

## Agronomic effectiveness of selected fertilisers in supplying copper to perennial ryegrass

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### Abstract

A glasshouse trial using perennial ryegrass as a test plant was conducted with granular fertilisers to evaluate the effectiveness of three CuSO<sub>4</sub>-based fertilisers and a Cu(OH)<sub>2</sub>-based fertiliser. Two soils, contrasting in soil organic matter content, were chosen for the study. The Cu(OH)<sub>2</sub>-based fertiliser was less effective than the CuSO<sub>4</sub>-based fertilisers in supplying Cu to ryegrass. In general, among the three CuSO<sub>4</sub>-based fertilisers, Ca-caseinate-CuSO<sub>4</sub> resulted in the highest Cu uptake by ryegrass grown in both soils. It is recommended that field trials be carried out to determine the true agronomic value of this product.

### Key words

Copper fertiliser, copper uptake, soil solution, perennial ryegrass

### Introduction

Copper deficiency in grazing animals is widespread in New Zealand (Liao, 2000), costing the farming industry several million dollars in animal remedies each year. Overcoming the problem with Cu fertilisers has met with mixed success, with generally low uptake of Cu by pasture plants. The currently used CuSO<sub>4</sub> fertiliser is highly corrosive to fertiliser spreader equipment. It was believed that coating of CuSO<sub>4</sub> with organic materials should reduce the corrosiveness of this fertiliser, and produce a granular Cu fertiliser that could be mixed easily and uniformly with physical blends of phosphatic fertilisers (Liao, 2000). A Ca-caseinate-CuSO<sub>4</sub> granule fertiliser has been developed with the aim of both increasing Cu uptake by pastures and reducing the corrosiveness of the fertiliser to top-dressing plane airframes.

The objective of the present study was to compare the agronomic effectiveness of the granular Ca-caseinate-CuSO<sub>4</sub> with that of Cu(OH)<sub>2</sub>-based fertiliser (provided by Ravensdown Fertiliser Coop Ltd) and the currently used CuSO<sub>4</sub>.5H<sub>2</sub>O fertiliser on plant Cu uptake in supplying to perennial ryegrass (*Lolium perenne* cv. Nui).

### Materials and methods

A 4×4×2 factorial design with three replicates was used. There were four copper fertilisers: Ca-caseinate-CuSO<sub>4</sub> (granule size 1.4-2 mm), Cu(OH)<sub>2</sub>-based product (granule size 1.4-2 mm), CuSO<sub>4</sub>.5H<sub>2</sub>O (granule size 1.4-2 mm), and CuSO<sub>4</sub>.5H<sub>2</sub>O (fine powder <0.5 mm); four copper application rates expressed as kg Cu ha<sup>-1</sup> based on topsoil weight: 0 (control), 12.5, 25 and 50 kg Cu ha<sup>-1</sup>; two soils: Ashhurst soil, Wairoa soil. Samples of Ashhurst and Wairoa soils were obtained from a 0-15 cm soil depth under permanent pastures. Both soils had received very little Cu fertiliser in the past.

Subsamples of 400 g air-dried soil were weighed into pots. Fertilisers were then evenly applied at the soil surface. The fertilisers were covered with a further 100 g soil. The moisture content of the soil was maintained at 80% of "pot field capacity". The germinated ryegrass seeds were sown and seedlings were thinned to 15 plants per pot. The pots were kept inside a glasshouse where the temperature was partly controlled (heated at 13 °C and ventilated at 25 °C). A nutrient solution (800 mg NH<sub>4</sub>NO<sub>3</sub>, 150 mg L<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub>, 150 mg L<sup>-1</sup> K<sub>2</sub>HPO<sub>4</sub>, 100 mg L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub>, 100 mg L<sup>-1</sup> MgCl<sub>2</sub>.6H<sub>2</sub>O, 25 mg CaCO<sub>3</sub>, pH 5.5) was added twice a week. Thirty days after thinning of seedlings, the plants were cut 2 cm above the soil surface, dried for 48 hours at 60°C in oven and weighed. A total of 6 harvests at 30-day intervals were

made. Copper concentrations in nitric acid digests of plant shoots were measured using flame atomic adsorption spectrometry (FAAS).

At the final harvest, one set of pots (one replicate) was sliced horizontally through the fertilised zone and any visible fertiliser granules were recovered. The dry weights of the granules were recorded. Each fertiliser granule was weighed and dissolved in 5 mL 2M HCl overnight, Cu concentration of the solution was determined using FAAS. The remaining replicates of each treatment were used for soil solution studies. Soil solutions were extracted from moist soils (80% pot field capacity) by centrifugation at 10 000 rpm (12 000 RCF) in a refrigerated centrifuge at 5°C for 30 minutes (Elkhatib et al. 1987).

Soil solution pH and electrical conductivity (EC) were measured immediately using a portion of the soil solution, and the remainder of the solution was filtered through 0.22-µm millipore filters. Total dissolved Cu concentrations in the soil solutions were measured using graphite furnace atomic adsorption spectrometry. The free Cu<sup>2+</sup> concentrations were measured using an Orion 9629BN Ionplus™ Cupric Electrode. The concentrations in solution were transformed into activities using the Davies equation (Stumm and Morgan, 1981). The proportion of total soluble Cu present as Cu<sup>2+</sup> ions varies with solution pH and provides a 'signature' for the Cu-organic complex system.

## Results and discussion

### Cu fertiliser solubility

The low solubility of Cu(OH)<sub>2</sub>-based products was illustrated by the recovery of 67% of the Cu within visible granules after more than 7 months. For CuSO<sub>4</sub>-based fertilisers, however, there were not visible granules recovered. These further confirmed the low solubility of Cu(OH)<sub>2</sub>-based product.

### Cumulative shoot Cu uptake

Application of CuSO<sub>4</sub>-based fertilisers resulted in significantly higher cumulative shoot Cu uptake compared to Cu(OH)<sub>2</sub>-based fertiliser. Among the three CuSO<sub>4</sub>-based fertilisers, Ca-caseinate-CuSO<sub>4</sub> was significantly more effectiveness than the others were (Fig. 1). Liao et al. (1999) found a similar result for chicory plants grown in Manawatu silt loam. The lower Cu uptake from finely divided CuSO<sub>4</sub> fertiliser may be due to higher Cu fixation in the soils. The cumulative ryegrass shoot Cu uptake significantly increased with the increases of Cu applications (Fig. 1). At a given Cu application rate, the Ca-caseinate-CuSO<sub>4</sub> product resulted in the highest cumulative Cu uptake, and Cu(OH)<sub>2</sub>-based Cu fertilisers resulted in a significant lower cumulative Cu uptake than did the other three Cu fertilisers (Fig. 1). When grown in Ashhurst soil, Ca-caseinate-CuSO<sub>4</sub> fertiliser resulted in a significantly higher Cu uptake than CuSO<sub>4</sub>.5H<sub>2</sub>O fertilisers (powder) did (Fig. 1).

### Recovery of fertiliser Cu

An index for the apparent recovery of applied fertiliser Cu ( $R_f$ ) was calculated for each fertiliser form and application rate:  $R_f = (C_t - C_0)/C_a * 100$ , where  $C_t$  is the cumulative shoot Cu uptake from a Cu fertilised treatment;  $C_0$  is the cumulative shoot Cu uptake from the control treatment;  $C_a$  is the rate Cu applied.

The apparent recovery of Cu from the CuSO<sub>4</sub>-based fertilisers was significantly higher compared to the Cu(OH)<sub>2</sub>-based product (Fig. 2). This is due to the lower rate of dissolution of the Cu(OH)<sub>2</sub>-based fertiliser. In general, there were no significant differences among CuSO<sub>4</sub>.5H<sub>2</sub>O (both granules and powder) and Ca-caseinate-CuSO<sub>4</sub>.5H<sub>2</sub>O granule fertiliser except when applied at 12.5 kg Cu ha<sup>-1</sup> to Ashhurst soil (Fig. 2). The apparent recovery of fertiliser Cu decreased with increasing Cu application when ryegrass was grown in both Ashhurst and Wairoa soils (Fig. 2). The apparent recovery of fertiliser Cu from the Ashhurst soil was significantly higher than that from the Wairoa soil (Fig. 2). The results showed that the percentage Cu recovery ranges between 0.15 - 0.94% in Ashhurst soil and 0.10- 0.41% in Wairoa soil. The lower recovery in Wairoa soil is probably due to the higher organic matter content of this soil (8.2% organic carbon in Wairoa soil compared to 4.1% organic carbon in Ashhurst soil).

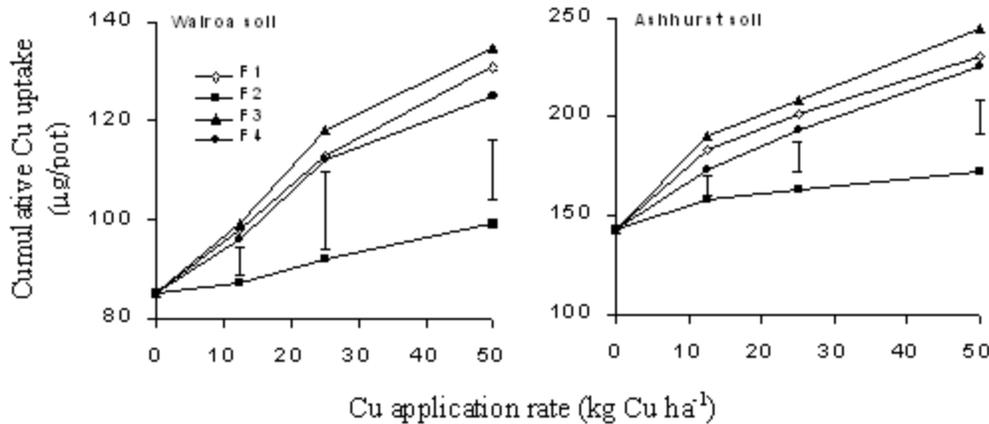


Fig. 1. Effect of Cu source and application rate on cumulative shoot Cu uptake, over 6 harvests, of ryegrass grown in Wairoa soil and Ashhurst soil. F1:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  chips (1.4-2 mm); F2:  $\text{Cu}(\text{OH})_2$ -based product (1.4-2 mm); F3: Ca-caseinate- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (1.4-2 mm); F4:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  powder (<0.5 mm). Vertical bars represent LSD at  $P = 0.05$ . Copper application rates were expressed as  $\text{kg Cu ha}^{-1}$  based on topsoil weight.

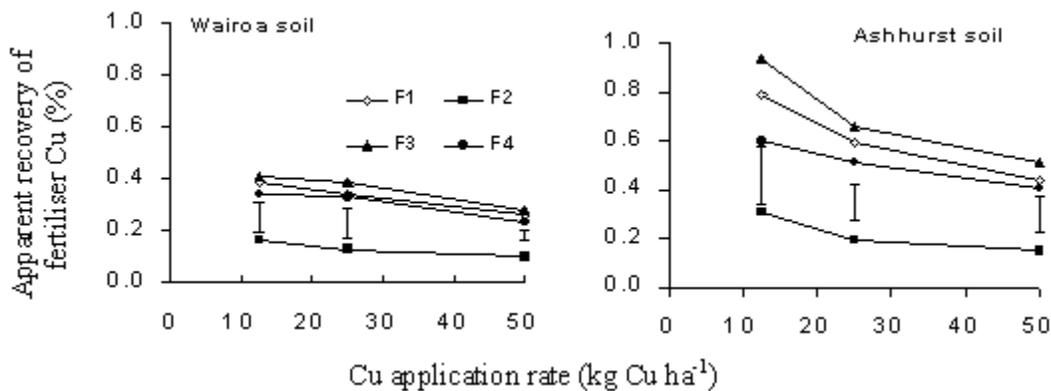


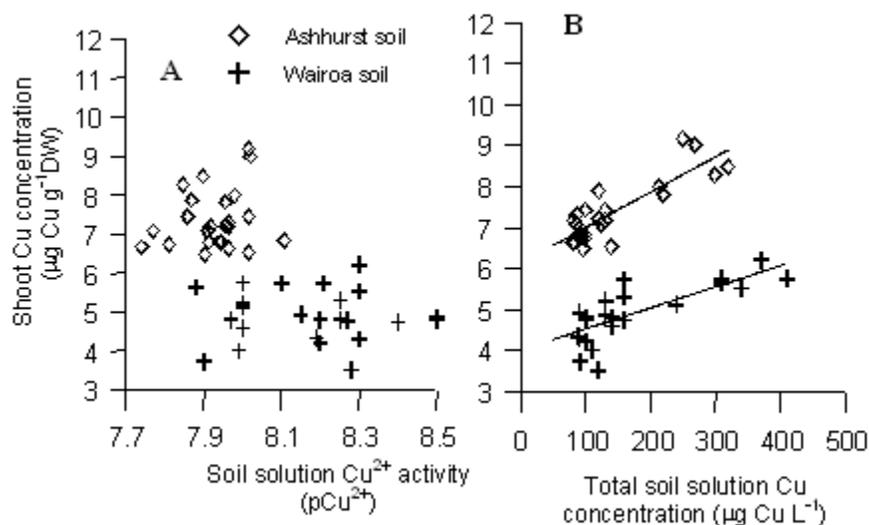
Fig. 2. Effect of Cu sources and rates on the apparent recovery of Cu from fertilisers, over 6 harvests, of ryegrass grown in Ashhurst soil and Wairoa soil. F1:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  chips (1.4-2 mm); F2:  $\text{Cu}(\text{OH})_2$ -based product (1.4-2 mm); F3: Ca-caseinate- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (1.4-2 mm); F4:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  powder (<0.5 mm). Vertical bars represent LSD at  $P = 0.05$ . Copper application rates were expressed as  $\text{kg Cu ha}^{-1}$  based on topsoil weight.

#### Relationship between soil solution Cu pools and shoot Cu concentration

Copper is generally considered to be taken up by plant roots in the form of free  $\text{Cu}^{2+}$  and therefore one would expect a good relationship between  $\text{Cu}^{2+}$  concentration in soil solution (expressed as  $\text{pCu}^{2+}$ ) and Cu concentration in plants. The results from our pot trial, however, showed that there was no such relationship for either the Wairoa soil or the Ashhurst soil (Fig. 3A). Instead, significant linear relationships were found between total soil solution Cu and shoot Cu concentration at the last harvest within each soil (Wairoa soil:  $y = 0.0053x + 3.963$ ,  $r^2 = 0.590$ ,  $P < 0.001$ ; Ashhurst soil:  $y = 0.00875x + 6.108$ ,  $r^2 = 0.734$ ,  $P < 0.001$ ) (Fig. 3B). A single relationship, however, cannot be derived for both soils (Fig. 3B). These results indicate that the plant Cu uptake patterns from Wairoa soil and Ashhurst soil are different.

Sauv? et al. (1996) hypothesised that copper bioavailability in soils is controlled by the free  $\text{Cu}^{2+}$  activity in the soil solution and the soil's capacity to maintain or buffer that  $\text{Cu}^{2+}$  activity. At constant  $\text{Cu}^{2+}$  activity (but variable total Cu), Checkai et al. (1987) suggested that the enhanced Cu uptake is due to chelates to

enhance diffusion of Cu across the undisturbed layer of water surrounding the roots, rather than to uptake of some Cu as the intact Cu chelate. Therefore, the importance of maintaining high total concentrations near the plant root surfaces should not be disregarded because both ionic and complexed species contribute to diffusive transport, which may be the major factor limiting the uptake rate in natural soil systems (Checkai, et al., 1987). The positive relationships (Fig. 2A), between the total soil solution Cu concentrations and ryegrass shoot Cu concentration are consistent with the agreement that diffusive flux of soluble Cu to roots is the limiting factor for Cu uptake in the Wairoa soil and Ashhurst soil.



**Fig. 3. The lack of a relationship between the soil solution Cu<sup>2+</sup> activity and shoot Cu concentrations (A), and the linear relationships between total soil solution Cu concentration and shoot Cu concentrations (B) at the last harvest in both Ashhurst soil and Wairoa soil.**

### Conclusions and future studies

Granulated Cu(OH)<sub>2</sub>-based fertiliser was less effective than CuSO<sub>4</sub>-based fertilisers in supplying Cu to ryegrass. This is due to the low solubility of the Cu(OH)<sub>2</sub>-based fertiliser. Addition of casein to granulated CuSO<sub>4</sub> can improve Cu availability to ryegrass, but the Cu recovery by plants remains soil type dependent. Increased Cu uptake by ryegrass fertilised with Ca-caseinate-CuSO<sub>4</sub> fertiliser is likely caused by: (1) lower dissolution rate compared to CuSO<sub>4</sub>·5H<sub>2</sub>O fertiliser; (2) decomposition of caseinate stimulating soil microbial activity, and then facilitating Cu-SOM moving to the root surface.

The combination of low corrosiveness and improved agronomic effectiveness of the caseinate-CuSO<sub>4</sub> product suggests that this material has the potential to use in Cu top-dressing of pastures. It is recommended that field trials be carried out to determine the true agronomic value of this product.

### References

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