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Novel Chelating Agents Increase Micronutrient Solubility

Potential is there not only to increase solubility of micronutrients in fluid fertilizers but also retain them in forms that are readily available to plant roots.

Summary: *Both polyethylenimine (PEI) and rhamnolipid increased zinc (Zn) uptake by canola and wheat grown on highly alkaline soils in the field (PEI) and in glasshouse trials (rhamnolipid). The lipophilic properties of micronutrients complexed by rhamnolipid could markedly assist crop uptake of elements complexed by this chelate. This was confirmed spectroscopically using synchrotron x-ray techniques where Zn complexed by rhamnolipid was found to move intact into canola roots. These new types of chelates, which do not form anionic micronutrient complexes, have the potential not only to increase the solubility of micronutrients in fluid fertilizers, but also retain them in forms that are readily available to plant roots.*

Millions of acres of arable land worldwide, particularly in arid and semi-arid regions, are deficient in plant-available micronutrients and this can markedly affect human nutrition. The major reason for the widespread occurrence of deficiency of micronutrients is the low availability of micronutrients to plant roots rather than their low concentration in soils. The low solubility of most micronutrient cations--copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn)--in soils means that after the addition to alkaline soil as the soluble form, the metal is rapidly sorbed or precipitated. One method to reduce these reactions in soil is through the use of chelates. Chelates are organic compounds that bind the metal and increase water solubility. Common chelates are ethylene diminetetraacetic acid (EDTA) and dimethylamine pentaacetic acid (DTPA) and these molecules increase micronutrient solubility through reversal of charge on the metal. The metallic cation M^{2+} becomes ML^{n-}, where M is the micronutrient cation and L the chelate, i.e., the chelate makes the micronutrient anionic.

It is well known that both EDTA and DTPA markedly increase the solubility of micronutrient cations in soil and aid their diffusion to plant roots. Indeed, the high mobility of these compounds raised concerns regarding their potential use in industrial and household chemicals due to their ability to transport heavy metals in the environment. While these chelates have an excellent ability to retain micronutrient cations in soluble forms, the form in which the micronutrient exists in solution is, however, not readily available for uptake by plant roots. It is well known that plants absorb micronutrient cations through defined metal transporters in the plant root membrane that principally recognize the free metal cation M^{2+}. These transporters do not recognize all complexed forms of micronutrients (an exception would be Fe-phytosiderophore). Indeed, addition of EDTA or DTPA to nutrient solutions markedly depresses the uptake of micronutrients by the plant due to complexation of the free metal cation (M^{2+}).

Thus, the efficiency of chelates such as EDTA and DTPA in terms of improving crop nutrition is compromised by the poor ability of the complexed forms of micronutrient to be absorbed by plant roots.

A better way?

In this article we shall examine new potential applications for two new chelates--polyethylenimine (PEI) and rhamnolipid--to improve crop micronutrient nutrition through exploitation of different physical and chemical behaviors of the chelates.

Ko/w values for the metals complexed by rhamnolipid were high. Normally, metallic cations are hydrophilic and do not partition to the octanol phase (and hence have very low Ko/w values). High Ko/w values for micronutrient cations found with rhamnolipid indicated that the chelate had formed a lipophilic complex with the cation, a property likely to assist in uptake by plant roots. PEI forms cationic complexes with micronutrients, so Ko/w values were low for this chelate (Figure 1).

Shoot concentration. Canola plants were grown under Zn deficient conditions. Therefore, on Streaky Bay soil, shoot Zn concentrations were below the published critical tissue concentrations for Zn of 7-8 mg Zn/kg dry matter (DM). Canola plants grown on Birchip soil had Zn concentrations at or above the critical Zn concentration; treatment with rhamnolipid and PEI increased shoot Zn concentration above the critical levels (Figure 2). Rhamnolipid also significantly increased concentration ($P<0.05$) of Zn in canola shoots grown on the highly calcareous Streaky Bay soil. EDTA did not significantly ($P>0.05$) increase Zn uptake from either soil, compared to the $ZnSO_4$ control even though EDTA substantially increased the solution concentrations of Zn in both soils (data not shown).

Root concentration. Examination of canola roots exposed to $ZnSO_4$,

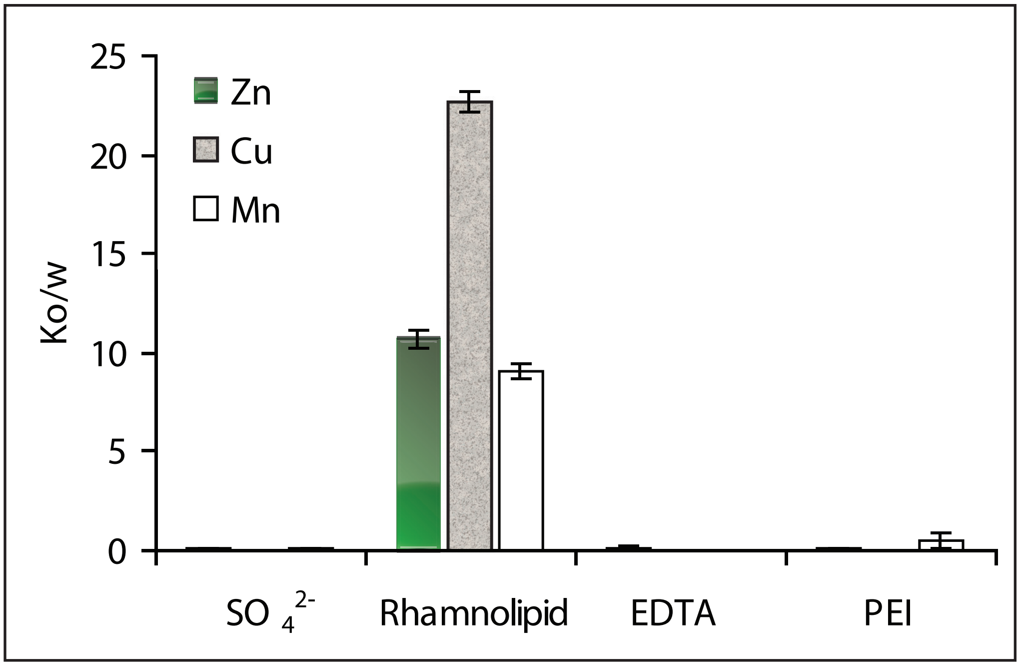

Figure 1. Octanol/water partition coefficients (Kw/o values) for Cu, Mn, and Zn with sulphate, EDTA, rhamnolipid and PEI), Stacey, 2007.

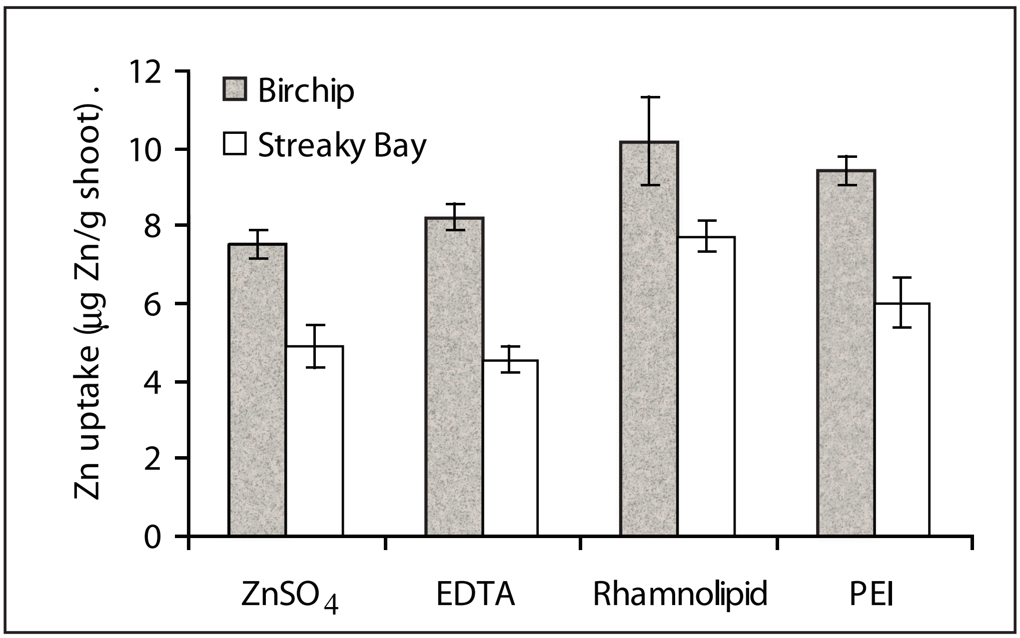

Figure 2. Uptake and translocation of Zn to canola shoots.

Zn-EDTA, and Zn-rhamnolipid revealed a significantly different pattern of accumulation, and a different speciation of Zn within the plants (Figure 3). The lowest Zn x-ray fluorescence signal was obtained from the Zn-EDTA treated roots (Figure 3, top), probably due to a reduction in Zn absorption by roots due to low solution Zn^{2+} activities in the presence of EDTA. The Zn signal was higher in $ZnSO_4$-treated roots and highest in Zn-rhamnolipid roots. EXAFS data (taken from XAS spots labeled in Figure 3) suggested that Zn was predominantly in the form of Zn-phytate-like compounds in Zn-free, $ZnSO_4$, and Zn-EDTA treated roots with 70-87 percent of total root Zn present as Zn-phytate-like compounds in these treatments. Zn-EDTA complexes were not detected inside root cross sections, consistent with published literature that showed Zn-EDTA complexes are not readily absorbed by intact roots via active or passive uptake pathways. In roots treated with Zn-rhamnolipid, EXAFS suggested that 55.3 and 87.6 percent of Zn was probably in the form of Zn rhamnolipid at spots A and B, respectively (Figure 3, bottom). These results suggest that Zn-rhamnolipid complexes may have been absorbed intact by roots, possibly due to the lipophilic properties of these complexes.

Conclusions

EDTA, DTPA and other chelates that form anionic complexes with cationic micronutrients are effective in solubilizing these elements in soil but ineffective in allowing them to be taken up by plant roots. Addition of these chelates to fluid fertilizer blends may increase the micronutrient solubility in the blend, but the resultant form of micronutrient is not one that crops can easily use. New types of chelates, which do not form anionic micronutrient complexes, have the potential not only to increase the solubility of micronutrients but also retain them in forms that are readily available to plant roots. The fact that some of these products have lipophilic properties is an added advantage, as they appear to be able to be readily transported (intact) into the plant root.

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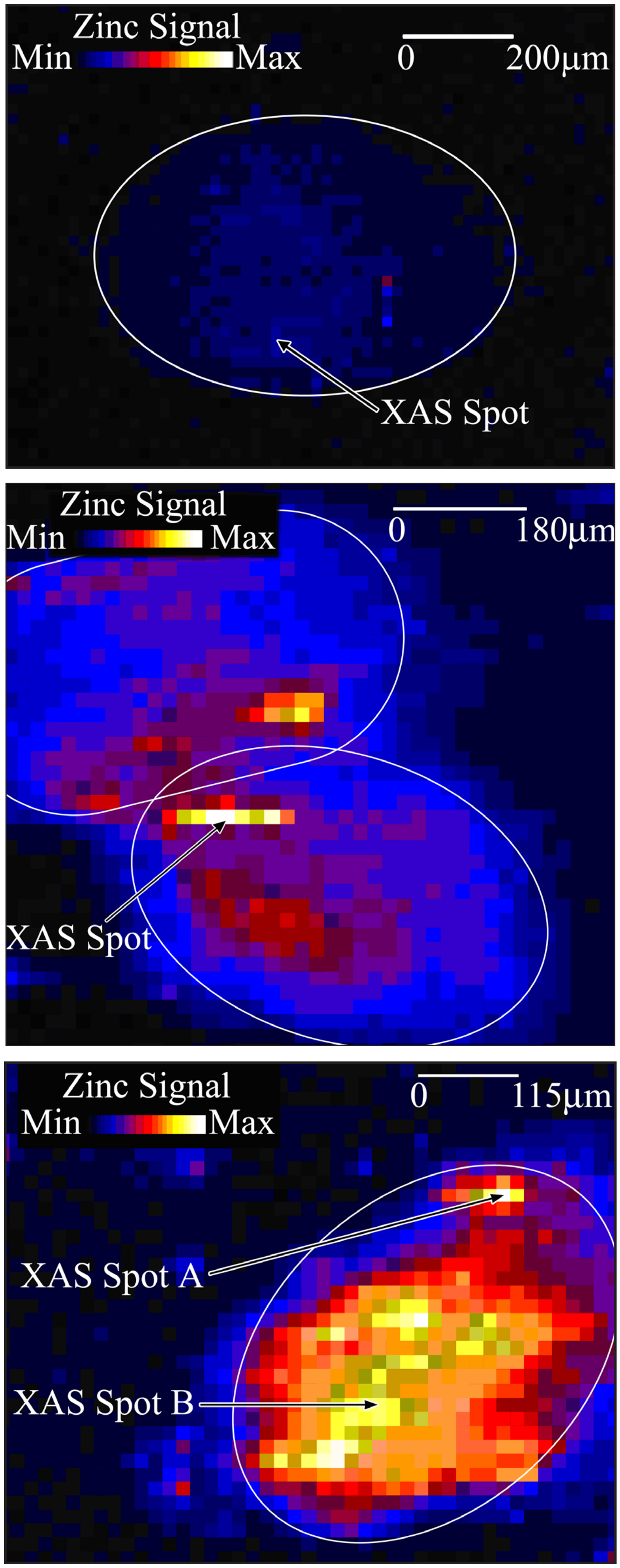

Figure 3. Zinc x-ray fluorescence maps showing the distribution of Zn in a canola root treated with Zn-EDTA (top), $ZnSO_4$ (middle), and Zn-rhamnolipid (bottom). Speciation of Zn forms was undertaken at the XAS spots marked. Stacey, 2007.