Improving Micronutrient Fluid Fertilizers using Novel Chelating Agents

Mike McLaughlin[1,2] and Samuel Stacey[1]

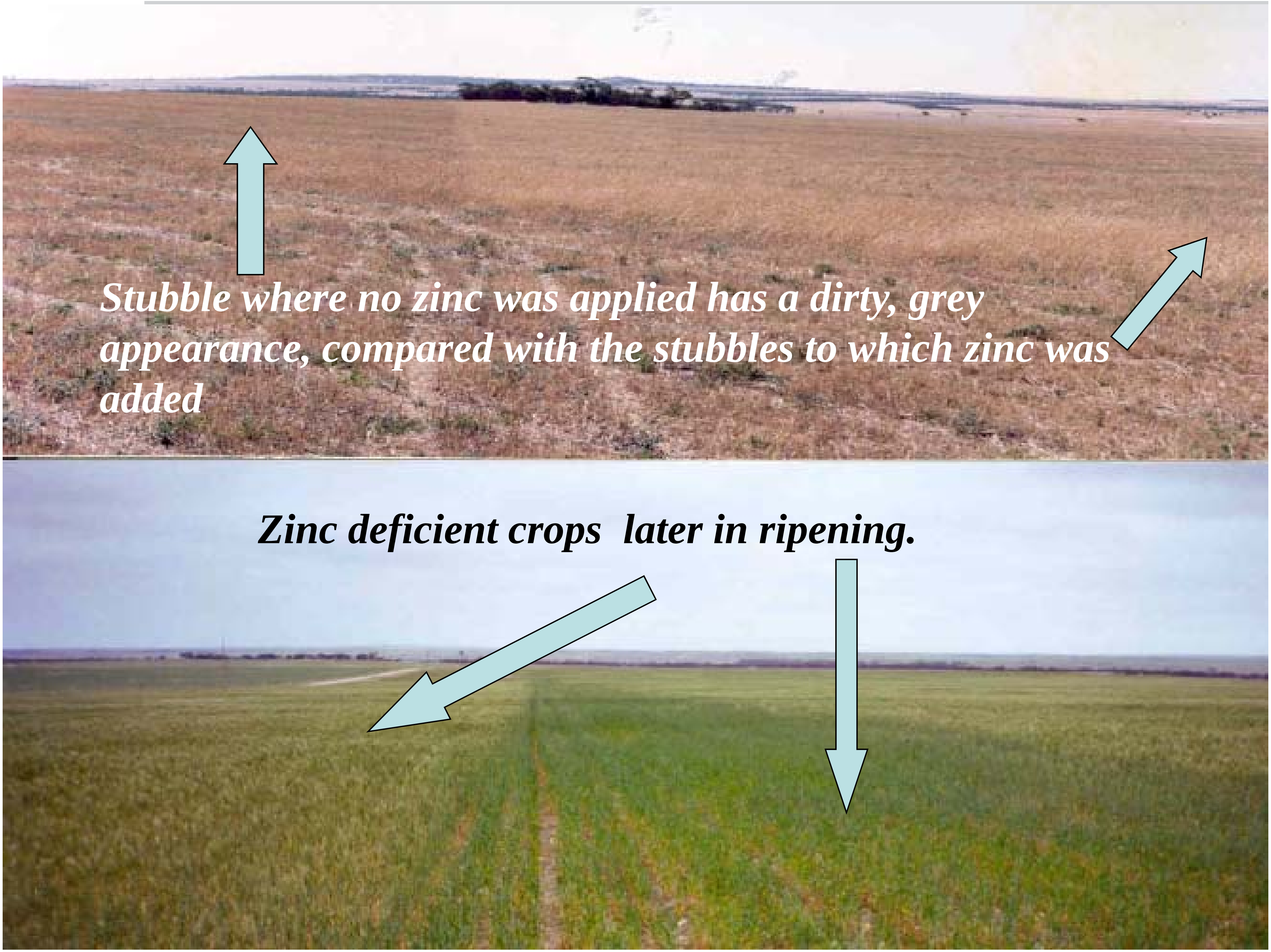
[1]Earth and Environmental Sciences, The University of Adelaide, AUSTRALIA
[2]CSIRO Land and Water, Urrbrae, AUSTRALIA

Areas of the world prone to micronutrient deficiency

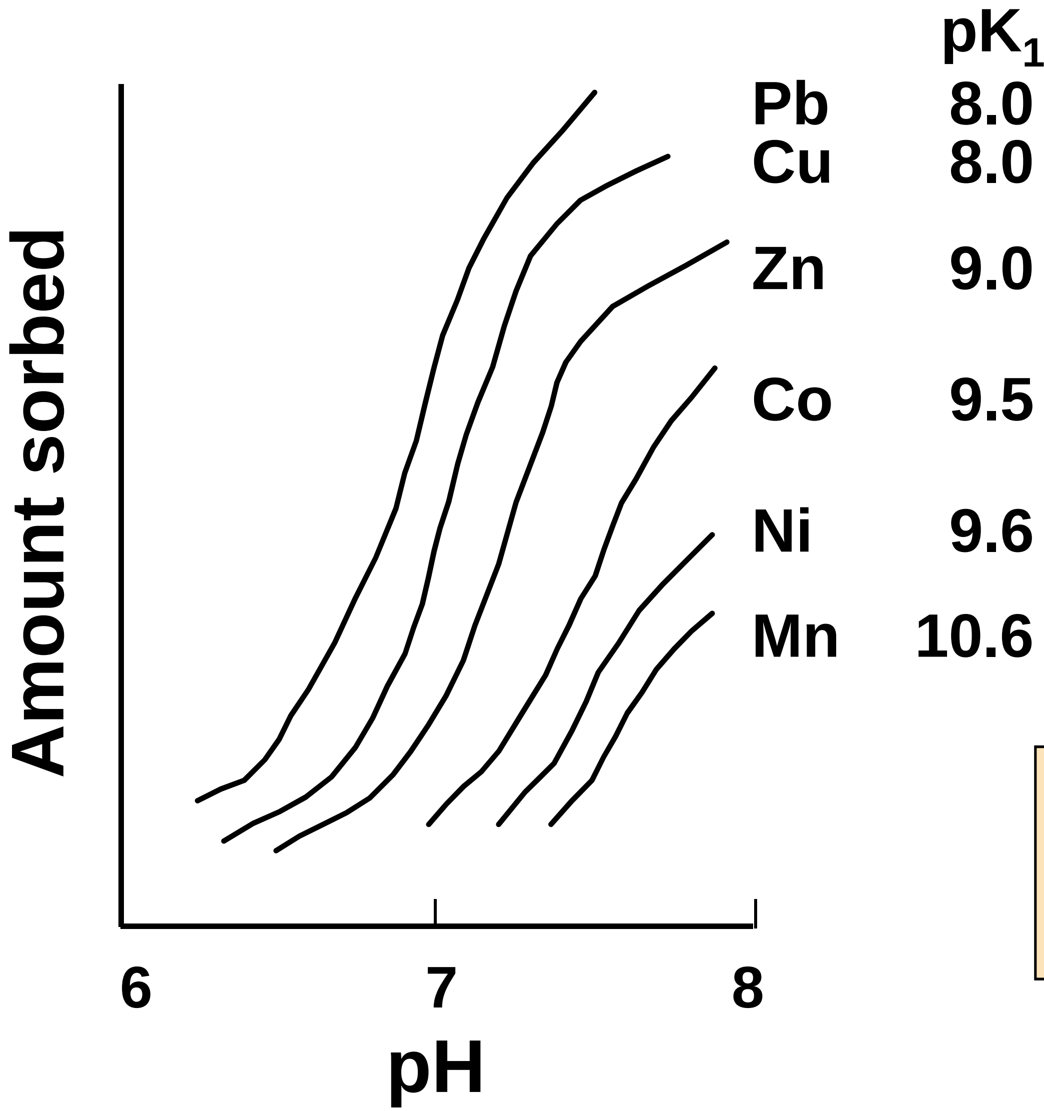
Combined Global Distribution of the Main Types of Soils Associated with Zinc Deficiency Derived from the World Reference Base for Soil Resources Atlas by Bridges, Batjes and Nachtergaele (1998)

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

Alloway 2003


Stubble where no zinc was applied has a dirty, grey appearance, compared with the stubbles to which zinc was added
Zinc deficient crops later in ripening.

Reactions of micronutrients 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 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.

Compound	pK_{sp}
$CaCO_3$	$1.0 \times 10^{-8.3}$
$Cu(OH)_2$	1.6×10^{-19}
$CuCO_3$	1.4×10^{-10}
$Cu_3(PO_4)_2$	1.4×10^{-37}
$Mn(OH)_2$	2.0×10^{-13}
$MnCO_3$	2.2×10^{-11}
$ZnCO_3$	1.5×10^{-10}
$Zn(OH)_2$	1.2×10^{-17}
$Zn_3(PO_4)_2$	9.0×10^{-23}

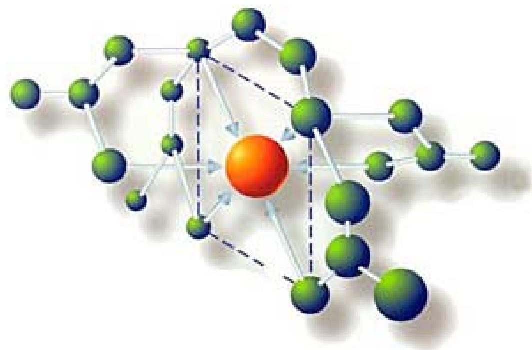
Compatibility issues

Solubility of ZnO in polyphosphate solutions (from Mortvedt, 1991).

	Fertiliser Solution pH		
Polyphosphate content	5.0	6.0	7.0
(% of total P)	------------------	% Zn	------------------
40	0.6	1.3	1.6
50	0.7	1.6	1.9
60	0.7	1.7	2.0
70	0.7	1.7	1.6
80	0.7	1.4	2.6

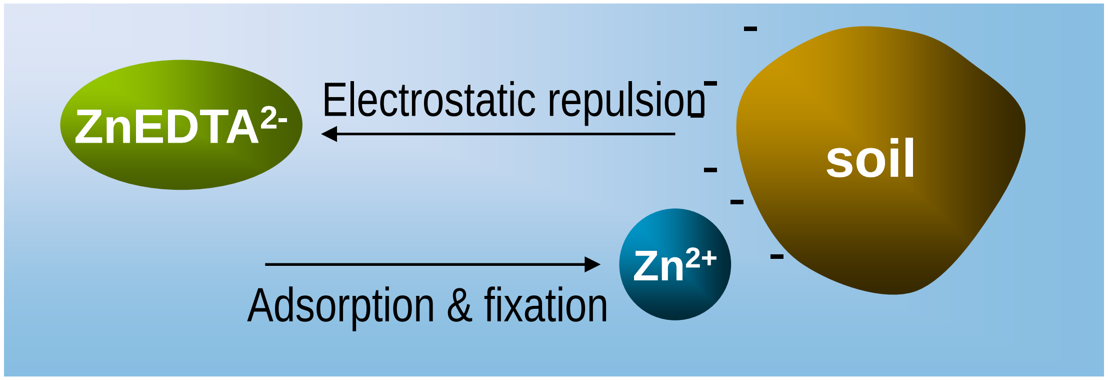
Chelates used to complex micronutrient ions

- Organic molecules that complex micronutrient (metal) cations



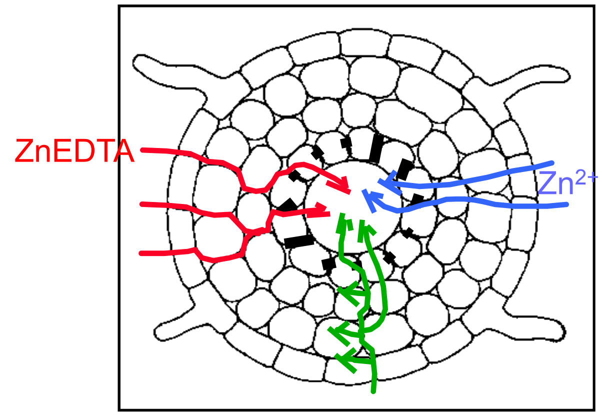
- Alters the charge of the fertiliser ion, which changes its fate in soil and affects absorption by plants

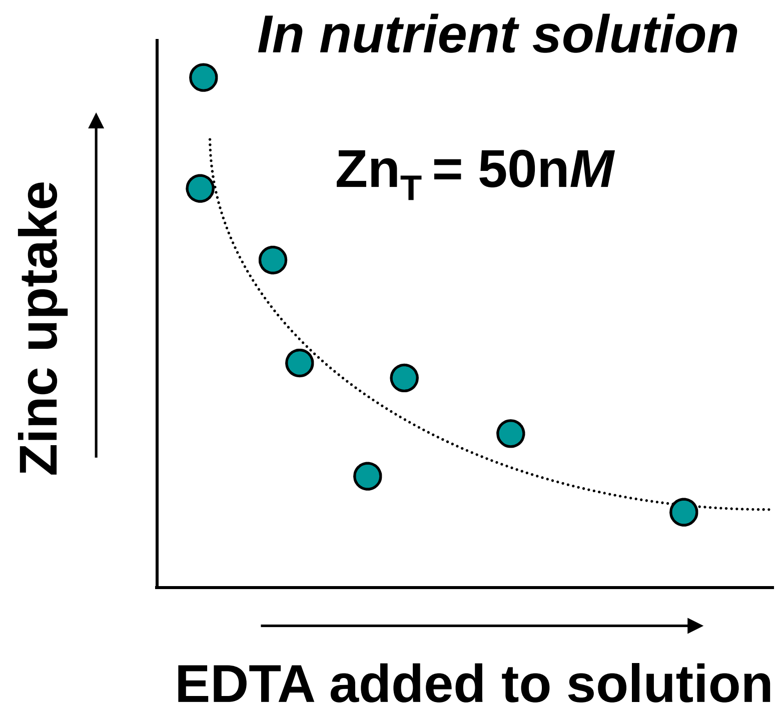
$$Zn^{2+} + EDTA^{4-} \rightleftharpoons ZnEDTA^{2-}$$



Problems with anionic chelates

- Charge reversal allows the cation to be mobile in the soil environment (subject to wash off/leaching)
- Plants *do not* absorb –vely charged metal-chelate complexes readily due to negative membrane potentials





Current Trace Element Fertilizers

Limitations to their effectiveness:

- Current trace element fertilizers are relatively ineffective on alkaline and calcareous soils, where micronutrient deficiencies are most severe;
- Synthetic chelates (e.g. EDTA) are not readily absorbed by roots due to membrane exclusion;
- Negatively charged complexes may be electrostatically repelled from plant roots;
- Product cost has mainly limited their use to high-value crops.

Environmental Pollution:

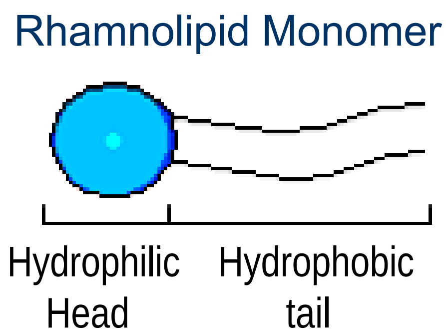
- EDTA is a persistent substance, has been found ubiquitously in the environment and has caused environmental degradation;
- NTA is carcinogenic and has been banned in the USA.

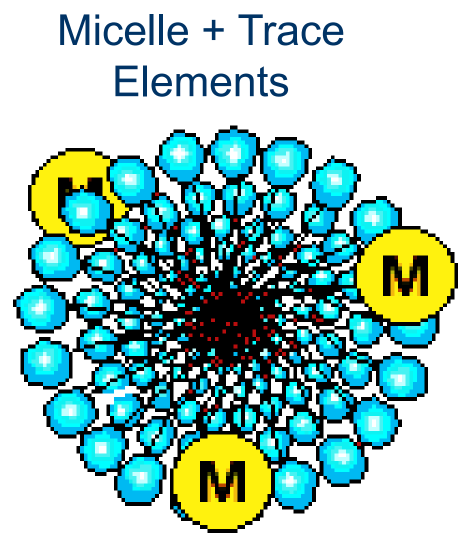
Requirements for effective micronutrient fertilizers

- Reduce trace micronutrient adsorption or precipitation.
- Increase solution metal concentration (to aid mass flow and diffusion)
- Increase labile pool of metal in soil
- Membrane permeable or actively transported by root uptake mechanisms (minimises –ve charge on metal complex)
- Environmentally friendly
- Inexpensive

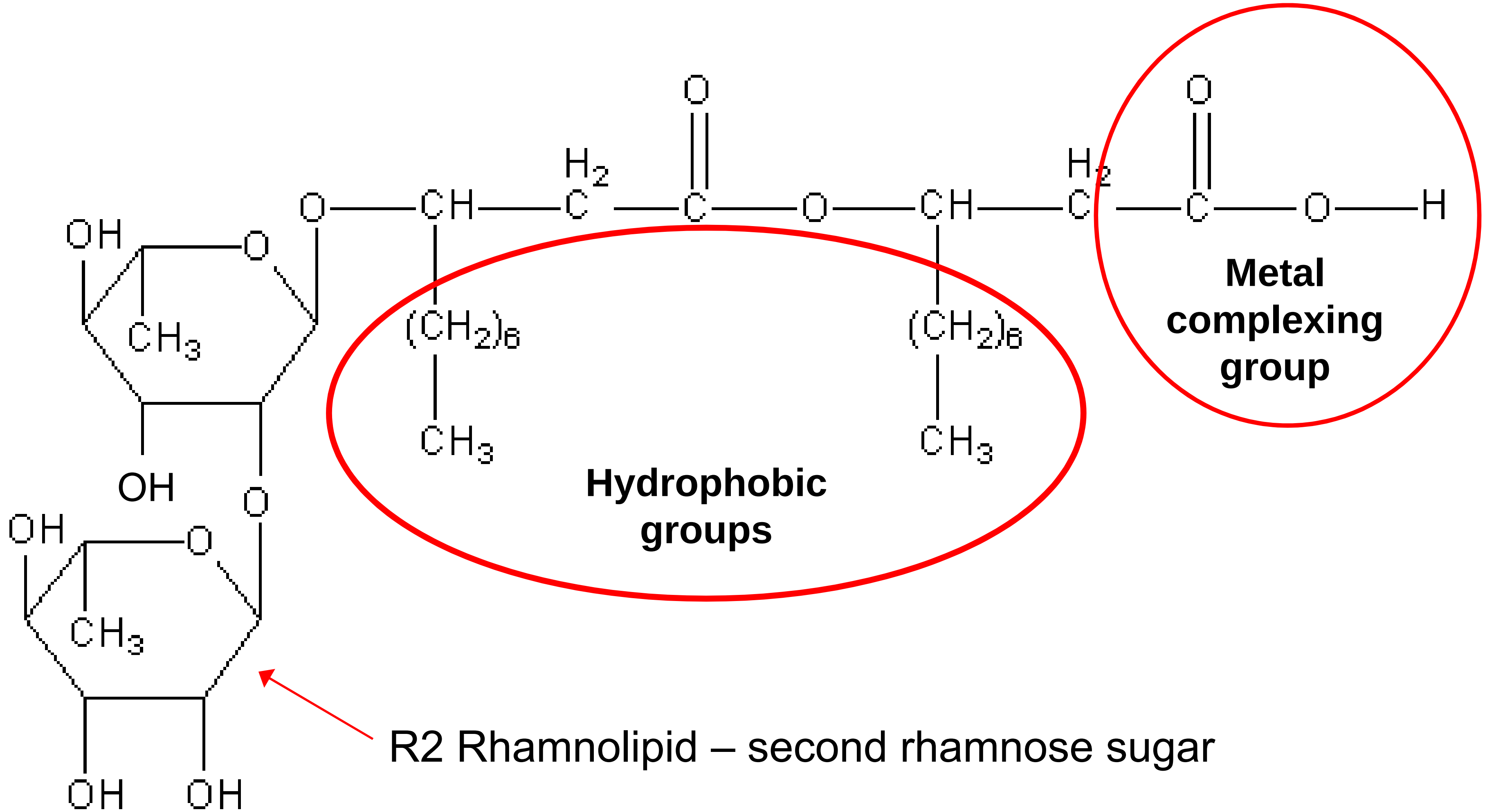
Rhamnolipid: a ‘lipophilic’ chelate

- Rhamnolipid is a biological chelating agent produced by bacteria;
- Non-toxic, biodegradable, can be synthesised or purchased;
- Product complexes trace elements (Zn, Cu, Mn etc) into a ‘lipophilic’ state;
- The chelate can be readily absorbed by plant roots;
- Less prone to leaching or surface runoff than EDTA and DTPA.



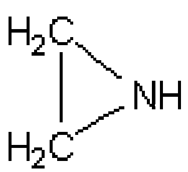


R1 Rhamnolipid biosurfactant

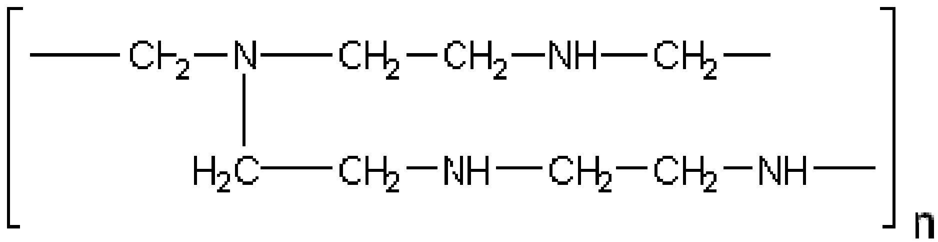


Polyethyleneimine - PEI: a plant-available polymer?

- Chelating polymer with an extremely high complexing capacity for trace elements (chelate rates could be reduced by 75%);
- Used for transmembrane delivery of DNA and other pharmaceuticals
- Less prone to leaching or surface runoff than EDTA;



Ethyleneamine



Polyethyleneamine

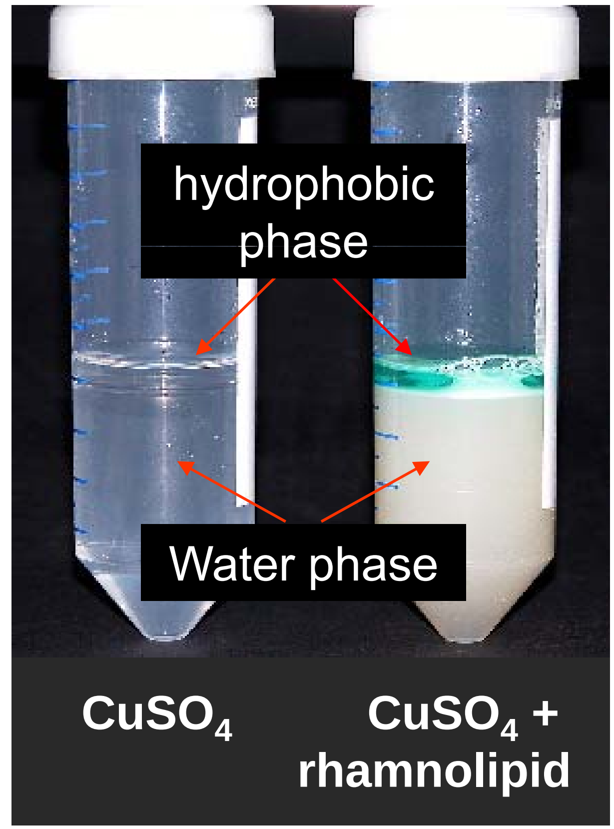
Cu^{2+} complexing capacity of EDTA and PEI

Chelate	Max. Complexing Capacity (g Cu^{2+}/g chelate)
EDTA	0.37
PEI	1.49

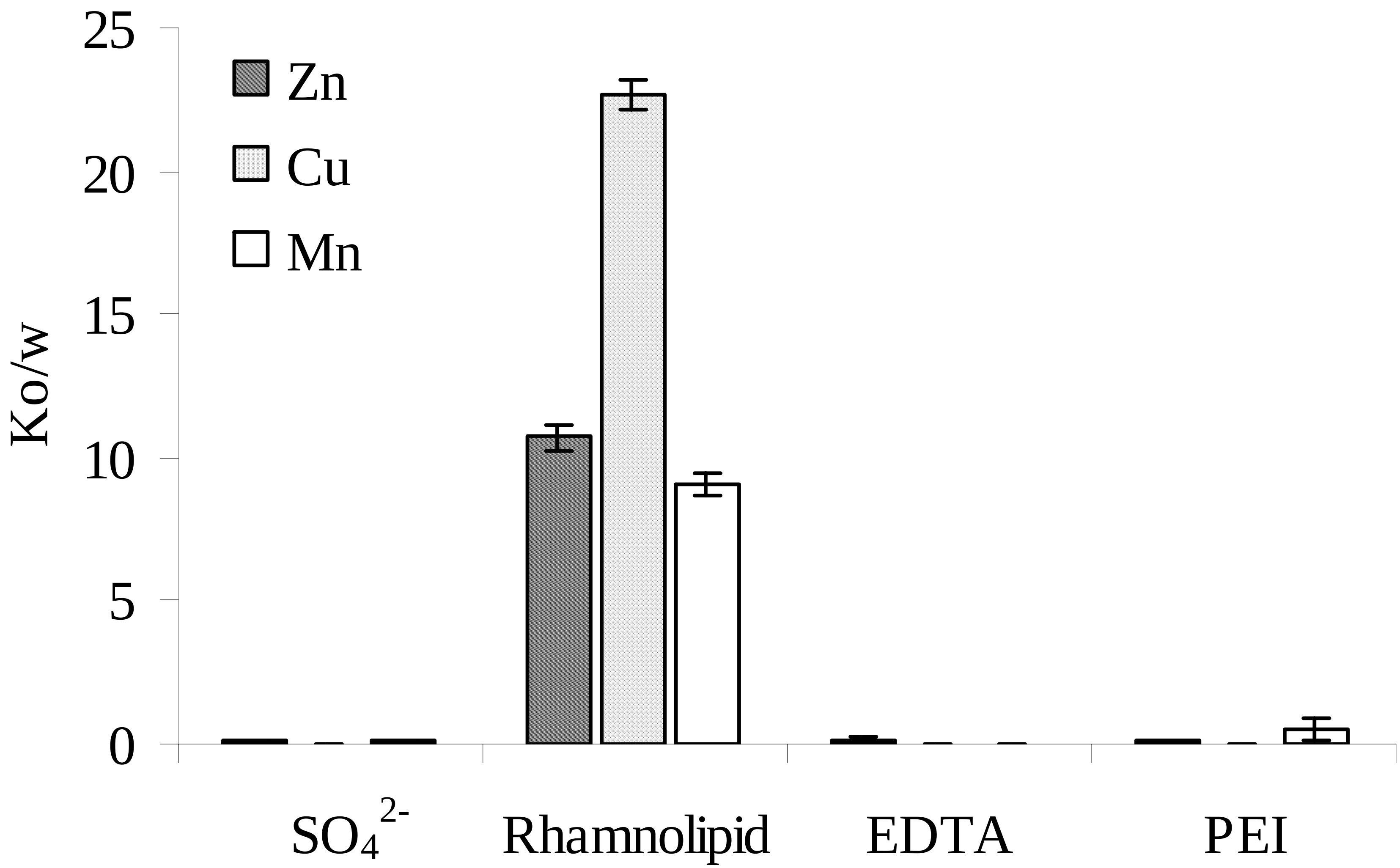
Measuring lipophilicity of rhamnolipid

Normally used to measure biomagnification potential of pesticides and other organic chemicals

$$K_{o/w} = \frac{[\text{Fert}]\ \text{octanol}}{[\text{Fert}]\ \text{water}}$$



Lipophilic complexes with rhamnolipid



Response of Zn deficient to rhamnolipid: Glasshouse trial on calcareous soil in Turkey (Ismail Cakmak)

0 0.75 2 4 6

Rhamnolipid (mg/kg). All pots 2ppm Zn

Response of Zn deficient soil to PEI: Glasshouse trial in Turkey (Ismail Cakmak)

0 0.05 0.2 0.5 1

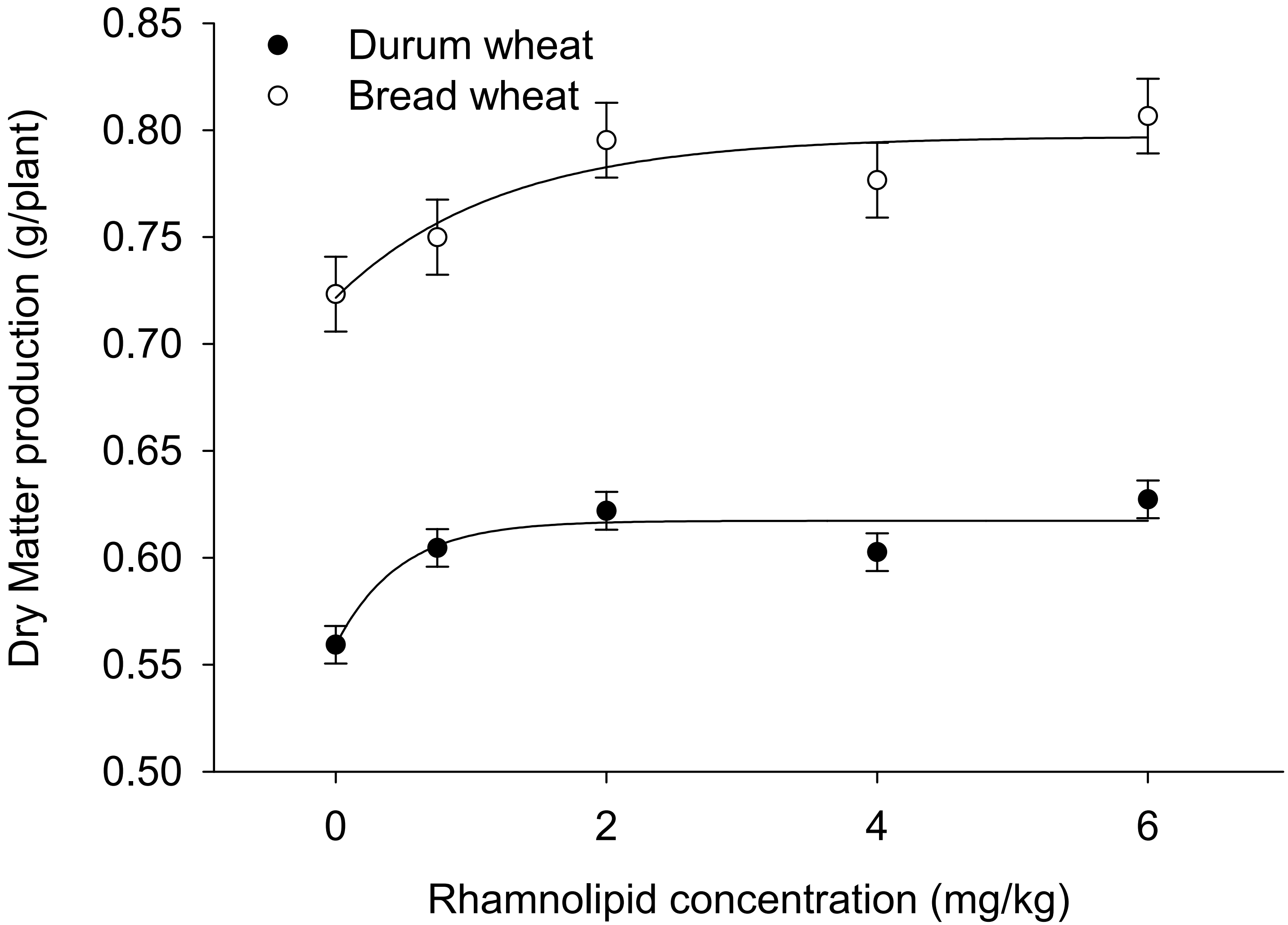
PEI (mg/kg). All pots 0.05 mg/kg Zn

Response of Zn deficient soil to PEI: Glasshouse trial in Turkey (Ismail Cakmak)

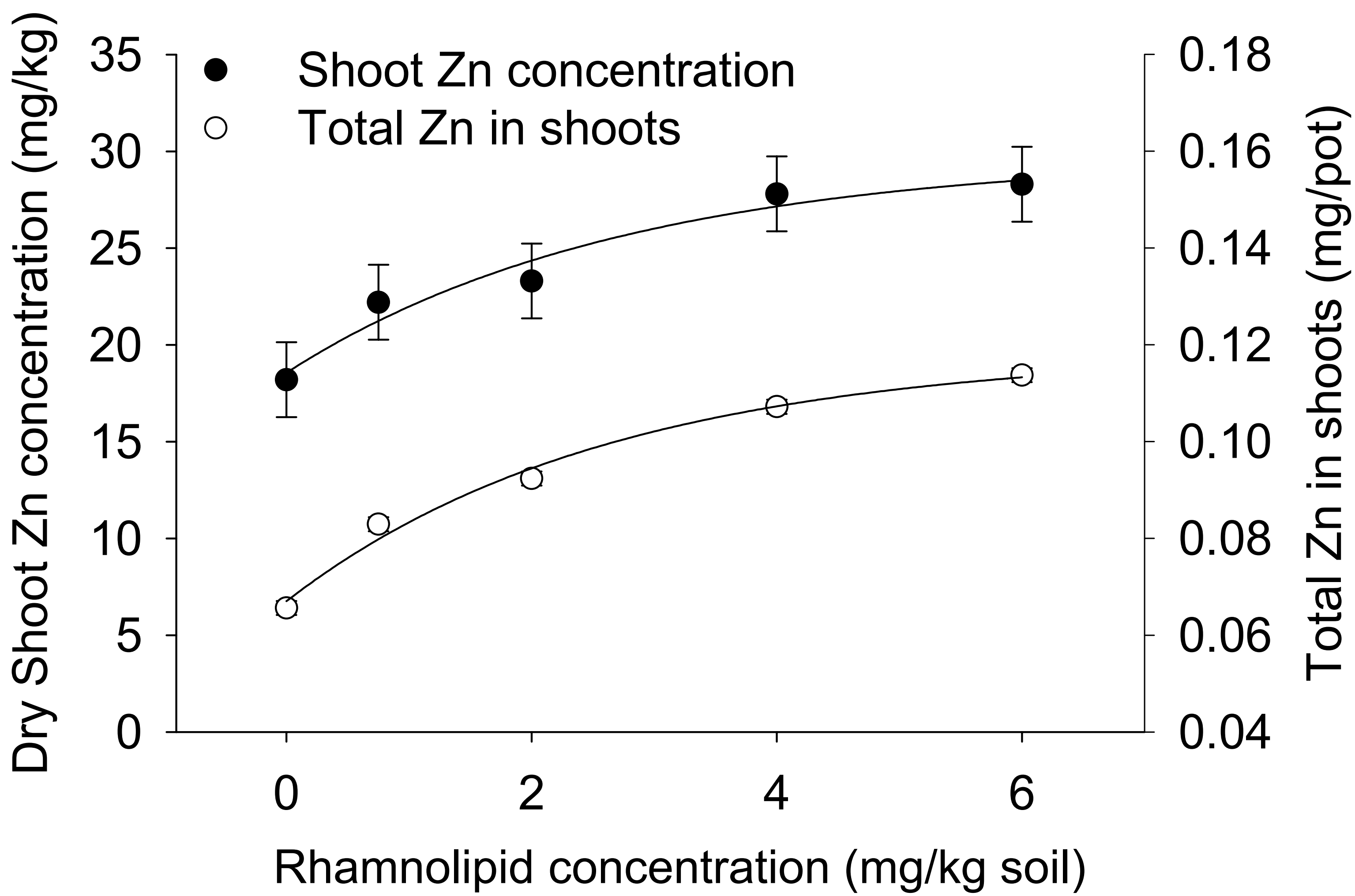
0 0.05 0.2 0.5 1

PEI (mg/kg). All pots 2ppm Zn

Wheat dry matter response to rhamnolipid.
Bars denote L.S.D. ($p \leq 0.05$)

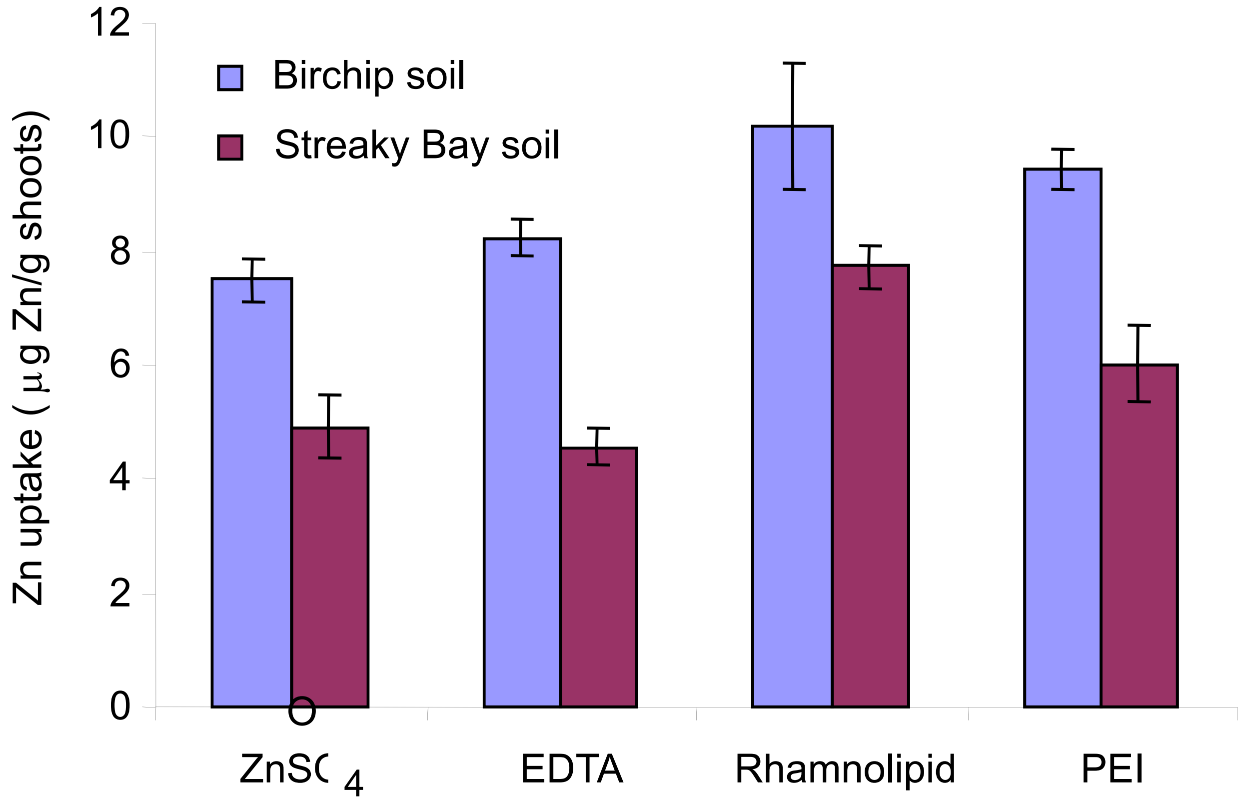


Effect of rhamnolipid application on Zn uptake by bread wheat. Bars denote LSD ($P \leq 0.05$)



Glasshouse trial on Zn uptake by canola

- The new products are more effective trace element fertilizers than EDTA on alkaline and calcareous soils.



Absorption of Zn complexes by canola roots

EDTA, rhamnolipid and PEI compared as Zn chelants

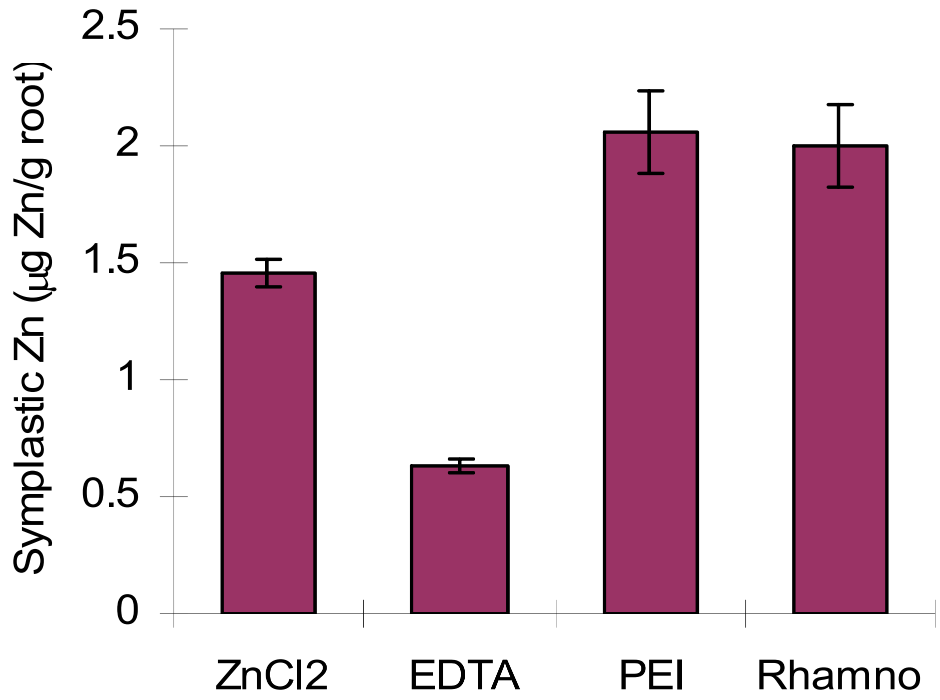
Canola plants, kinetic uptake of chelated fertilizers

Zinc speciation determined by Anodic Stripping Voltammetry

New chelates are readily absorbed by plant roots

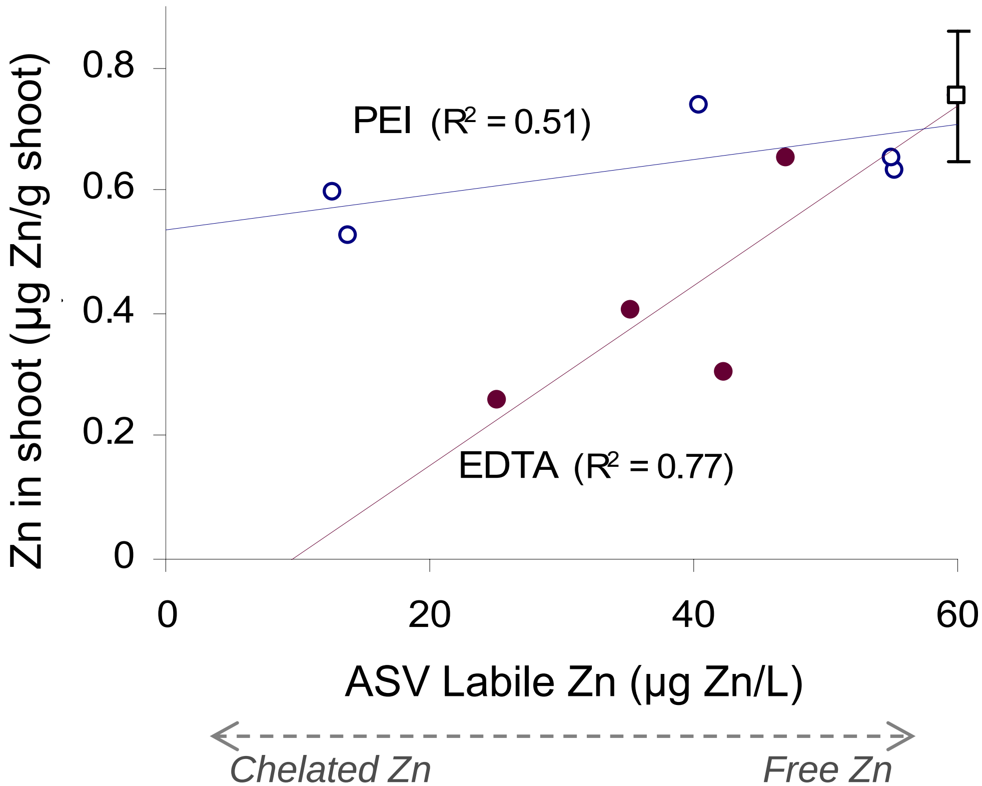
- Both new products were readily taken up by canola roots.
- Zn EDTA was excluded at the root membrane surface and not readily absorbed by canola.

Uptake of Zn by canola roots in solution culture

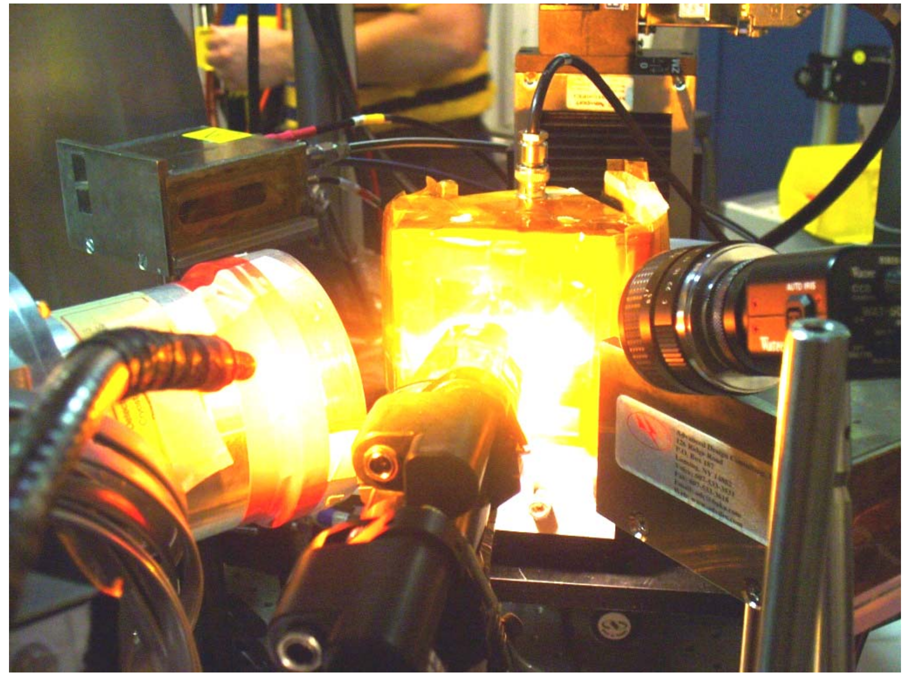


New chelates are readily absorbed by plants

- Zn PEI was readily absorbed and translocated to canola shoots.
- Zn EDTA was not taken up by the plants.



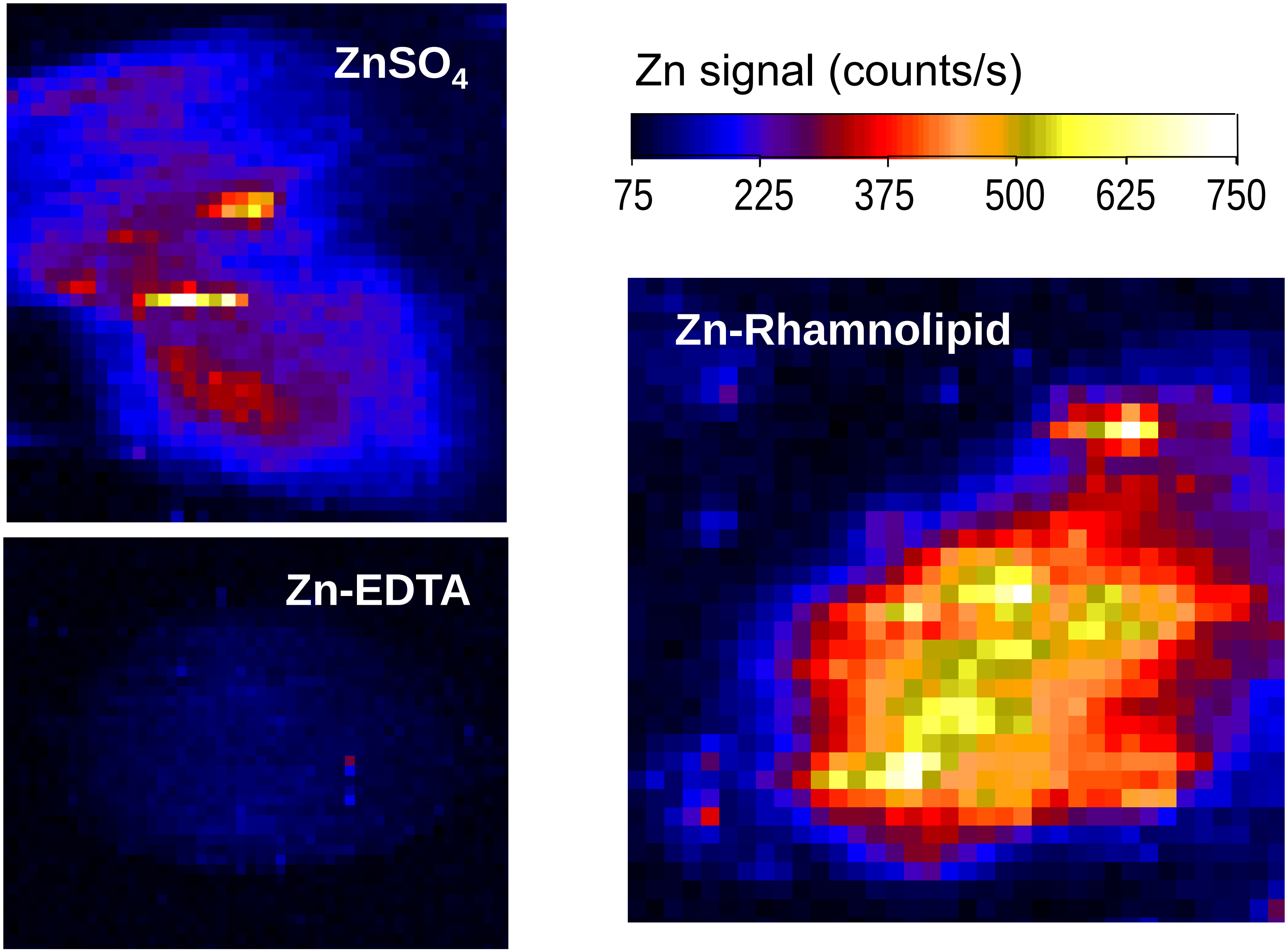
Zinc distribution and speciation in canola roots



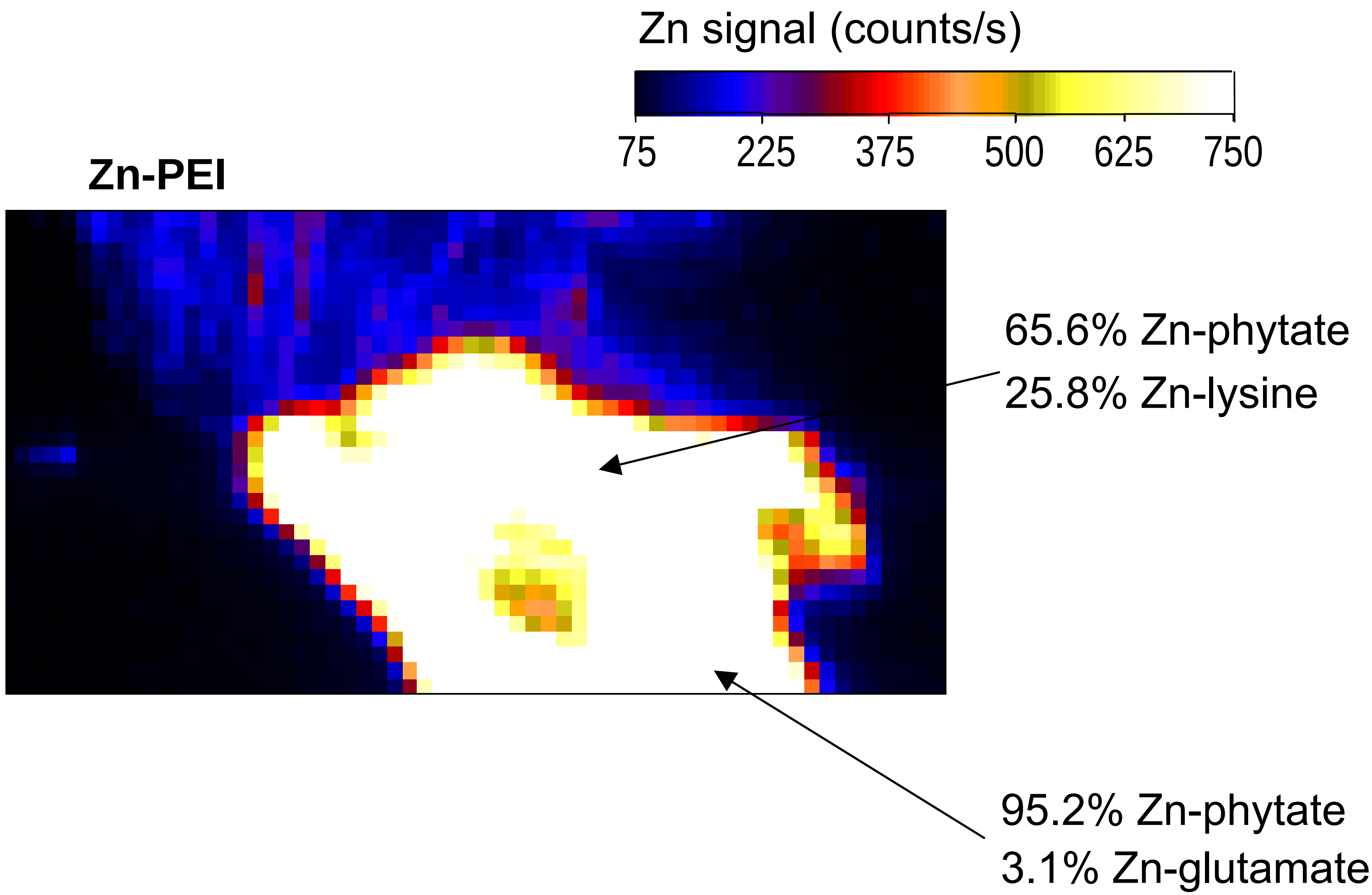
13-BM at the Advanced Photon Source, Argonne National Laboratory.

- Zn mapped in root cross-sections using X-ray Microprobe fluorescence;
- Zn speciated using X-ray Absorption Fine Structure Spectroscopy.

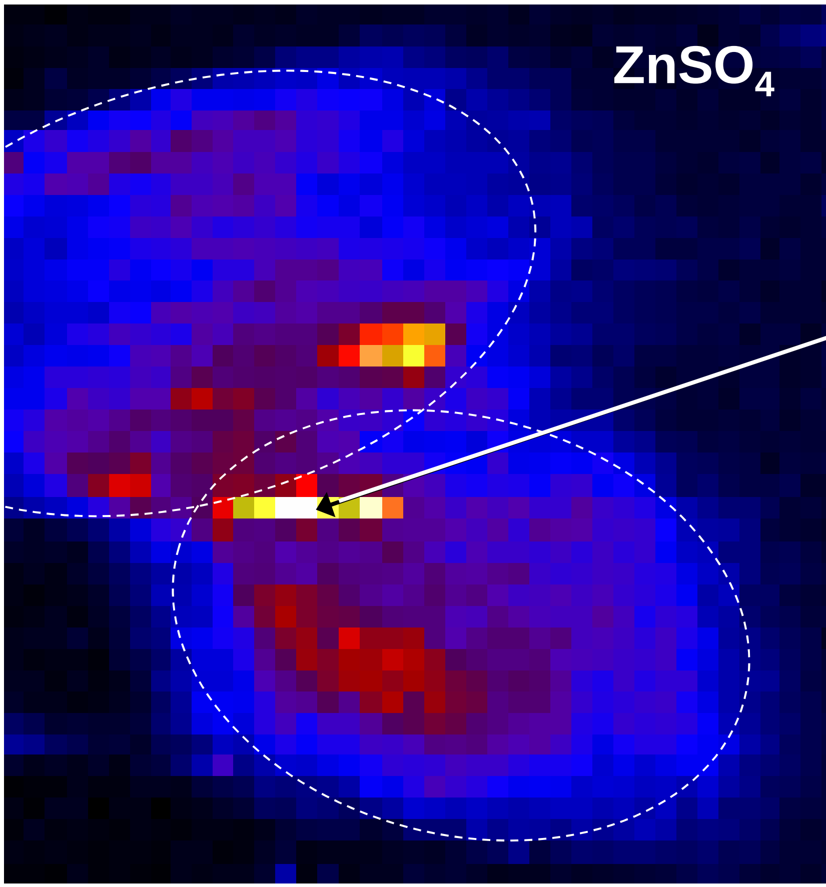
Synchrotron Zn X-ray fluorescence maps



Zinc distribution and speciation in roots from different fertilizer sources



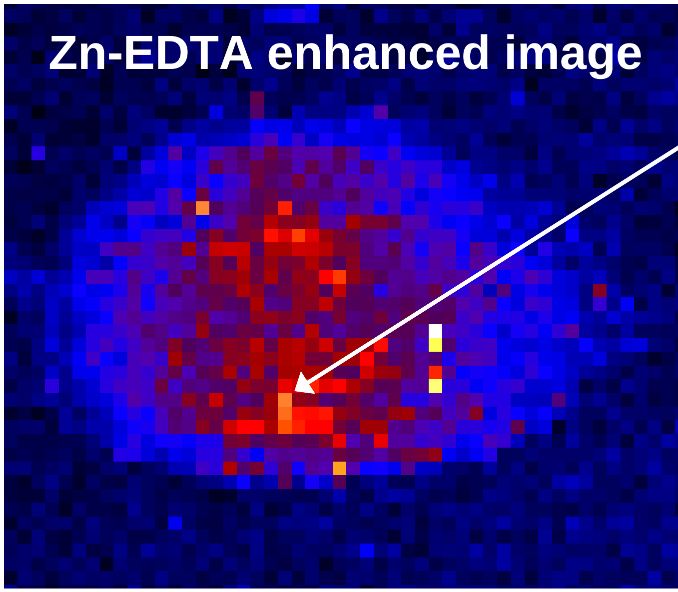
XAS speciation of Zn in $ZnSO_4$ treated root sections



77% Zn-phytate
23% Zn-proline

- Zn was predominantly stored in the root as Zn-phytate

XAS speciation of Zn in Zn-EDTA treated root sections

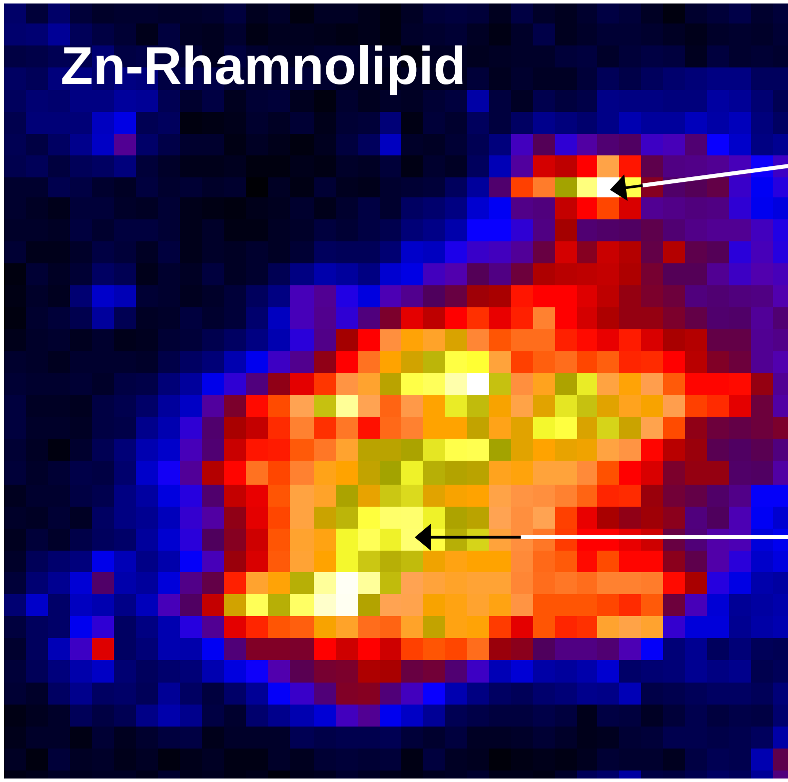


81.2% Zn-phytate
18.8% Zn-glutamate

- Zn-EDTA was not detected inside the root symplast;
- Zn was predominantly stored in the root as Zn-phytate, even at low (environmentally relevant) Zn levels.

XAS Zn speciation in controls (no Zn)
84.4% Zn-phytate 15.6% Zn-glutamate

XAS speciation of Zn in Zn-rhamnolipid treated root sections



61.3% Zn-rhamnolipid
24.4% Zn-proline
14.3% Zn-phytate

80.0% Zn-rhamnolipid
16.1% Zn-phytate
3.9% ZnSO4 (or Zn2+)

- Zn was predominantly found in the root as Zn-rhamnolipid, rather than Zn-phytate;
- Intact Zn-rhamnolipid may have been absorbed by roots.

Canola field response to PEI in Southern Australia

Conclusions

- Rhamnolipid formed lipophilic complexes with micronutrients and PEI has a high metal-complexing capacity;
- Soil application of these compounds with Zn increased DM production and Zn uptake in canola and bread/durum wheat grown on calcareous Turkish and Australian soils;
- Rhamnolipid significantly ($P \leq 0.05$) increased Zn uptake by canola in ice-cold nutrient solutions despite reducing the (Zn^{2+}) - Zn-rhamnolipid was the predominant form of Zn in roots supplied with 5µM Zn-rhamnolipid.
- PEI also dramatically increased Zn uptake by canola roots in solution culture and suggests very effect transmembrane transport
- Both products show potential to improve micronutrient delivery in fluid fertilizers

Acknowledgements

Mosaic™

Fluid Fertilizer Foundation