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Micronutrient status of a group of soils in Canterbury, New Zealand, as measured by extraction with EDTA, DTPA and HCl, and its relationship with plant response to applied Cu and Zn

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SUMMARY

The Cu, Zn and Mn status of 44 fields from the Canterbury region of New Zealand under winter wheat was investigated in Spring 1993. Micronutrient status was assessed using EDTA, DTPA and HCl as extractants. The Mn status of soils was generally high and unaffected by soil development. However, when samples were separated according to soil series, it was found that extractable Cu and Zn levels in both the 0–15 and 15–30 cm soil layers generally decreased with increasing soil development (increasing soil age and annual rainfall). Twenty-three percent of fields had EDTA-extractable Cu levels < 1 μg g^{-1} whilst 34% had EDTA-extractable Zn levels < 1 μg g^{-1}.

Twenty-two of the soils were used in a glasshouse experiment in which wheat was grown in the soils with or without the addition of added Cu and/or Zn. Plant dry matter responses to added Cu were recorded in soils with extractable Cu levels $< 1{\cdot}1$ μg g^{-1} EDTA, 0·4 μg g^{-1} DTPA and 0·9 μg g^{-1} HCl. Responses to added Zn occurred in soils with extractable Zn levels $< 0{\cdot}8$ μg g^{-1} EDTA, 0·25 μg g^{-1} DTPA and 1·4 μg g^{-1} HCl. Significant linear correlations were found between EDTA-, DTPA- and HCl-extractable Cu and Zn and Cu and Zn uptake respectively by wheat. Correlation coefficients were closer for Cu than for Zn uptake. It was concluded that many sites on the more strongly developed soils of the Canterbury Plains are potentially deficient in Cu and/or Zn and that these can be identified using conventional micronutrient soil tests.

INTRODUCTION

Soil testing for micronutrients such as Cu and Zn involves extracting the 'potentially plant-available' fraction from the soil. This is achieved with a wide variety of reagents which are often either chelating agents (e.g. ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA)) or weak acids (e.g. 0·1 M HCl) (Knezek & Ellis 1980).

Soil samples are normally air-dried prior to chemical analysis. Drying increases the amount of micronutrients extracted from soils, although oven-drying has a more pronounced effect than air-drying (Khan & Soltanpour 1978; Leggett & Argyle 1983; Haynes & Swift 1991). These increases have been observed to vary with different elements, different extractants and different soils (Haynes & Swift 1991). However, air-drying does ensure that micronutrients are extracted at similar soil moisture contents. This is an important consideration since Shuman (1980) showed that when soil samples of widely differing moisture contents were used, initial moisture content significantly influenced the amounts of Fe, Mn, Zn and Cu that were extracted with DTPA. Thus, one source of variability (different soil moisture contents) is removed by air-drying, but another is created since drying itself causes a variable increase in micronutrient extractability. Haynes & Swift (1991) questioned the agronomic significance of micronutrient extractability measured in air-dried soils.

The Canterbury Plains region covers over 750000 ha and is the main cereal-growing area of New Zealand. Amounts of extractable Cu and Zn in many of the soils of the region are low and appear to be potentially deficient (Haynes & Swift 1984; McLaren *et al.* 1984). Despite this, there are few reports of deficiencies of these nutrients in cereal

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crops or, indeed, positive responses to their application (Haynes 1994).

In this study, the Cu and Zn status of 44 fields from the Canterbury region of New Zealand under winter wheat was investigated using EDTA, DTPA and HCl as extractants. Wheat was grown in 22 of these soils in a glasshouse experiment with or without the addition of Cu and/or Zn and the relationship between Cu and Zn extractability from field-moist and air-dried soils and plant uptake was determined.

MATERIALS AND METHODS

Forty-four fields in the Canterbury Plains region of New Zealand were sampled in spring. Samples were taken from winter wheat fields on sites representative of some of the main soil series used for arable cropping. These included the Lismore, Ruapuna, Mayfield, Lyndhurst, Templeton, Wakanui, Paparua and Temuka series (Kear *et al.* 1967). Twenty soil cores (i.d. 2·5 cm) were taken from each field and sectioned into 0–15, 15–30, 30–45 and 45–60 cm depths. Samples from each depth were bulked, sieved (< 2 mm) and a portion of each sample was air-dried at 22 °C in a drying cabinet with air circulation for 48 h. For the soils sampled (0–15 cm soil layer), the pH range was 5·6–6·5, organic C content 2·0–4·1% and the effective CEC 136–239 mmol kg^{-1}. There were no significant differences between soil series for these soil properties.

Cu and Zn were extracted from field-moist and air-dried soil with (i) 0·04 M EDTA (disodium salt adjusted to pH 6·0) using a 1:2·5 soil:extractant ratio for 2 h (Williams & McLaren 1981); (ii) DTPA soil test extractant (0·005 M DTPA, 0·1 M triethanolamine and 0·01 M $CaCl_2$ at pH 7·3) using a 1:2 soil:extractant ratio for 2 h (Lindsay & Norvell 1978); and (iii) 0·1 M HCl using a 1:2·5 soil:extractant ratio for 2 h (Haynes & Swift 1985). Concentrations of Cu and Zn in centrifuged extracts were measured by atomic absorption spectrophotometry.

The 0–15 cm layer of 22 of the sites (randomly chosen) was resampled and sieved (< 4 mm). 1500 cm^3 of soil was placed in plastic pots (32 replicates per site) and a basal fertilizer dressing was applied. This consisted of 200 g N m^{-3} as NH_4NO_3, 150 g K m^{-3} as KH_2PO_4, 50 g Mg m^{-3} as $MgSO_4$, 1·5 g B m^{-3} as H_3BO_3 and 0·08 g Mo m^{-3} as $(NH_4)_6Mo_7O_{24}.4H_2O$. Experimental treatments consisted of (i) control, (ii) Cu applied at 10 g Cu m^{-3} (+Cu), (iii) Zn applied at 20 g Zn m^{-3}(+Zn), and (iv) a combination of treatments 2+3(Cu+Zn). The pots were maintained at 70% field capacity for 6 weeks in a glasshouse, thermostatically controlled with a fan vent temperature of 25 °C and a heat temperature of 15 °C. At the end of this period, four replicates of each treatment were removed for analysis of extractable Cu and Zn as outlined above. Ten seeds of wheat (*Triticum aestivum* L. cv. Sapphire) were sown in each of the other four replicates and seedlings were subsequently thinned to 5 per pot. Above-ground plant material was harvested after 13 weeks, oven-dried (70 °C), weighed and ground. Plant samples were digested with nitric and perchloric acids and the digests were analysed for Cu and Zn as outlined above.

RESULTS

Mean values, along with standard deviations, for extractable Cu, Zn and Mn in field-moist and air-dried samples for the 44 fields surveyed are presented in Table 1. Air-drying substantially increased EDTA- and DTPA-extractable Cu and Zn and DTPA-extractable Mn. By contrast, EDTA-extractable Mn and HCl extractable Zn and Mn were not greatly increased by drying. The frequency distribution of EDTA-extractable Cu, Zn, and Mn for air-dried soils is shown in Fig. 1. Similar patterns of distribution were observed for DTPA- and HCl-extractable micronutrients (data not presented). A value of 1 μg g^{-1} for EDTA-extractable Cu and Zn can be taken as a rough guideline for the approximate level below which deficiencies may occur in cereals (Haynes 1994). Twenty-three percent of fields had EDTA-extractable Cu levels < 1 μg g^{-1} and 34% had extractable Zn levels less than that value. Concentrations of EDTA-extractable Mn were generally high (McLaren *et al.* 1984) in these soils.

Mean values for EDTA-extractable Cu, Zn and Mn in the study soils when separated according to soil series are shown in Table 2. A similar pattern was evident when data for DTPA- and HCl-extractable micronutrient contents were separated by soil series (data not presented). Concentrations of extractable Mn in soils were generally unaffected by the soil series from which they originated (Table 2). In the 0–15 and

Table 1. *Mean values for EDTA-, DTPA- and HCl-extractable Cu, Zn and Mn for 44 study soils in New Zealand (0–15 cm) analysed using field-moist or air-dried samples*

Extractant and sample state	Cu Mean ± S.D.	Zn Mean ± S.D.	Mn Mean ± S.D.
EDTA			
Field-moist	0·99 ± 0·89	0·93 ± 0·49	30 ± 26
Air-dried	1·81 ± 1·61	1·3 ± 0·68	32 ± 30
DTPA			
Field-moist	0·28 ± 0·25	0·31 ± 0·17	0·98 ± 0·56
Air-dried	0·95 ± 0·88	0·65 ± 0·46	2·8 ± 2·5
HCl			
Field-moist	0·92 ± 0·30	1·6 ± 0·98	17 ± 15
Air-dried	1·3 ± 0·34	1·8 ± 1·3	21 ± 18

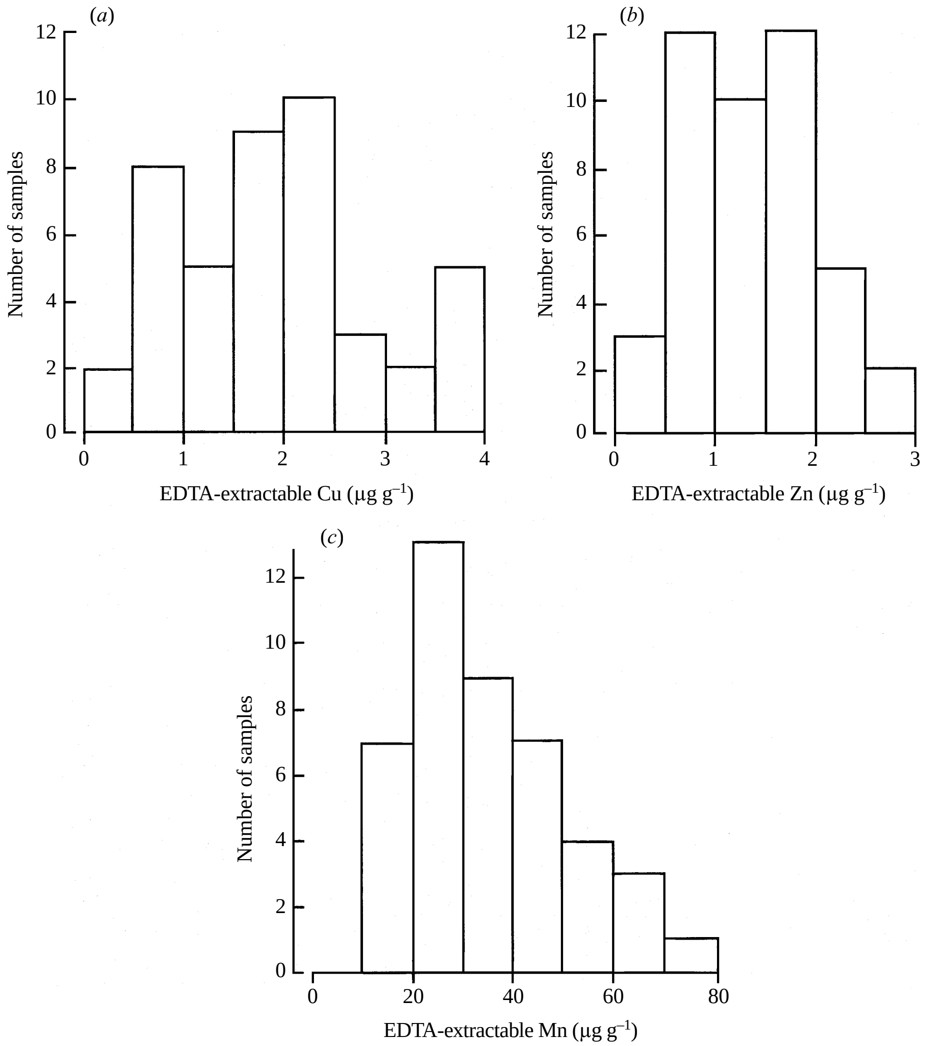
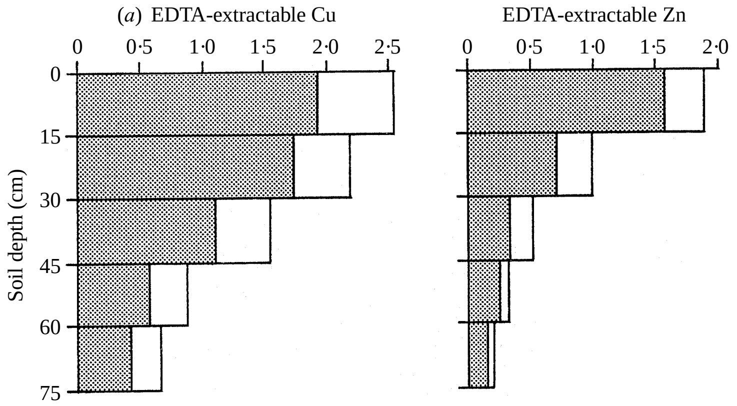


Fig. 1. Frequency distribution of EDTA-extractable (*a*) Cu, (*b*) Zn and (*c*) Mn in the 0–15 cm layer of 44 soils (air-dried samples) from under winter wheat crops in the Canterbury region of New Zealand.

Table 2. *Mean values for EDTA-extractable Cu, Zn and Mn contents (air-dried samples) for different soil series in New Zealand studied at two different soil depths*

Soil series	Sample size	Cu		Zn		Mn	
		0–15	15–30	0–15	15–30	0–15	15–30
Lismore	6	0·59	0·60	0·56	0·39	30	25
Ruapuna	3	0·62	0·54	0·62	0·41	28	27
Mayfield	4	0·78	0·49	1·18	0·49	21	12
Lyndhurst	5	0·64	0·66	0·67	0·37	16	9·5
Templeton	7	2·2	1·17	2·0	0·89	44	27
Wakanui	7	2·2	0·99	1·8	0·53	18	9·7
Paparua	6	1·8	0·83	1·6	0·74	29	19
Temuka	6	2·5	2·0	1·8	1·18	57	34



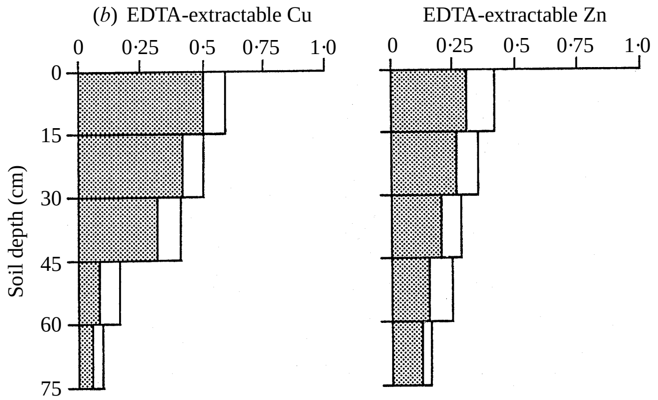


Fig. 2. Concentrations of EDTA-extractable Cu and Zn in the soil profile (field-moist ▨ and air-dried ▨☐ samples of (*a*) a soil from the Temuka series and (*b*) one from the Lismore series.

to a lesser extent 15–30 cm layer, mean concentrations of extractable Cu and Zn were, however, lower for the more developed Lismore, Ruapuna, Mayfield and Lyndhurst soil series than for the younger Templeton, Wakanui, Paparua and Temuka soils. Differences were less marked in the 30–45 and 45–50 cm layers (data not shown). Nonetheless, when an individual soil from the Temuka series is compared with that from the Lismore series (Fig. 2), it is evident that EDTA-extractable Cu and Zn are considerably lower in the Lismore soil in all layers down to 60 cm. Air-drying increased EDTA-extractable Cu and Zn in both profiles (Fig. 2) down to 60 cm.

Of the 22 soils used in the pot experiment, wheat plants showed a significant dry matter (DM) response to applied Cu and/or Zn in six of them. Amounts of extractable Cu and Zn in field-moist and air-dried samples from these six soils either unamended or amended with Cu or Zn are shown in Figs 3 and 4. All of these soils had EDTA-extractable Zn contents (air-dried soils) of < 1 μg g^{-1} (Fig. 4) and five of them also had EDTA-extractable Cu < 1 μg g^{-1} (Fig. 3). Air drying the field-moist soils generally increased the extractability of Cu and Zn both from unamended soils and those where Cu and/or Zn had been added (Figs 3 and 4). The relative increase was generally greater for unamended soils.

Dry matter yields of wheat grown in the six soils (out of 22) where a response to added Cu and Zn was recorded are presented in Fig. 5. Responses to added Cu were recorded in the Lismore 1 and 2, Ruapuna 1 and Lyndhurst soils and responses to added Zn were measured in the Lismore 1, Ruapuna 1 and 2, Mayfield and Lyndhurst soils. When results for all 22 soils were compared, responses to added Cu occurred in soils with extractable Cu values (air-dried soils) of $< 1{\cdot}1$ μg g^{-1} EDTA, 0·4 μg g^{-1} DTPA and 0·9 μg g^{-1} HCl. Responses to added Zn were measured in soils with extractable Zn values of $< 0{\cdot}8$ μg g^{-1} EDTA, 0·25 μg g^{-1} DTPA and 1·4 μg g^{-1} HCl. Soils with extractable Cu and Zn contents above these values showed no significant responses to added Cu and Zn. As would be expected where soils are deficient in both Cu and Zn, in several instances (e.g. Lismore 1,

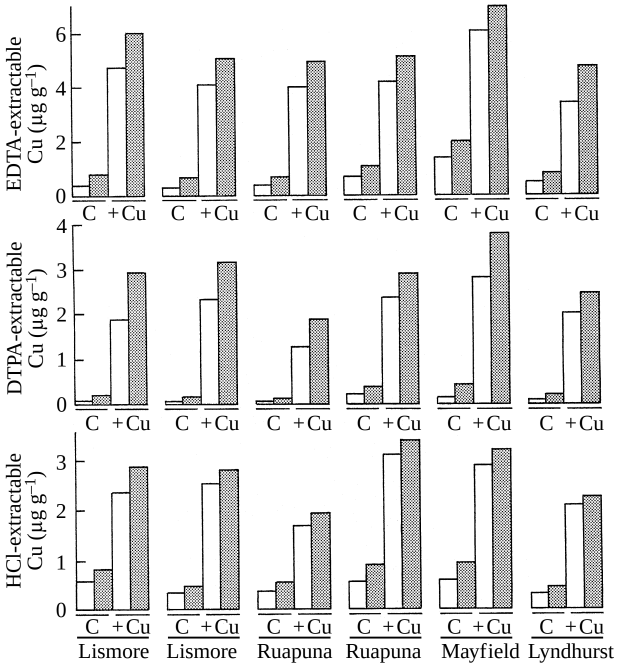


Fig. 3. Concentrations of extractable Cu from field-moist □ and air-dried ▨ samples of control (C) soils and those amended with Cu (+Cu) for six soils that showed a significant plant response to added Cu and/or Zn in a glasshouse experiment. Soil series from which each sample originates is shown.

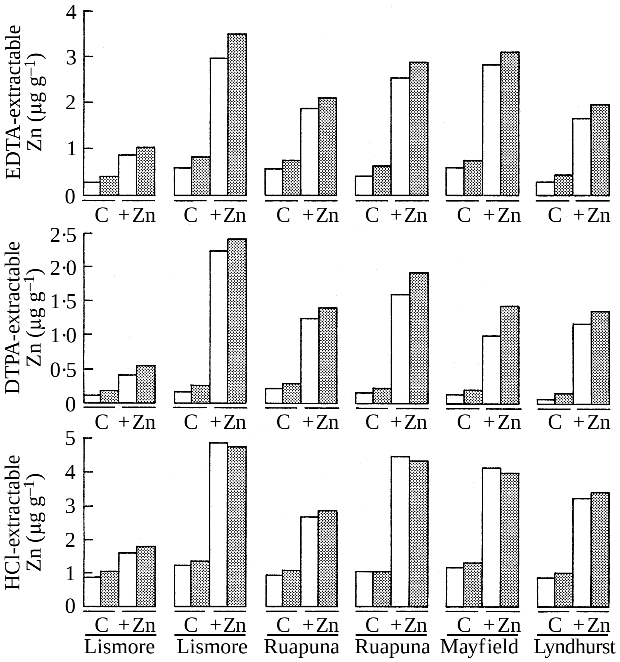


Fig. 4. Concentrations of extractable Zn from field-moist □ and air-dried ▨ samples of control (C) soils and those amended with Zn (+Zn) for six soils that showed a significant plant response to added Cu and/or Zn in a glasshouse experiment. Soil series from which each sample originates is shown.

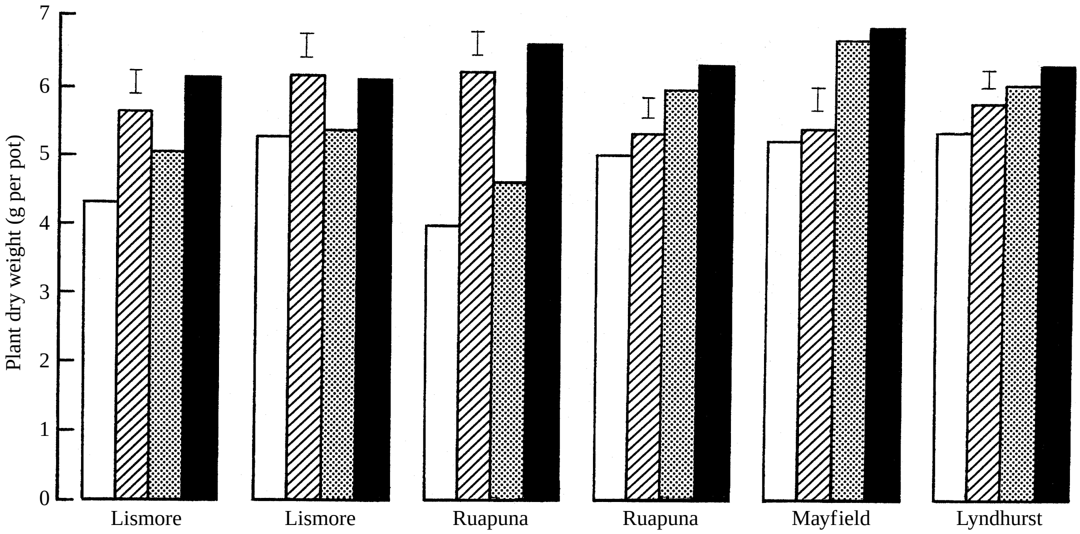


Fig. 5. Dry matter yields of wheat grown in a glasshouse experiment in control □ soils or those amended with the addition of Cu ▨, Zn ░ or Cu + Zn ■ for six soils that showed a significant plant response to added Cu and/or Zn. Soil series from which each sample originates is shown. Vertical bars indicate S.E. (D.F. = 12).

Ruapuna 1 and Lyndhurst soils), DM yields showed a positive interaction when Cu and Zn were added together.

Correlation coefficients between extractable soil Cu and Cu uptake by wheat (where basal Zn had been applied) and extractable soil Zn and Zn uptake by wheat (where basal Cu had been applied) are shown in Table 3. Correlations were closer for extractable Cu *v.* Cu uptake than for extractable Zn *v.* Zn uptake and air-drying did not significantly affect the relationships. The closest relationship observed was between EDTA-extractable Cu and Cu uptake (Table 3).

DISCUSSION

Since the Canterbury Plains are the major area for cereal production in New Zealand, soil fertility is of major economic importance. In order to appreciate the effect of soil series on extractable micronutrient levels, some understanding of the factors influencing soil formation in the area is required. The plains are made up of the terraces, fans and floodplains of four major rivers that run from mountains to the sea (Molloy 1988). The most important factors influencing fertility are the depth of loess mantling the outwash gravels, the age of the soils and the annual rainfall of the locality. The more fertile soils are generally the deeper, younger soils. Soil development increases with increasing age of terraces (from 3000 to 20000 years old) and with increasing rainfall (from 600 to 1000 mm). Previous research in the study area (Haynes & Swift 1984; McLaren *et al.* 1984) has suggested that extractable Cu and Zn contents generally tend to decrease with increasing soil development. Results of this research confirm such findings, since Lismore and Ruapuna soils are shallow soils formed on the high (oldest) terrace 10000–20000 years ago. The deeper Mayfield and Lyndhurst soils are from the intermediate terrace formed 3000–10000 years ago but are in a high rainfall area and are more highly leached and weathered than Templeton, Wakanui and Paparoa soils. For example, above an annual rainfall of 900 mm, Templeton soils grade into Mayfield soils and these had a lower Cu and Zn status than Templeton soils. Deep, fertile soils on the intermediate and youngest (formed in the last 3000 years) terraces are also used for intensive horticultural production and have generally been found to have relatively high amounts of extractable Cu and Zn (Haynes 1990).

The decrease in Cu and Zn extractability with increasing soil development could be caused by leaching losses and/or immobilization of Cu and Zn into non-extractable forms. Williams & McLaren (1982), for instance, showed that even in relatively short periods of time, Cu added to soils can be transformed into forms non-extractable with EDTA. Haynes & Swift (1984), however, found decreases in both total and extractable Cu and Zn with increasing soil development in a sequence of loess soils of the Canterbury Plains. Preliminary results suggest that both factors may be important, since soils from the younger, more fertile, series tend to have higher total Cu and Zn contents and in addition, extractable Cu

Table 3. *Linear correlation coefficients between EDTA-, DTPA- and HCl-extractable Zn and Cu measured on field-moist (FM) and air-dried (AD) soil samples and plant uptake of Zn and Cu**

Micronutrient uptake	EDTA		DTPA		HCl	
	FM	AD	FM	AD	FM	AD
Zn uptake	0·61	0·64	0·66	0·69	0·65	0·64
Cu uptake	0·85	0·86	0·74	0·79	0·79	0·76

* r values for significance at $P < 0.05$, < 0.01 and < 0.001 are 0·59, 0·68 and 0·80 respectively (D.F. = 42).

and Zn represent a higher proportion of the total content than for the older and shallower soil series.

The increase in extractability of Cu and Zn upon air-drying has been found to be reversible upon rewetting (Haynes & Swift 1991). This has been attributed primarily to the disruption of organic-mineral components upon drying, resulting in the increased extractability of micronutrients acting as bridges between clay-organic matter colloids, both those weakly held to mineral surfaces as well as those complexed with organic matter (Haynes & Swift 1985, 1991). The increased extractability of Mn is not readily reversed upon rewetting and may be caused by direct effects related to changes in mineral structure. Drying, for example, may induce a decrease in the stability of Mn oxides, thereby rendering a portion of the Mn soluble (Bartlett & James 1980; Leggett & Argyle 1983).

The increases in micronutrient extractability upon air-drying differed with different elements, different soils and different extractants. Such a finding is not altogether unexpected when one considers the complexity of the 'extractable' fraction of micronutrients in soils. The relative contribution of the various labile forms of micronutrients to the extractable fraction will differ for different elements in the same soil and for the same element in different soils. For example, HCl may preferentially remove ions from mineral surfaces while EDTA may remove the same ions preferentially from organic matter.

It was concluded by Haynes & Swift (1991) that air-drying soils may well decrease the reliability of soil test data for micronutrients, since it would constitute an additional source of variability when correlations between extractable micronutrients and crop response were being attempted. Nonetheless, in this study, similar correlation coefficients between extractable Cu and Cu uptake and extractable Zn and Zn uptake were measured for field-moist and air-dried soils. Differences in the extractability of Cu and Zn between soils were much more substantial than any relatively small differences caused by air-drying the soil. As a consequence, the drying effect did not significantly influence correlations between extractable micronutrients and plant uptake.

The reason why extractable Cu was more closely correlated with Cu uptake than extractable Zn was with Zn uptake is unclear. Nonetheless, in the same general locality McLaren *et al.* (1984) also found that EDTA-extractable Cu was more closely correlated with concentrations of Cu in lucerne than was EDTA-extractable Zn with tissue Zn concentrations. It appears that some factor other than extractable soil Zn is substantially affecting the availability of Zn to crops in these soils. Although soil pH is known to be an important factor influencing micronutrient availability, in this study, multiple regressions in which soil pH data were included with extractable Zn (and Cu) data did not significantly improve correlations with Zn (or Cu) uptake. Since the soils had a narrow pH range (5·9–6·4) this was not, however, unexpected. The better correlation between EDTA-extractable Cu than DTPA- or HCl-extractable Cu and plant uptake may reflect the importance of Cu complexed with labile soil organic matter to Cu availability in these soils. EDTA has been used as an extractant of soil organic matter and presumably it preferentially extracts micronutrients associated with organic matter as well as those bound to mineral components (Haynes & Swift 1983).

Tests for micronutrient cation (e.g. Cu, Zn and Mn) availability based on soil extraction are not in routine use for New Zealand soils. However, based on data from other parts of the world, critical levels for extractable Zn are *c.* 1 $\mu g\ g^{-1}$ for EDTA and HCl and 0·5 $\mu g\ g^{-1}$ for DTPA and for Cu they are *c.* 1 $\mu g\ g^{-1}$ for EDTA and 0·2 $\mu g\ g^{-1}$ for DTPA (Caldwell 1971; Cox & Kamprath 1972; Lindsay & Norvell 1978; Kabata-Pendias & Pendias 1984). Using these guidelines and data for air-dried soils, the majority of the sites on the strongly developed soils (Lismore, Ruapuna, Mayfield and Lyndhurst) are potentially deficient in both Cu and Zn. By contrast, all of the sites surveyed had DTPA-extractable Mn levels well above the approximate critical level of 1 $\mu g\ g^{-1}$ (Lindsay & Norvell 1978).

Overall < 40 % of the fields surveyed under winter wheat had EDTA-extractable Cu and Zn contents < 1 $\mu g\ g^{-1}$. By contrast, in a survey of 182 sites on the Canterbury Plains under lucerne, McLaren *et al.*

(1984) found that 76 and 85% respectively of sites had EDTA-Zn and EDTA-Cu contents < 1 μg g^{-1}. The reason for this is that stands of deep-rooting lucerne tend to be concentrated on shallow, drought-prone soils (e.g. Lismore and Ruapuna soils) where concentrations of extractable Cu and Zn are characteristically low. On the other hand, a considerable proportion of the winter wheat crop is grown on the deeper, more fertile, soils which have an inherently high Cu and Zn status.

The glasshouse experiment confirmed that a significant proportion of the soils were deficient in Cu and Zn. As noted previously, responses to added Cu were recorded in all soils with extractable Cu concentrations $< 1{\cdot}1$ μg g^{-1} EDTA, 0·4 μg g^{-1} DTPA and 0·9 μg g^{-1} HCl. Responses to added Zn occurred in soils with extractable Zn contents $< 0{\cdot}8$ μg g^{-1} EDTA, 0·25 μg g^{-1} DTPA and 1·4 μg g^{-1} HCl. It is notable that these concentrations are very similar to those quoted above for critical soil test values recorded by other workers. Nonetheless, neither Cu nor Zn deficiency symptoms are generally observed in winter wheat in the study area. Unpublished trials in the 1970s found no significant responses of winter wheat to applied fertilizer Cu (R. C. Stephen, personal communication). The long growing period (8 months) probably enables the crop to extract sufficient micronutrients from the soil to meet its nutritional requirements. In comparison, under glasshouse conditions, the crop grows extremely rapidly (over only 2 or 3 months) and as a result, the nutrient-supplying capacity of the soil is placed under stress and Cu and Zn deficiencies are induced. Cu and Zn deficiencies are most likely to be encountered under field conditions for rapidly growing crops with a high nutrient demand, especially where soil pH is high. Irrigated spring wheat or barley, particularly where high rates of N have been applied (e.g. 150–200 kg N ha^{-1}) could well encounter such deficiencies. Certainly, on limed fields where applications have been doubled-up in a strip down the field (producing a strip of high soil pH), Zn deficiency symptoms have been noted (Haynes 1994). There is a need to investigate whether field responses to applied Cu and Zn are measurable on the more strongly developed soils of the Canterbury Plains. If economic responses are recorded then the use of a routine soil test procedure to predict the likelihood of such a response should be practicable.

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