# Reactions of Fluid and Granular Copper and Molybdenum-Enriched Compound Fertilisers in Acidic and Alkaline Soils

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# Areas of the world prone to micronutrient deficiency

**Combined Global Distribution of the Main Types of Soils Associated with Zinc Deficiency Derived from the World Reference Base for Soil Resources Atlas by Bridges, Batjes and Nachtergaele (1998)**

Note: Not all the areas of soil shown on this map have conditions suitable for crop production (e.g. desert areas)

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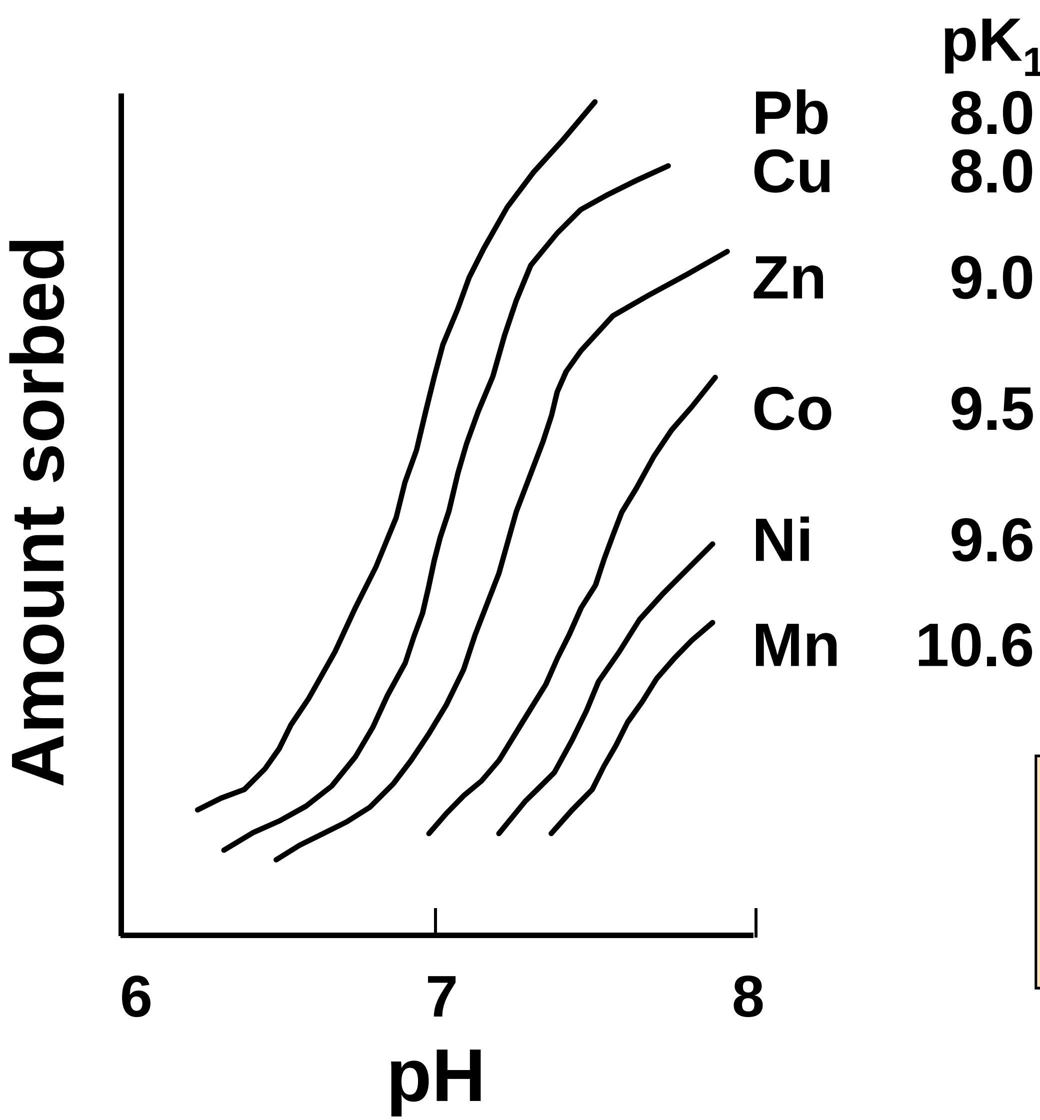
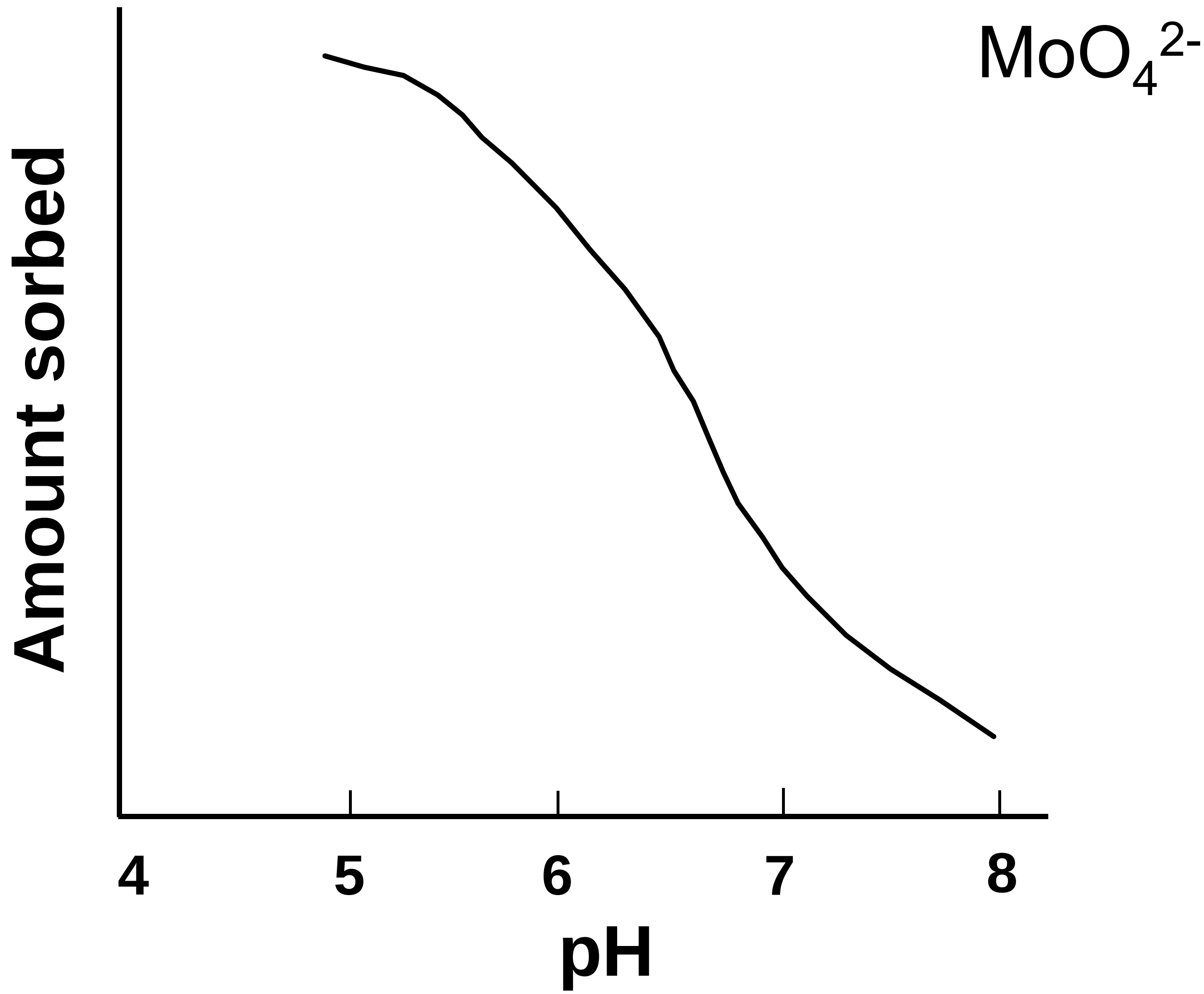
# Reactions of micronutrient cations in soils




- Soils are predominantly negatively charged, and sorb trace elements very strongly, especially in alkaline soils

$$M^{2+} + H_2O = MOH^{+} + H^{+}$$

# Reactions of micronutrient anions in soils



# Reactions of micronutrients in soils

- Trace elements also form very insoluble precipitates in soils, especially with phosphate, carbonate and hydroxide ions.  This is a particular problem in phosphatic fertiliser formulations in alkaline soils, where P concentrations in the fertilised band are high.
- Copper and molybdenum can form a range of insoluble compounds in soils or in the vicinity of fertiliser bands

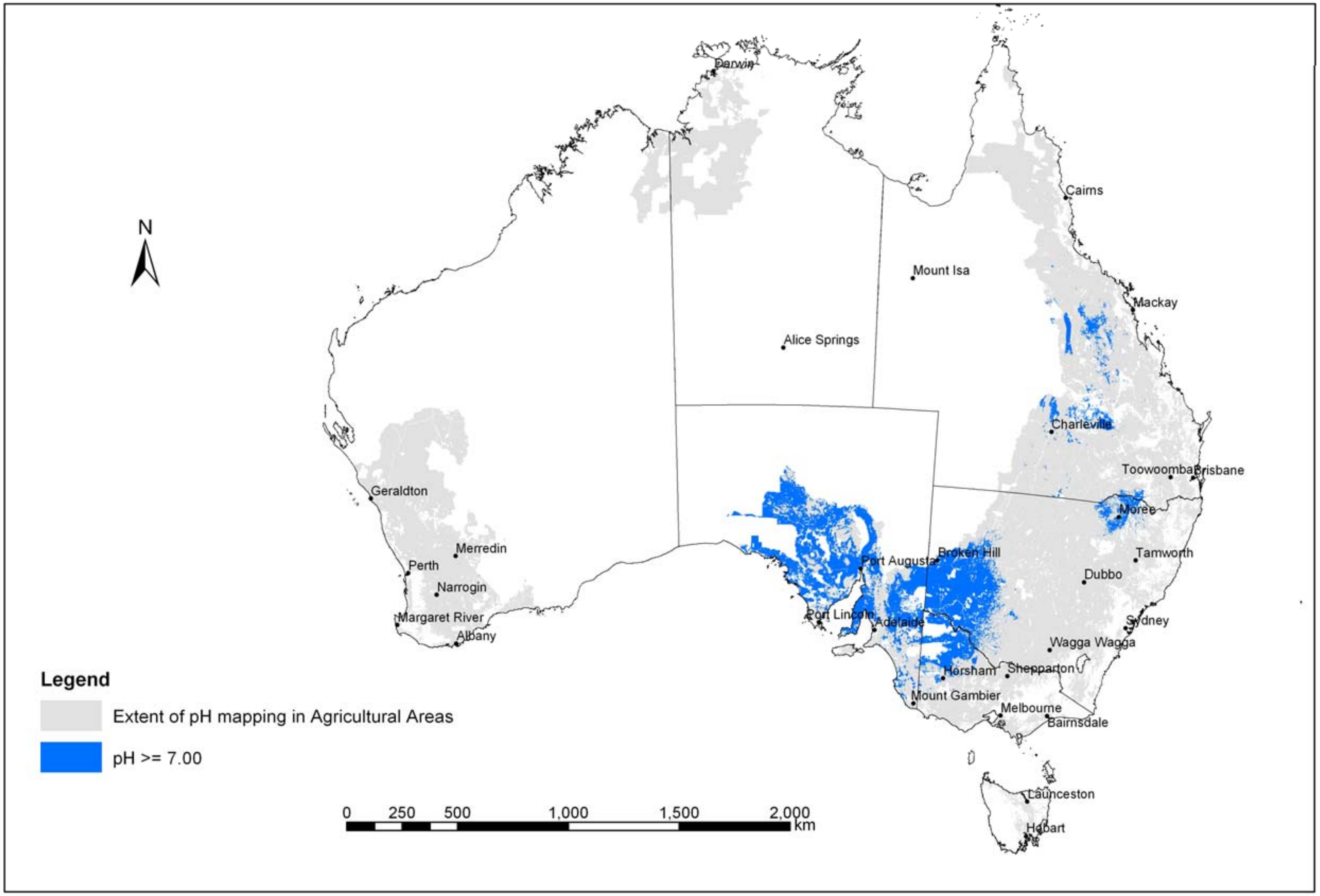
| Compound | p$K_{sp}$ |
|---|---|
| $CaCO_3$ | $1.0 \times 10^{-8.3}$ |
| $Cu(OH)_2$ | $1.6 \times 10^{-19}$ |
| $CuCO_3$ | $1.4 \times 10^{-10}$ |
| $Cu_3(PO_4)_2$ | $1.4 \times 10^{-37}$ |
| $CaMoO_4$ | $1.0 \times 10^{-7.9}$ |

# Background

- Copper is an essential element for crop growth in many soils in Australia – several areas have reported significant responses to applied Cu, in both acidic and alkaline soils

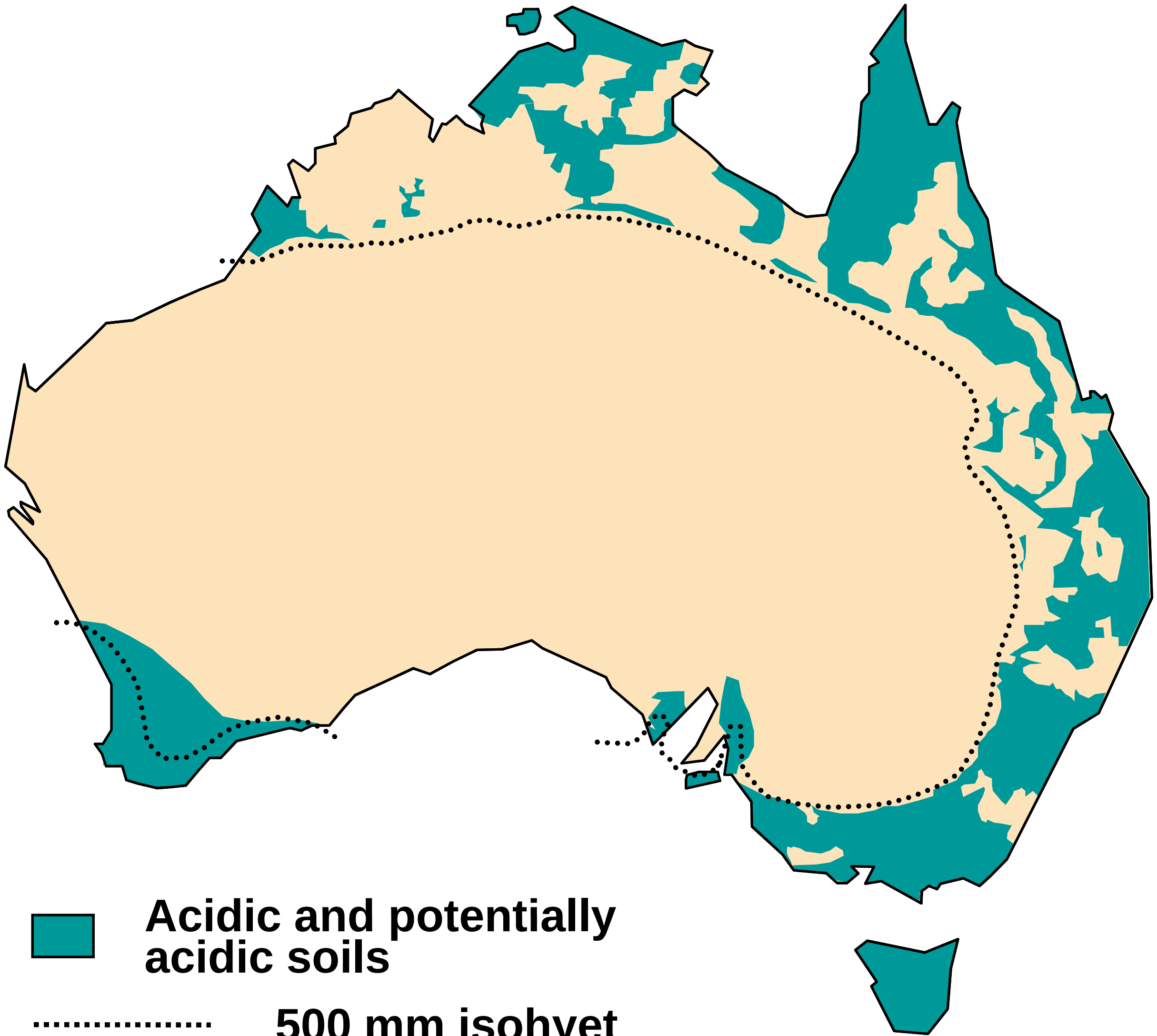
- Molybdenum plays an important role in many biochemical reactions in soils and plants – reduction of nitrate, nitrogen fixation and oxidase reactions. Deficiency is widespread in acidic soils

# Alkaline soils in Australia




Calcareous soils

# Acidic soils in Australia



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# Acidic soils

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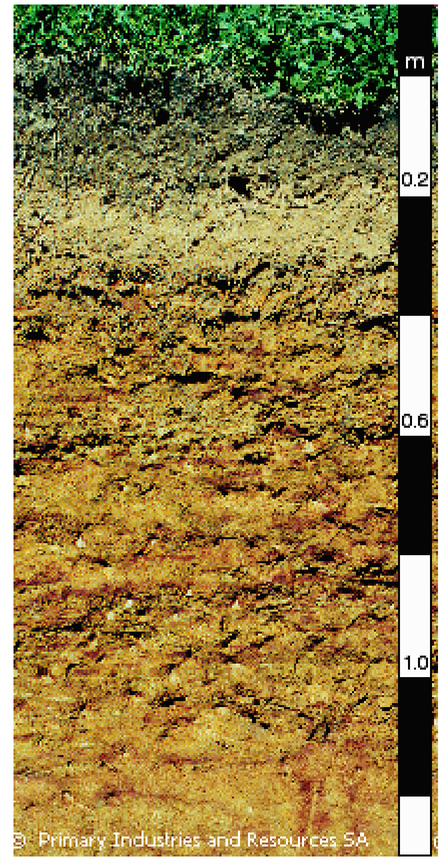
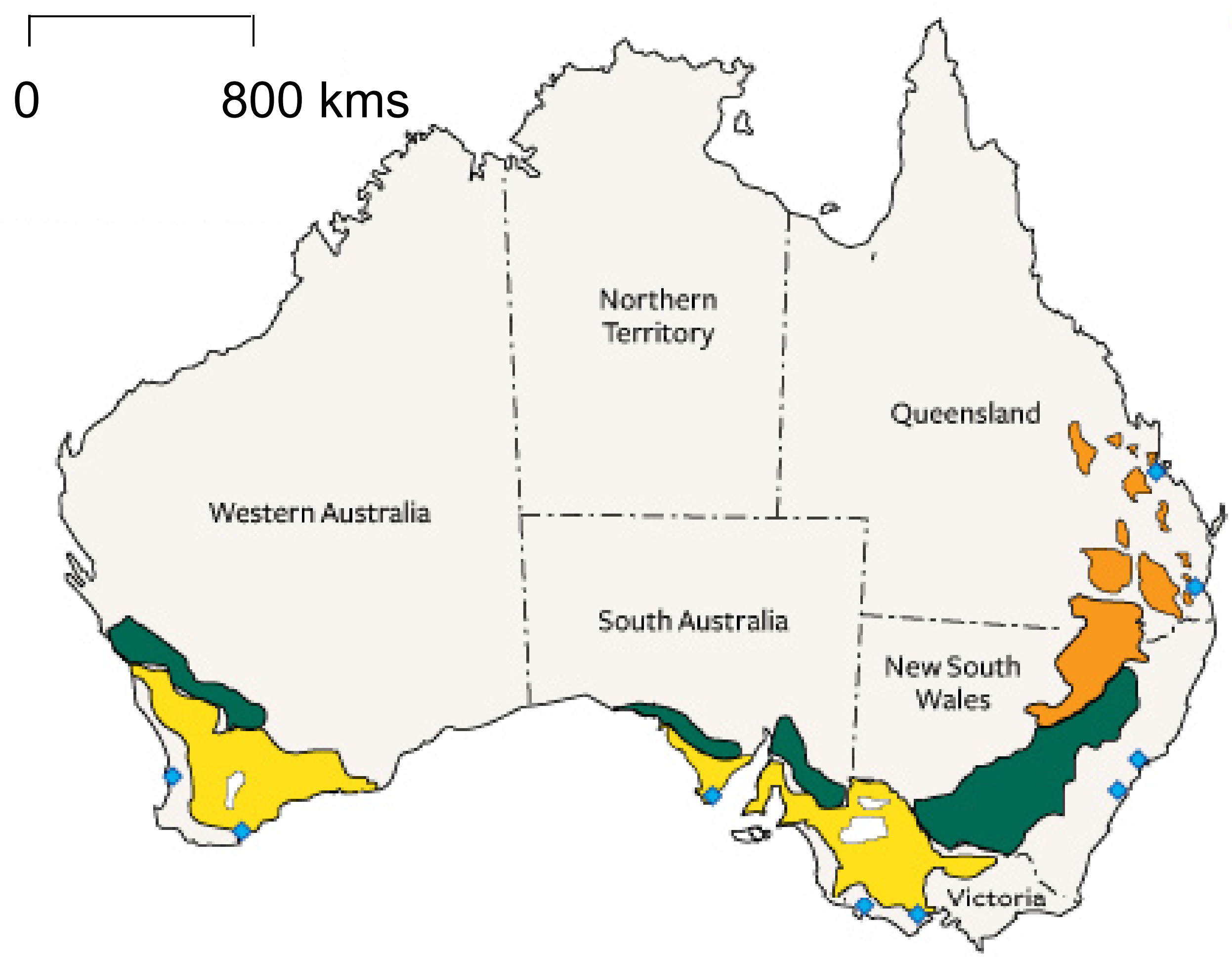


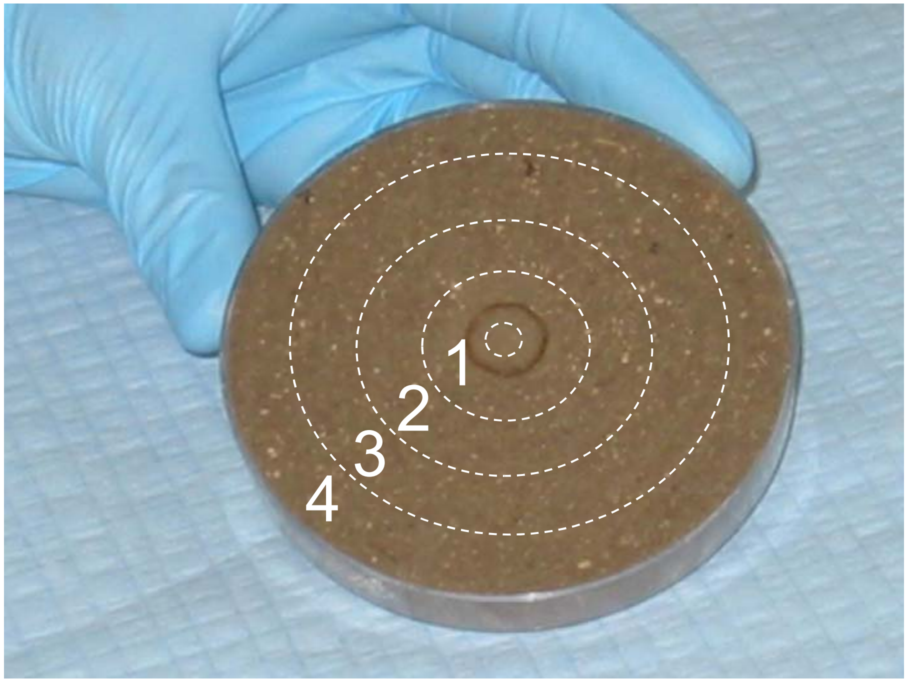
# Broadacre cropping soils in Australia



# Methods

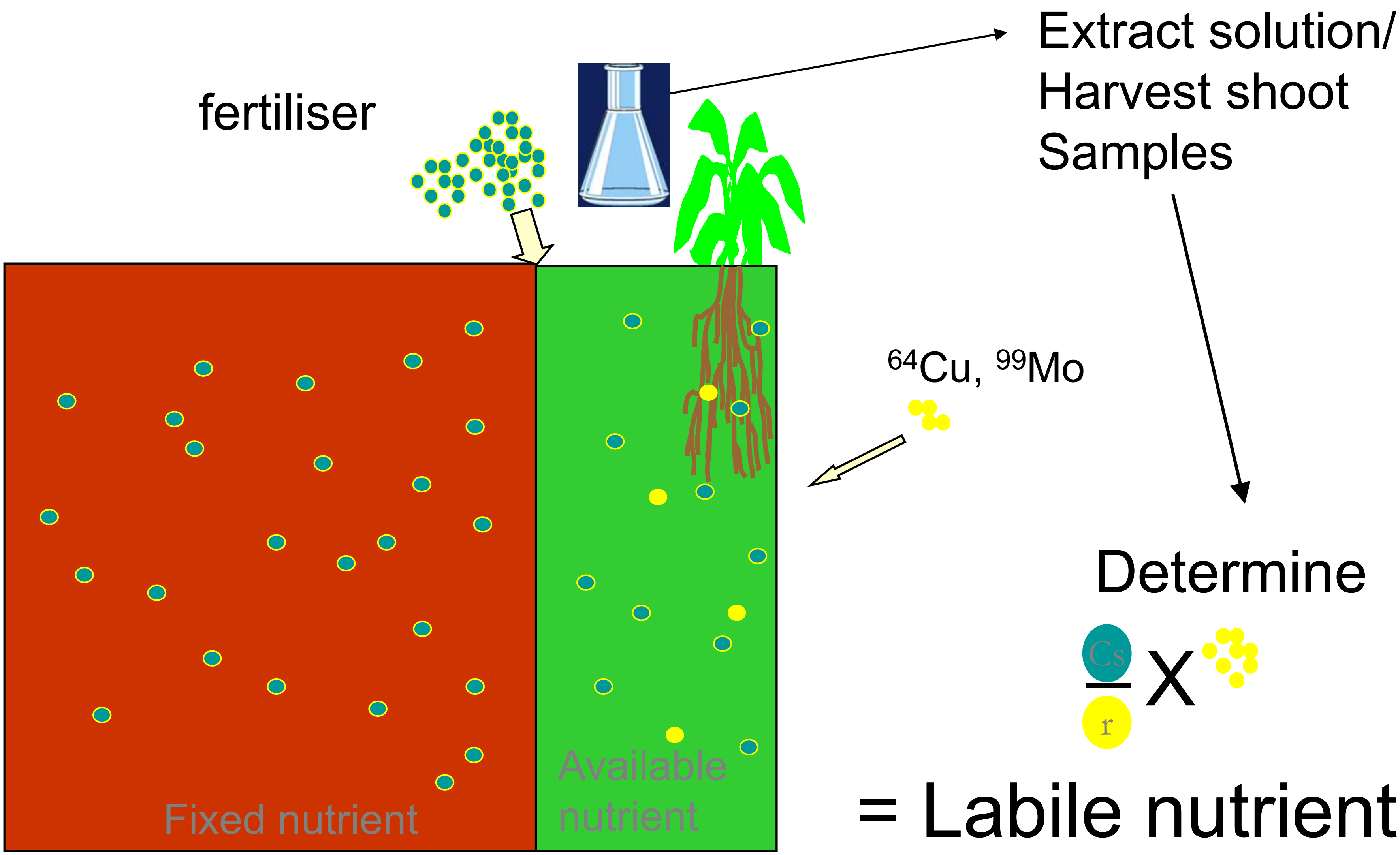
- Soils (3) were
  Alkaline calcareous (Warramboo, SA)
  Neutral sandy (Eneabba, WA)
  Acidic loamy sand (Kambellup, WA)
- Fertilisers used were
  Granular MAP+0.6%Cu and 0.04%Mo
  Fluid MAP+Cu+Mo (equiv)
  APP+Cu+Mo (equiv)
- Soils placed in Petri dishes at field capacity and fertilisers added at centre of dish
- Soils incubated for 5 weeks at field capacity

# Isotopic assessment of fertiliser efficiency

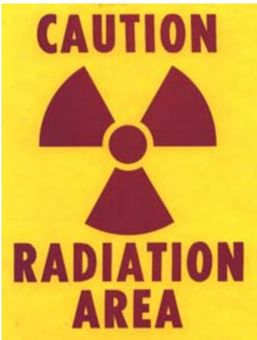



- Incubate granule in soil
- Measure nutrient release with time
- Distance of diffusion
- Using isotopes, measure fertiliser fixation or partitioning in the soil solution or exchangeable phase.

# E/L value to measure lability



# Use of radioactive $^{64}Cu$

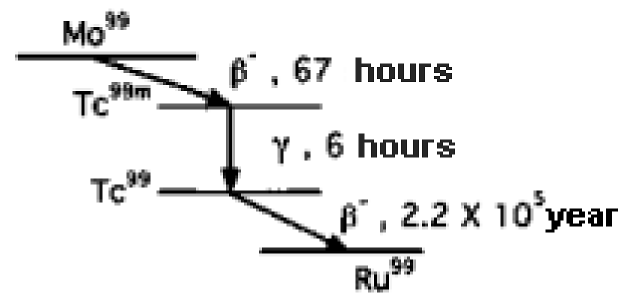



Half life of only 12.7 hours!

# Use of radioactive $^{99}$Mo

66-hour half life
γ-emitter decays to $^{99m}$Tc (6h half life)

Measure $^{99m}$Tc by γ-spectroscopy




Do soil extractions and wait 3 days, then measure radioactivity

# Synchrotron based x-ray analysis

**Advanced Photon Source, Argonne, IL**

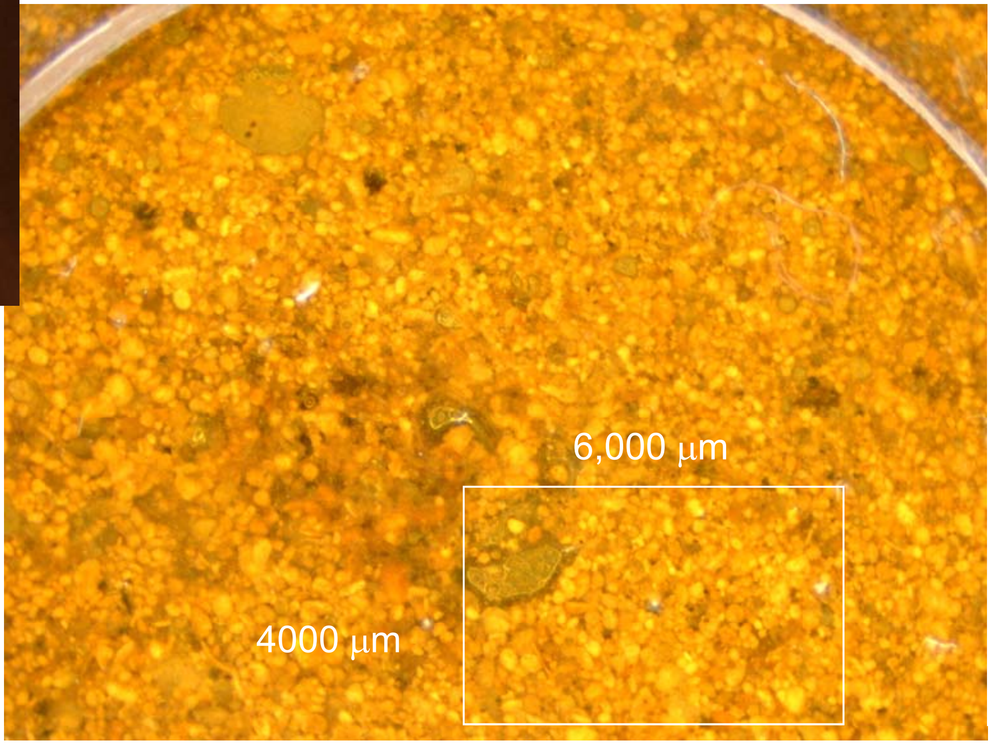
**µ-XRF, and -XANES collected *in situ* at GSE CARS, 13-BM, Advanced Photon Source) Argonne, IL, USA**

**Bulk k-edge Zn and Mn XANES/EXAFS collected at Australian National Beamline, Photon Factory Tsukuba, Japan**

# Methods

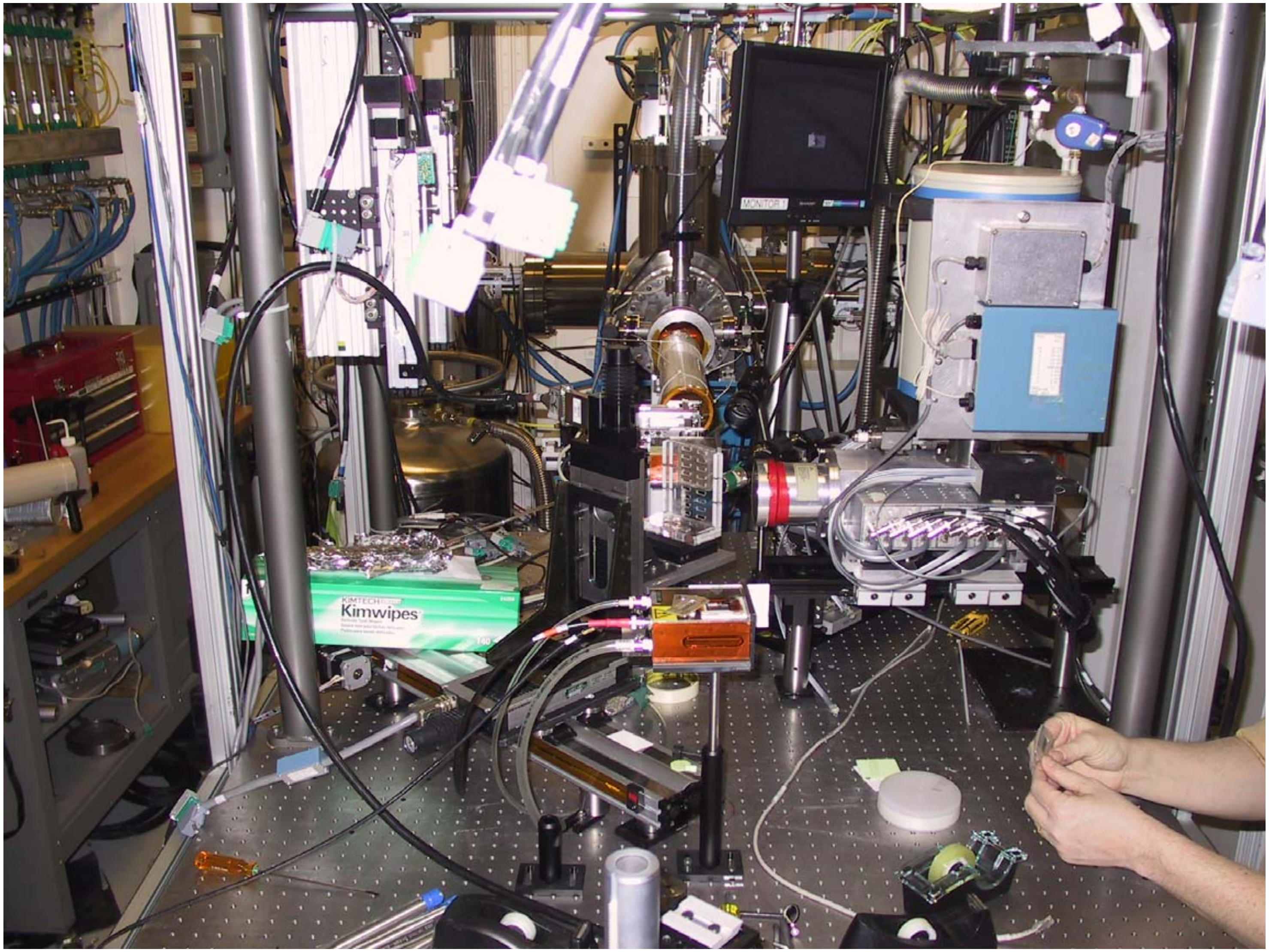
Experimental "Cell"

A calcareous soil treated with granular- and liquid -Cu and -Mo and incubated for 5 weeks

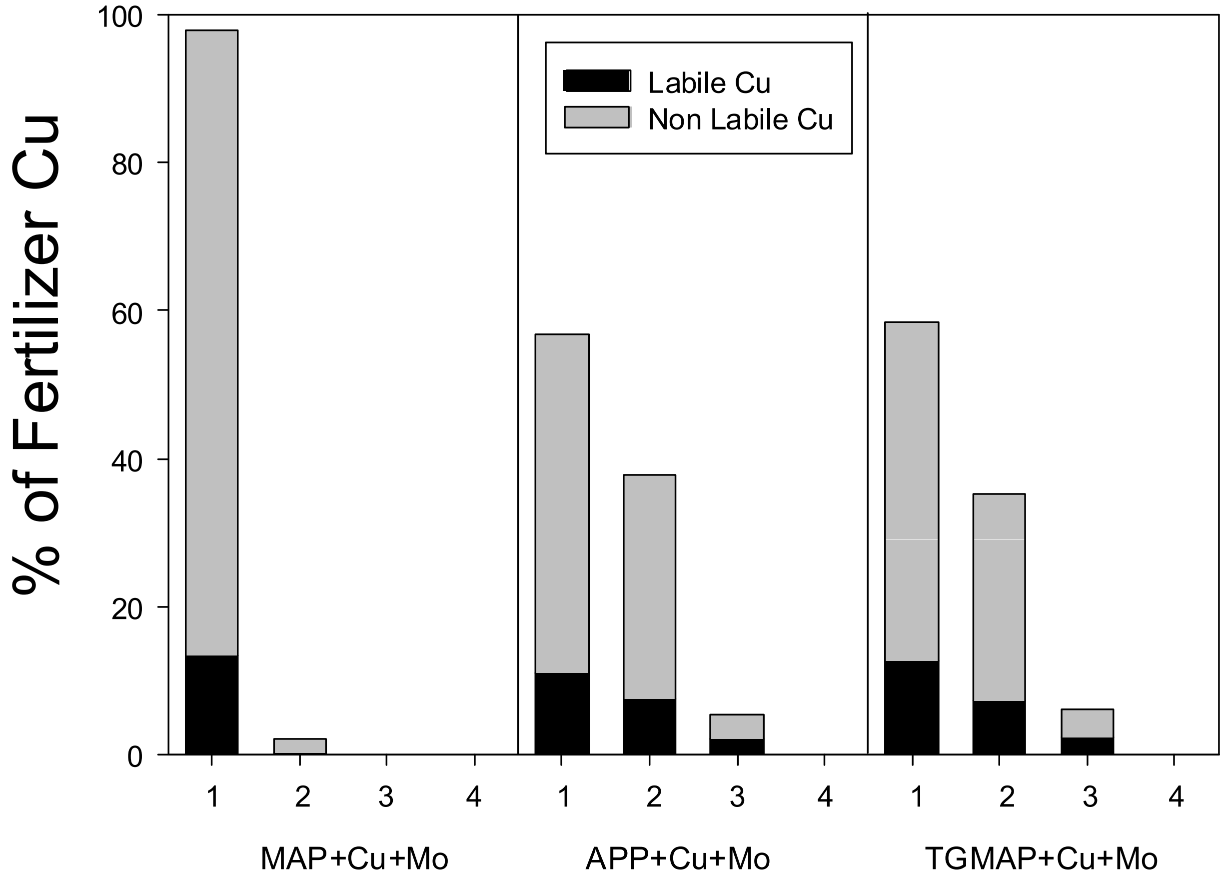



Area Mapped

# Methods



# Results – labile Cu in acidic soil




1 = 0 to 4 mm section
2 = 4 - 7.5 mm section
3 = 7.5 to 13.5 mm section
4 = 13.5 to 25.5 mm section

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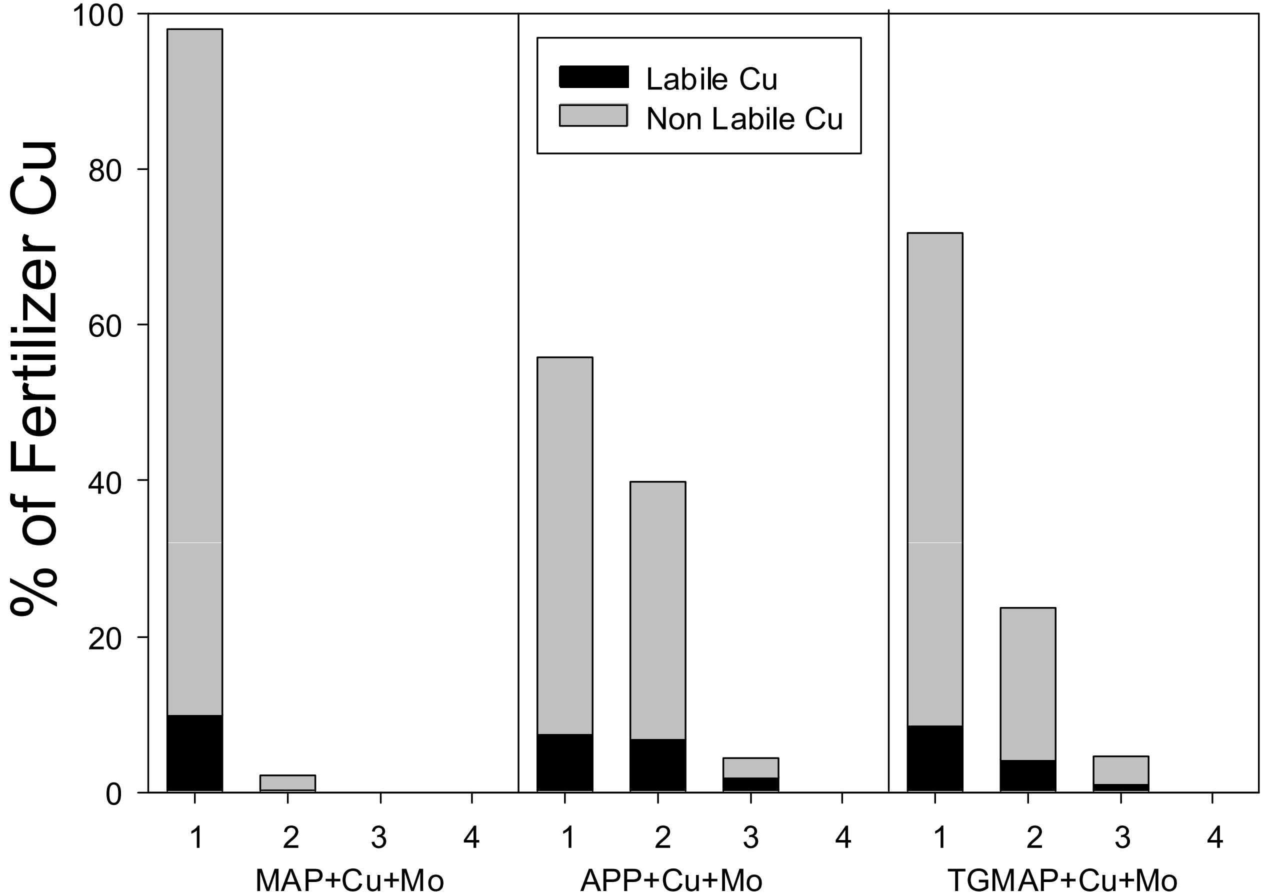


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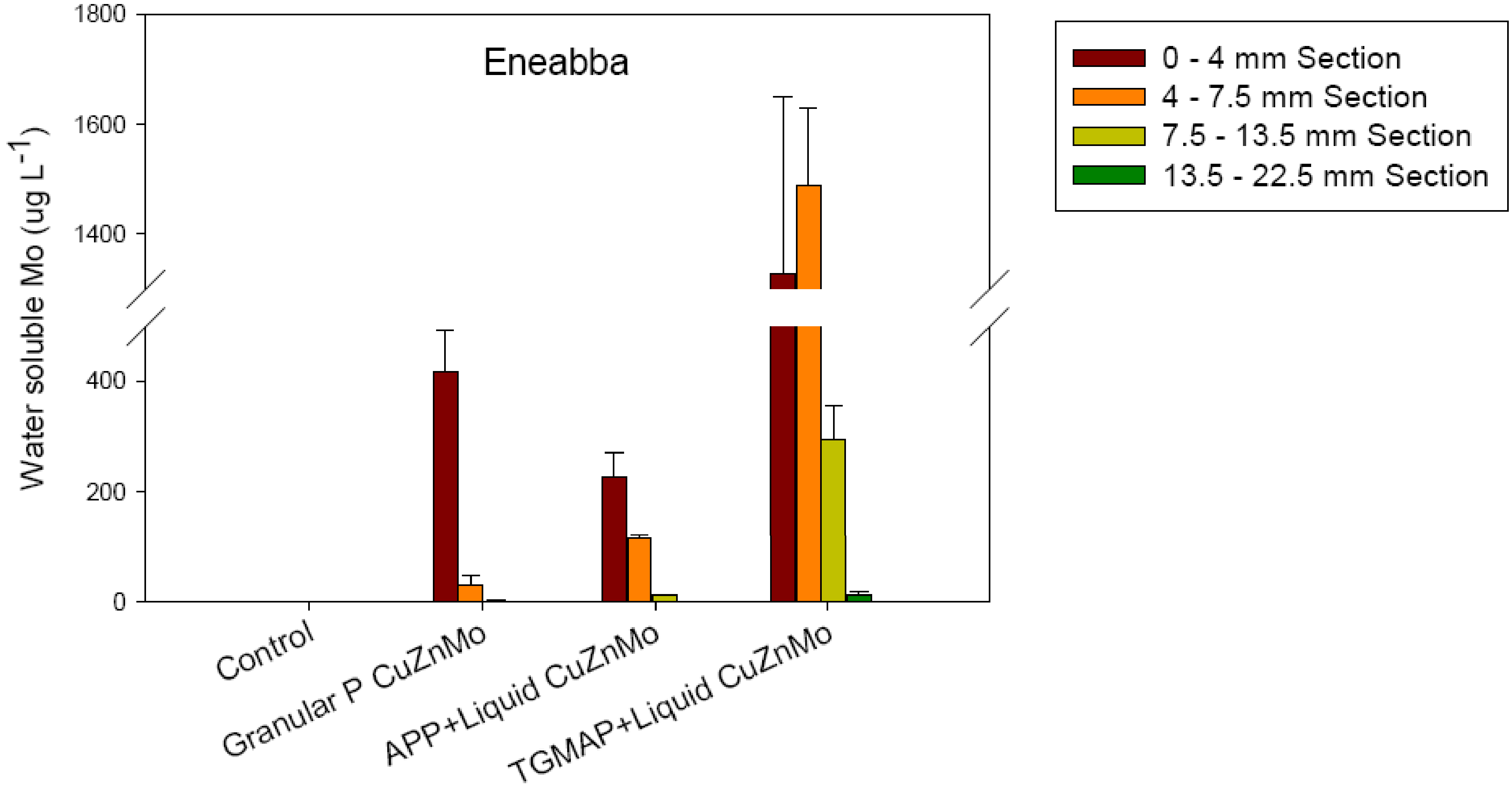

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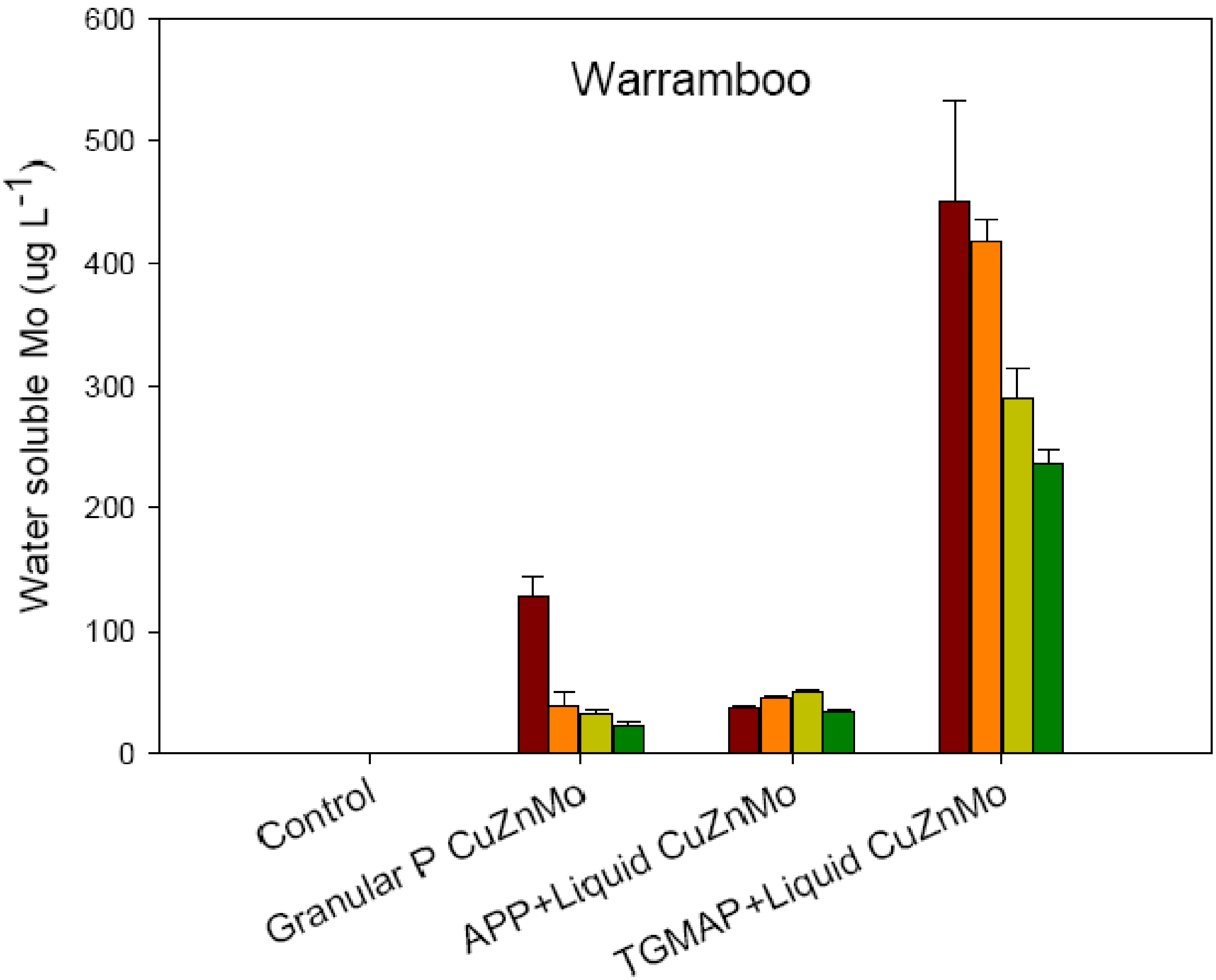
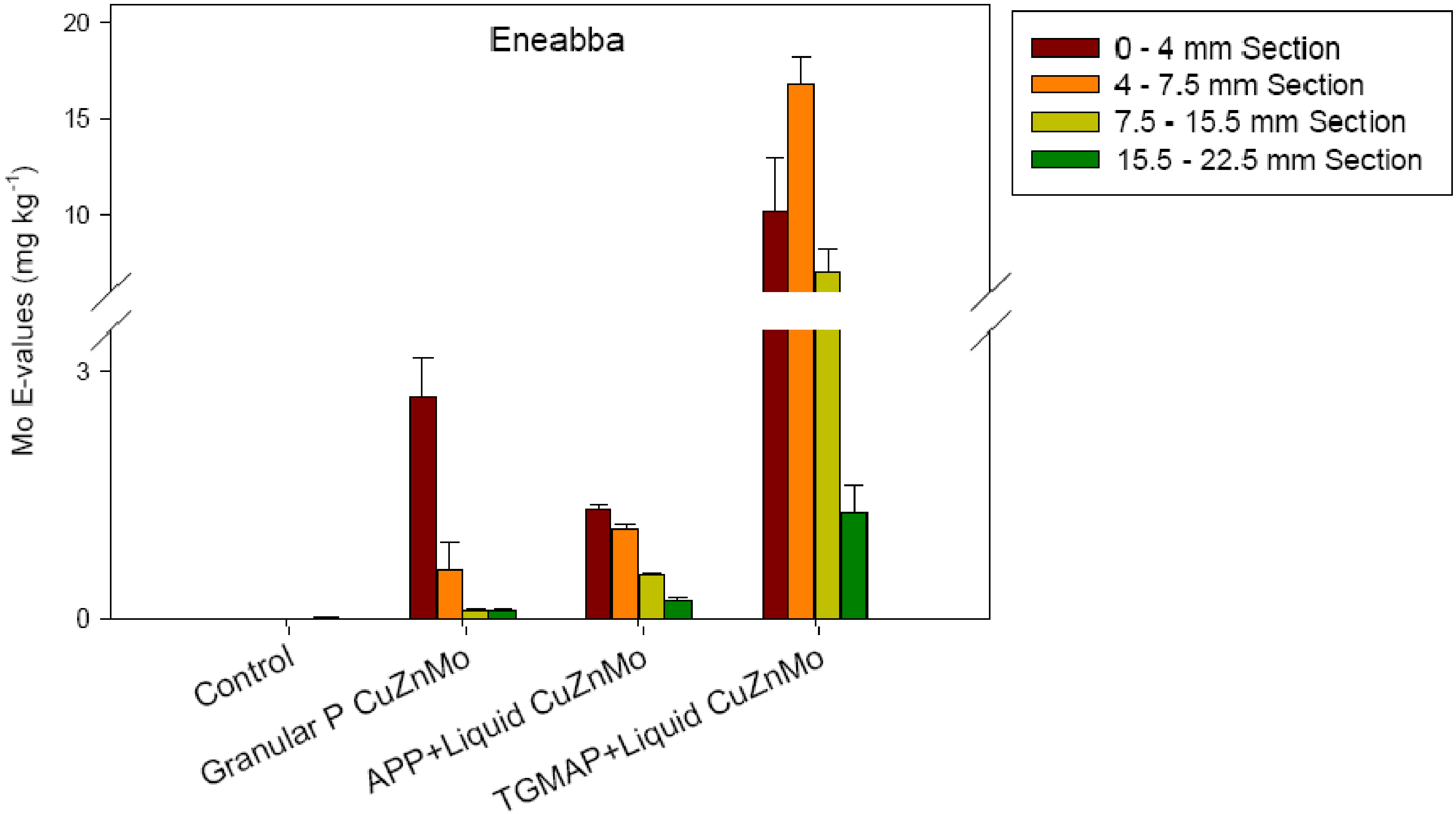


# Results – labile Mo, acidic soil



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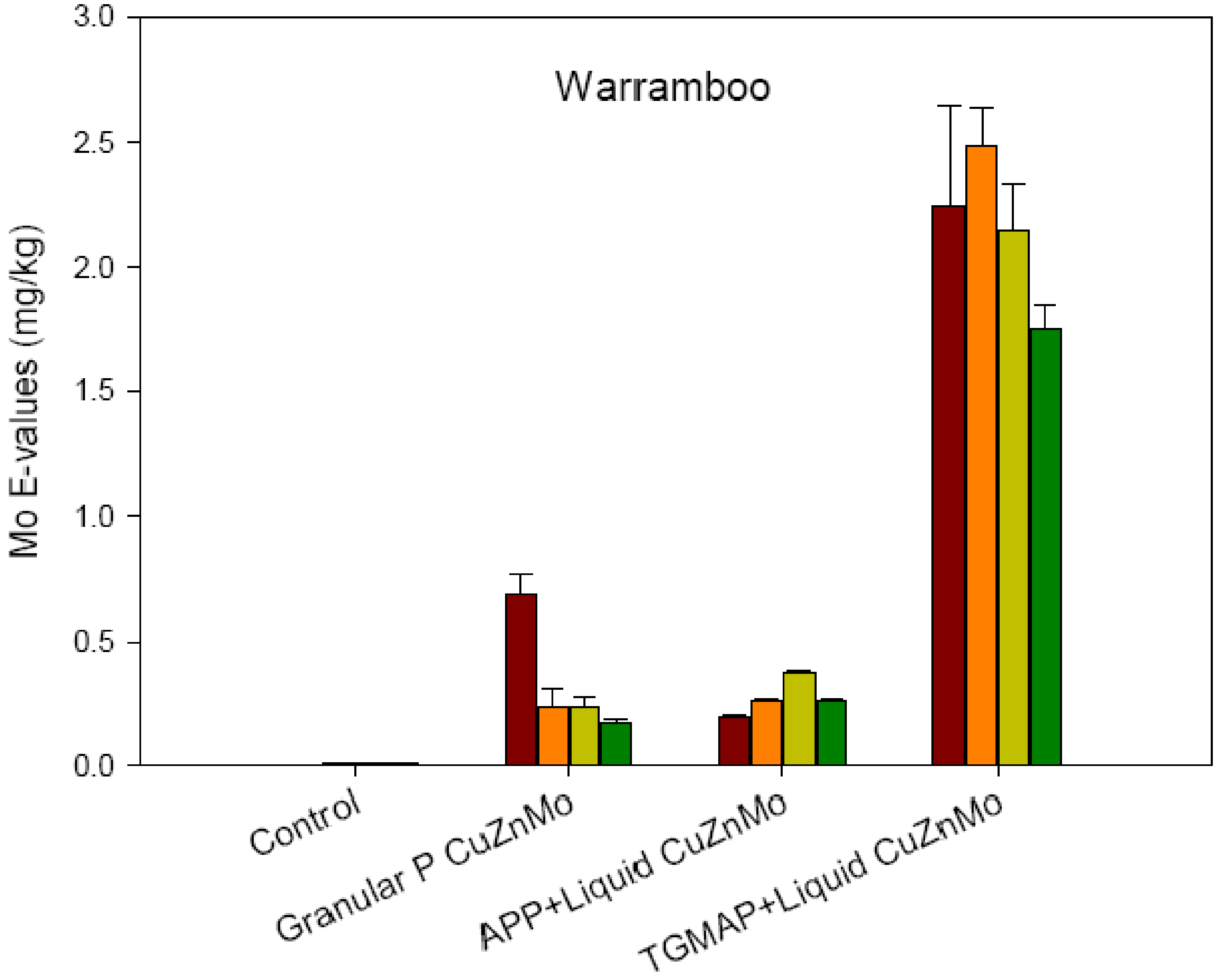
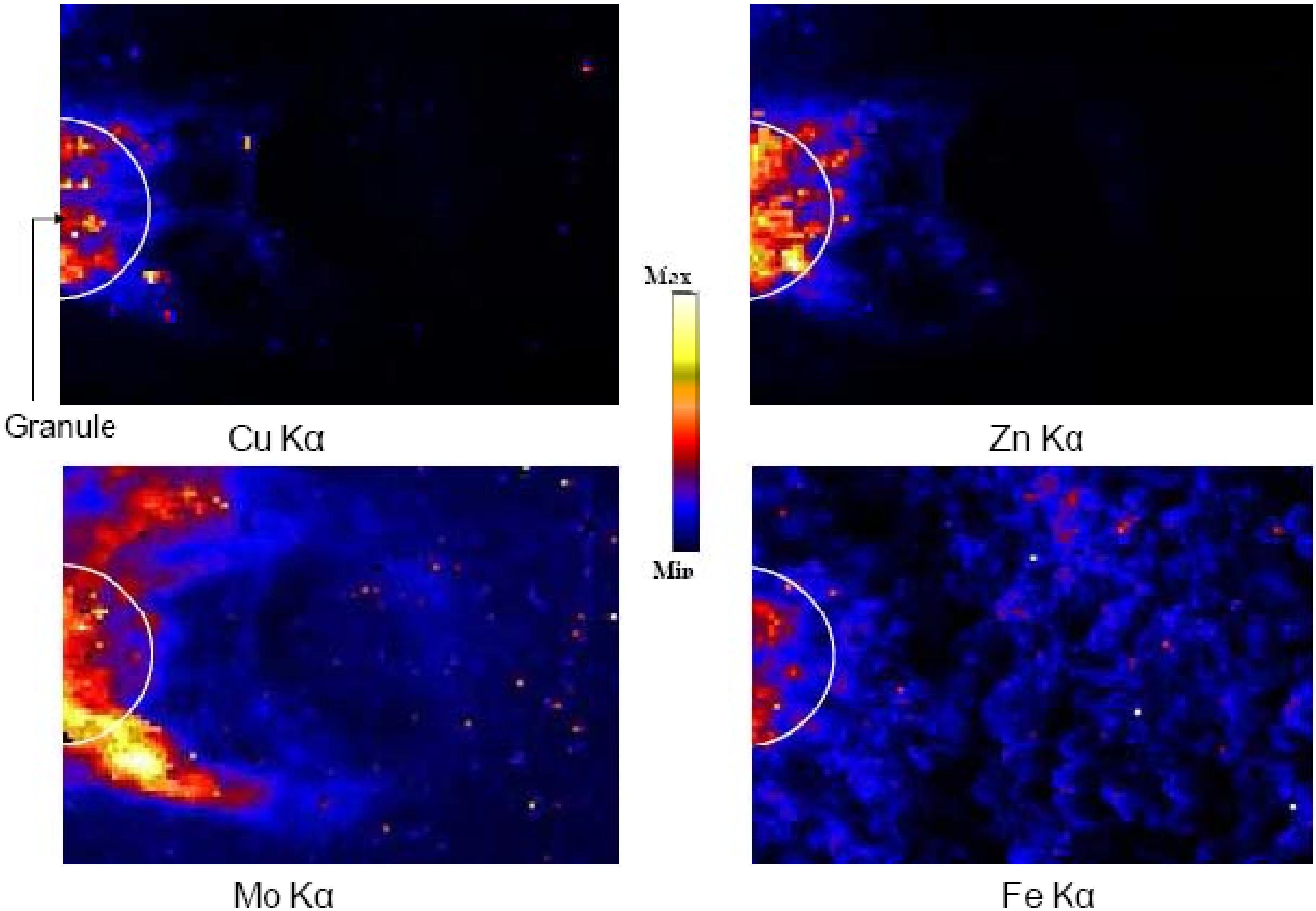


# Results – X-ray mapping of granular product alkaline soil



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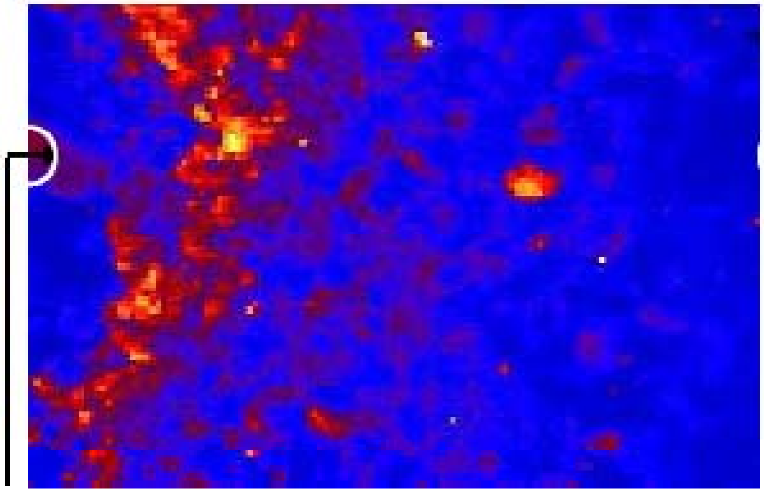
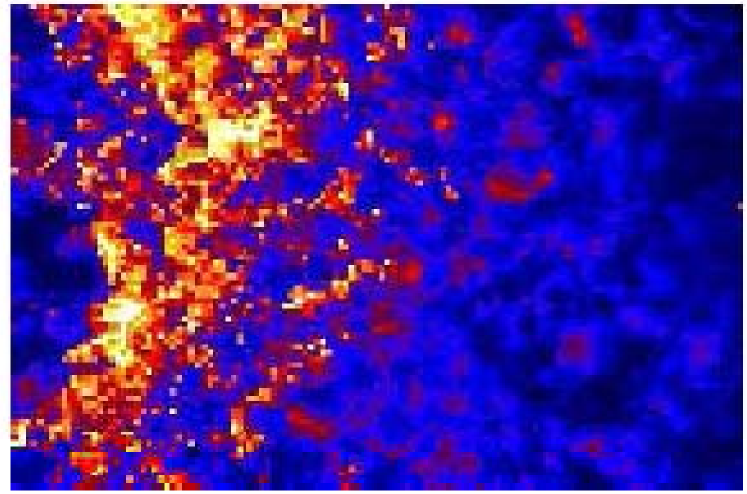
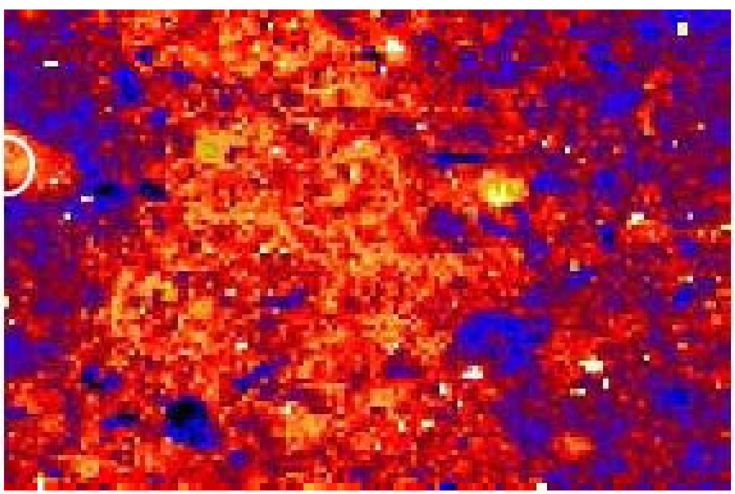


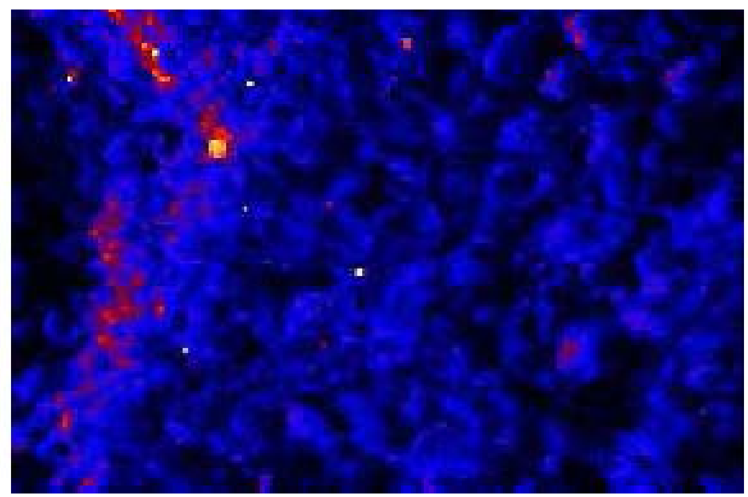

Cu Kα



Zn Kα



Mo Kα

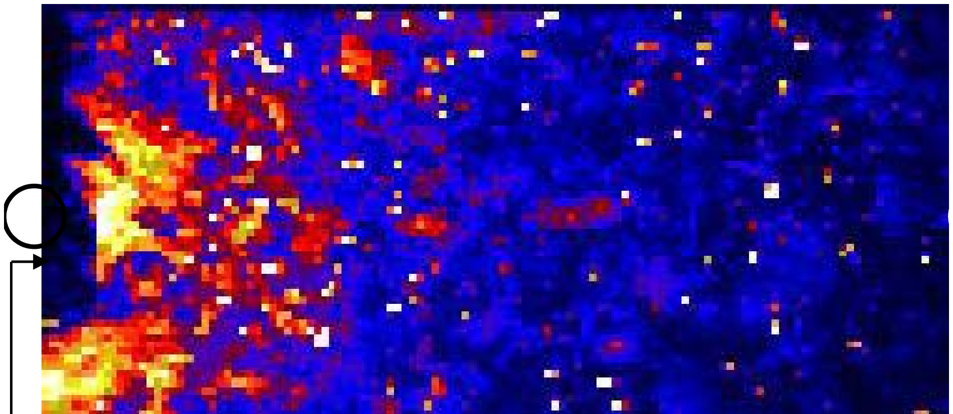


Fe Kα

# Results – X-ray mapping of granular product acidic soil

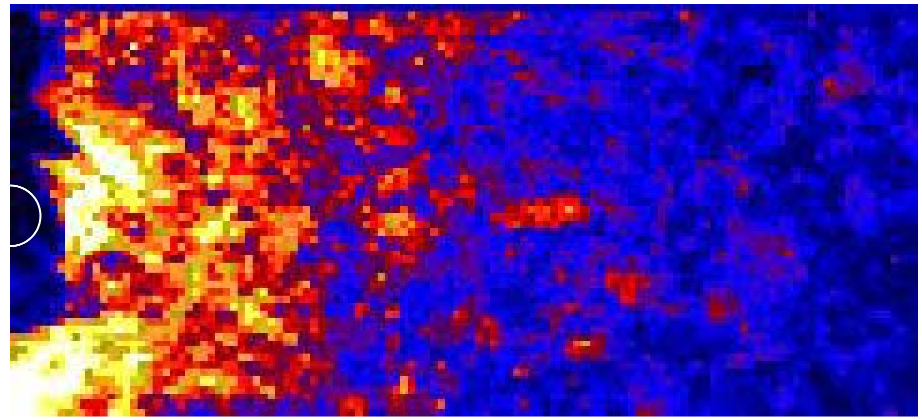


Liquid treated acid soil (Kambellup) maps
size: 6000 x 2250 µm

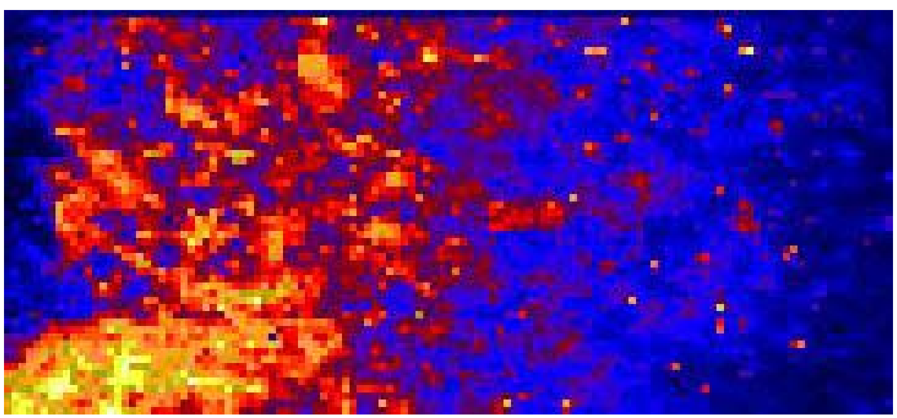


Cu Kα

Point of application



Zn Kα



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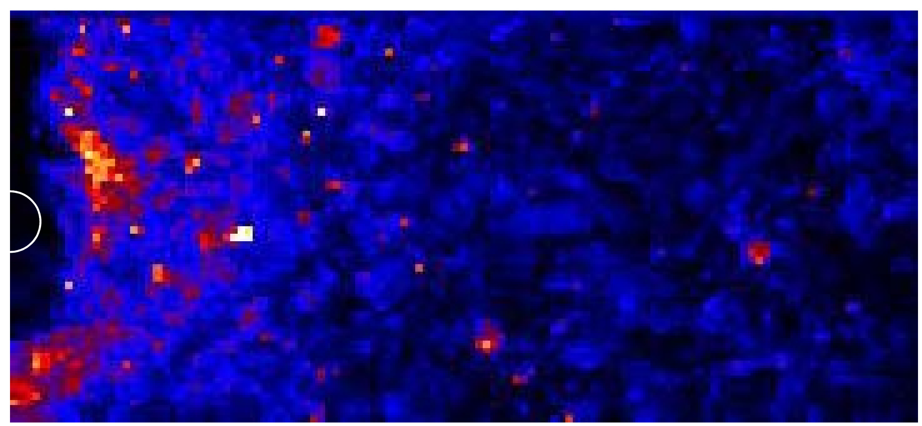

Fe Kα

# Conclusions

- Diffusion of Cu from the granular fertilisers was limited in all soils. Fluid forms diffused further from the point of application compared to granular products
- Most of the granular Cu was in non-labile forms (either initially in granule or fixed by soil). A large percentage of non-labile Cu for the fluid fertiliser also indicates a problem in supplying Cu with soluble P i.e. rapid fixation in fertiliser band
- Better techniques are needed to supply cationic micronutrients with phosphatic fertilisers
- Water soluble and labile Mo were greater in the acidic soil – likely that precipitation of $CaMoO_4$ reduced Mo availability in the alkaline soil (to be confirmed by synchrotron speciation data)
- In all soils, Mo diffused further from the point of fluid application compared to Cu (and Zn) in all soils

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# Acknowledgements

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Australian Research Council