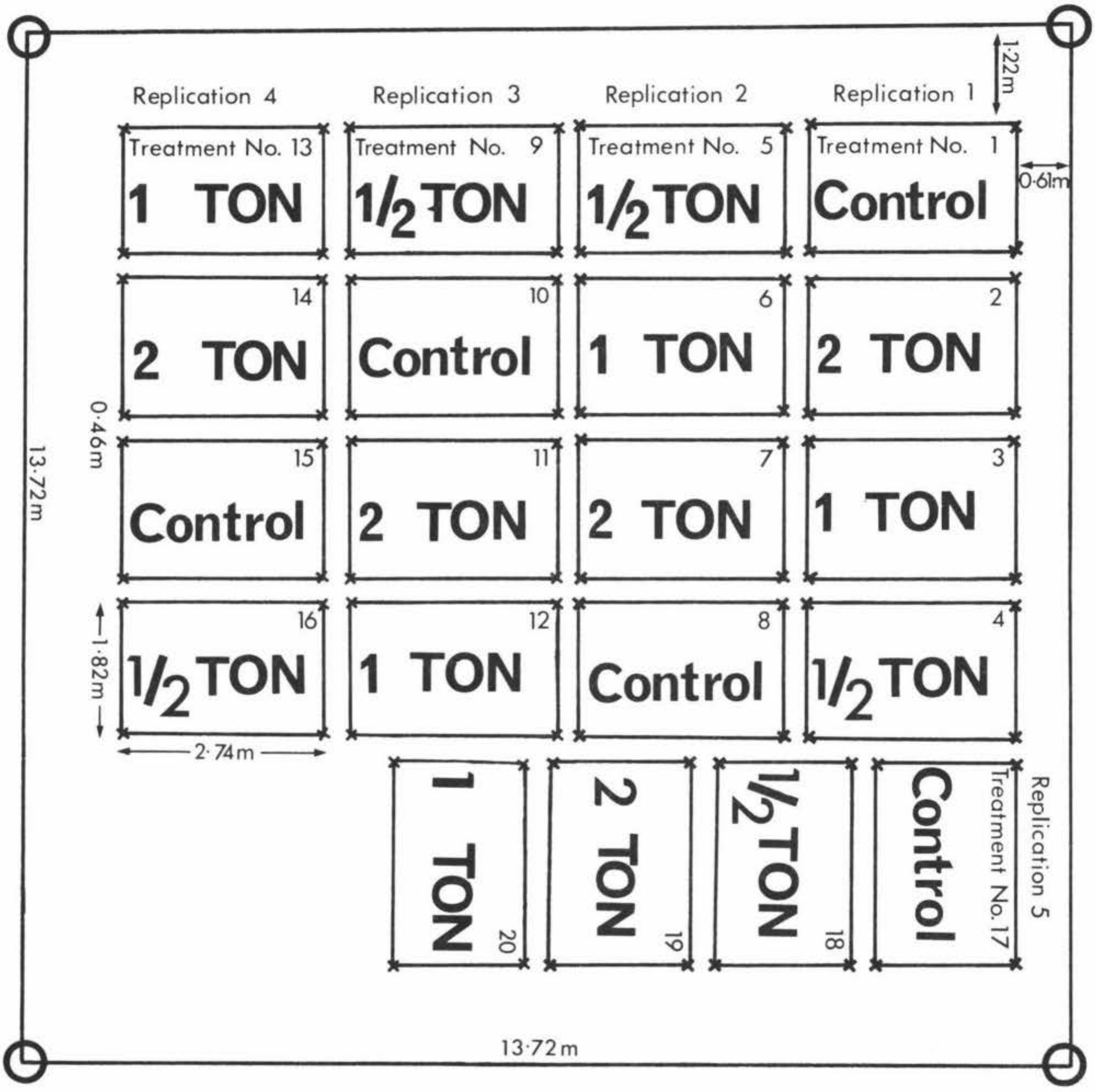


FIGURE 2. PLAN OF THE EXPERIMENTAL SITE A SHOWING LIME TREATMENTS

⊕ FENCE

X MARKER PEGS

B. METHODS

1. Methods of soil and herbage sampling

(a) Soil sampling

(i) Soil sampling frequency

Soil samples were taken before lime application and then at approximately 8-week intervals from the time of liming for a period of 40 weeks. Initially both sites were included at each sampling time until 22/6/72. Subsequently sampling of site B was discontinued because of similar trends at the early sampling times, and in order to reduce the number of analyses to be performed. The sites sampled, dates of samplings and analyses performed (including herbage samplings and analyses) are summarized in Table II.

TABLE II : Summary of sites sampled, dates of samplings and analyses performed.

Dates of samplings	Soil	Herbage	Sites sampled A	B
15/5/71	x	-	x	x
7/8/73	x	-	x	x
9/10/71	x	x	x	x
7/12/71	x	x	x	x
25/1/72	x †	-	x	x
22/6/72	x ‡	x	x	-

- no samples
x samples taken
† no water-soluble Mn analysed
‡ limited samples only

(ii). Soil Sampling method

Five cores 10 cm in length were randomly taken from each plot using a 2-cm diameter hand-operated soil core-extracting device. The top 1 cm of each core, comprising the litter and root mat was removed and discarded. The cores were placed in plastic bags, labelled, sealed, and stored in a polystyrene container which was cooled using blocks of ice. Samples were transported to the laboratory, where the five cores from each plot were crumbled and mixed thoroughly to form a composite sample.

(iii). Storage of soil samples

To investigate the effect of storage condition on the transformations of Mn forms in soils, two representative samples were stored for varying time periods in the field moist condition in a refrigerator at 4°C. In addition, separate samples were air-dried at ambient temperature or oven-dried at 105°C.

Exchangeable, easily-reducible, and total Mn contents of these samples were estimated using procedures outlined in Section B.3. Results are shown in Tables III and IV. All results in this report are computed on an oven-dry soil basis.

TABLE III : The effect of time of storage of soil samples on forms of soil Mn.

	Forms of Soil Mn :											
	Exchangeable Mn:			Easily-reducible Mn (pH 7) :			Easily-reducible Mn (pH 3.5)			Total Mn:		
	Storage time (weeks):											
	0	8	24	0	8	24	0	8	24	0	8	24
	µg/g Mn extracted:											
SOIL A	16	12	16	146	174	139	87	73	69	551	550	551
SOIL B	14	10	12	142	104	125	67	74	79	553	553	553

TABLE IV : The effect of sample pretreatment on amounts of extractable soil Mn.

	Forms of soil Mn :											
	Exchangeable Mn :			Easily-reducible Mn (pH 7) :			Easily-reducible Mn (pH 3.5) :			Total Mn :		
	Sample pretreatment :											
	F.M.	A.D.	O.D.	F.M.	A.D.	O.D.	F.M.	A.D.	O.D.	F.M.	A.D.	O.D.
	µg/g Mn extracted											
SOIL C	12	18	66	184	153	127	91	92	88	666	617	638
SOIL D	17	21	63	127	107	76	73	73	69	522	485	473

F.M. = field moist
A.D. = air-dried
O.D. = oven-dried

From the results in Table III it is evident that storage in the field moist condition at 4°C resulted in minimal changes in measured forms of soil Mn for storage periods up to 24 weeks. The results in Table IV showed that whereas air drying appeared to result in small increases in exchangeable Mn and decreases in easily-reducible Mn (pH7), results for total Mn content suggest that sample variation may have been a problem. However, it is clear that oven drying at 105°C caused release of much exchangeable Mn, presumably at the expense of the easily-reducible form.

Reports in the literature differ on the effect of air-drying soils on transformations of soil Mn. Fujimoto and Sherman (1945) reported increased exchangeable Mn following air drying whereas Hammes and Berger (1960) considered that air drying was not likely to increase exchangeable Mn levels. Boken (1952) found no immediate effect of drying on the levels of exchangeable Mn but levels tended to increase with storage. Boken also confirmed that storage in the moist condition for up to 3 weeks resulted in minimal changes in exchangeable Mn content of soil samples.

In view of the need to store samples prior to analysis, all samples were maintained in the field moist condition at 4°C in an effort to minimise transformations between the various forms of Mn.

(b) Herbage sampling

(i) Frequency of sampling

Herbage samples were taken concurrently with soil samples whenever possible. Because of the seasonal pattern of growth of this area it was not possible to obtain herbage samples at all soil sampling dates. The actual frequency of herbage sampling is shown in Table II.

(ii) Method of sampling

Random grab samples of herbage were collected from each plot using hand clippers. No attempt was made to sample particular plant species. Samples were clipped approximately 1 cm above ground level and placed in cloth bags for transport to the laboratory.

(iii) Preparation of plant tissue for analysis

Plant tissue was dried in a Wilco Electric oven for 72 hours at 65-75°C then crushed by hand and thoroughly mixed prior to chemical analysis.

(iv) Soil contamination

A preliminary experiment was conducted to determine the degree of soil contamination present on harvested plant material. Representative samples were quickly washed by immersion in distilled water. Washed and unwashed samples of herbage were then analysed for Mn content as described in section B. 3. The results are shown in Table V.

TABLE V : Mn content of unwashed and washed herbage samples.

Mn extracted ($\mu g/g$) :

washed	unwashed
600	600
325	225
237	188
300	213
500	285
453	325
250	205
543	375

The results in Table V show that washing often resulted in considerable reductions of up to 40% in Mn content of herbage samples. It was considered that much of the loss of Mn due to washing was probably due to removal of soluble Mn from plant tissue in addition to any removal of adhering soil particles. Hereafter, Mn analyses reported were for unwashed herbage samples.

2. Methods for chemical fractionation of soil Mn

Preliminary experiments were conducted to establish appropriate techniques for delineating recognisable fractions of soil Mn.

(a) Soil/extraction ratios

In order to establish amounts of soil required for the Mn fractionation procedures, four soil/extractant ratios using 0.5, 1, 2 and 4 g of soil in 80 ml of extractant (1N NH_4OAc, pH7 containing 0.2% hydroquinone) were investigated. The extractions were made in 100 ml polypropylene tubes on an end-over-end shaking machine using extraction times of 1 or 4 hours. The results are shown in Table VI.

TABLE VI : Effect of soil/extractant ratio and time of shaking on extraction of Mn by 1N NH_4OAc containing 0.2% hydroquinone.

Soil/extractant ratio (80 ml of extractant)	Mn extracted (µg/g) Time of extraction (Hr.)	
	1	4
0.5	149	182
1	147	158
2	138	164
4	145	170

From these results it can be seen that there was a negligible effect of soil/extractant ratio, at either shaking time, on the amounts of Mn extracted. Four grams of soil was chosen as standard quantity for succeeding extractions.

(b) Determination of extracting pH and extraction time for the estimation of exchangeable soil Mn.

Using a fixed soil/extractant ratio (1:20) an investigation was made of the effect of extraction pH and extraction time for the estimation of exchangeable Mn content of the same soils.

(i) Effect of pH of extractant

Duplicate soil samples were shaken for 8 hours with 1N NH_4OAc adjusted to pH 2, 3, 4, 5, 6, or 7 using either NH_4OH or HOAc. A soil/extractant ratio of 1:20 was used. The results are shown in Table VII.

TABLE VII : Effect of extraction pH on determination of exchangeable Mn.

pH of extraction :	Mn extracted ($\mu g/g$) :
7	10
6	16
5	29
4	50
3	49
2	41

It is seen from the results in Table VII that as the pH of the extractant decreased, more Mn tended to be extracted by NH_4OAc. Peak amounts were extracted around pH 4.

(ii) Effect of extraction time.

Extraction times of 2, 8, 16, 24, and 48 hours were carried out using 1N NH_4OAc adjusted to either pH 3.5 or 7.0, at a soil extractant ratio of 1:20. The results are presented in Table VIII.

TABLE VIII : Effect of pH of extractant and extraction time on amount of NH_4OAc - extractable soil Mn.

Extraction time (Hr.)	Mn extracted (µg/g) pH 7.0	pH 3.5
2	6	20
8	9	24
16	13	77
24	14	104
48	16	163

From Table VIII it is apparent that at pH 7.0 most of the exchangeable Mn was extracted after 16 hours shaking. However, at pH 3.5 additional Mn was still being extracted after 48 hours. Because it appeared that at this lower pH, forms of Mn other than that present as exchangeable Mn were being extracted, further extractions at this pH were not attempted.

Measurement of pH following each extraction verified that initial pH's were maintained throughout the extraction period.

(c) Determination of extractant pH and extraction time for the estimation of easily-reducible Mn

Because extractant pH and extraction time were shown to influence the amounts of exchangeable soil Mn, a similar investigation was then made for content of easily-reducible soil Mn.

(i) Effect of extraction pH

Duplicate soil samples were shaken for 8 hours with 1N NH_4OAc containing 0.2% hydroquinone as reducing agent. Results for Mn extracted by this procedure are presented in Table IX.

TABLE IX : Effect of extraction pH on amounts of easily-reducible Mn extracted from soils by 1N NH_4OAc with hydroquinone.

pH of extraction:	Mn extracted ($\mu g/g$) :
7	130
6	154
5	173
4	187
3	176
2	138

From the results in Table IX it can be seen that, as with exchangeable Mn, more easily-reducible Mn was extracted at pH 3 and 4 than at pH 7. Further experiments were designed to investigate the nature of Mn release at pH's 3.5 and 7.0.

(ii). Effect of extraction time

Duplicate soil samples were extracted with 1N NH_4OAc containing 0.2% hydroquinone at pH 3.5 or 7.0 using extraction times of 4, 8, 16 and 48 hours. The soil extractant ratio was 1:20. The results are shown in Table X. In addition, following the 24-hour extraction with NH_4OAc/hydroquinone at pH 7, the soil samples were washed once with 50 ml of the same extractant and then extracted for a further 24 hours using NH_4OAc/hydroquinohe at pH 3.5. Aliquots of all extractions were analysed for both Fe (by atomic absorption) and Mn contents.

TABLE X : Effect of extraction time on amounts of Fe and Mn removed by 1N NH_4OAc/hydroquinone at two pH values.

Extraction time (Hr.)	Mn extracted (µg/g)			Fe extracted (µg/g)		
	pH 3.5	pH 7	pH 3.5† after pH 7	pH 3.5	pH 7	pH 3.5† after pH 7
4	247	156	-	385	0	-
8	253	175	-	474	0	-
24	332	181	105	688	0	1036
48	352	186	103	799	37	370

† 24-hour extraction.

From the results in Table X it is apparent that the amounts of Mn extracted from the soils at a pH of 3.5 and 7.0 continued to increase up to the 24-hour extraction time. Beyond 24 hours there was little further release of Mn.

At pH 7 there was no measurable extraction of Fe which is interpreted to indicate that, either Fe was not extracted at this pH and consequently any Mn released was not associated with Fe components, or that any Fe released was resorbed or precipitated at this pH and did not appear in the extractant. It is of interest to note that recovery studies for Fe additions to NH_4OAc/hydroquinone at pH 7 have shown an almost total loss of Fe from solution during the extraction period, thereby demonstrating that if Fe were released from the soil it would most certainly be resorbed or precipitated by the soil under the pH conditions of the extraction (Turner - pers. comm.).

Furthermore, it can be seen that extraction with NH_4OAc/hydroquinone pH 3.5 following extraction at pH 7 resulted in a further release of Mn from the soil together with significant release of Fe (1000 µg/g soil).

(d) Effect of NH_4OAc concentration on extractability and recovery of exchangeable and easily-reducible soil Mn.

The recovery of added Mn (60 µg/g) during NH_4OAc/hydroquinone extraction at pH 7 was determined. Recovery was also checked in the presence of 2N NH_4OAc. The extraction period was 24 hours and the results are shown in Table XI.

TABLE XI : Recovery of added Mn (60 µg/g) by NH_4OAc/hydroquinone extraction at pH 7, for 2 normalities of NH_4OAc.

Normality of NH_4OAc :	Extractable Mn (µg/g soil)		
	no added Mn :	added Mn :	% recovery
1N	312	366	90
2N	353	414	100

The results obtained for this series of experiments are slightly higher than those reported earlier due to the selection of a different soil sample. However, it can be seen that greater recovery was obtained using the 2N NH_4OAc extractant.

A final series of extractions was made using 1N and 2N NH_4OAc. For this series, duplicate soil samples were successively extracted once with NH_4OAc pH 7 (24 hour), twice with NH_4OAc/hydroquinone pH 7 (24 hour) and twice with NH_4OAc/hydroquinone pH 3.5. Between each extraction, the soil samples were washed with 50 ml of the preceding extractant. Results of these extractions are presented in Table XII.

TABLE XII : Amounts of Mn extracted by successive 24-hour extractions with NH_4OAc pH 7, NH_4OAc/hydroquinone pH 7, and NH_4OAc/hydroquinone pH 3.5 (µg/g soil).

NH_4OAc normality :	Exchangeable Mn :	NH_4OAC/hyd. pH 7 1st :	2nd	NH_4OAc :pH 3.5 1st	2nd	Total Mn extracted :
1N	12	277	65	113	16	483
2N	12	321	49	89	10	481

From the results in Table XII it is evident that more Mn was removed in the NH_4OAc/hydroquinone pH 7 extractions using 2N NH_4OAc as compared with 1N NH_4OAc. This higher recovery was apparently the result of a decreased tendency for resorption of released Mn during the extraction procedure. It appears that the increased recovery at pH 7 was at the expense of that measured in subsequent pH 3.5 extractions, as evidenced by the same total extractable Mn obtained for both 1 and 2N NH_4OAc extraction sequences.

3. Manganese extraction procedures

The general procedures for soil Mn extraction adopted in this study are shown in Figure 3 and discussed below. All extractions were made at 20°C.

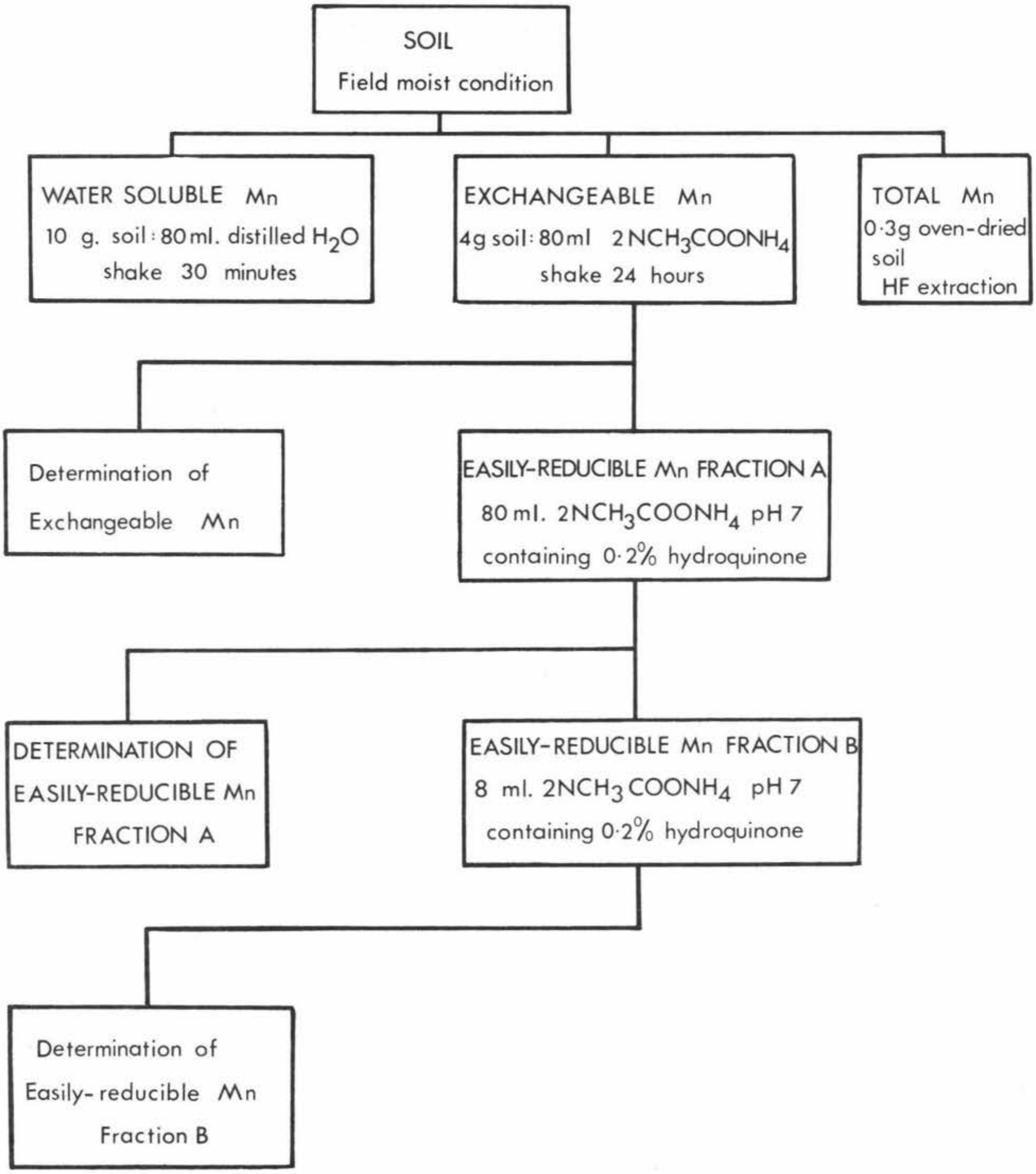


FIGURE 3. FLOW DIAGRAM FOR SOIL MANGANESE EXTRACTION PROCEDURES

(a) Water-soluble Mn.

Ten grams of field-moist soil were shaken on an end-over-end shaker at 20 r.p.m. with 80 ml of distilled water in 100-ml polypropylene tubes. After shaking, the tubes were centrifuged at 2,500 r.p.m. for 15 minutes followed by filtration (Whatman No. 1) to remove floating organic materials. A 50-ml aliquot of the filtrate was pipetted into a 100-ml beaker and evaporated to dryness on a hot plate. The residue was treated with 2 ml of 30% H_2O_2 and 5 ml of conc. HNO_3 to destroy soluble organic matter. The beaker was covered with a cover glass and digested on a hot plate for 30 minutes. The cover glass was then removed and the contents evaporated to dryness. This procedure was repeated twice prior to development of the colour, as outlined in section (f).

(b) Exchangeable Mn.

Separate four-gram samples of soil were shaken in 100 ml of 2N NH_4OAc solution adjusted to pH 7. After shaking, the tubes were centrifuged at 2,500 r.p.m. for 15 minutes, and filtered to remove floating organic material. A 50-ml aliquot of filgrate was pipetted into a 100-ml beaker and evaporated to dryness. Digestion of acetate and soluble organic material was achieved using the same method as outlined above (3. (a)) for water-soluble Mn. The soil remaining in the centrifuge tube was washed once with 50 ml of 2N NH_4OAc at pH 7 prior to the determination of the easily-reducible Mn, fraction A.

(c) Easily-reducible Mn fraction A.

Eighty ml of 2N NH_4OAc adjusted to pH 7 and containing 0.2% hydroquinone was added to the tube containing the soil from which exchangeable Mn had been extracted. The tubes were shaken for 24 hours. After centrifugation and filtration, a 10-ml aliquot was pipetted into a 100-ml beaker and evaporated to dryness. Acetate and soluble organic material were destroyed as previously described (3. (a). The remaining soil in the centrifuge tube was washed once with 50 ml of 2N NH_4OAc pH 7 containing 0.2% hydroquinone prior to determination of easily-reducible Mn, fraction B.

(d). Easily-reducible Mn fraction B.

Eighty ml of 2N NH_4OAc solution adjusted to pH 3.5 and containing 0.2% hydroquinone was added to the soil in each tube and extracted for a further 24 hours. After centrifugation and filtration a 10-ml aliquot was removed and treated to remove acetate and soluble organic material.

(e). Total Mn.

0.3 g of oven-dry soil was weighed into a 50-ml polypropylene beaker. Ten ml of a 1:1 solution (v/v) of 48% HF and conc. HNO_3 was added to the beaker and the contents were digested on a steam bath by taking to dryness. The procedure was repeated at least twice to ensure complete destruction of the sample. The residue was then taken up in 5 ml of 18N H_2SO_4 and 15 ml of distilled water and the solution gently heated on a steam bath for 30 minutes. After cooling, the solution was filtered into a 100-ml volumetric flask and made to volume with distilled water. A 50 ml aliquot was pipetted into a 100 ml beaker and evaporated to dryness on a hot plate. Mn was determined colorimetrically as described in section (f).

(f). Colorimetric determination of Mn.

Mn was determined colorimetrically according to the method of Adams (1965). To the residue in a 100-ml beaker was added 20 ml of distilled water, 2 ml of 85% H_3PO_4, and 0.5 g of solid KIO_4. The beaker was covered with a watch glass and the contents heated to boiling on a hot plate. The permanganate colour developed within 20 minutes. Heating was continued until the solid KIO_4 was completely dissolved. The solution was transferred to a 50-ml volumetric flask, made to volume with distilled water, and thoroughly mixed. The colour was read using a Beckman model DU spectrophotometer at 540 mμ using 10 cm path length cells. The Mn content was read from a standard curve covering the range 0 to 3 μg/ml Mn.

4. Soil pH

Soil pH was measured using a Radiometer Model 24 pH meter. A soil to water ratio of 1 to 2.5 was used (Metson, 1971) and readings were taken after allowing to stand overnight.

5. Soil moisture

Soil moisture content was determined after oven drying at 105°C for 24 hours.

6. Plant Mn

Mn in herbage was analysed according to Peech (1958). One gram of oven-dried herbage was weighed into a 250-ml beaker and ashed in a muffle furnace at 450°C for 4 hours. After ashing and cooling, 25 ml of 1N HNO_3 was added and the contents evaporated to dryness on a hot plate. The beaker was returned to the furnace for 10 minutes at 400°C. After cooling, 15 ml of 18N H_2SO_4 and 30 ml of distilled water were added and the contents heated for 30 minutes on a hot plate. After cooling, the contents were filtered into a 100-ml volumetric flask and the solution made to volume with distilled water. A 20-ml aliquot was pipetted into a 100-ml beaker and the colour developed as described in section (f).

IV. RESULTS AND DISCUSSION

A. EFFECT OF LIME ADDITIONS ON FORMS OF SOIL Mn

The effect of lime additions on each form of soil Mn are considered separately in this section.

1. Water-soluble Mn

Results for water-soluble Mn are presented in Tables XIII and XIV.

TABLE XIII : The effect of lime addition and sampling time on water-soluble Mn at Site A

Treatment (kg/ha lime)	Dates of sampling			
	15/6/71	7/8/71	9/10/71	7/12/71
Control	2	2	2	2
1270	3	3	2	2
2540	2	3	2	1
5080	2	3	2	1

TABLE XIV : The effect of lime addition and sampling time on water-soluble Mn at Site B

Treatment (kg/ha lime)	Dates of sampling			
	15/6/71	7/7/71	9/10/71	7/12/71
Control	3	4	3	2
1270	4	4	3	2
2540	2	4	3	2
5080	3	5	3	2

Values for water-soluble Mn ranged between 1 and 5 µgMn/g soil. However, there was no obvious effect of lime application on the amounts of water-soluble soil Mn. Also, the levels remained reasonably constant throughout the experimental period. The results obtained for water-soluble Mn produced very low absorbance readings which in the absence of a concentration procedure, may not have given the necessary sensitivity for reflecting changes resulting from seasonal or liming factors.

2. Exchangeable Mn

Results for exchangeable Mn are presented in Tables XV and XVI.

TABLE XV : Effect of lime addition and sampling time on exchangeable Mn at Site A

Treatment (kg/ha lime)	Dates of sampling						
	15/6/71	7/8/71	9/10/71	7/12/71	15/1/72	22/6/72	Analysis of variance result
Control	19	15	18	23	14	11	N.S.
1270	20	15	21	22	12	7	N.S.
2540	20	14	19	18	10	14	N.S.
5080	17	13	18	19	9	9	N.S.
Results of analysis of variance	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	

TABLE XVI : Effect of lime addition and sampling time on exchangeable Mn at Site B

Treatment (kg/ha lime)	Dates of sampling					
	15/6/71	7/8/71	9/10/71	7/12/71	15/1/72	Analysis of variance result
Control	18	18	17	19	18	N.S.
1270	15	15	17	15	12	N.S.
2540	13	13	16	13	10	N.S.
5080	13	19	21	17	11	N.S.
Results of analysis of variance	N.S.	N.S.	N.S.	N.S.	N.S.	

The results for exchangeable Mn show no significant effects due to either seasonal factors or liming treatments. Absolute value for exchangeable Mn varied between 7 and 22 µgMn/g. These results were somewhat surprising in view of previous reports (Fujimoto and Sherman, 1948; Christensen et al, 1950; Messing, 1965; Cheng and Quellete, 1971a; Truong et al, 1971), which indicate that exchangeable Mn decreased following lime application.

3. Easily-reducible Mn (Fraction A)

The effect of lime addition on this fraction of soil Mn at both sites is shown in Tables XVII and XVIII.

TABLE XVII : The effect of lime addition and sampling time on easily-reducible Mn fraction A at Site A .

Treatment (kg/ha lime)	Dates of sampling						
	15/6/71	7/8/71	9/10/71	7/12/71	25/1/72	22/6/72	Analysis of variance result
Control	220	200	236	201	232	204	N.S.
1270	224	227	247	190	243	198	N.S.
2540	216	209	245	185	242	212	N.S.
5080	181	158	193	157	202	185	N.S.
Results of analysis of variance	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	

TABLE XVIII : The effect of lime addition and sampling time on easily-reducible Mn fraction A at Site B

Treatment (kg/ha lime)	Dates of sampling					
	15/6/71 :	7/8/71 :	9/10/71 :	7/12/71 :	25/1/72	Analysis of variance result
Control	153	151	162	141	146	N.S.
1270	143	144	157	125	137	N.S.
2540	127	114	127	120	127	N.S.
5080	140	135	146	125	131	N.S.
Results of analysis of variance	N.S.	N.S.	N.S.	N.S.	N.S.	

It can be seen that easily-reducible (fraction A) soil Mn in Site A ranged from 157 to 247 ugMn/g soil with an average of 195 ug/g. At Site B this form ranged from 120 to 140 ugMn/g soil. In addition, levels of this fraction remained essentially constant at each sampling time throughout the experimental period.

4. Easily-reducible Mn (Fraction B)

The results for easily-reducible (fraction B) soil Mn at both sites are shown in Tables XVIV and XX.

TABLE XVIV : The effect of lime addition and sampling time on easily-reducible Mn fraction B at Site A.

Treatment (kg/ha lime)	Dates of sampling						
	15/6/71	7/8/71	9/10/71	7/12/71	25/1/72	22/6/72	Analysis of variance results
Control	104	100	75	64	52	146	* *
1270	118	111	82	70	76	176	* *
2540	119	103	77	65	55	182	* *
5080	102	85	70	59	62	120	* *
Results of analysis of variance	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	

TABLE XX : The effect of lime addition and sampling time on easily-reducible Mn fraction B at Site B.

Treatment (kg/ha lime)	Dates of sampling					
	15/6/71	7/8/71	9/10/71	7/12/71	25/1/72	Analysis of variance results
Control	92	80	68	70	60	N.S.
1270	79	81	68	59	55	N.S.
2540	78	66	56	59	49	N.S.
5080	77	77	62	56	59	N.S.
Results of analysis of variance	N.S.	N.S.	N.S.	N.S.	N.S.	

The results in Tables XVIV and XX show that substantial amounts of soil Mn are removed using this extraction procedure but again no effect of lime application could be detected. An interesting seasonal variation in this form of soil Mn was detected at Site A

(Table VII) where extractable levels were lowest at the October-December-January sampling times corresponding to the driest soil conditions for the experimental period.

It is difficult to envisage how changes in this category of soil Mn could be related to the availability of Mn to plants, in view of the fact that availability of Mn is usually explained in terms of water-soluble, exchangeable, and easily-reducible (fraction A) soil Mn. However, further work is required to assess the nature of this category of soil Mn in view of the apparent cyclic seasonal effect demonstrated in this experiment.

5. Total Mn

Total soil Mn analyses for both sites at two sampling times are presented in Table XXI.

TABLE XXI : Total soil Mn for sites A and B at two sampling times.

Site :	Sampling Date :	
	9/10/71	7/12/71
	ug/g	
A	657 ± 140	655 ± 141
B	532 ± 148	531 ± 146

From Table XXI it is seen that the soils used in this experiment contained between 531 and 657 ug/g total Mn. Values obtained at Site A were slightly higher than those at Sibe B although no significance is attached to this result. Although no change in total Mn content of the soil would be expected, results obtained at the 16 and 24 week samplings were used as evidence for the adequacy of the sampling methods adopted in this study.

B. EFFECT OF LIME ON SOIL pH

The effect of lime addition on soil pH at the two experimental sites is shown in Tables XXII and XXIII.

TABLE XXII : Effect of lime addition and sampling time on soil pH at Site A.

Treatment (kg/ha lime)	Dates of sampling						
	15/6/71	7/8/71	9/10/71	7/12/71	25/1/72	22/6/72 †	Analysis of variance results.
Control	5.75	5.84	5.82	5.62	5.44	5.49	* *
1270	5.66	5.87	5.98	5.87	5.56	5.65	* *
2540	5.60	5.90	6.08	6.10	5.75	5.86	* *
5080	5.67	5.92	6.36	6.36	6.09	6.23	* *
Results of analysis of variance	N.S.	* *	* *	* *	* *	* *	

† data for 2 replicates only.

TABLE XXIII : Effect of lime addition and sampling time on soil pH at Site B.

Treatment (kg/ha lime)	Dates of sampling						
	15/6/71	7/8/71	9/10/71	7/12/71	25/1/72	22/6/72 †	Analysis of variance results.
Control	5.65	5.77	5.75	5.73	5.37	5.42	* *
1270	5.71	5.80	5.91	5.93	5.51	5.72	* *
2540	5.73	5.93	6.05	6.14	5.73	5.87	* *
5080	5.75	5.94	6.16	6.26	5.86	6.05	* *
Results of analysis of variance	N.S.	* *	* *	* *	* *	* *	

† data for 2 replicates only.

It can be seen from Table XXII and XXIII that the soil pH's prior to liming were relatively uniform for the two sites, giving measured values between pH 5.60 and 5.75. These values were only slightly higher than those previously quoted for Purimu silt loam (pH 5.5) (Soil Bureau Bulletin n.s. No. 5, 1954). It should be noted that these soils were sampled in June when the soils were relatively moist (approximately 50% moisture content) and pH was measured on field moist samples, which may account in part for the higher-than-expected pH readings.

A feature of the results in Tables XXII and XXIII is the marked seasonal variation of soil pH for both the limed and unlimed treatments at both sites. In general, soil pH values on the unlimed areas tended to be the highest in the 7/8/71 - 9/10/71 samplings, when soil moisture was greatest and lowest in the 25/1/72 - 22/6/72 samplings when soil moisture was much lower.

Soil pH measurement on samples at field moisture content is influenced markedly by moisture content, especially when pH is measured by the standard procedure used in this study. Similar seasonal variation is evident for the limed areas but is complicated by the tendency for pH values to increase as the liming reaction proceeds with time. However, the results suggest that again measured pH values for limed areas tended to be lowest when the soils were driest.

It is noted that the pH values for the control plots at the June sampling 1972, were considerably lower than the corresponding values for 1971 reflecting, again, the different moisture contents of samples at the time of analyses.

Significant differences in soil pH due to liming were detected at the 8-weeks sampling time following application of lime and were still increasing at the final sampling.

These results suggest that changes in pH of 0.3-0.4 units could be expected per 2450 kg/ha of lime addition, after 8-12 months from time of application.

C. EFFECT OF LIME ON CONTENT OF Mn IN HERBAGE

Results for the effect of lime addition on concentration of Mn in bulk herbage samples are shown in Tables XXIV and XXV.

TABLE XXIV : The effect of lime addition and sampling time on herbage Mn at Site A.

Treatment (kg/ha)	Dates of sampling		
	9/10/71	7/12/71	22/6/72
Control	306	234	226
1270	185	165	144
2540	172	118	128
5080	134	87	79
Results of analysis of variance	* *	* *	* *

TABLE XXV : The effect of lime addition and sampling time on herbage Mn at Site B.

Treatment (kg/ha lime)	Dates of sampling	
	9/10/71	7/12/71
Control	338	311
1270	169	133
2540	170	122
5080	165	136
Results of analysis of variance	* *	* *

From these results it can be seen that for the sampling time corresponding to five months after lime addition when the first herbage samples were taken, the average concentration of Mn in the unlimed controls was 306 µg/g and 338 µg/g for sites A and B, respectively. Addition of 1270 kg lime/ha resulted in reduction of herbage Mn concentrations of approximately 40 to 50% at sites A and B, respectively. Larger additions of lime did not appear to further decrease Mn levels in the herbage, except possibly for the heaviest rate (5080 kg/ha) at site A.

The maximum depression in concentration of Mn in herbage was noted for the heaviest rate of lime addition at the 6-month sampling period. At this time Mn reduction to approximately 72% of the unlimed controls was achieved. Evidence for marked seasonal variation in the uptake of Mn by herbage is shown by the pronounced fluctuation in Mn concentration found for the unlimed controls, especially at site A. It is noted that this seasonal variation appeared to parallel the soil moisture status in that the highest Mn uptake was found when soil moisture content was greatest. This suggests that moisture content and its relationship to redox phenomena may be important in controlling Mn availability to plants on these soils.

V. GENERAL DISCUSSION

Lime application and soil pH

A feature of the results obtained for soil pH in this experiment was the marked seasonal variation exhibited by these soils. For the unlimed controls, measured pH varied by up to 0.4 of a pH unit, depending on sampling time. Part of this variation is possibly due to the use of field-moist samples for pH measurement, and highlights the problem of using fixed soil/solution ratios for undried soil samples.

The addition of 2540 kg lime/ha resulted in pH shifts of approximately 0.3-0.4 units one year after application, which agrees well with published information on expected lime responses for New Zealand silt loams (During, 1972).

Lime application and Mn in herbage

It was apparent in this experiment that the lowest rate of lime addition produced, at least initially, a considerable reduction in herbage Mn concentration. Such an effect is consistent with the findings of Mann (1930), Fujimoto and Sherman (1948) and Truong et al (1971) who reported that the first light application of lime markedly reduced the uptake of Mn by the plant and the further additions of lime, produced more gradual reductions in Mn uptake. Although no obvious explanation can be advanced for the nature of this lime effect, in the present experiment possibilities would include :

(a) Approach to pH 6.0 achieved at the lowest liming rate (Leeper, 1935; Walker and Barber, 1960). Leeper has reported that Mn availability decreased markedly around pH 6.0.

(b) Initial increment of Ca addition which may antagonise uptake of Mn (Hopkins et al, 1944; Fried and Peech, 1946; Quellette and Dessureaux, 1958: Cheng and Quellette, 1968). Cheng and Quellette (1968) have reported that normal plants should have a Ca : Mn ratio of approximately 350 and a Mn : Fe ratio of approximately 30. Plants show Mn toxicity symptoms when the Ca : Mn ratio falls below 70 or when the Mn : Fe ratio is higher than 100. Truong et al (1971) found that in solution culture, high Ca supply alleviated Mn toxicity by reducing the proportion of absorbed Mn moving to the shoots of legumes, The effect was due to an influence on plant processes rather than to its influence on Mn absorption and translocation (Quellette and Dessureaux, 1958).

Herbage and analyses in the present study were made on grab samples of bulk herbage. No attempt was made to assess either the relative contribution of individual species in the mixed pasture sward at the various sampling times or the Mn content of these species and their response to lime. Undoubtedly, some of the variation reported may be the result of the varying contribution from the different pasture members.

Forms and amounts of soil Mn

Water-soluble Mn varied between 1 and 5 ugMn/g soil with an average of 2 ugMn/g soil for site A and 3 ugMn/g soil for site B. However, there was no apparent seasonal or liming effect on the levels of this form of Mn. Reports by other workers suggest that water-soluble Mn can vary from a trace to 25 ugMn/g soil (Morris and Pierre, 1947; Morris, 1948; Randhawa et al, 1961; Siman et al, 1970 and Gupta, 1972) and that the amounts in this form tend to decrease with increasing pH (Mann, 1930; Piper, 1931; Morris, 1948; Mulder and Gerretsen, 1952). Values of 1 to 10 ug/ml have been reported to be toxic to various legumes in culture solutions (Morris and Pierre, 1949). Siman et al (1970) reported evidence for toxicity of French beans at 7-15 ug/ml water-soluble Mn. Gupta (1972) showed that toxicity in barley under greenhouse conditions occurred at values around 0.25 ug/ml. Comparative values for water-soluble Mn in New Zealand soils are not available. It would not be expectedm however, that the levels of water-soluble Mn obtained in the present experiments would result in toxicity or deficiency problems for resident plant species.

Exchangeable soil Mn values ranged from 11 to 32 ugMn/g soil on site A and from 9 to 25 ugMn/g soil in site B. Seasonal variation in exchangeable Mn has been reported previously (Sherman and Harmer, 1942; Dorp and Peterson, 1950; Korregarten, 1956; Nozdrunova et al, 1958). Dorp and Peterson (1950) and Nozdrunova et al (1958) found 5 to 10 times as much exchangeable Mn in summer as in winter, whereas Sherman and Harmer (1942) claim that winter conditions favour manganous, and summer conditions manganic, forms of the element. This latter conclusion was based on work with alkaline soils. Fujimoto and Sherman (1946, 1948) and Hurtwitz (1948) found that the level of exchangeable Mn was raised as the temperature increased. Organic matter decomposition and high moisture favour the reduction of Mn. Rich (1956) reported that exchangeable Mn tended to increase under the anaerobic condition of waterlogging and easily reducible Mn tended to decrease under drying conditions. Although reports differ on when exchangeable Mn can be expected to increase, all agree that the pattern of change is closely associated with soil temperature and pH conditions. In these present experiments it was found that exchangeable Mn tended to be highest in the October-December period when soil moisture was at its greatest.

Easily-reducible Mn (fraction A) was approximately 200 µg Mn/g soil in site A and 130 µg Mn/g soil for site B. Leeper (1935) considered the quantity of easily-reducible Mn dioxide to be of major importance in the supply of Mn to plants. He found that any soil having less than 15 µgMn/g soil of easily-reducible Mn dioxide would be deficient in Mn for plant growth. A soil having more than 100 µgMn/g soil of easily-reducible Mn dioxide would provide an adequate supply of Mn. However, it must be noted that his method for determining this form of soil Mn was different from that used in the present study. Using Leeper's data it could be concluded that the soil used for the present experiment would be potentially capable of an ample or excessive supply of Mn for plants.

Patrick and Turner (1968) pointed out that the sum of exchangeable and easily-reducible Mn accounted for most of the Mn present in Crowley silt loam soil; of the total Mn, 80% existed as easily-reducible Mn, 16% as exchangeable Mn, and 2% as water-soluble Mn. In the present experiment, easily-reducible Mn represented approximately 20-30%, exchangeable Mn 3%, and water-soluble Mn 0.3-0.5% of the total Mn content of Purimu silt loam. Sherman and Harmer (1942) reported that to avoid Mn deficiency, soils should contain at least 3.3 µg/g of exchangeable Mn and 100 µg/g of easily-reducible Mn. Jones and Leeper (1951a) pointed out that a soil should contain more than 20 µg/g of easily-reducible Mn to support normal growth of plants; when the soil content is less than 20 µg/g, plants exhibit Mn-deficiency symptoms. From these values it can be concluded that the soil used in present experiment contains relatively high reserves of a potentially available form of Mn (approximately 200 µgMn/g soil). The possibility of Mn deficiency is therefore remote, whereas an excessive Mn supply, especially under wet or waterlogged conditions, would be possible.

In terms of the total Mn content of the soils used in this experiment, values of 1000 μgMn/g soil could not be considered excessively high. Comparative values for total soil Mn in a range in New Zealand soils are presented in Table XXVI (Soil Bureau Bulletin, 1968).

TABLE XXVI : Values for total soil Mn in some New Zealand soils.

Soil name:	Classification :	Sampling depth :	Total Mn :
Hamilton clay loam	Moderately leached strongly weathered clay illuvial brown granular loam (transitional between central and northern yellow-brown earth	0 - 7.5	8800
Tirau silt loam	Moderately leached central yellow-brown loam	0 - 7.5	8600
Dannevirke silt loam	Strongly leached yellow-brown loam to yellow-brown earth intergrade	0 - 7.5	1200
Marton silt loam	Weakly leached gleyed net-gammate central yellow-grey earth	0 - 7.5	980
Taupo sandy silt	Moderately leached yellow-brown pumice soil	0 - 7.5	820
Timaru silt loam	Moderately leached southern yellow-grey earth	0 - 9.0	400

Lime application and forms of Mn in soil

In spite of the considerable effect of lime application on measured soil pH and on the levels of Mn in herbage, it was not possible to detect changes in the amounts of the forms of soil Mn using common procedures for soil Mn fractionation. Typically, previous workers have shown the equilibrium between exchangeable and easily-reducible Mn to be influenced by soil pH (Sherman *et al*, 1942; Messing, 1965), and that increasing pH generally favours formation of easily-reducible Mn at the expense of exchangeable Mn. This transformation was not observed in the present experiment. In particular no effect of lime on levels of exchangeable Mn was detected. The inherent experimental errors associated with the field sampling techniques or laboratory measurement of each form of Mn may have masked the real liming effect.

An even more fundamental problem however, relates to the use of a buffered (pH 7) NH_4OAc extractant for both limed and unlimed soils. Such an extractant could alter the distribution of Mn existent at field pH conditions and tend to obscure real lime effects. In spite of this problem many reports are available in the literature indicating that changes in soil Mn fractions consequent to lime application can be obtained (Sherman *et al*., 1942; Peech *et al*., 1947 and Sanchez and Kamprath, 1959) using procedures similar to those used in this study. In addition, such transformations have been observed even where no precautions were taken to preserve the field moisture status of the soils prior to extraction. It will be remembered that in this study samples were maintained in a field moist condition to minimise oxidation during the storage and preparation of samples prior to extraction.

The apparent lack of correlation between soil pH and changes in the forms of soil Mn has, however, been reported previously (Healy, 1953). It was found that acidification of

Hastings silt loam using sulphur additions did not result in measurable changes in either exchangeable or easily-reducible forms of soil Mn, at least during the first year of the experiment, even when pH was altered to a value less than 6.0. On the other hand Leeper (1947), typically, found a strong correlation between soil pH and ammonium acetate-extractable Mn, with a marked increase in exchangeable Mn occurring as the soil pH decreased below pH 6.0.

The inability to detect changes in the forms of soil Mn following liming may have been due in part to the method adopted in this study for sampling and analysis of soil cores. As a result broadcasting lime over the soil surface, a gradient in soil pH would likely extend down from the soil surface. Such a gradient would be dissipated throughout the whole sample when a 10 cm soil core was mixed prior to analysis. This may have lead to problems in the detection of changes in the forms of Mn occurring, especially in the upper part of the core. To avoid such possible effects would necessitate a more detailed analysis of portions of each soil core and this was not attempted in the present study. Allowing for the dilution effect discussed above, however, significant changes in the pH of the mixed soil cores were found in this experiment but these were not paralleled by any apparent changes in the forms of soil Mn. Most studies relating forms of Mn to lime treatments have involved the uniform incorporation of lime throughout the soil sample (White, 1970; Truong _et al._, 1971). No reports are available where lime has been surface-applied to soils in the field.

The statistically significant seasonal variation in amounts of easily-reducible Mn (fraction B) at site A cannot as yet be interpreted since it is by no means clear that this fraction of soil Mn is in any way related to the supply of available Mn for plant use. It is of interest to note, however, that the amount of this fraction tended to be lowest when the soils were driest and that this corresponded to the lowest herbage Mn values, for the control plots, obtained during the experiment. Unfortunately, insufficient plant and soil data are available to further assess the significance of this result.

SUMMARY

A field study was made to determine the forms of native soil Mn, and the effect of lime additions on Mn transformations, in a previously-unlimed yellow-brown earth (Purimu silt loam) of the Wairarapa district.

Five forms of Mn were measured and changes in these forms were assessed, at two-monthly sampling intervals, for a twelve-month experimental period following lime application. Lime was applied at four rates corresponding to 0, 1270, 2540 and 5080 kg/ha.

Soil pH changes and, where possible, Mn concentrations in bulked herbage samples were also determined.

The results showed that lime additions increased soil pH and decreased the concentration of Mn in the bulk herbage. The magnitude of pH shift obtained was consistent with previous reports for New Zealand Silt Loams. Likewise the decrease in herbage Mn concentration following liming agreed with previous findings.

A feature of the results in this study was the failure to detect changes in the various forms of soil Mn following lime addition. This result cannot be satisfactorily explained at the present time. Problems in the sampling procedure adopted for this study and the choice of pH 7.0 for extraction of soil Mn forms may be partially responsible for the lack of expected correlations. In addition, there was no evidence for significant seasonal variation in amounts of exchangeable or easily reducible forms of soil Mn.

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