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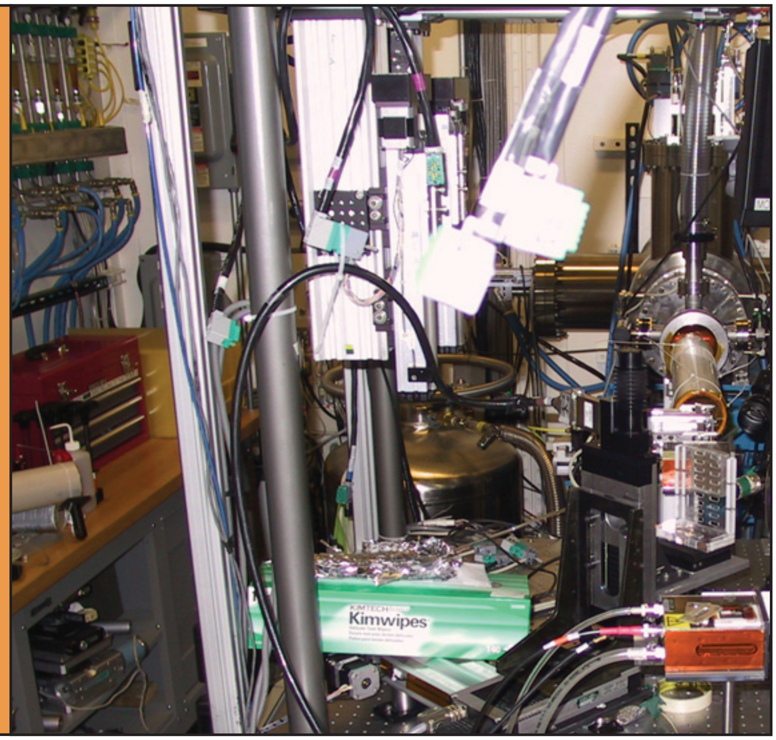
Copper Diffusion Superior With Fluids In Acidic and Alkaline Soils

Preliminary data suggest difference in diffusion between fluid and dry may not be as great for molybdenum.

Summary: *The reactions of copper (Cu)- and molybdenum (Mo)-enriched phosphorus (P) fertilizer 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 (Mn)- and zinc (Zn)-enriched P fertilizers. Reactions of Cu and Mo in and around fertilizer granules or fluid bands have not been evaluated before. 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 in both acidic and alkaline soils. The results of our work have shown that diffusion of Cu from granular phosphatic fertilizer is limited, thus reducing the likelihood that plant roots would intercept Cu. However, diffusion of fertilizer Cu away from the point of application was greater for fluid fertilizers, in line with previous experiments with P, Mn, and Zn, and is likely due to the microscopic difference in solute flow in and around granular and fluid fertilizers after application into the soil.*



Millions of acres of arable land worldwide, particularly in arid and semi-arid regions, are deficient in plant-available micronutrients that more than ever today are needed by human populations requiring more trace elements in their diets. Copper and Mo are essential trace elements in all agricultural systems, yet these elements are often overlooked in fertilization programs. The major reason for the widespread occurrence of micronutrient deficiency 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

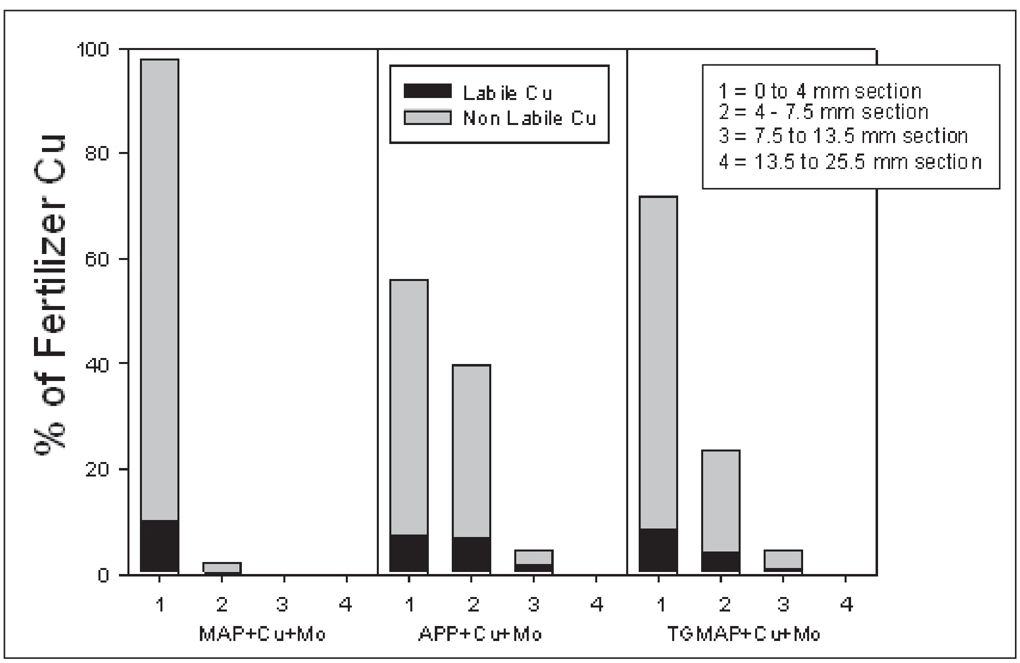


Figure 1. *Distribution and lability of Cu in alkaline calcareous soil (Warramboo) 5 weeks after incubation with fertilizers.*

Australia and Asia. Of the soils in China, for example, up to 30 percent are estimated to be deficient in Cu and Mo, and Mo was central to the agricultural development of high rainfall acid soils in Australia for legume-based pastures. While Cu deficiency occurs predominately in alkaline soils where availability of Cu is low, it also may occur in highly leached soils where total available Cu concentrations are very low due to leaching over geologic time scales (e.g., Western Australia). By contrast, availability of Mo is lowest in acidic soils as it is anionic and is increasingly attracted to the positive charges on clay minerals as soil pH drops.

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. Further, recent laboratory experiments using isotopic dilution techniques using Mn and Zn 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.

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

Movement and lability

Copper. A large percentage of the Cu in the fertilizers remained in the fertilized zone (0-4mm) in and around the granule/fluid injection point and this was consistent across all soils. Data for the most alkaline soil (Warramboo) and the most acidic soil (Kambellup) are shown in Figures 1 and 2. Diffusion of Cu

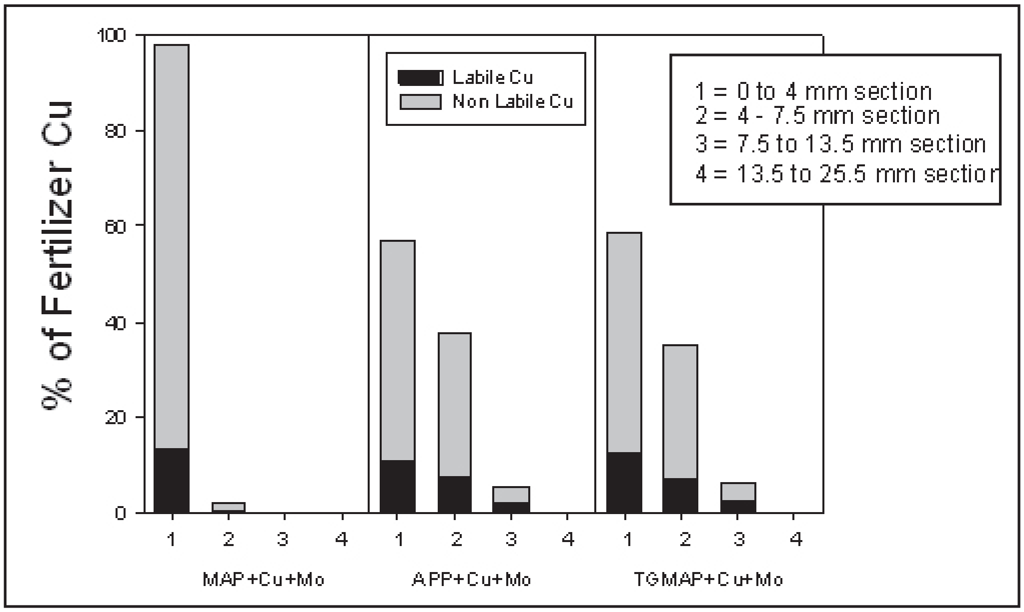


Figure 2. *Distribution and lability of Cu in acidic soil (Kambellup) 5 weeks after incubation with fertilizers.*

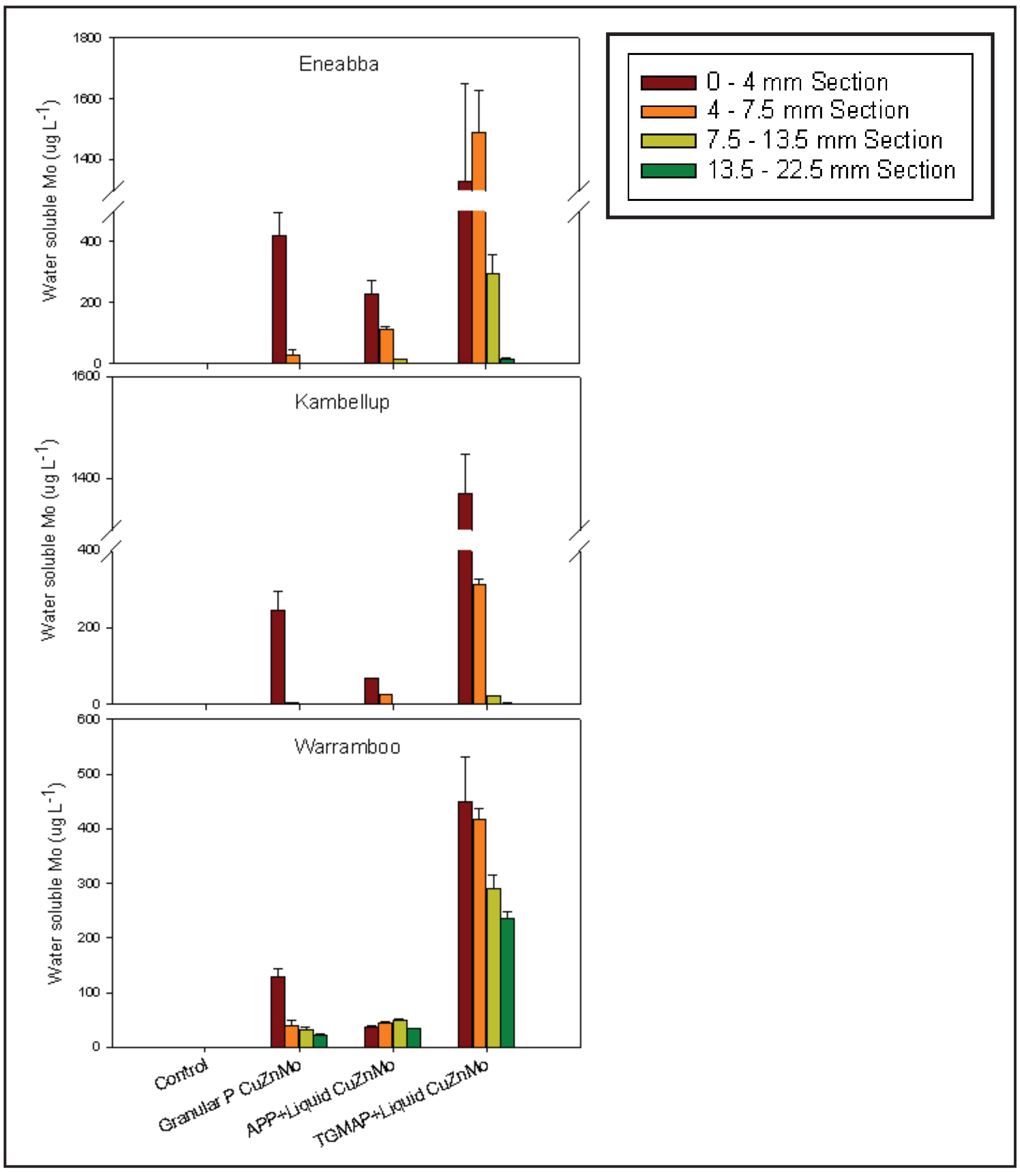


Figure 3. *Preliminary data for concentrations of water soluble Mo in three soils (note data have not yet been normalized for different amounts of Mo added between treatments (e.g., TGMAP treatment had equivalent to 9 times more Mo added compared to APP).*

away from the fertilizer into the surrounding soil was greatest with the fluid products, with only small differences evident between the two fluid formulations (TGMAP and APP).

Most of the fertilizer-derived Cu in the soil was not water soluble (data not shown) and non-labile--e.g., was not readily exchangeable with the 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. 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 the 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 percent or more of the added Cu, indicating that the agronomic effectiveness of this micronutrient in these fertilizers would be low in winter-rainfall dryland cereal cropping systems.

Molybdenum. 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 normalized for differing amounts of Mo added in the fertilizers. Comparing the same fertilizer between soils, however (Figures 3 and 4), it is evident that soluble and labile Mo (E values) were much lower in the Warramboo soil than the two other soils, yet Warramboo is the most alkaline soil. The highly calcareous nature of this soil likely leads to the immobilization of added soluble Mo as insoluble Ca-molybdenite (powellite – $CaMoO_4$).

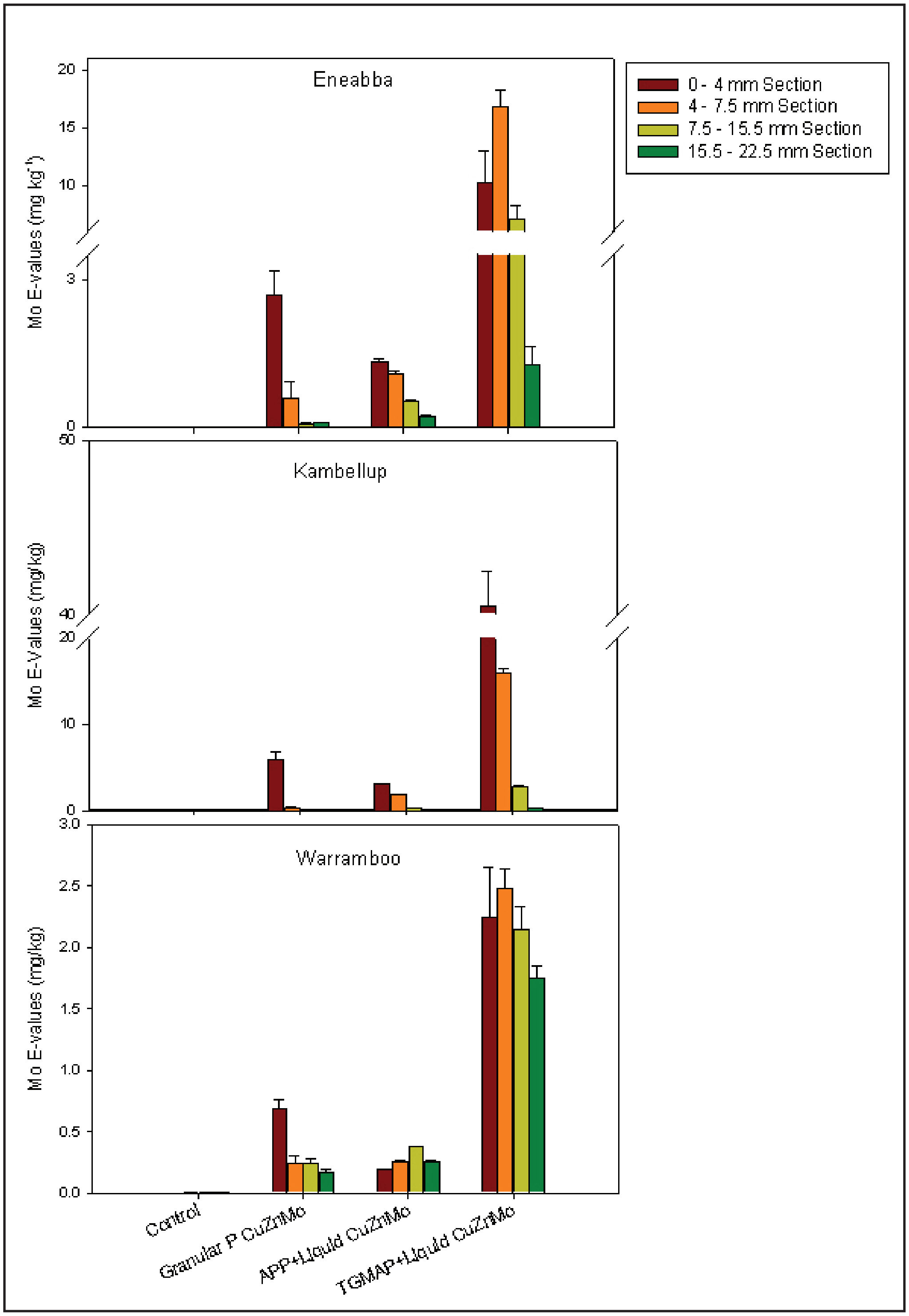


Figure 4. *Preliminary data for concentrations of labile Mo in three soils (note data have not been normalized for different amounts of Mo added between treatments, e.g., the TGMAP treatments had equivalent to 9 times more Mo added compared to APP).*

Comparing the distribution of Mo across the soil sections for any given fertilizer treatment indicates that fertilizer Mo is slightly more mobile than fertilizer Cu and diffuses a greater distance away from the zone of fertilization, especially in the Warramboo soil. This might seem contradictory, as the Warramboo 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 the 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.

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

Spectroscopy

A large percentage of the Cu in fertilizers remained in the fertilized zone (0-4mm) in and around the granule/fluid injection point and this was consistent across all soils. Data for the most alkaline soil (Warramboo) 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 fertilization with the fluid product (Figure 5). Diffusion of Mo was much greater in the alkaline soil than in the acidic soils (data not shown), supporting conclusions from the Petri dish experiments.

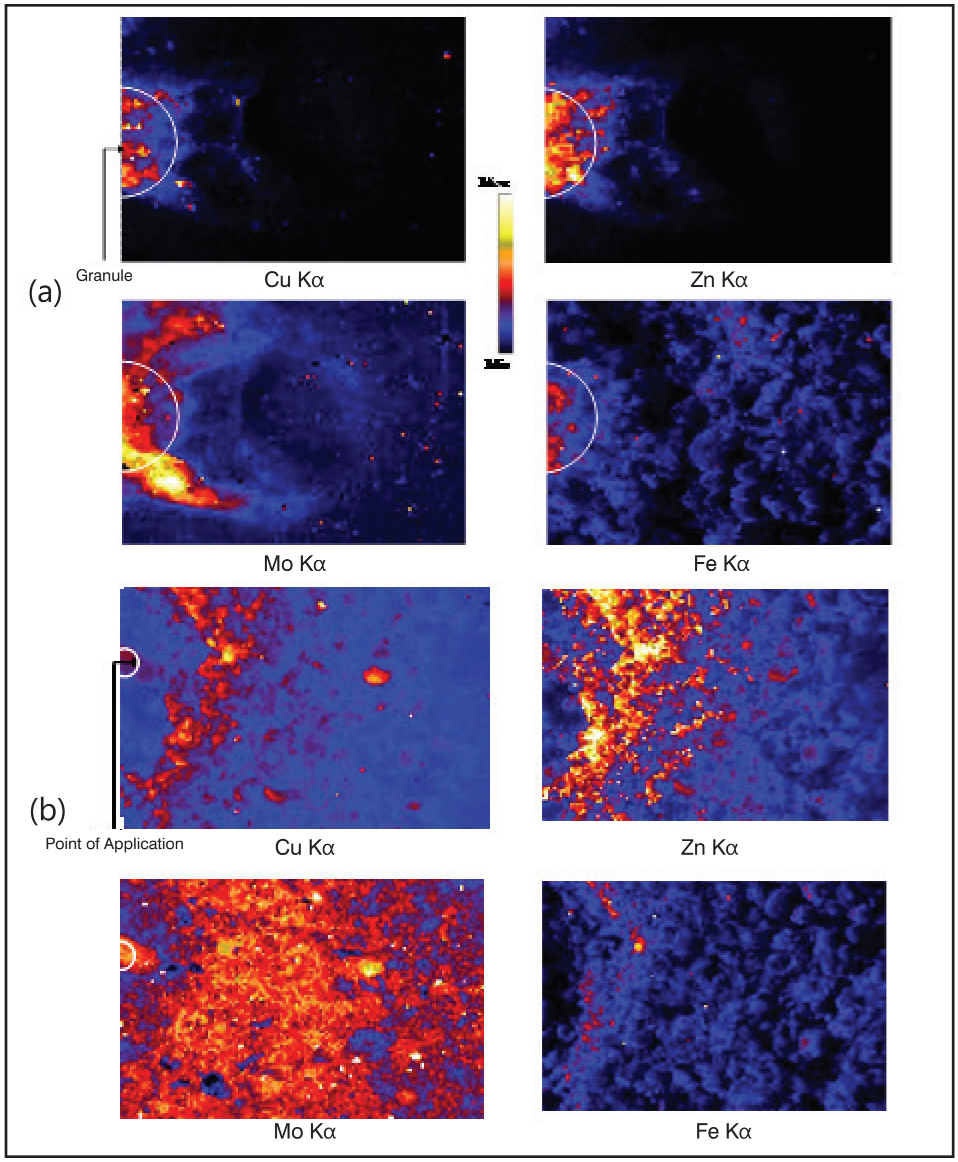


Figure 5. *μ-XRF maps for Cu, Zn, Mo, and Fe in alkaline calcareous soil (Warramboo) for a) granular (MAP+Cu+Zn+Mo, and b) fluid (TGMAP+Cu+Zn+Mo) treatments. The boxes represent an area of 8,000 x 3,500 μm granular and 8,000 x 4,000 μm fluid and the circle is the estimated granule/fluid injection location.*

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