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**MECHANISMS OF COPPER UPTAKE
AND TRANSPORT IN PLANTS**

**A thesis presented in partial fulfilment of the requirements of the
degree of Doctor of Philosophy in Soil Science at
Massey University, New Zealand**

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ABSTRACT

The Cu concentration in plants varies considerably between species. This suggests different abilities to either absorb Cu from soils or translocate Cu from root to shoot. The main objective of the thesis was to provide a fuller understanding of the mechanisms of Cu uptake and transport in plants which may lead to the development the strategies to improve Cu uptake by pasture crops.

Glasshouse experiments with the Cu hyperaccumulator *Haumaniastrum katangense* showed that Cu hyperaccumulation in shoots was not found. It was concluded that *H. katangense* plants tested in these experiments were Cu tolerant rather than having hyperaccumulator status. The mechanism of high tolerance to Cu could be due to the restriction of Cu transport from roots to shoots.

Nutrient solution culture experiments with the Ni hyperaccumulator plants *Alyssum bertolonii* and *Berkheya coddii* showed that co-hyperaccumulation of Cu and Ni did not exist. *Alyssum bertolonii* was not a Cu-tolerant plant, whereas *B. coddii* exhibited a much greater degree of tolerance to this metal, and the tolerance of *B. coddii* to Cu was not at the expense of Ni uptake. It was concluded that *B. coddii* should be considered as a possible plant for phytoremediation of soils contaminated with both Cu and Ni and it is recommended that field trials be carried out to establish this potential.

NFT nutrient solution culture experiments showed that a large proportion of total Cu uptake by chicory and tomato plants was retained by roots except when plants were grown in the basal nutrient solution (0.05 mg Cu L⁻¹). Copper retention by roots, limited Cu translocation to xylem and shoots. Large differences between measured and predicted Cu accumulation by shoots of tomato and chicory suggested that some xylem-transported Cu is recirculated to roots via the phloem.

A Cu speciation study showed that more than 99.7% of total Cu in tomato and chicory xylem sap was in a bound form. Increased Cu concentrations in the rooting media induced selective synthesis of certain amino acids which include NA, His, Asn and Gln, all of which have high stability constants with Cu.

Nicotianamine and His have the highest binding constants for Cu and the concentrations of NA and His in chicory and tomato xylem saps can account for all the bound Cu carried in the sap.

Copper recirculation within plants was demonstrated by an experiment with hydroponically grown tomato plants in a split-root system. Significant amounts of Cu were translocated from roots bathed in a solution of high Cu concentration to another half root system exposed to low Cu. Shoot Cu concentrations were positively correlated to plant water use ($\text{mL g}^{-1} \text{DM}$). A Cu recirculation model was suggested.

Efforts have been made to develop the strategies to improve Cu uptake by pastures. The initial uptake of Cu from CuSO_4 -fertilised soil can be increased by 10-21 % by addition of His and casein. Casein was generally more effective at increasing plant Cu uptake than His and other amino acids.

The $\text{Cu}(\text{OH})_2$ -based fertiliser was less effective than the CuSO_4 -based fertilisers in supplying Cu to ryegrass grown in pots of Ashhurst stony silt loam and Wairoa pumice soil. In general, among the three CuSO_4 fertilisers, Ca-caseinate- CuSO_4 resulted in higher Cu uptake by ryegrass grown in both soils.

The factors constraining Cu uptake by ryegrass plants from Cu-fertilised soils were elucidated. Linear relationships between ryegrass Cu uptake and total soil solution Cu concentration were soil type dependent, despite each soil having similar soil solution Cu concentrations. Between 98.5-99.5% of the soil solution Cu was in complexed forms. No relationship between the Cu^{2+} concentration in soil solution (expressed as pCu^{2+}) and Cu concentration in plants was found. Free Cu^{2+} concentrations in soil solution were sensitive to pH change. The extent of the increase in free Cu^{2+} concentration per unit decrease in pH was dependent on soil type. It is suggested that the rate of Cu uptake by plants is likely to be dependent on both the concentration of organically complexed Cu in the soil solution and the stability of this complex to pH change.

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LIST OF ABBREVIATIONS

3 Mh	3-methylhistidine
Aaba	α -aminobutyric acid
AAD	α -aminoadipic acid
Ala	alanine
Arg	arginine
Asn	asparagine
Asp	aspartic acid
β -Aib	β -aminoisobutyric acid
Carn	carosine
Cyst	cystathionine
DM	dry matter
EDTA	ethylene-diaminetetraacetic acid
FAAS	flame atomic absorption spectrometry
Gaba	γ -aminobutyric acid
GFAAS	graphite furnace atomic absorption spectrometry
Gln	glutamine
Glu	glutamic acid
His	histidine
Hyp	hydroxyproline
Ile	isoleucine
Leu	leucine
Lys	lysine
Met	methionine
NA	nicotianamine
NFT	nutrient film technique system
Orn	ornithine
Phe	phenylalanine
PITC	phenylisothiocyanate
Pro	proline

RP-HPLC	reversed phase high performance liquid chromatography
Ser	serine
Thr	threonine
Tyr	tyrosine
Val	valine
WUE	plant water use efficiency ($\text{g DM L}^{-1} \text{H}_2\text{O}$)