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Fluids Excel In Supplying Mn And Zn In Calcareous Soils

Australian microscopic and spectroscopic studies show superiority of fluids over granular.

Millions of acres of arable land worldwide, particularly in arid and semi-arid regions, are deficient in plant available micronutrients. The major reason for the widespread occurrence of deficiency of micronutrients in soils is their low availability to plant roots rather than their low concentration in soils. Various organic and inorganic Mn and Zn fertilizers have been used to correct their deficiencies. Inclusion of Mn and Zn as well as other micronutrients in commercial macronutrient fertilizers is a common practice throughout the world because it is much more practical than a separate application of micronutrients. The cost of these fertilizers, as well as yield loss due to their inefficient use, is considerable, which is why the most efficient use of micronutrients in such compound fertilizers by plants is very important.

Recent field studies conducted by our group have shown an increased response to fluid 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 purpose of this study was to investigate the reaction products of Mn and Zn in fertilizer in highly calcareous South Australian soils using several laboratory and synchrotron based x-ray techniques after addition of these micronutrients to the soil either in granular or fluid form.

SUMMARY

The benefits of trace elements (Mn and Zn) supplied in fluid forms over conventional granular products in calcareous sandy loam soils have been agronomically demonstrated. We hypothesized that the differences in the effectiveness between granular and fluid micronutrient fertilizers may be due to different reaction processes in and around fertilizer granules and fluid fertilizer bands. We employed a combination of 1) several laboratory based x-ray techniques, 2) scanning electron microscopy combined with energy dispersive x-ray analysis, and 3) synchrotron based x-ray techniques to identify chemical forms of different fertilizer-derived Mn and Zn in highly calcareous soils. Combined use of these different x-ray techniques suggested that when fluid micronutrients were supplied to the soil, Mn and Zn remained in comparatively more soluble solid forms whereas granular Mn and Zn tended to transform into comparatively less soluble solid forms. This confirmed findings from previous studies using isotopic dilution analyses, and from field agronomic studies.

Movement

Manganese. Most of the fertilizer Mn diffused out of the granular Mn sources but was retained/precipitated around the granule whereas fluid Mn diffused farther away from the point of application. This pattern was confirmed by the microphotograph of the granular Mn extracted from the soil (Figure 1). This observation is in agreement with our previous experiments that showed that nearly 90 percent of the Mn in the granule dissolved and diffused out of the granule but was retained within 4 mm of the point of placement.

Zinc. Most of the fertilizer Zn was retained in the granule whereas fluid Zn diffused away from the point of application (Figure 2). This observation is in agreement with our previous studies in the same soil where 85 percent of the Zn in the granular Zn fertilizer source remained in the granule after 4 weeks of incubation.

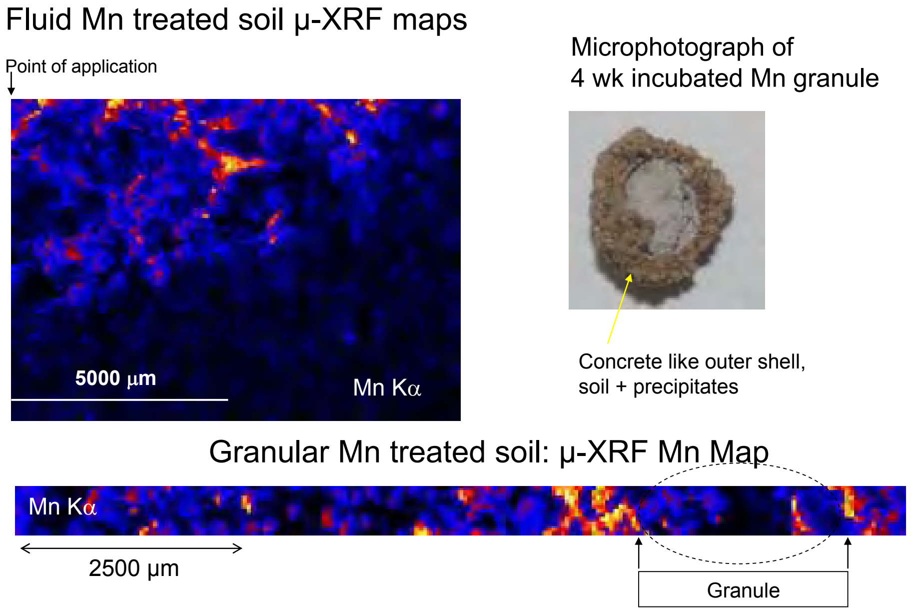

Figure 1. Mn XRF maps for fluid Mn and granular Mn treated in experimental cells. Fertilizer granule extracted from soils clearly shows the presence of concrete-like precipitate adjacent to the granule.

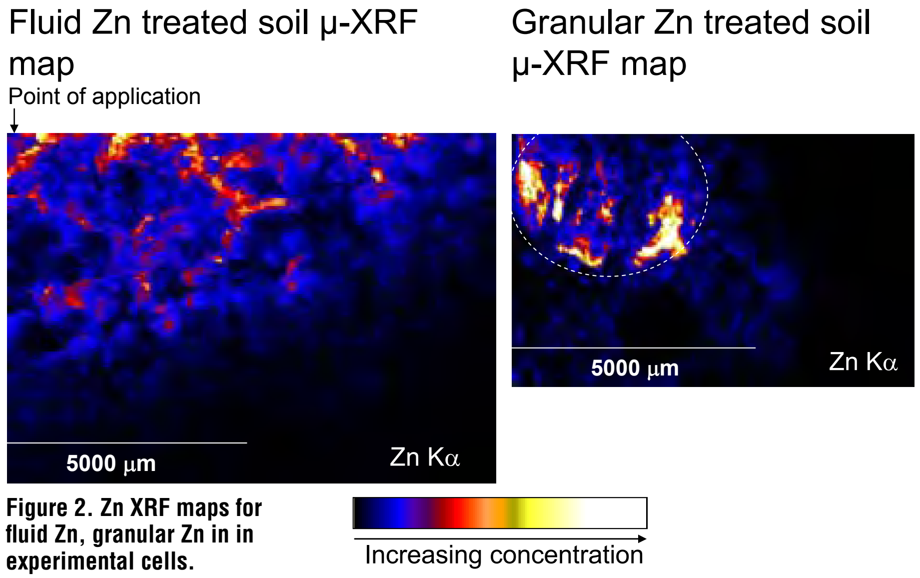

Figure 2. Zn XRF maps for fluid Zn, granular Zn in in experimental cells.

X-ray diffraction

Manganese. X-ray diffraction analysis of the original granular Mn showed that granules mainly contained Mn in the form of the mineral szmikite [$MnSO_4$ (H_2O)], the original form that Mn was introduced into the granule during manufacturing, Moreover, it appeared from the XRD pattern that some manganese hydrogen phosphate and hydroxylapatite were present in these Mn granules (data not shown). In the granules incubated in soil, Mn remaining in the granule stayed in these same minerals with little transformation to other forms.

Both micro and bulk x-ray absorption spectra suggested that the majority of Mn in the soil adjacent to the granule was present as Mn-carbonate [$MnCO_3$ or rhodochrosite] and Mn-oxide mixtures whereas the spectra for fluid-treated soil suggested the major form of Mn in the is soil was a Mn(II) phosphate mineral called hureaulite (Figure 3). Our calculations using solubility data showed that when P and Ca solubility are controlled by hydroxyapatite and calcite (typical in fertilized calcareous soils) and at typical CO_2 concentrations, $MnCO_3$ can be comparatively less soluble than hureaulite or various other Mn phosphates. Thus x-ray absorption spectroscopy analysis agreed with previous isotopic dilution techniques indicating that when Mn is added to the soil in liquid forms, more Mn remains in comparatively more soluble minerals. By contrast, granular Mn tends to transform into comparatively less soluble minerals.

Zinc. X-ray diffraction analyses of the original granular Zn showed the major crystalline form of Zn in the granule was zincite (ZnO). No other crystalline forms of Zn were observed by the XRD analysis (data not shown). Both XRD and SEM-EDAX analyses indicated that the concentration of Zn species in the incubated granules became higher following their incubation in soil possibly due to the decreased concentration of major nutrient elements (i.e., N and P). XRD analysis of incubated Zn granules showed that some ZnO was still present. Furthermore, both XRD and SEM-EDAX analysis suggested that a significant amount of Zn remaining in the incubated granules was present in mixed metal phosphate forms (i.e., Zn, Ca, and Al phosphates).

The chemistry of Zn in fertilized soil appeared to vary little with the form of Zn fertilizer added. Analysis of both the micro and bulk x-ray absorption data indicated that for granular Zn, Zn phosphate-like and Ca/Zn phosphate-like compounds dominated the reaction products. For fluid Zn, adsorbed Zn or Zn silicate-like compounds appeared to dominate the Zn spectra (data not shown). Nriagu (1984)* suggested the formation of sparingly soluble mixed metal-Zn phosphates as a possible mechanism restricting Zn solubility in alkaline environments.

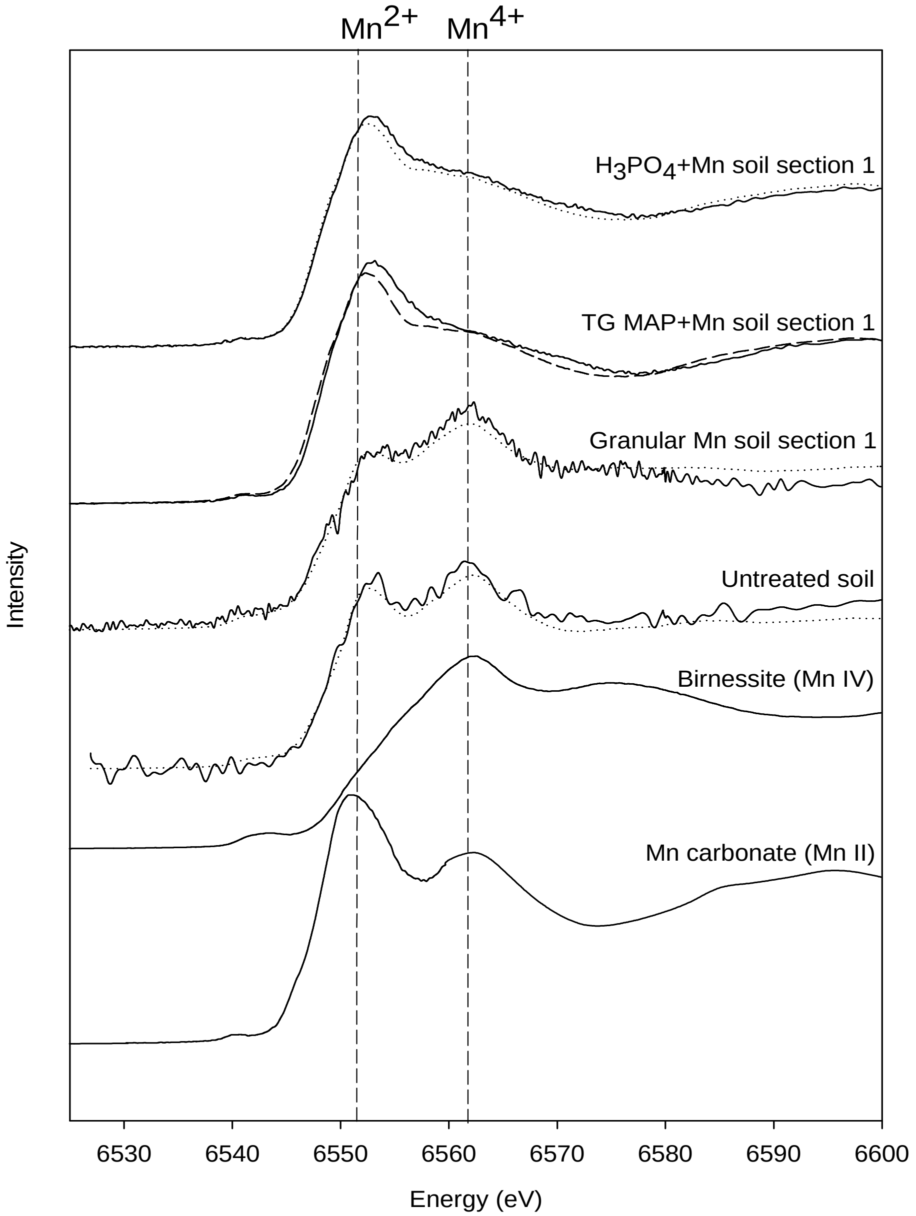

Figure 3. Mn x-ray absorption spectra for different treatments and the line of best fit by combining various mixtures of spectra of pure Mn minerals. Dotted lines indicate where peaks are expected for the two oxidation states of Mn (Mn^{2+} and Mn^{4+}).

Conclusions

XRF mapping of soil/fertilizer reaction zones indicated that the mobility of Mn and Zn from fluid fertilizer was greater than observed for equivalent granular sources of these trace elements in a calcareous soil. X-ray microscopic and spectroscopic analyses agree with our previous isotopic dilution techniques and provide evidence that when fluid Mn and Zn were applied to soil, a considerably greater proportion of these micronutrients remained in relatively more soluble minerals compared to the granular forms. Our data suggest that the superior agronomic effectiveness of fluid Mn and Zn fertilizer observed in calcareous soils under field conditions may have resulted from the enhanced diffusion and/or solubility of these micronutrients in soil when applied in fluid form. Moreover, this study confirms that the combination of different x-ray techniques, including synchrotron-based x-ray techniques, is useful for identifying reaction products of micronutrients in the soil.

* Formation and stability of base metal phosphates in soils and sediments, p. 318-329. *In* J.O. Nriagu and B.P. Moore (Eds.) Phosphate Minerals. Springer-Verlag, Berlin.

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