

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

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ABSTRACT

The reactions of copper (Cu)- and molybdenum (Mo)-enriched phosphorus (P) fertilisers have rarely been studied, and we hypothesized that these elements supplied in fluid form would behave differently in soil to those supplied in granular form, based on previous work with manganese- and zinc-enriched P fertilisers. Reactions of Cu and Mo in and around fertiliser granules or fluid bands have not been evaluated before, and we employed a combination of several laboratory based isotopic and spectroscopic methods to evaluate lability and chemical forms of different fertilizer derived Cu and Mo and in both acidic and alkaline soils.

INTRODUCTION

Millions of hectares of arable land worldwide, particularly in arid and semi-arid regions, are deficient in plant available micronutrients and human populations require more trace elements in their diets (Welch and Graham 2005). Copper and Mo are essential trace elements in all agricultural systems (Kaiser *et al.* 2005; Welch 1995), yet these elements are often overlooked in fertilisation programs. The major reason for the widespread occurrence of deficiency of micronutrients in soils is the low availability of micronutrients to plant roots rather than their low concentration in soils. Copper and Mo deficiencies are widespread in Australasia and Asia – for example up to 30% of the soils in China are estimated to be deficient in Cu and Mo (Yang *et al.* 2007) and Mo was central to the agricultural development of high rainfall acidic soils in Australia for legume-based pastures (Anderson and Moye 1952). While Cu deficiency occurs predominantly in alkaline soils where availability of Cu is low, it may also occur in highly leached soils where total and available Cu concentrations are very low due to leaching over geologic time scales e.g. Western Australia (Brennan *et al.* 1980). By contrast, availability of Mo is lowest in acidic soils (Welch and Anderson 1962) as it is anionic and is increasingly attracted to the positive charges on clay minerals as soil pH falls (Barrow 1978).

Recent field studies conducted by our group have shown an increased response to fluid Cu, Mn and Zn (concentration in grain and/or grain yield) compared to granular fertilizers in calcareous sandy loam soils (Holloway *et al.*, 2002; 2006). Further, recent laboratory experiments using isotopic dilution techniques using ⁵⁴Mn, and ⁶⁵Zn revealed that granular Mn and Zn did not diffuse readily from the point of application in soil nor did they enter, or remain in, the labile (available) pool compared to fluid fertilizer micronutrients (Hettiarachchi *et al.*, unpublished data).

The aim of this study was to investigate the reaction products of Cu and Mo in fluid and granular fertilizers in highly acidic and calcareous soils using isotopic and spectroscopic procedures.

MATERIALS AND METHODS

The soil used in this study was a grey calcareous alkaline sandy loam from Upper Eyre Peninsula in South Australia (Warrambo, 5% clay, pH 8.5), a neutral sandy soil from Western Australia (WA) (Eneabba, 3% clay, pH 6.2) and a slightly acidic loamy sand also from WA (Kambellup, 13% clay, pH 6.1). Treatments were: Granular monoammonium phosphate with 0.6% Cu and 0.04% Mo (and 0.6% Zn), fluid technical grade MAP (TG MAP) with added Cu, Mo and Zn equivalent to that supplied in granular form, and ammonium polyphosphate (APP) with added Cu, Mo and Zn as above.

Soils at 60% of maximum water holding capacity were incubated for 5 weeks at 25°C in Petri dishes/experimental cells with fertilisers in the centre. After 5 weeks, concentric rings of soils were collected from Petri dishes, outwards from the fertilizer placement point (0-4 mm, 4-7.5 mm, 7.5-13.5 mm and 13.5-22.5mm). Soils from the 0-4 mm zone, including incubated fertilizer granules/fluid fertilizer injection point,

and from the 4 mm - 7.5 mm zone were dried in an oven maintained at 40°C. Soil pH and total, water-soluble and labile concentrations of Cu and Mo were determined by *aqua regia* digestion, and by isotope dilution, respectively. For determination of labile micronutrients (E-values) by isotope dilution, 1 MBq ⁶⁴Cu (half-life 12.8 days) or 100 kBq ⁹⁹Mo (half-life 67 days) were added to a pre-equilibrated (4 days end-over-end shaking) soil:water suspension (1:10 soil:water ratio) and equilibrated for 24 hours. Suspensions were then filtered (<0.2 µm) and assayed for radioisotopes by gamma spectroscopy. Concentrations of unlabelled Cu and Mo in the solutions were determined by inductively-coupled plasma mass spectroscopy. Percentages of Cu and Mo derived from the added fertilisers in each soil section were determined by subtracting the total and labile concentrations of these elements from those determined in similarly incubated unfertilized soil, and expressing this as a % of the fertiliser Cu and Mo added.

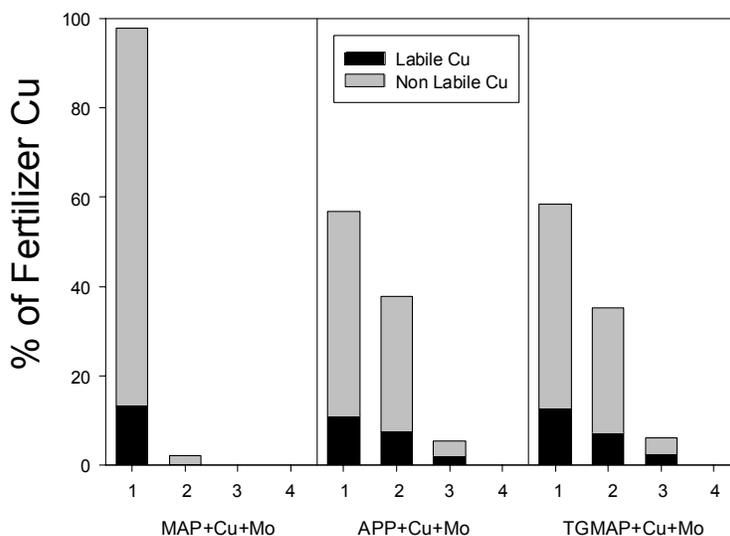
Incubated soils/fertilisers as outlined above were prepared in experimental cells were used for synchrotron-based micro scale x-ray fluorescence (to determine elemental distribution), and micro scale x-ray absorption spectroscopy (to determine chemical form of reaction products). Data were collected at GSE-CARS, 13-BM, Advanced Photon Source, Argonne, IL, U.S.A.

RESULTS AND DISCUSSION

Movement of and lability of fertilizer copper and molybdenum

A large percentage of the Cu in the fertilisers remained in the fertilised zone (0-4mm) in and around the granule/fluid injection point and this was consistent across all soils. Data for the most alkaline soil (Warrambo) and the most acidic soil (Kambellup) are shown on Figures 1 and 2. Diffusion of Cu away from the fertiliser into the surrounding soil was greatest with the fluid products, with only small differences evident between the two fluid formulations (TG MAP and APP).

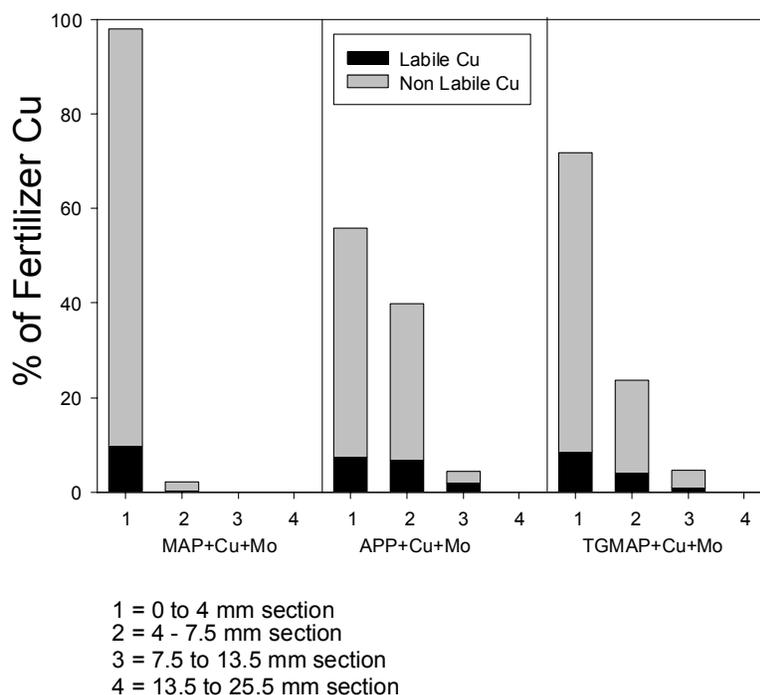
Figure 1. Distribution and lability of Cu in the acidic soil (Kambellup) 5 weeks after incubation with fertilisers.



- 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

Most of the fertiliser-derived Cu in the soil was not water soluble (data not shown) and non-labile i.e. was not readily exchangeable with Cu isotope in both alkaline and acidic soils (Figures 1 and 2), with only slightly more Cu remaining in the labile pool in the acidic soil (Kambellup). In the central section (0-4 mm) the non-labile Cu in the granular treatment could be derived from Cu in the granule that did not dissolve into soil solution, or from Cu that dissolved and was then immobilized quickly. For the fluid treatments, and for all soil sections other than the central one, all the Cu would have been initially soluble, so non-labile Cu in these sections/treatments represents Cu that reacted with the soil solid phase to convert labile Cu to non-labile forms. In all soils and treatments the non-labile Cu was 75% or more of the added Cu, indicating that the agronomic effectiveness of this micronutrient in these fertilisers would be low in winter-rainfall dryland cereal cropping systems.

Figure 2. Distribution and lability of Cu in the alkaline calcareous soil (Warrambo) 5 weeks after incubation with fertilisers.



Only preliminary data are available for Mo at this stage. Also, Mo data were subject to greater error due to the extremely small concentrations of Mo in soil and in soil extracts. At this stage Mo concentrations have not been normalised for differing amounts of Mo added in the fertilisers. Comparing the same fertiliser between soils however (Figures 3 and 4), it is evident that soluble and labile Mo (E values) were much lower in the Warrambo soil than the two other soils, yet Warrambo is the most alkaline soil. The highly calcareous nature of this soil likely leads to the immobilisation of added soluble Mo as insoluble Ca-molybdenate (powellite – CaMoO_4).

Comparing the distribution of Mo across the soil sections for any given fertiliser treatment indicates that fertiliser Mo is slightly more mobile than fertiliser Cu, and diffuses a greater distance away from the zone of fertilisation, especially in the Warrambo soil. This might seem contradictory as the Warrambo soil had the lowest concentrations of water-soluble and labile Mo – these data are likely explained by the fact that Mo availability in this soil is controlled by precipitation/dissolution. Once Mo concentrations are below the solubility product for powellite, Mo is free to diffuse through the soil as sorption of Mo is low. In the acidic soil on the other hand, while Mo concentrations were high in solution (as solubility is not limited by Ca), stronger sorption by soil minerals reduced the transport of Mo from the point of application.

These preliminary data also suggest that diffusion of Mo from the granular source of Mo-enriched MAP was not as effective as from fluid sources of the same compound, although differences were less marked than for Cu. This is further addressed in the spectroscopy data below.

Spectroscopic investigations of diffusion and mobility of fertilizer copper and molybdenum

A large percentage of the Cu in the fertilisers remained in the fertilised zone (0-4mm) in and around the granule/fluid injection point and this was consistent across all soils. Data for the most alkaline soil (Warrambo) show that fluid forms of Cu diffused more freely through the soil than Cu in the granular MAP. Similarly, there appeared to be a greater movement of Mo away from the point of fertilisation with the fluid product (Figure 5). Diffusion of Mo was much greater in the alkaline soil than in the acidic soils (data now shown), supporting the conclusions from the Petri dish experiments.

Figure 3. Preliminary data for concentrations of water soluble Mo in the three soils – note data have not yet been normalised for different amounts of Mo added between treatments e.g. the TGMAP treatment had ~9 times more Mo added compared to APP.

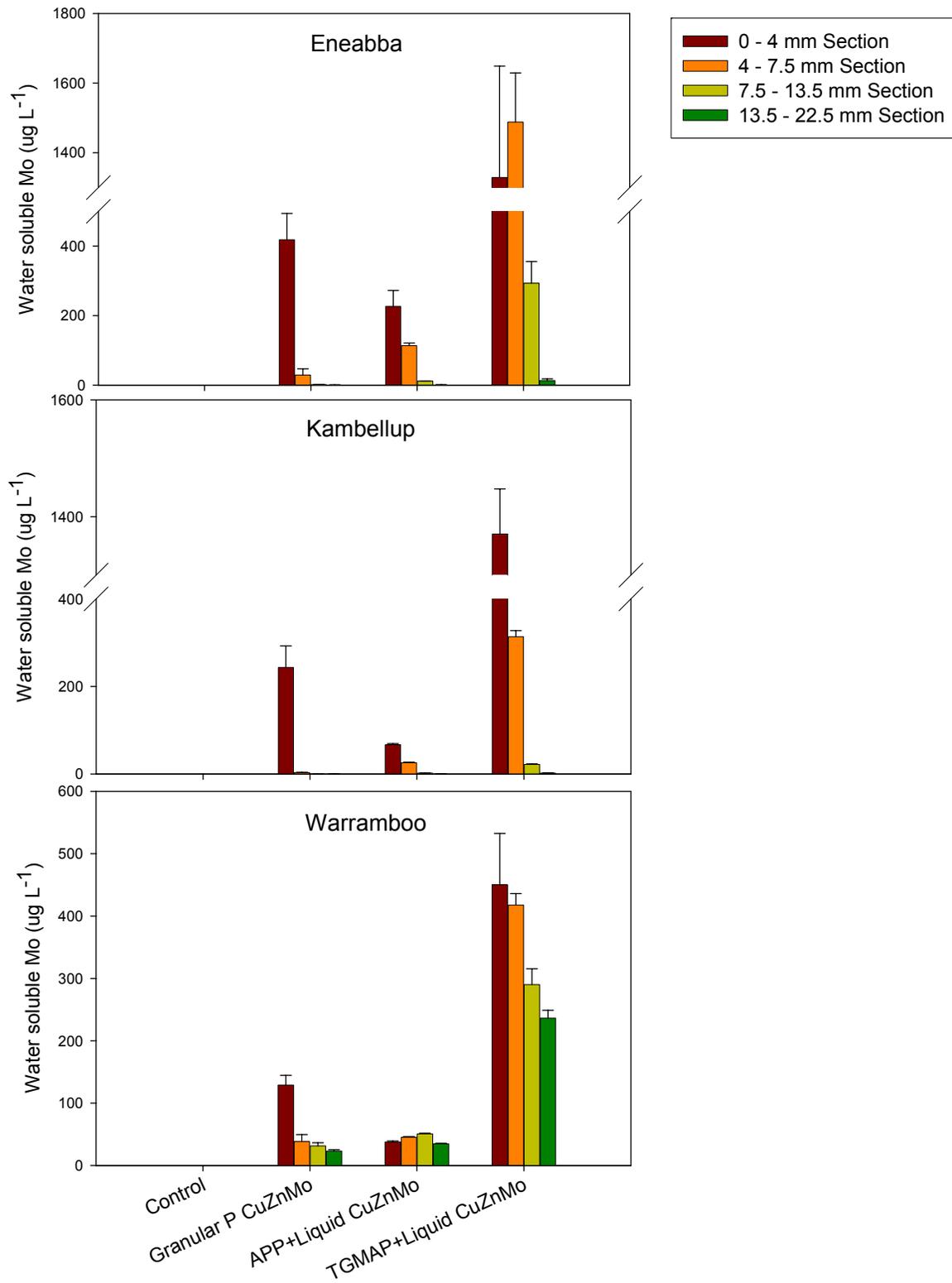


Figure 4. Preliminary data for concentrations of labile Mo in the three soils – note data have not yet been normalised for different amounts of Mo added between treatments e.g. the TGMAP treatment had ~9 times more Mo added compared to APP.

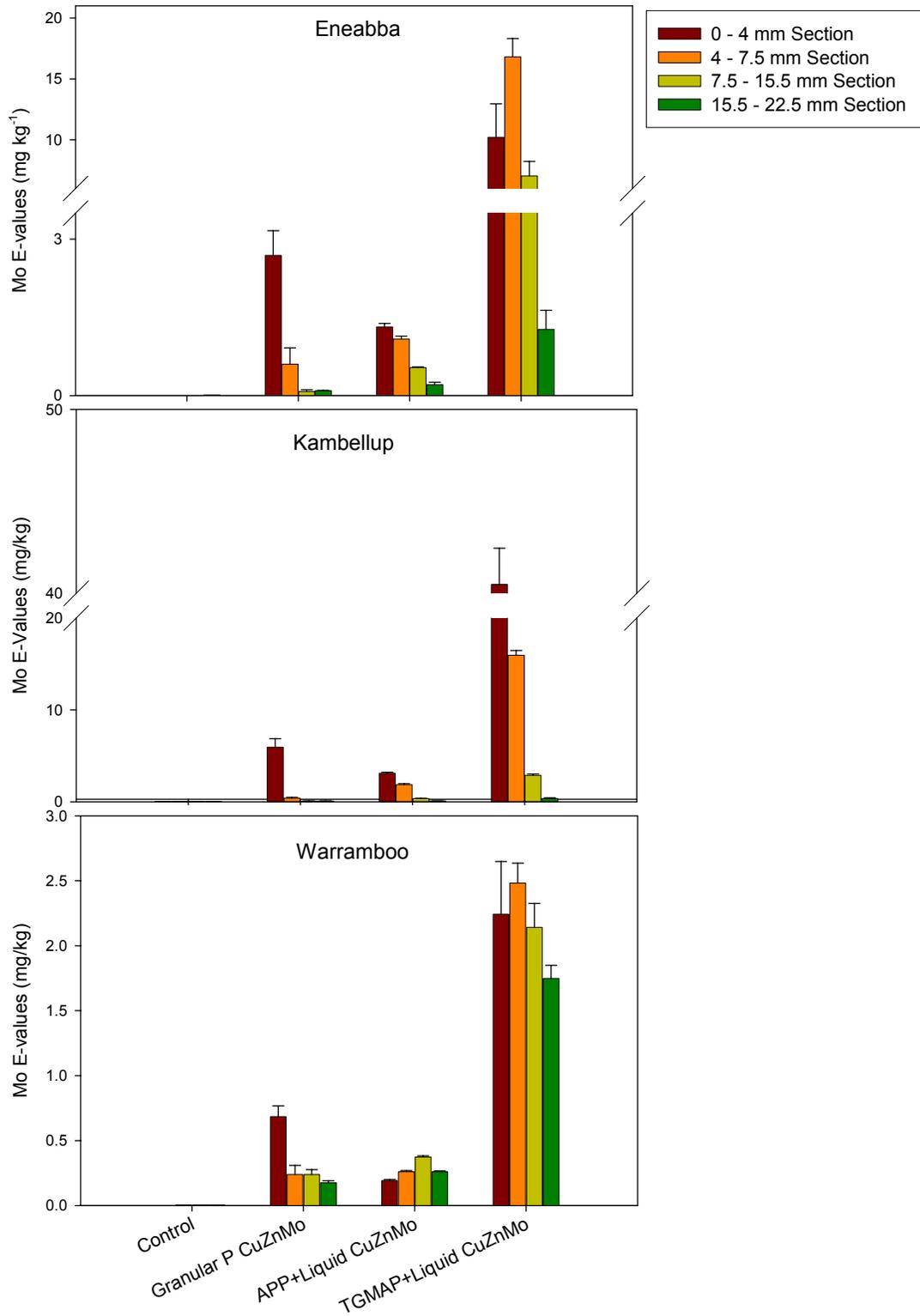
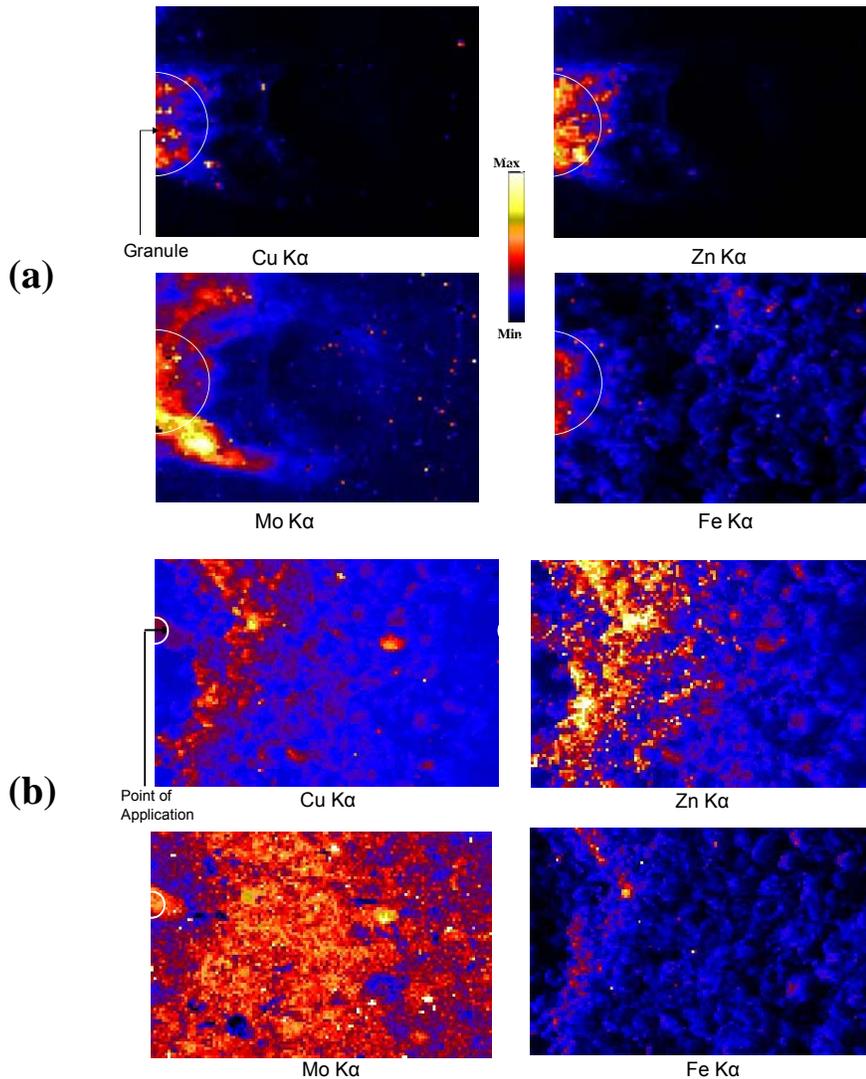


Figure 5. μ -XRF maps for Cu, Zn, Mo and Fe in the the alkaline calcareous soil (Warrramboo) for the (a) granular (MAP+Cu+Zn+Mo) (b) fluid treatment (TGMAP+Cu+Zn+Mo). The boxes represent an area of 8,000 x 3,500 μm (granular) 8,000 x 4,000 μm (fluid) and the circle is the estimated granule/fluid injection location.



CONCLUSIONS

This work demonstrates that diffusion of Cu from granular phosphatic fertilisers is limited, thus reducing the likelihood that plant roots would intercept Cu. This is especially the case in dryland cereal soils where rates of P (and micronutrient) application are low, and therefore the number of granules per metre of crop row is not large. Diffusion of fertiliser Cu away from the point of application was greater for the fluid fertilisers in line with previous experiments with P, Mn, and Zn (Hettiarachchi *et al.* 2008) and is likely due to the microscopic differences in solute flow in and around granular and fluid fertilisers after application to soil (Hettiarachchi *et al.* 2006). Granules tend to draw soil solution towards their surface, thus inhibiting the outward diffusion of fertiliser nutrients, and indeed contributing to fertiliser nutrient precipitation in and around the granule (Lombi *et al.* 2004). The flow of water is different around a fluid injection point (outward) which tends to reduce solute concentrations and assist diffusion and movement of fertiliser nutrients out into the soil.

In the calcareous soil APP appeared to provide some additional mobility for fertiliser Cu. It is well known that APP products can complex micronutrients and enhance their mobility in soils (Giordano *et al.* 1971; McBeath *et al.* 2007).

A large percentage of the applied Cu was found to be in non-labile forms 5 weeks after incubation in soils, and this was common across both granular and fluid fertiliser forms. Combining Cu with orthophosphate-

based fertilisers may be problematic, due to the precipitation of Cu with phosphate in the products, and better technologies for supplying cationic micronutrients with P fertilisers are required.

The preliminary data for Mo indicate that while fertiliser Mo mobility may be high in alkaline soils, the solubility and lability of fertiliser Mo in alkaline calcareous soils will be limited, likely through precipitation of CaMoO_4 close to the fertilised zone.

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REFERENCES

- Anderson AJ, Moye DV (1952) Lime and molybdenum in clover development on acid soils. *Australian Journal of Agricultural Research* **3**, 95-110.
- Barrow NJ (1978) Inorganic reactions of phosphorus, sulphur and molybdenum in soil. In 'Mineral nutrients of legumes in tropical and subtropical soils.' (Eds CS Andrew and EJ Kamprath) pp. 189-206. (CSIRO Melbourne: CSIRO Melbourne Australia)
- Brennan RF, Gartrell JW, Robson AD (1980) Reactions of copper with soil affecting its availability to plants. I. Effect of soil type and time. *Australian Journal of Soil Research* **18**, 447-459.
- Giordano PM, Sample EC, Mortvedt JJ (1971) Effect of ammonium ortho-phosphate and pyrophosphate on Zn and P in soil solution. *Soil Science* **111**, 101.
- Hettiarachchi GM, Lombi E, McLaughlin MJ, Chittleborough D, Self P (2006) Density changes around phosphorus granules and fluid bands in a calcareous soil. *Soil Science Society of America Journal* **70**, 960-966.
- Hettiarachchi GM, McLaughlin MJ, Schekel KG, Chittleborough DJ, Newville M, Sutton S, Lombi E (2008) Evidence for different reaction pathways for liquid- and granular-micronutrients in a calcareous soil. *Soil Science Society of America Journal* **72**, 98-110.
- Kaiser BN, Gridley KL, Ngaire Brady J, Phillips T, Tyerman SD (2005) The role of molybdenum in agricultural plant production. *Annals of Botany* **96**, 745-754.
- Lombi E, McLaughlin MJ, Johnston C, Armstrong RD, Holloway RE (2004) Mobility and lability of phosphorus from granular and fluid monoammonium phosphate differs in a calcareous soil. *Soil Science Society of America Journal* **68**, 682-689.
- McBeath TM, Lombi E, McLaughlin MJ, Bünemann EK (2007) Pyrophosphate and orthophosphate addition to soils: Sorption, cation concentrations, and dissolved organic carbon. *Australian Journal of Soil Research* **45**, 237-245.
- Welch LF, Anderson OE (1962) Molybdenum content of peanut leaves and kernels as affected by soil pH and added molybdenum. *Agronomy Journal* **54**, 215-217.
- Welch RM (1995) Micronutrient nutrition of plants. *Critical Reviews of Plant Sciences* **14**, 49-82.
- Welch RM, Graham RD (2005) Agriculture: the real nexus for enhancing bioavailable micronutrients in food crops. *Journal of Trace Elements in Medicine and Biology* **18**, 299-307.
- Yang XE, Chen WR, Feng Y (2007) Improving human micronutrient nutrition through biofortification in the soil-plant system: China as a case study. *Environmental Geochemistry and Health* **29**, 413-428.