Making more effective zinc fertilizers

Mosaic-supported Fertilizer Technology Research Centre

@ The University of Adelaide, Australia

Zinc is an essential element for humans

- Humans, animals, plants need zinc to function
- Affects over 300 enzymes in the body
- Supports normal growth and development
- Essential for metabolism and cellular growth
- Especially important during pregnancy, childhood and adolescence
- Key for immune system
- Activates wound healing
- Impacts taste, mood, hair, finger nails

Zinc deficiency – a global Issue

Leading 10 Risk Factors in Developing Countries as Percentage Causes of Disease Burden, Measured in Disability Adjusted Life Years (DALY)

Underweight	14.9%
Unsafe sex	10.2%
Unsafe water	5.5%
Indoor smoke	3.7%
Zinc deficiency	**3.2%**
Iron deficiency	3.1%
Vitamin A deficiency	3.0%
Blood pressure	2.5%
Tobacco	2.0%
Cholesterol	1.9%

Source: The World Health Report 2002

- 2 billion people at risk of zinc deficiency
- 195 million children < 5 years at risk of stunting
- 2 million children < 5 years die due to pneumonia
- 1.5 million children < 5 years die due to diarrhea
- 800,000 deaths attributed to zinc deficiency
- 450,000 children < 5 years die due to zinc deficiency
- Sub clinical zinc deficiency also prevalent in developed nations

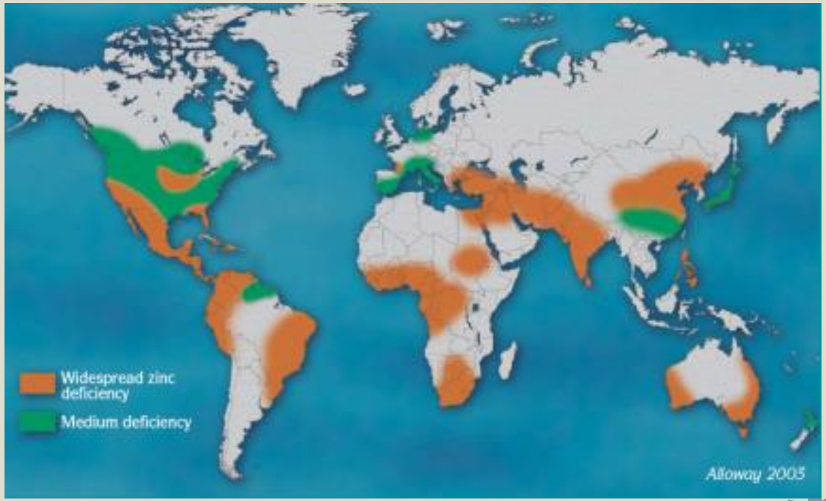
Zinc is an essential element for humans

- The International Zinc Association (IZA) in collaboration with UNICEF has a program to supplement children's diets with Zn

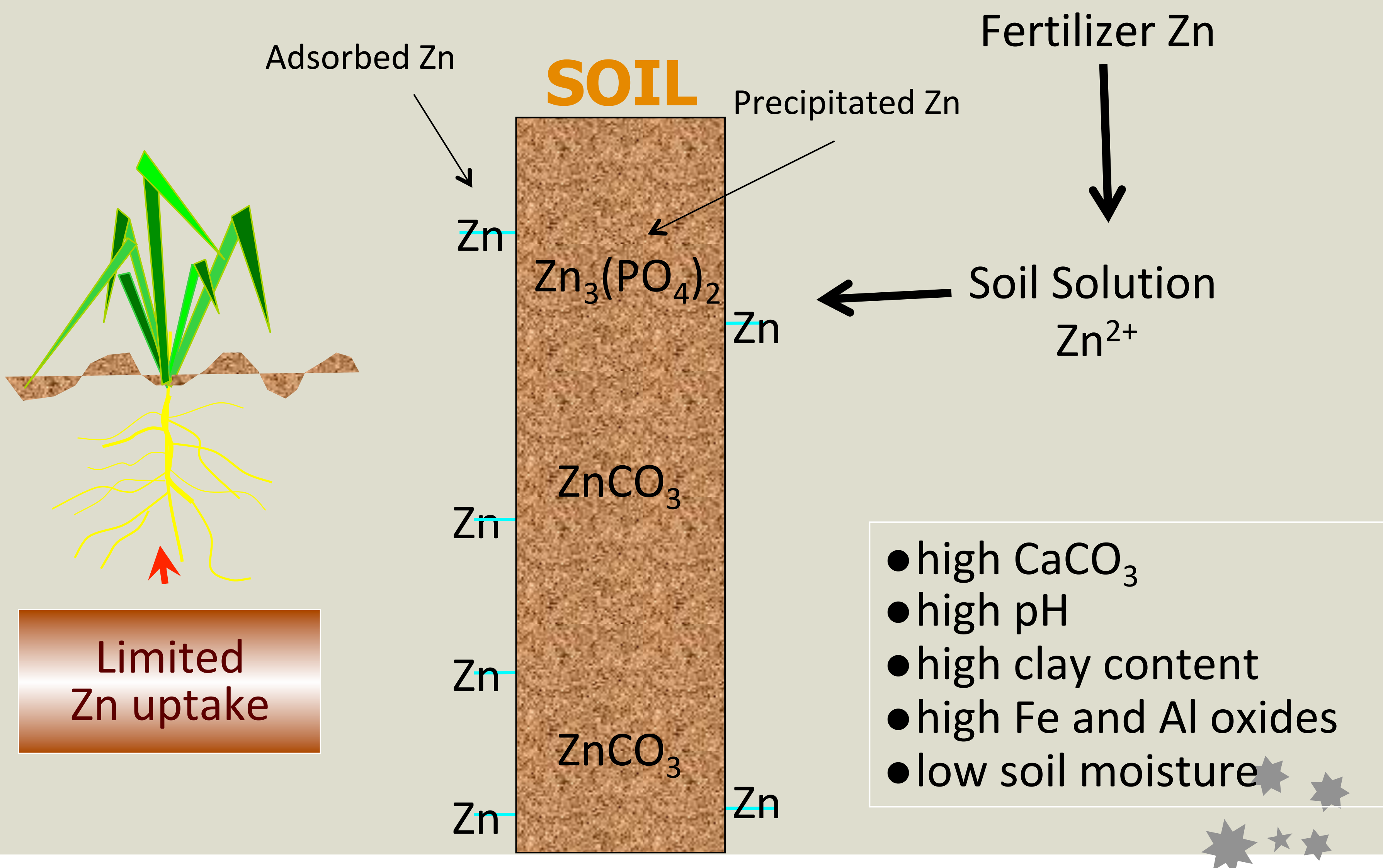
- IZA is also supporting promotion of zinc-fortified fertilizers in deficient areas

Zinc nutrition of crops

- Crops require Zn in small amounts to promote photosynthesis, seed production, growth regulation and for resistance to disease
- Deficiency of Zn is a global problem that affects soils and crops worldwide
- The crucial role Zn plays in human health is now recognised as a global issue



What limits crop Zn uptake from soils?



Zinc nutrition of crops

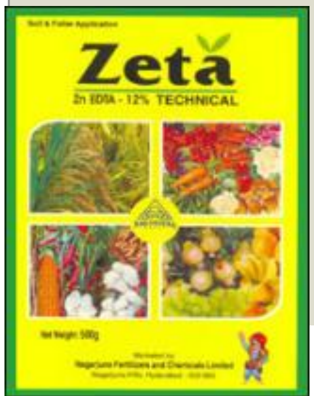
There are two main factors to consider in crop Zn nutrition

- Placement - physical accessibility of Zn in soil for access by crop root systems
- Solubility - rate and extent of release of Zn from fertilizer to the growing crop in relation to crop demand

Zinc fertilizers

ZnO or $ZnSO_4$-enriched NPK granular fertilizers e.g. MAP, DAP, MESZ

Granular Zn for bulk blending with NPK fertilizers



Zn chelates for foliar or fertigation

Zn powders for fertigation or foliar (commonly ZnO or $ZnSO_4$)

Pure Zn fertilizers and solubility

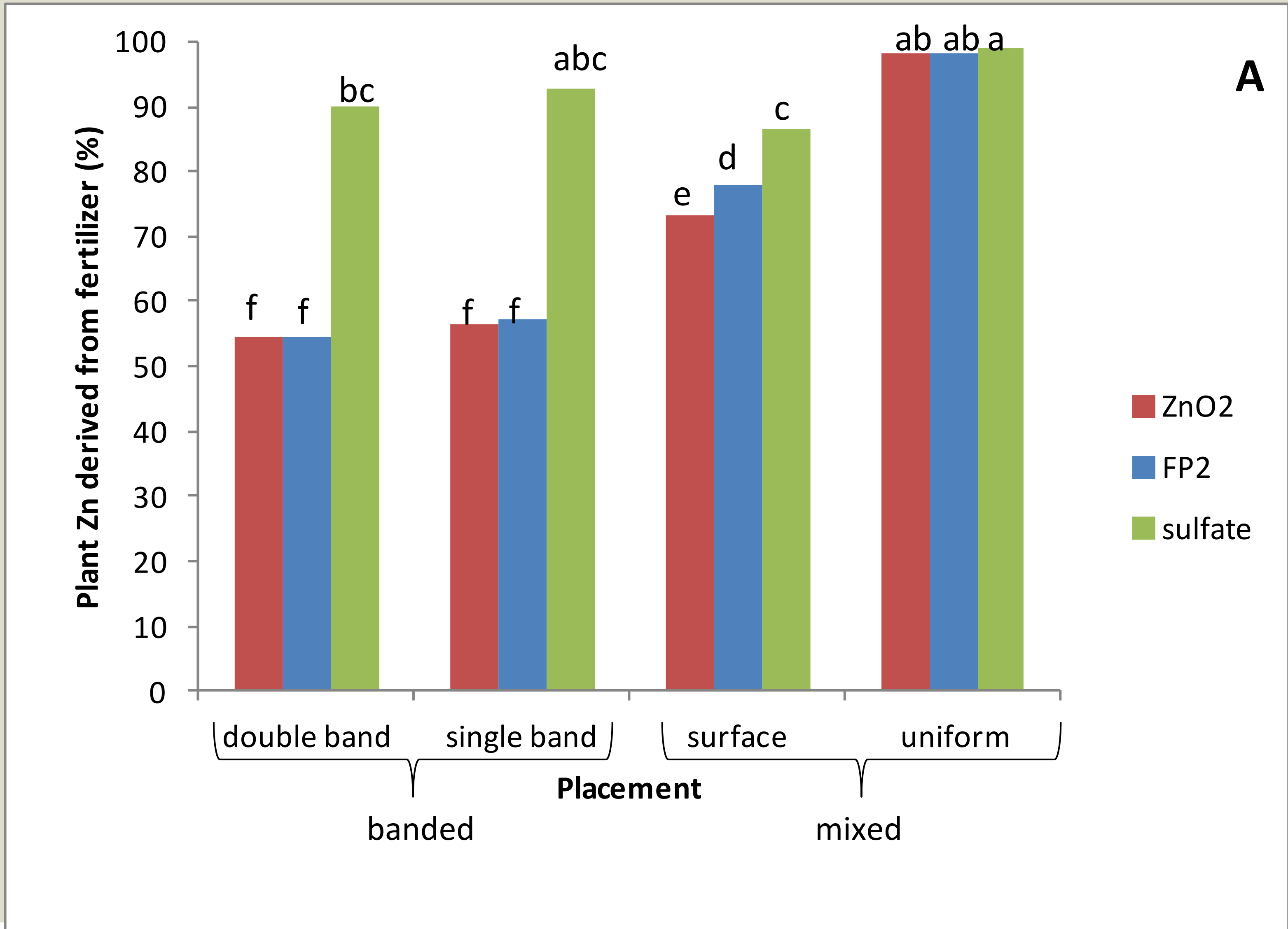
- The most soluble Zn source is Zn sulfate, usually sold as Zn sulfate heptahydrate (23% Zn) which has a water solubility of ~960 g/L
- Zinc oxide (ZnO) is 80% Zn, but has a much lower (~200,000 times lower) water solubility (1.5-5.0 mg/L) than Zn sulfate
- When ZnO dissolves it has an alkaline reaction (by consuming acid) – as H^+ ions are needed for dissolution, which causes its low solubility:

$$ZnO_{(solid)} + 2H^+ \rightarrow Zn^{2+}_{(solution)} + H_2O$$

Pure Zn fertilizers and solubility

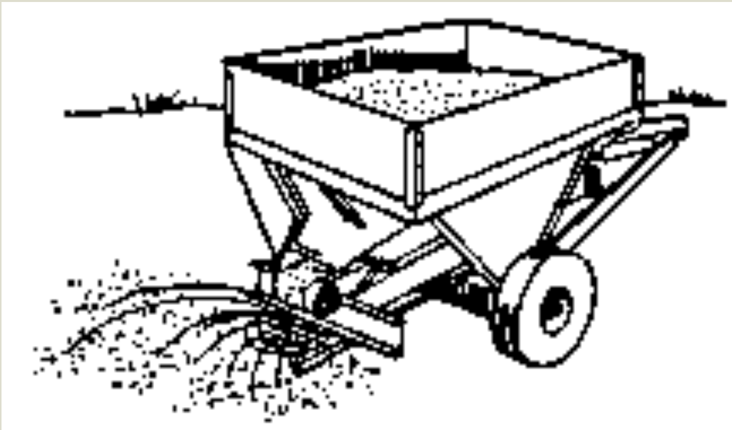
- Despite its low water solubility in water, ZnO can be effective if uniformly mixed throughout soil
- The soil provides a "pull" for Zn, and can stop pH increasing around the oxide particle or provide H^+ ions - all these promote dissolution of the oxide
- However, if ZnO is banded or present as large particles, its effectiveness is reduced compared to $ZnSO_4$ because of reduced surface area for dissolution, the alkaline reaction and the lower ability of soil to sorb the Zn

Pure Zn fertilizers and solubility



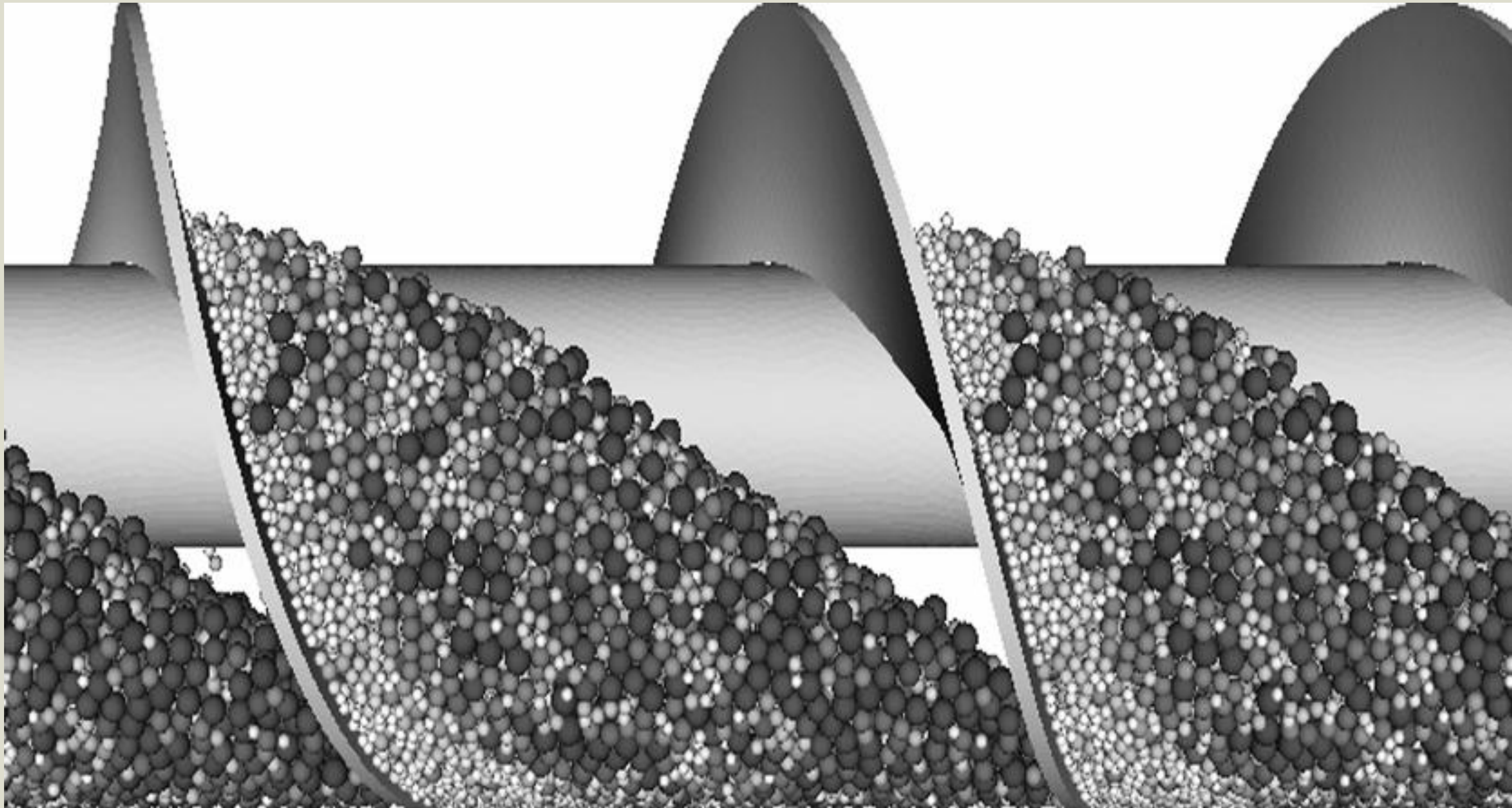
Bulk blends of Zn with macronutrient fertilizers

- Segregation of pure Zn fertilizers blended with other nutrients (e.g. N, P) results in poor distribution of nutrients in the field
- Granules segregate according to particle size rather than density
- Particle sizes need to be identical to prevent granule segregation



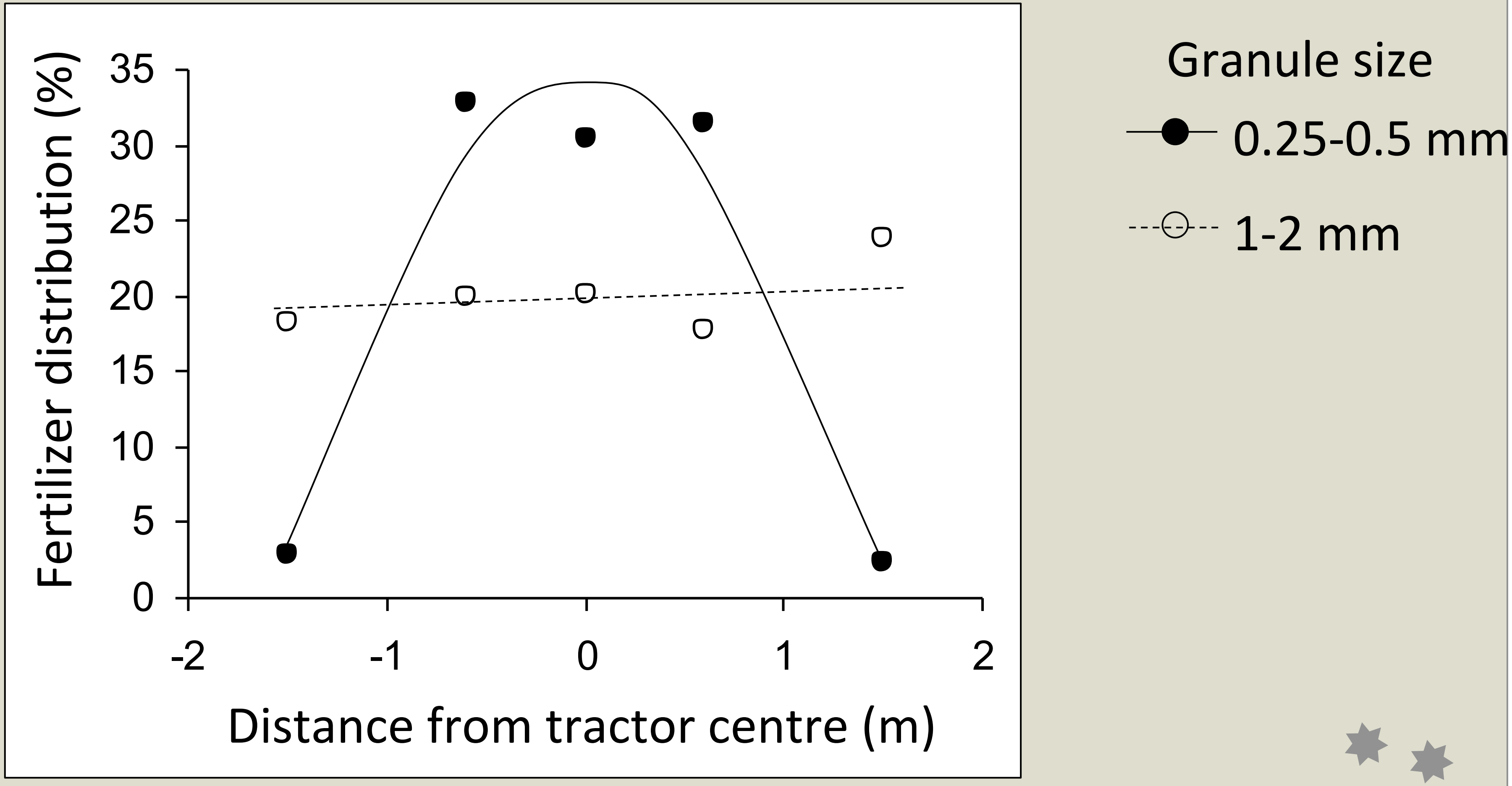
Bulk blends of Zn with macronutrient fertilizers

Particle size segregation during application



Bulk blends of Zn with macronutrient fertilizers

Ballistic segregation from rotary spreaders



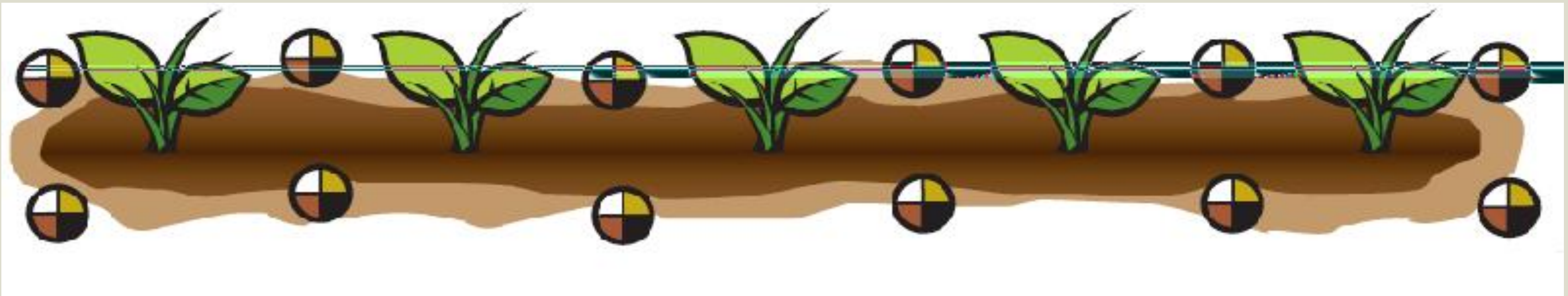
Source: Karnok (1986) The Segregation of Homogeneous and Blended Granular Fertilizers from a Rotary Spreader, *Agron. J.* 78:258-260

Bulk blends of Zn with macronutrient fertilizers

- Typical rates of Zn required by crops vary from 1 to 10 kg Zn/ha, generally 2-3 kg/ha
- Amounts of Zn are low and even with a low Zn content product e.g. Zn sulfate heptahydrate (23% Zn) the distribution of Zn in soil is poor
- Assuming normal granule size and broadcast at 2 kg/ha, there would be about 22 Zn granules ( ) per sq. m soil
- Zinc does not diffuse far from the granule – unlikely plant roots would “see” this Zn easily

Co-granulated Zn with macronutrient fertilizers

- Co-granulated NP+Zn products are typically 0.5-1% Zn
- Assuming normal granule size and broadcast Zn at 2 kg/ha, there would be about 500 1% Zn granules per sq. m soil – much more likely plant roots would "discover" this Zn
- Also a placement advantage that Zn is close to N and P nutrients – roots will "go there"

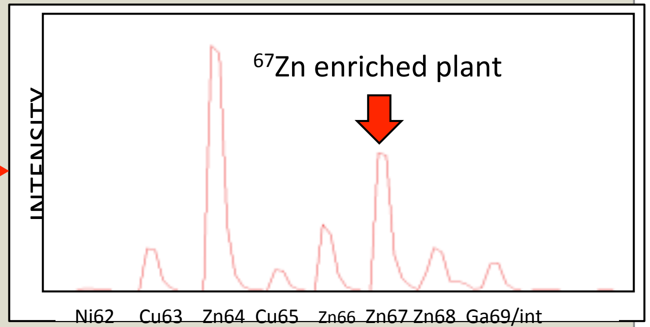


Co-granulated Zn with macronutrient fertilizers

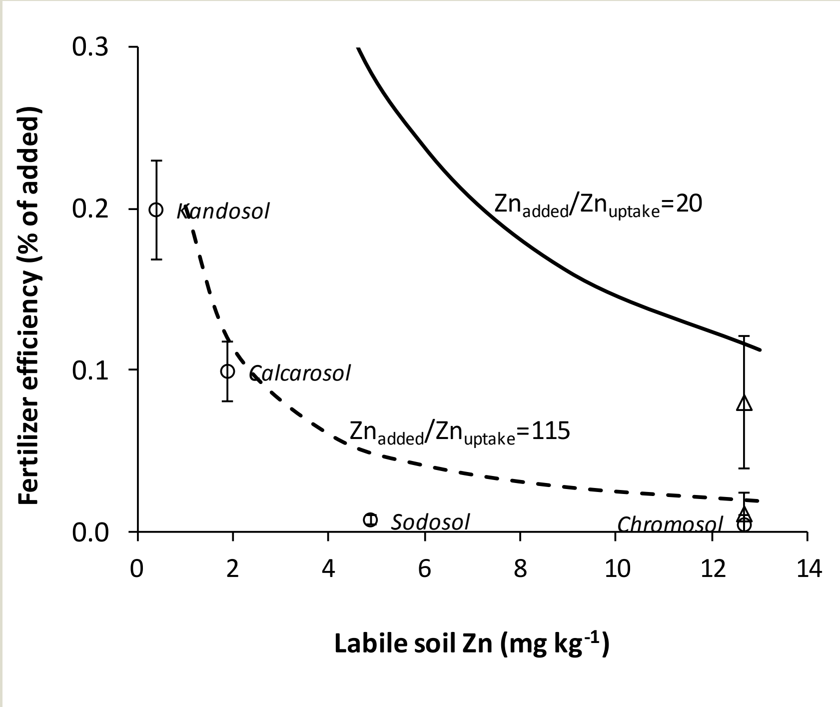
- Co-granulated products offer significant placement advantages over pure Zn fertilizers or bulk blends of Zn fertilisers with other nutrients

Co-granulated Zn

Fertilizer Zn efficiency is low in co-granulated products



<0.5% of added fertilizer Zn taken up in first year



McBeath T.M., McLaughlin M.J., Kirby J.K., Degryse F. (2013) A stable isotope methodology for measurement of soil applied zinc fertilizer recovery in Durum wheat (*Triticum durum*). *Journal of Plant Nutrition and Soil Science (in press).*

Issues with co-granulating Zn in P fertilizers

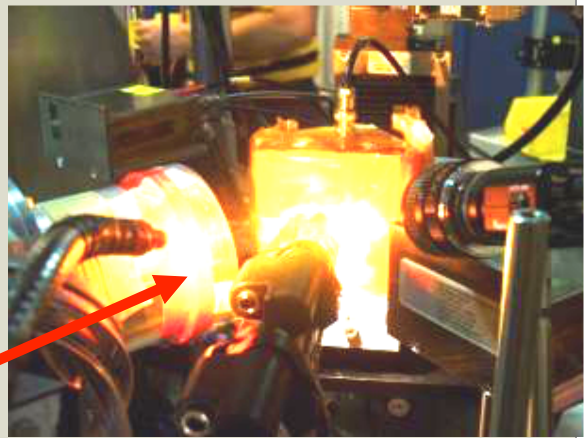
- The solubility of the raw Zn materials used to co-granulate with phosphatic fertilizers is not of great importance for final Zn water solubility
- Co-granulating either Zn sulfate or Zn oxide with NP fertilizers results in the same forms of Zn in the final product – predominantly Zn phosphate or Zn ammonium phosphate

$$3ZnO + 2H_3PO_4 \Leftrightarrow Zn_3(PO_4)_2 + 3H_2O$$

$$3ZnSO_4 + 2H_3PO_4 \Leftrightarrow Zn_3(PO_4)_2 + 3H_2SO_4$$

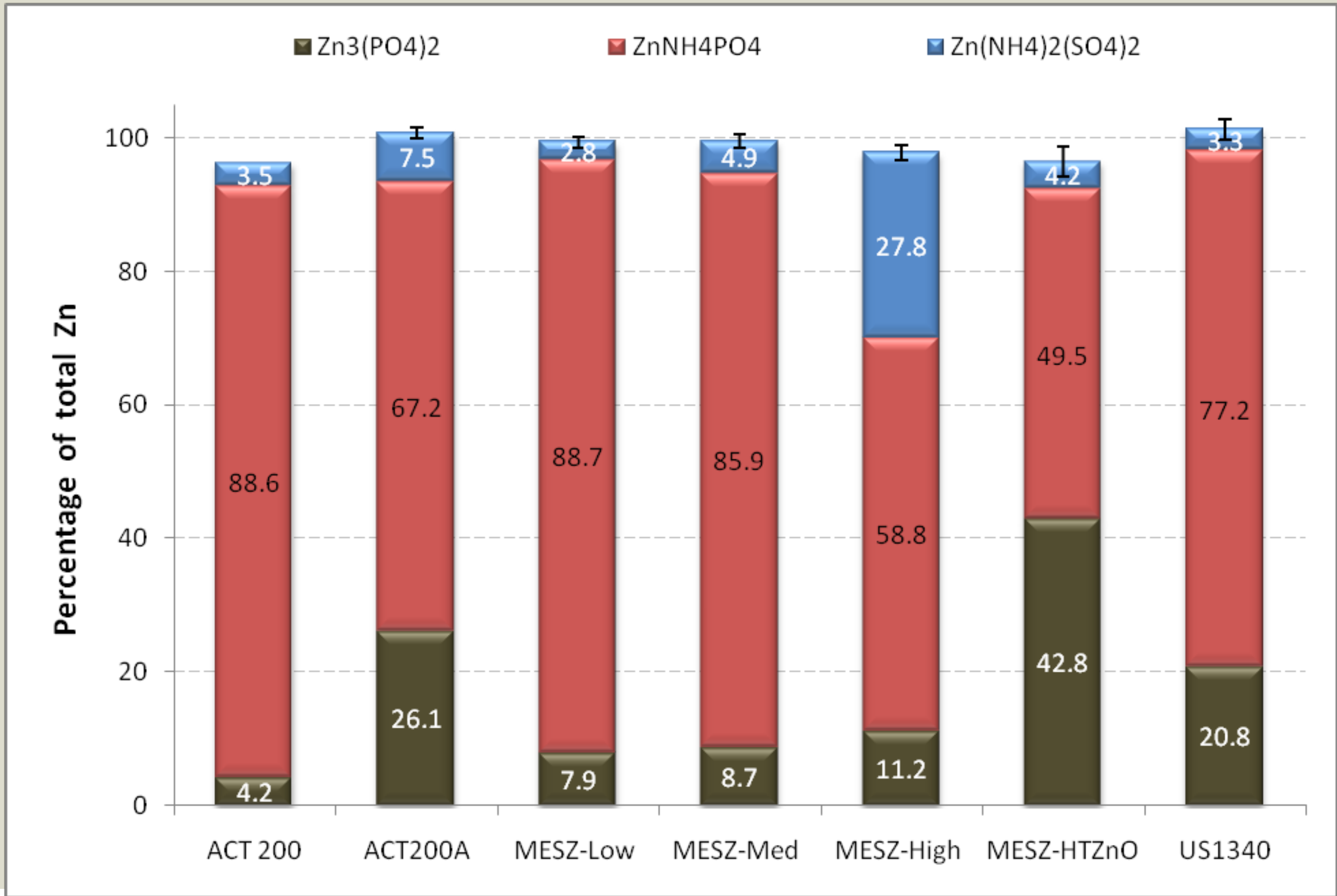
Issues with co-granulating Zn in P fertilizers

- The acidity at which granulation is performed (measured by pH) controls the relative amounts of each of these minerals
- We have measured Zn minerals in MESZ using synchrotron x-ray methods



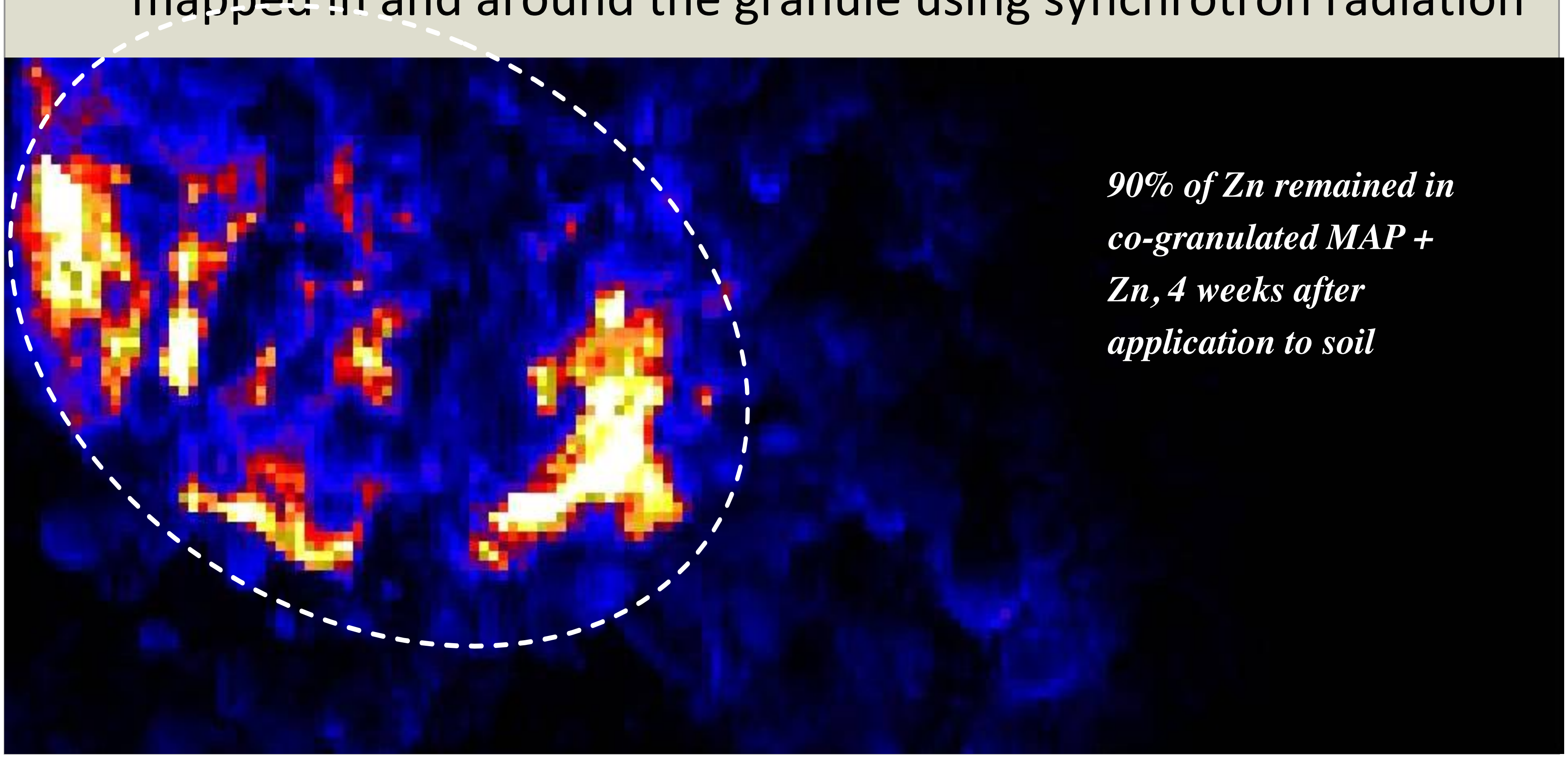
Issues with co-granulating Zn in P fertilizers

- Speciation of Zn in Microessentials and competitor granules



Issues with co-granulating Zn in P fertilizers

- In co-granulated products, release of Zn from the granule is limited in most soils due to the insolubility of Zn phosphate
- A MAP+Zn granule was incubated in soil for 4 weeks and Zn mapped in and around the granule using synchrotron radiation

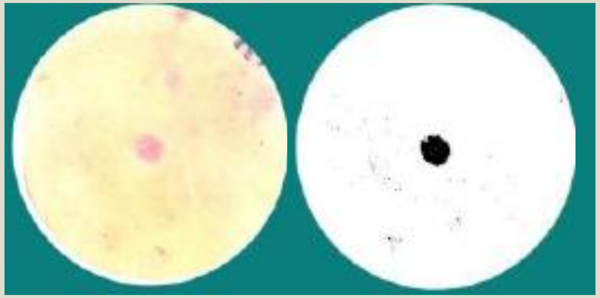


Issues with co-granulating Zn in P fertilizers

- Granule chemistry can affect how water soluble and diffusible the Zn becomes on granule dissolution

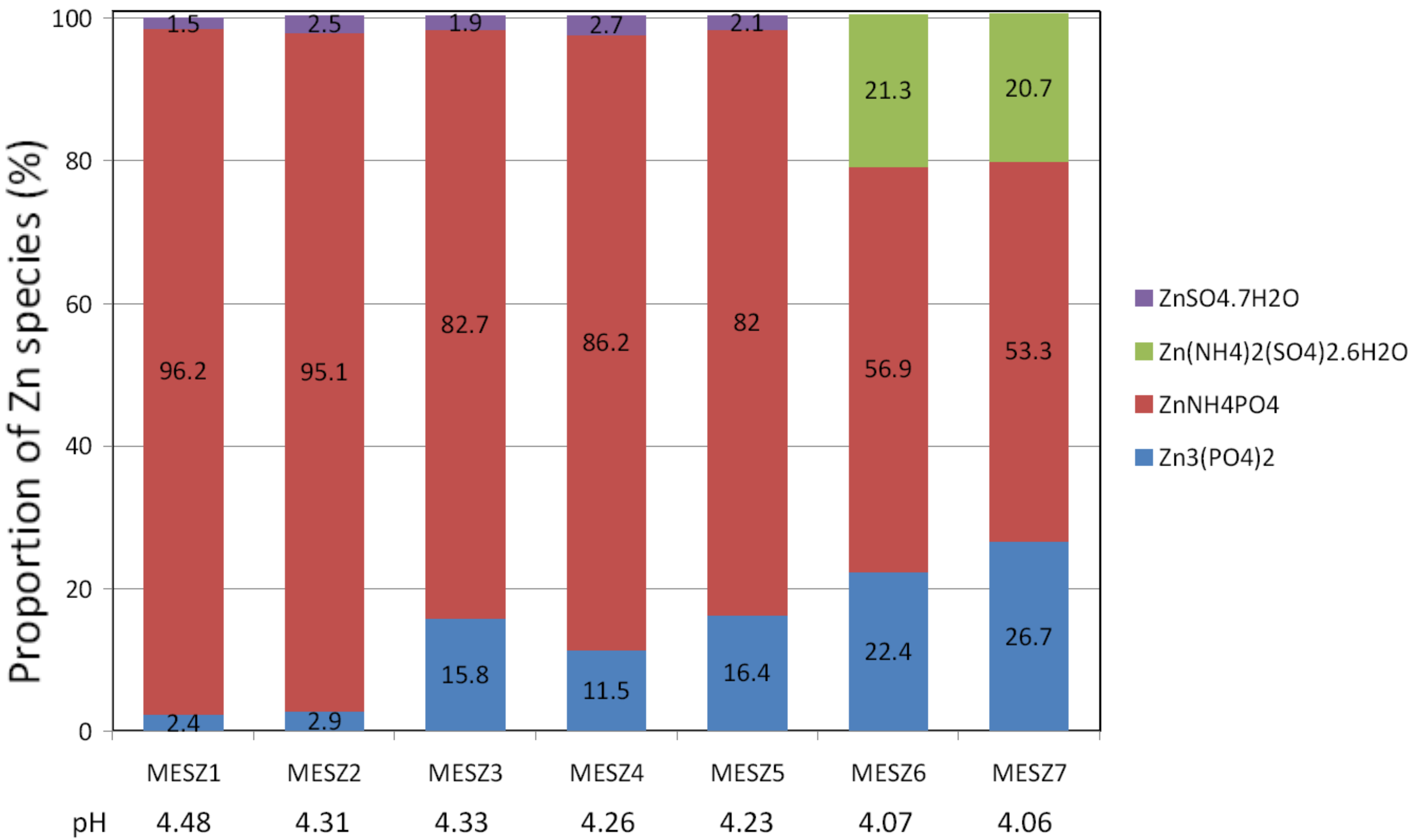
Granules placed in soil in centre of Petri dish and movement of Zn from granule evaluated colorimetrically

DAP + Zn

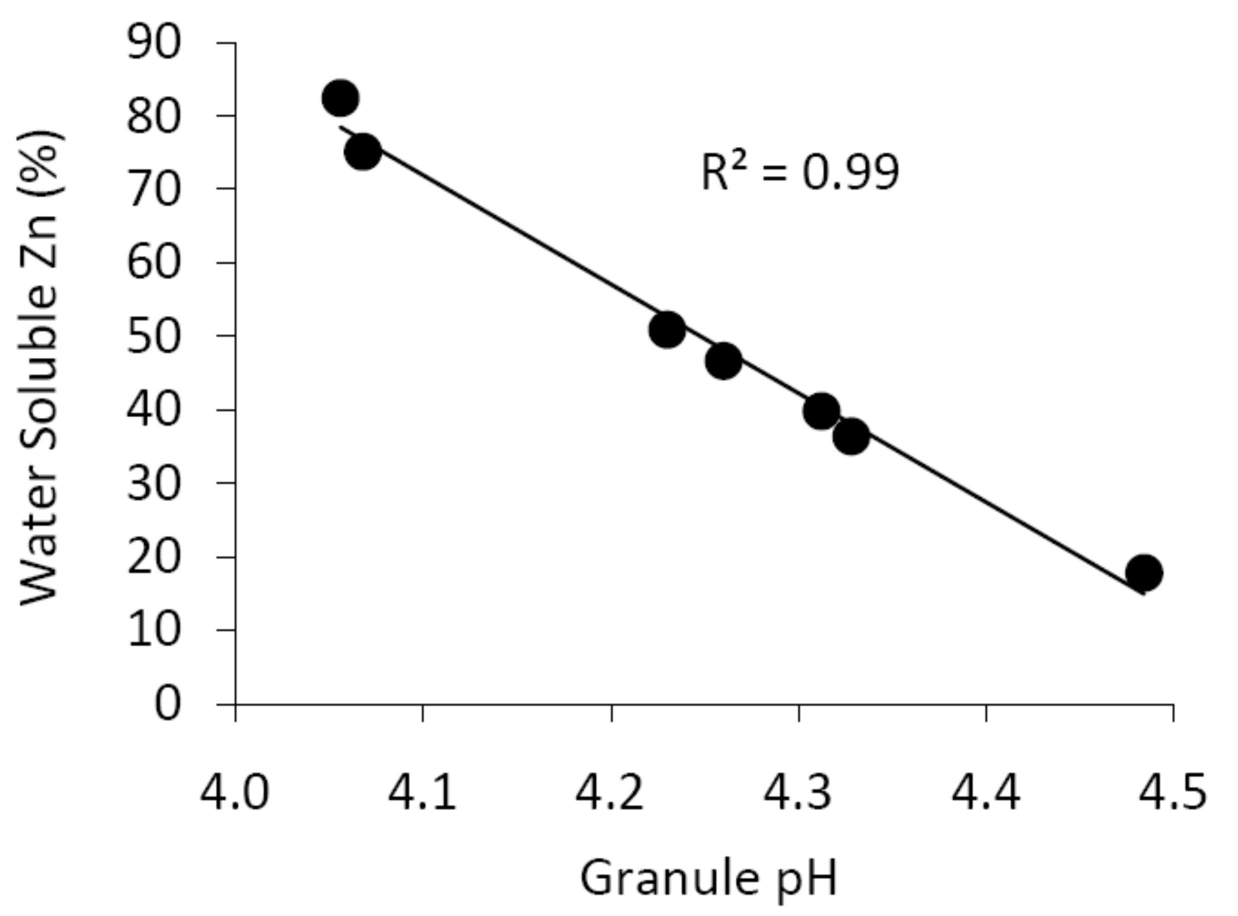


MAP+S+ Zn

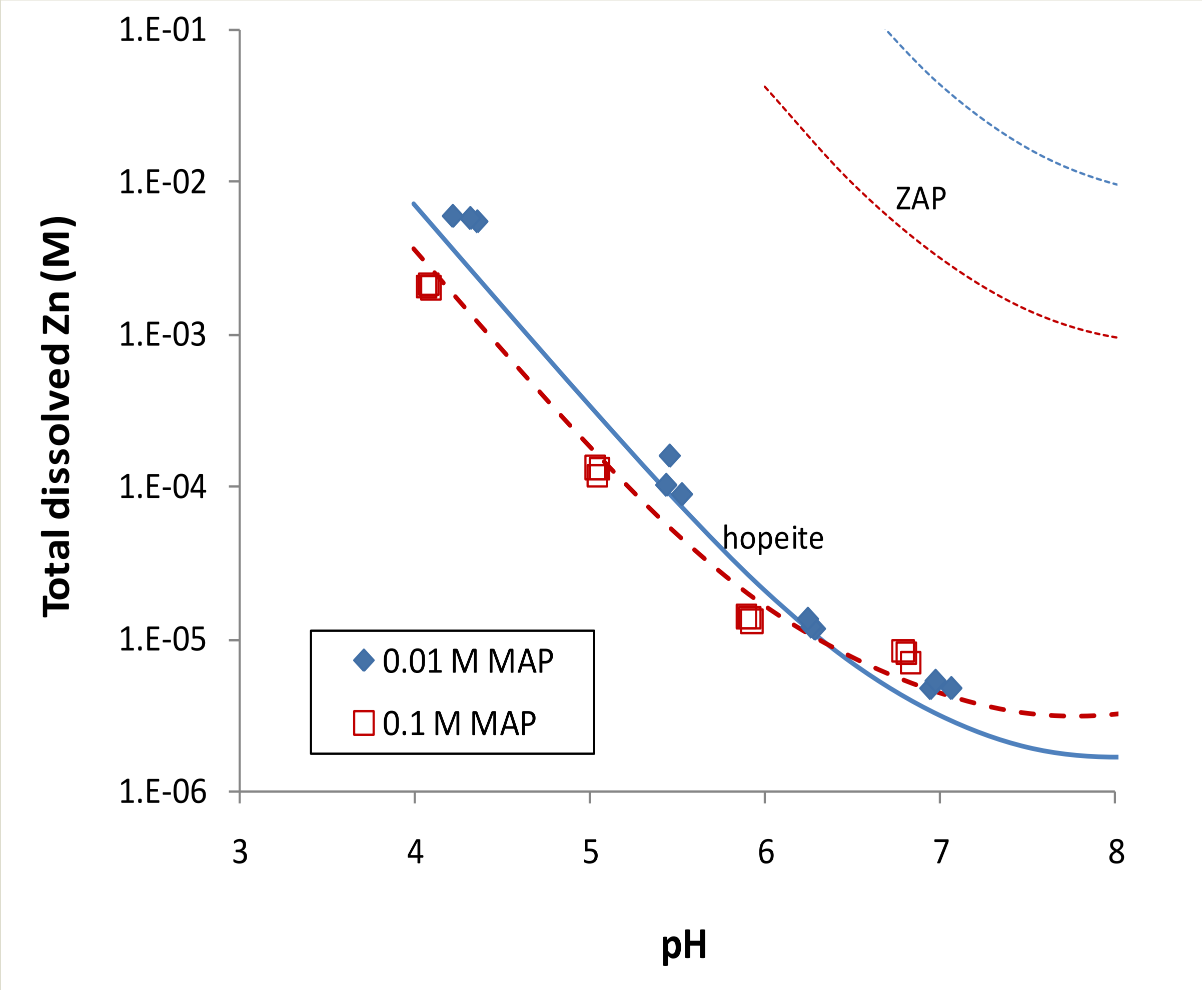
Speciation of Zn and granule pH



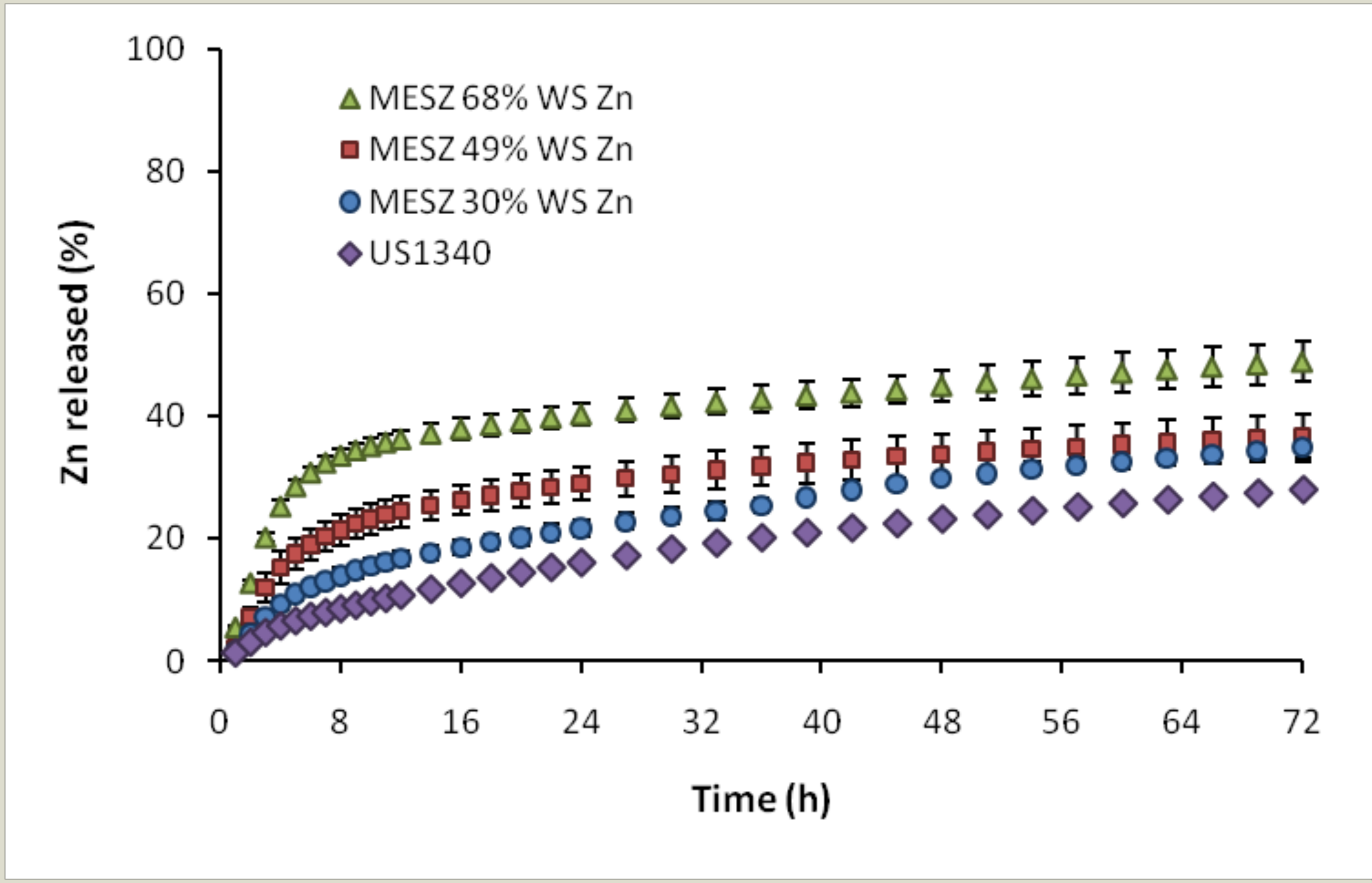
Water solubility of Zn and granule pH



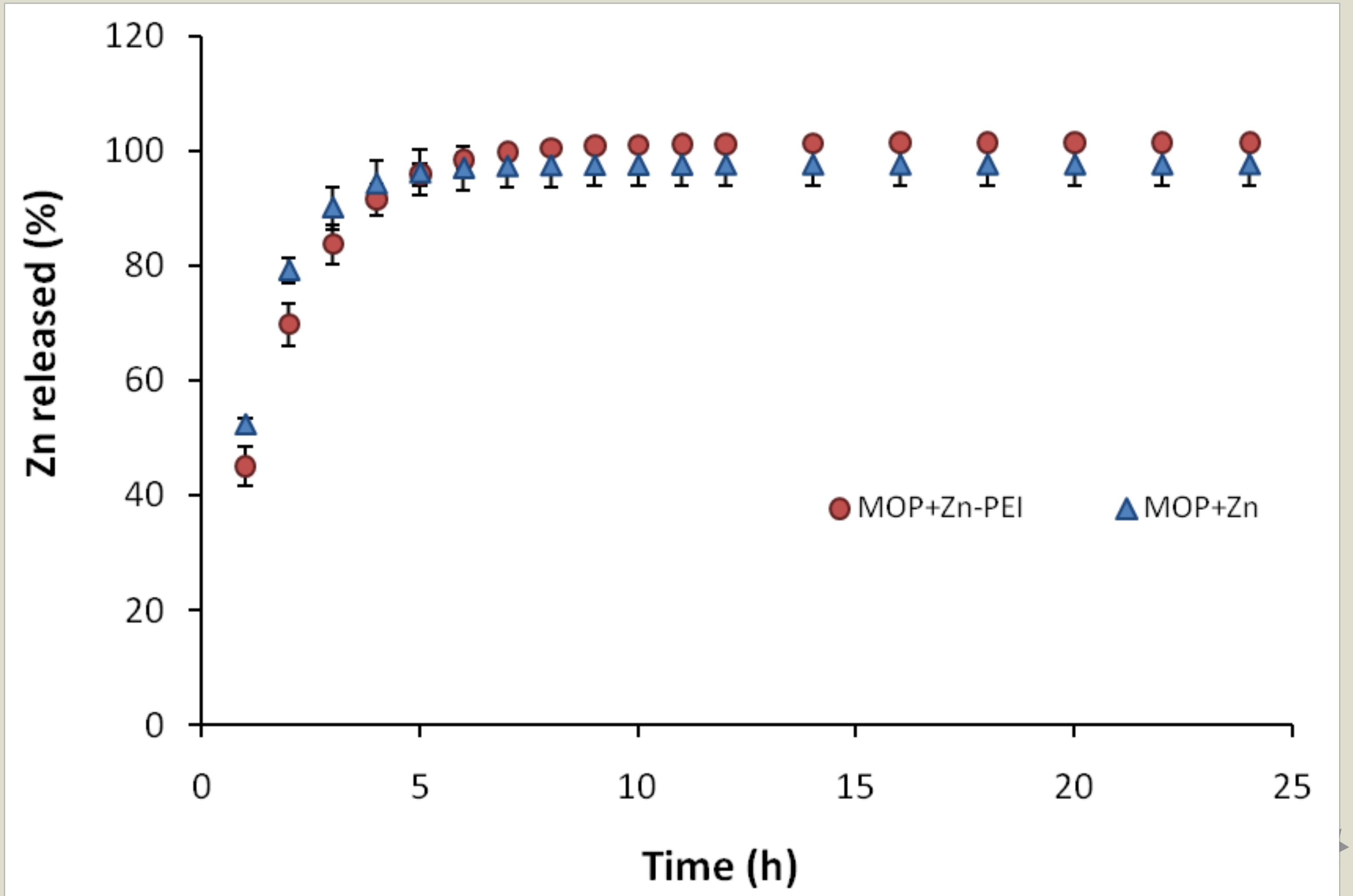
Hopeite ($Zn_3(PO_4)_2$) mineral controls Zn solubility



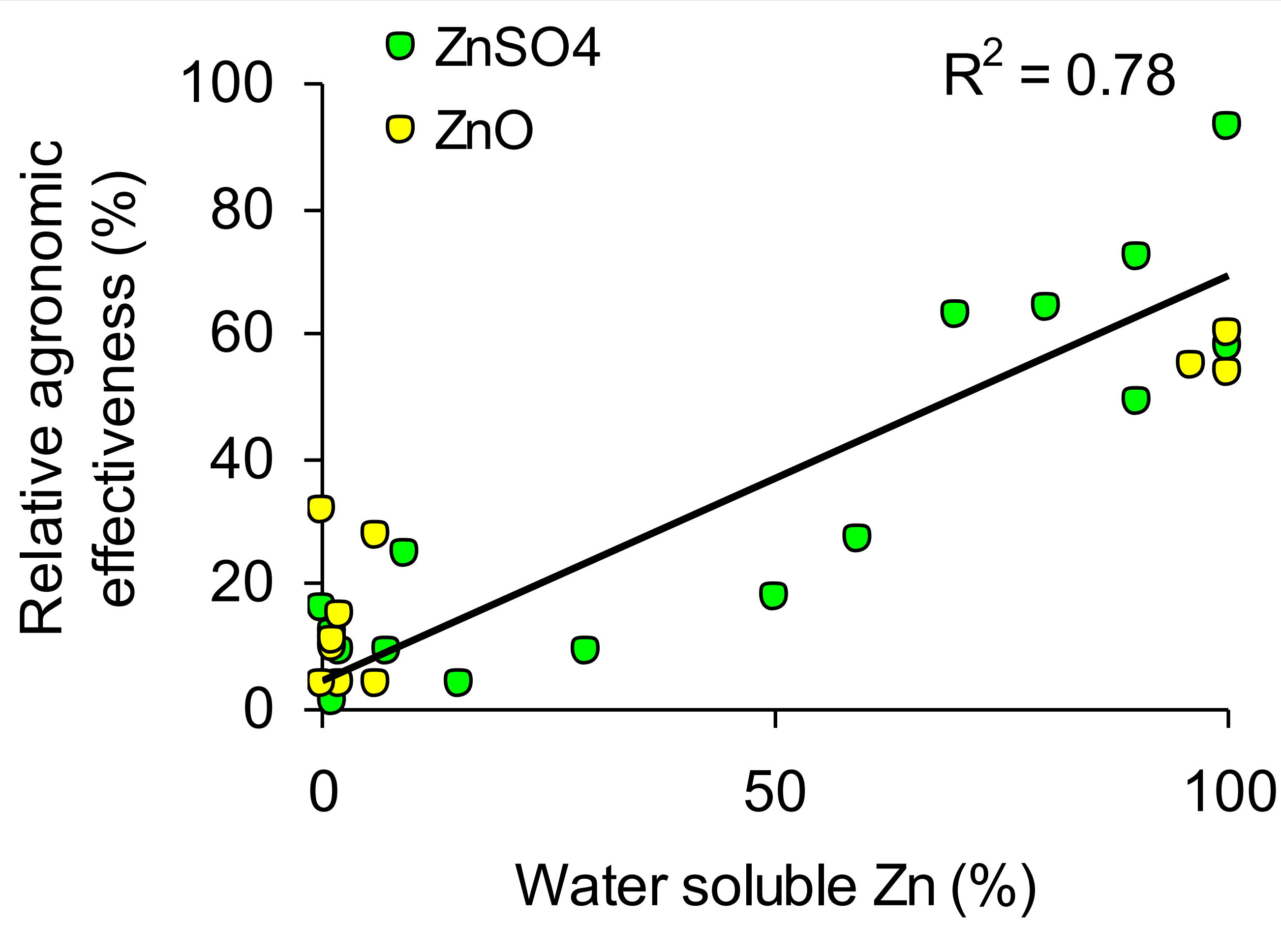
Rate of Zn release from granules



What about Zn in potash?



Agronomic effectiveness of Zn

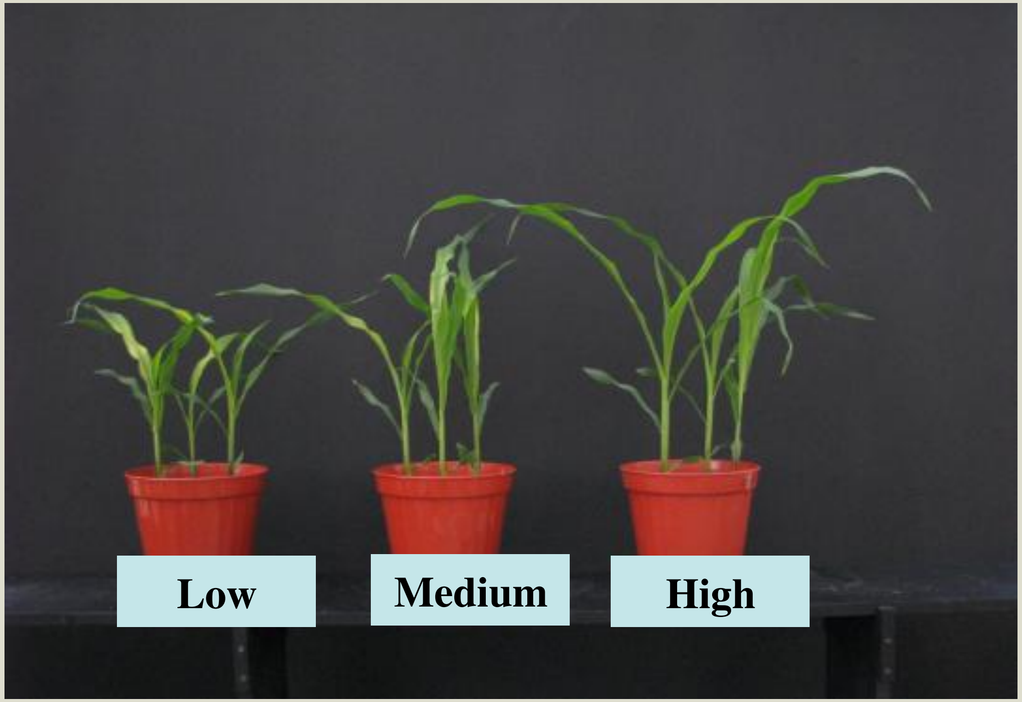


Early research from Mortvedt and Giordano (1969) demonstrated that high water solubility of fertilizer Zn is needed for fast-growing annual crops

Sli

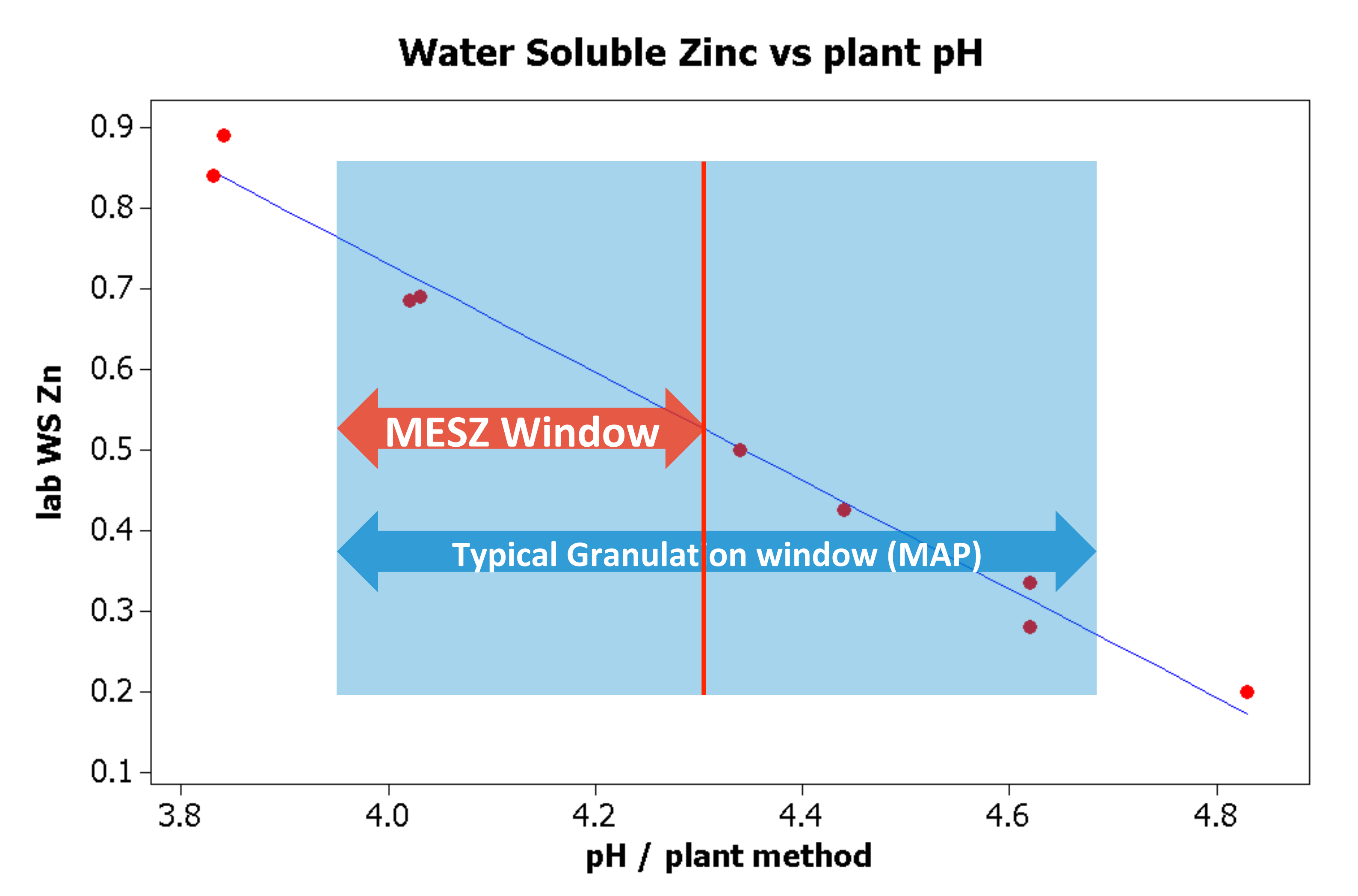
Agronomic effectiveness of Zn

- Water solubility of Zn in the fertilizer is the key attribute leading to fertilizer efficiency for annual crops



- The link between Zn species in the fertilizer and water solubility is not strong
- A key attribute to control is granule pH

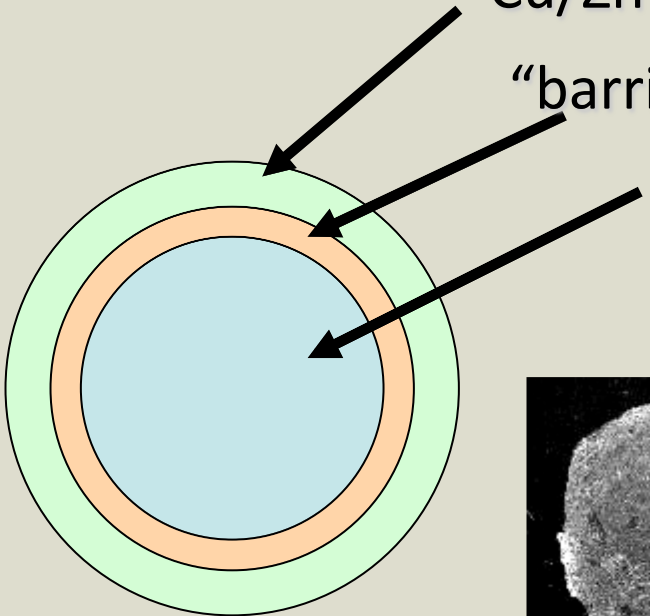
Controlling granule pH

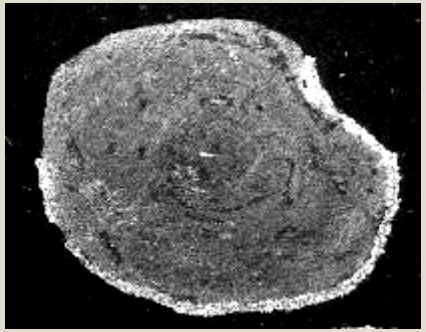


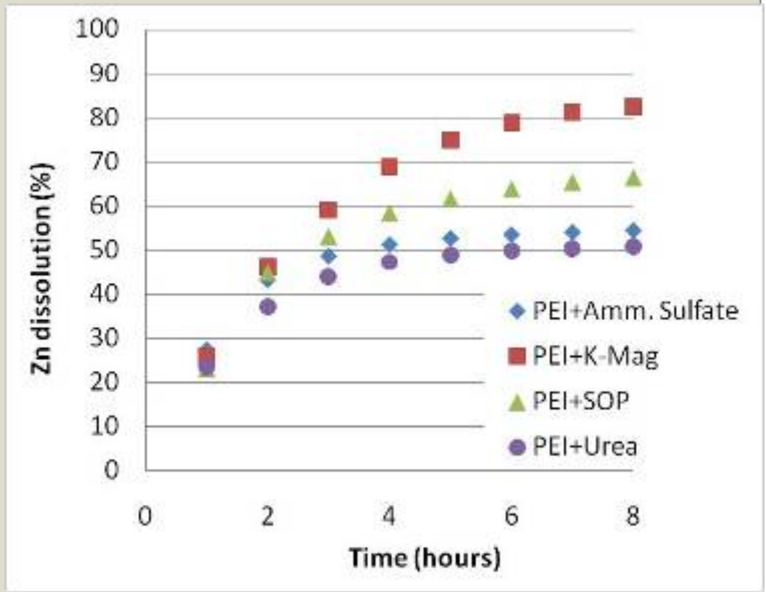
Increasing water soluble Zn in MESZ

- Need to retain flexibility in operating plant window for pH to allow good granulation
- Strategies to increase water soluble Zn
    - Physically separate Zn from P core of granule with coatings post granulation
    - Add chelates either prior or post granulation to complex Zn and reduce formation of hopeite on dissolution
    - Add acidifying agents post granulation to improve solubility of hopeite

Barrier coatings to separate Zn from P

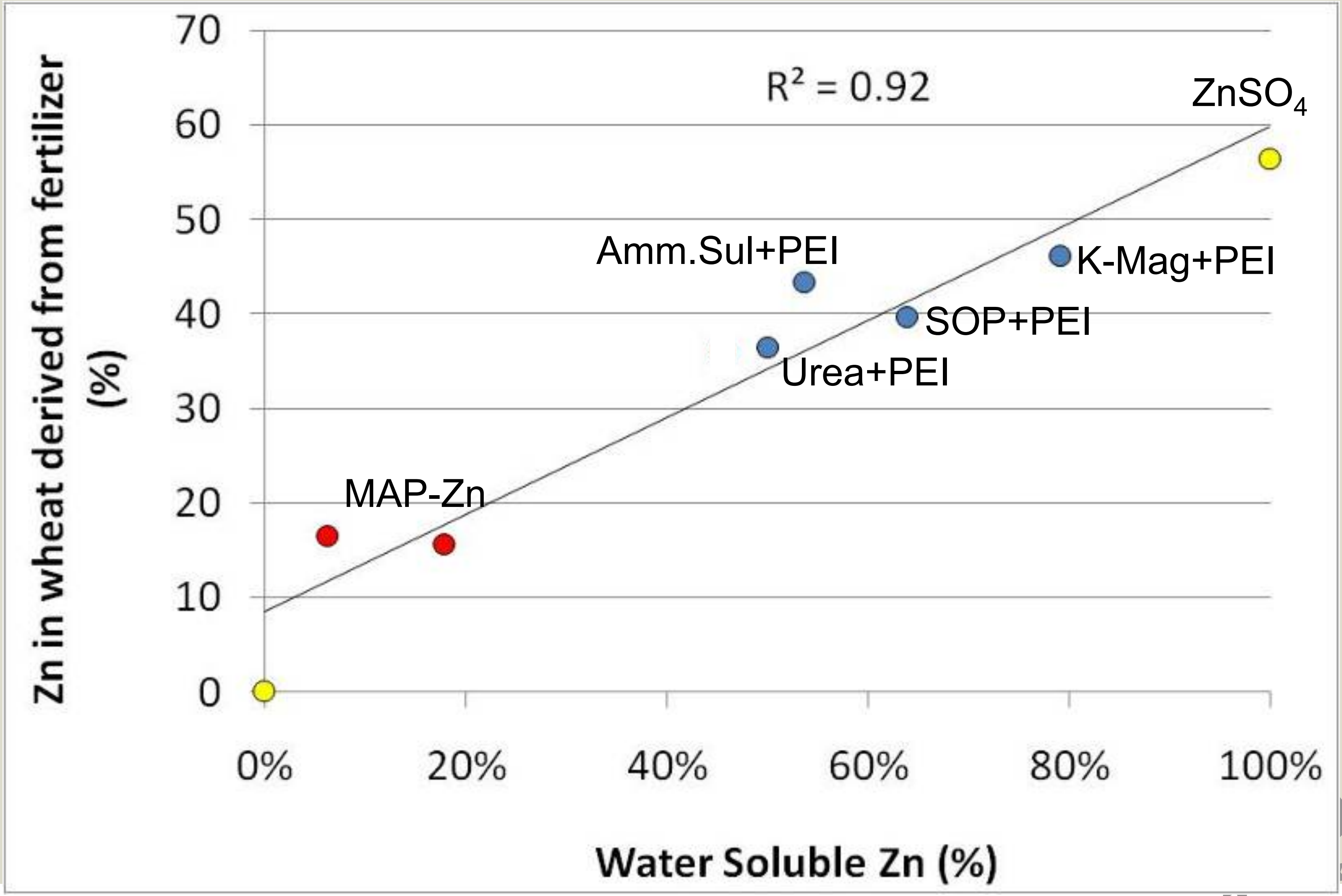






US PO Application Number 61/309,894 filed 3 March 2010

Zinc effectiveness in barrier-coated products



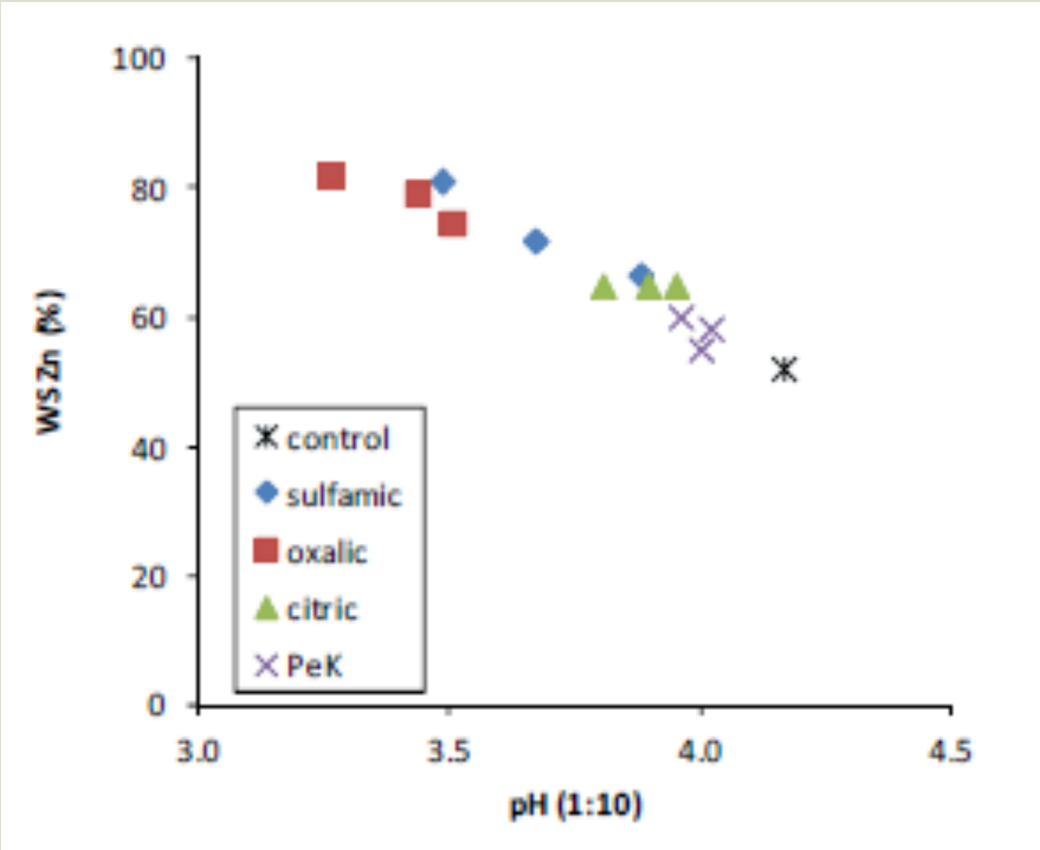
Acidifying agents - products tested

PHOSPHATE FERTILISERS **MESZ with 1% Zn wt/wt** **and 2, 3, 4% acid coatings**	**MOP-BASED FERTILISERS** **All with 1% Zn wt/wt** **Compacted and Coated**
MESZ + sulfamic acid	MOP $ZnSO_4$
MESZ + oxalic acid	MOP ZnO
MESZ + citric acid	MOP ZnO +1.5% sulfamic acid
MESZ + peK acid	MOP
MESZ (control)	

Sulfamic acid coated MESZ

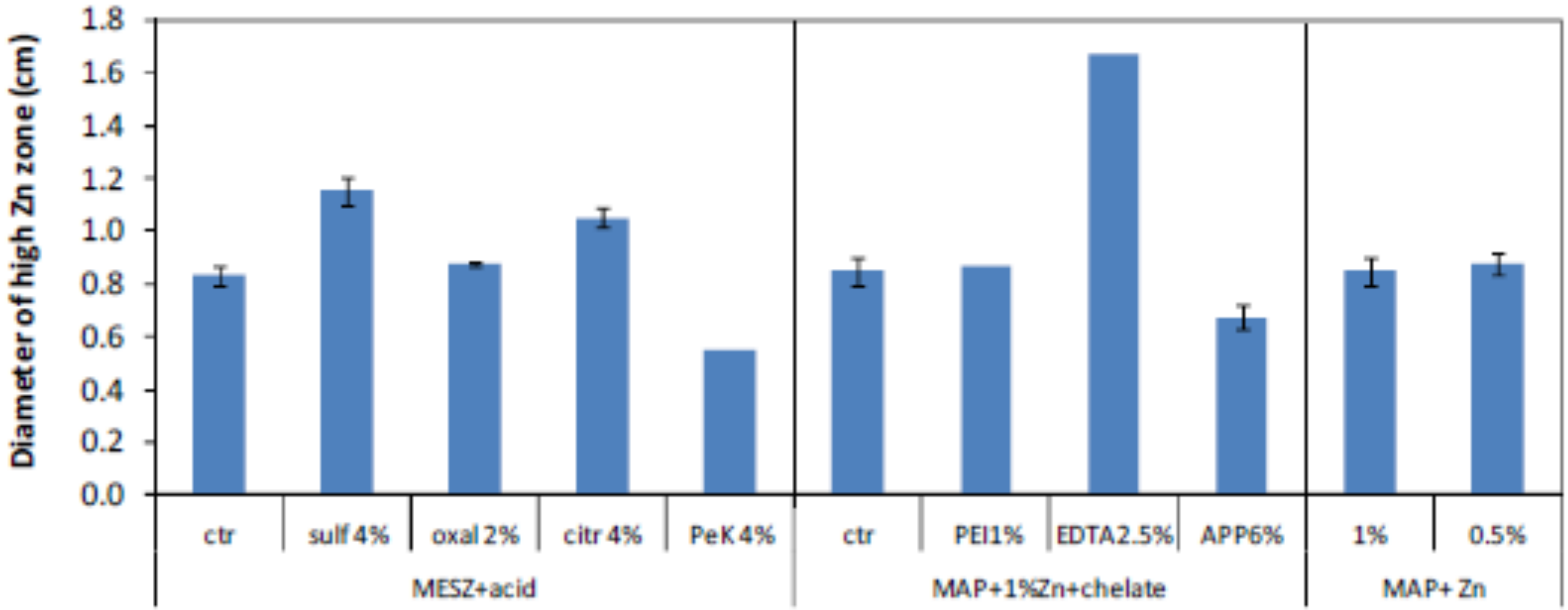
MESZ with	WS Zn (%)	Total Zn (%)	WS/Total (%)	pH (1:10)
2% acid	0.71	1.07	66.6	3.88
3% acid	0.79	1.09	71.9	3.67
4% acid	0.91	1.13	81.1	3.49

Acidifying agents and Zn solubility



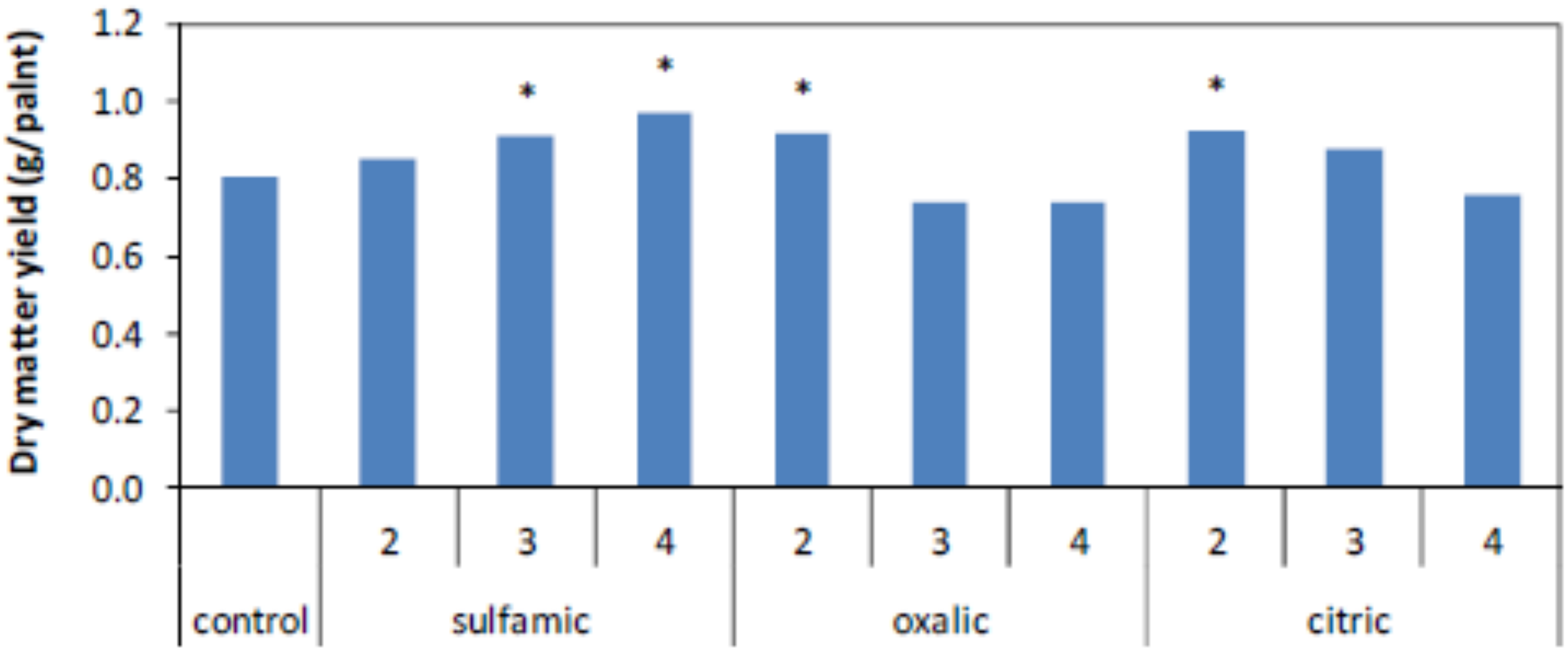
Acidifying agents were effective in increasing WS Zn

Acidifying/chelating agents and Zn diffusion



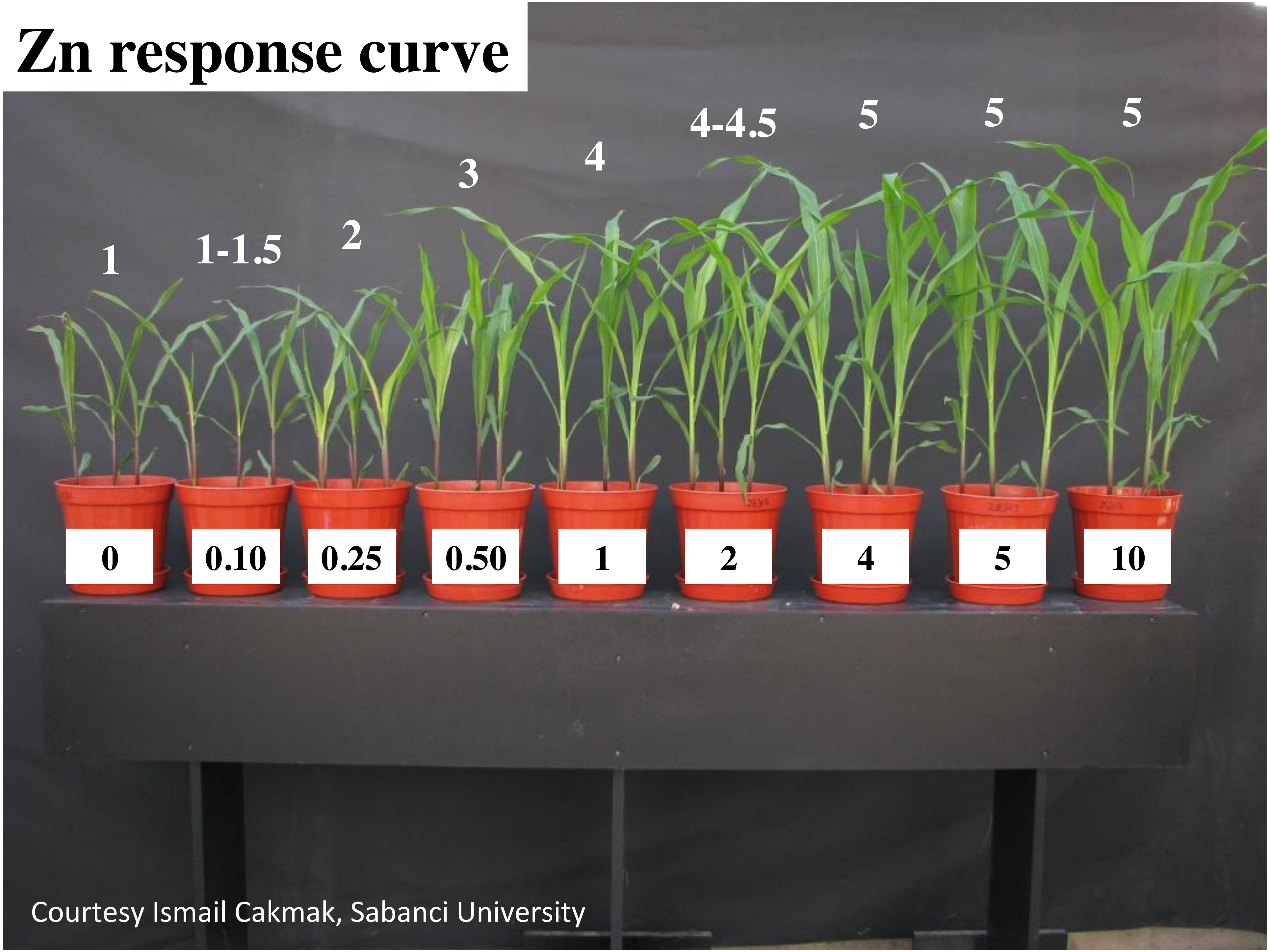
Acidifying agents and EDTA were effective in increasing Zn diffusion from granules

Acidifying/chelating agents and Zn diffusion

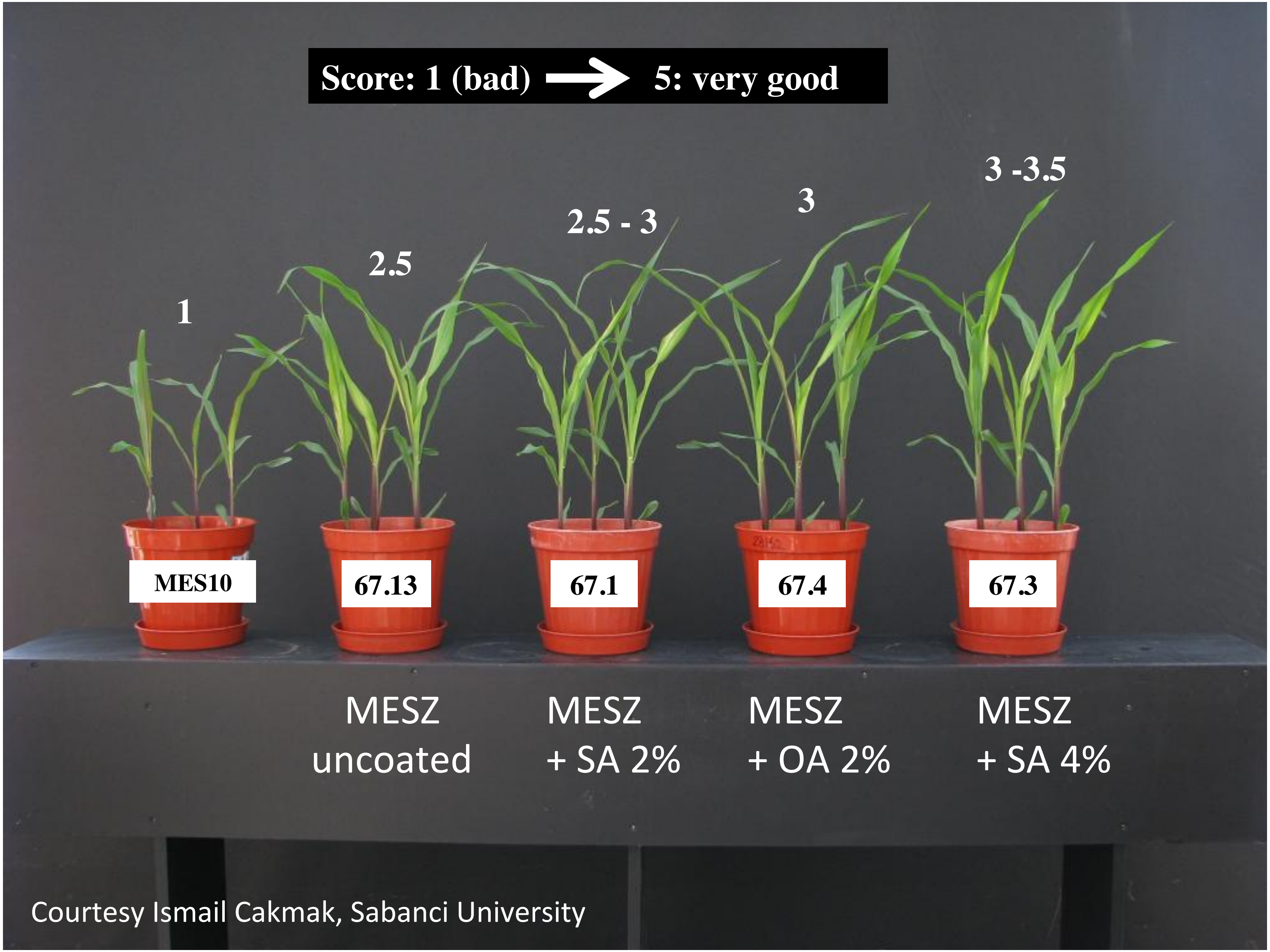


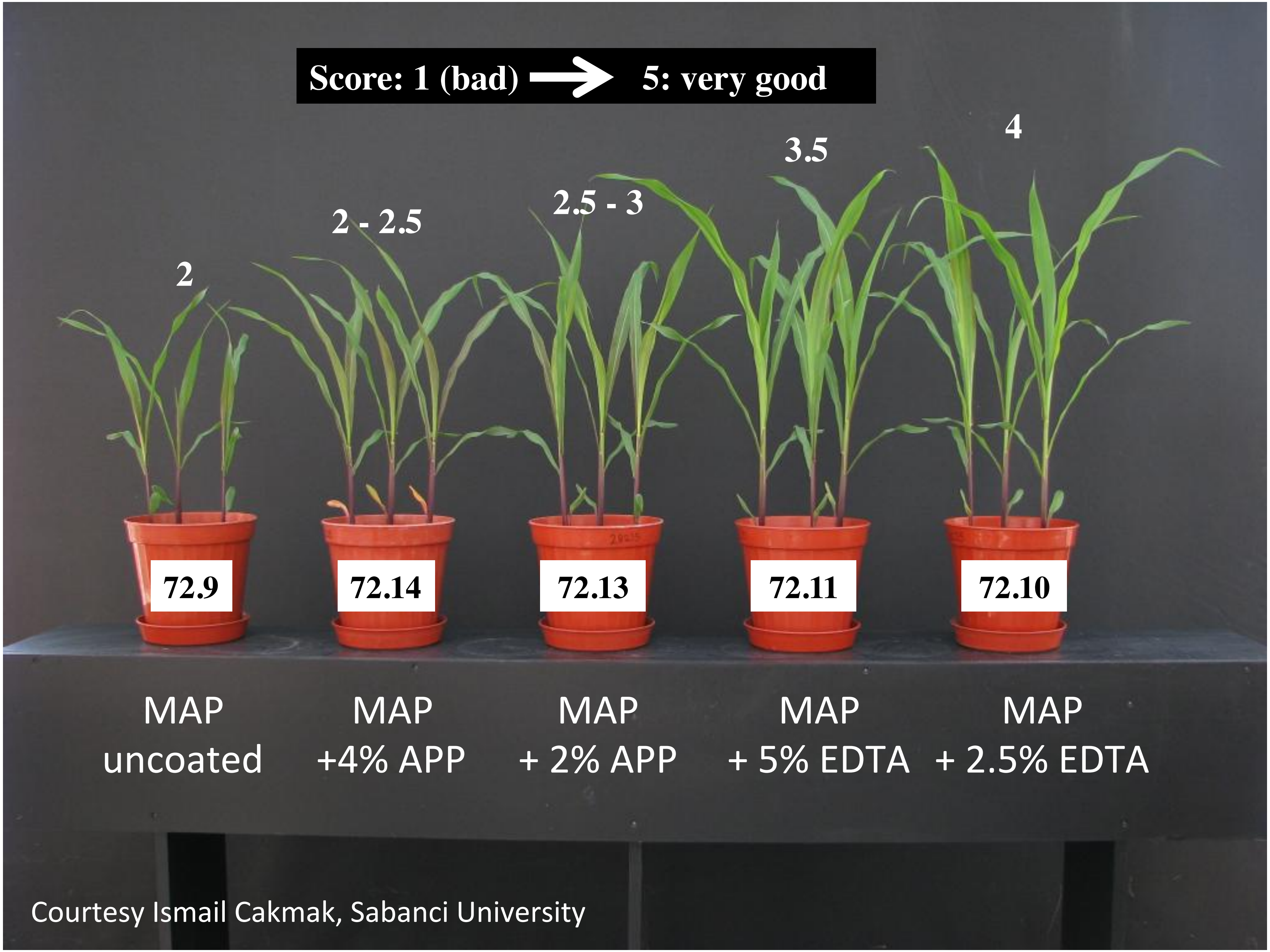
Citric and sulfamic acid effective in increasing Zn supply to plant in a deficient soil

Zn response curve



Courtesy Ismail Cakmak, Sabanci University

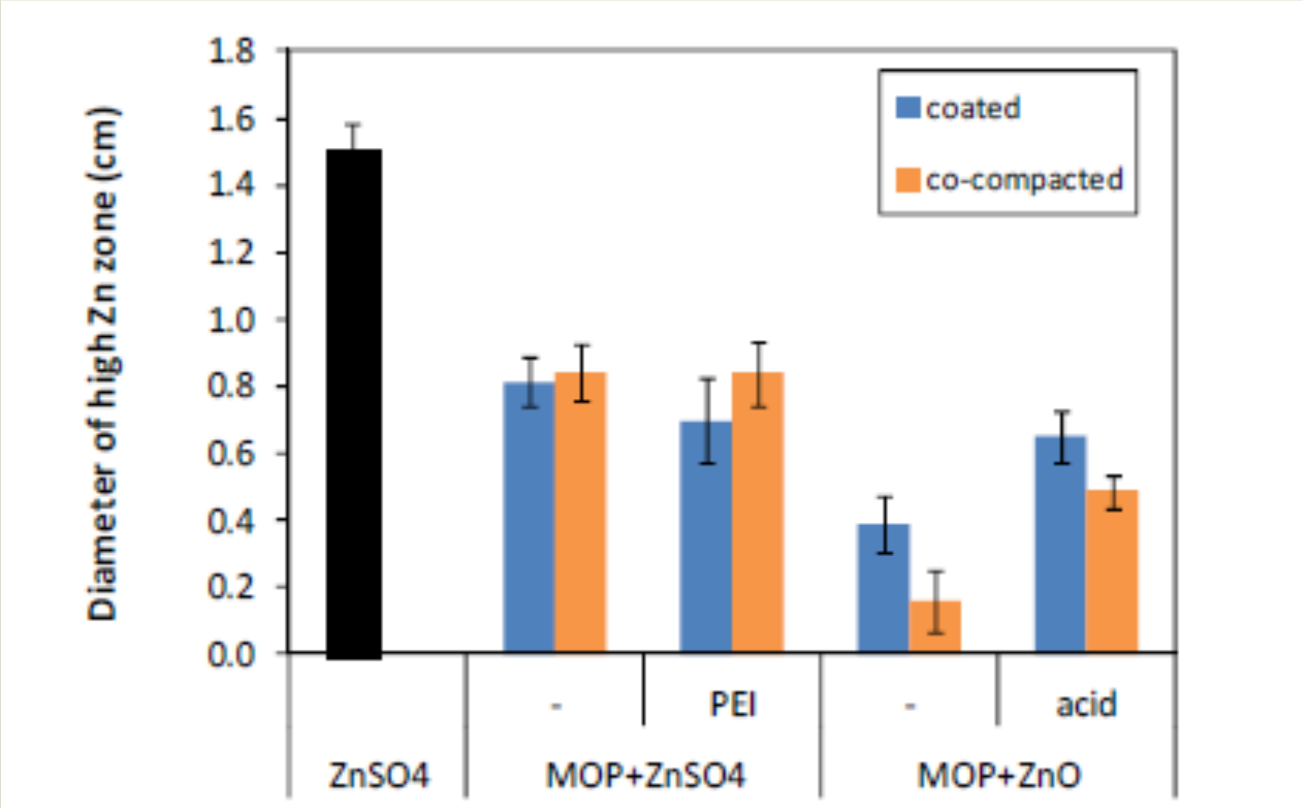

Score: 1 (bad) → 5: very good
1
2.5
2.5 - 3
3
3 -3.5
MES10
67.13
67.1
67.4
67.3
MESZ
uncoated
MESZ
+ SA 2%
MESZ
+ OA 2%
MESZ
+ SA 4%
Courtesy Ismail Cakmak, Sabanci University


Score: 1 (bad) → 5: very good
2
2 - 2.5
2.5 - 3
3.5
4
72.9
72.14
72.13
72.11
72.10
MAP uncoated
MAP +4% APP
MAP + 2% APP
MAP + 5% EDTA
MAP + 2.5% EDTA
Courtesy Ismail Cakmak, Sabanci University

Co-compacted MOP products

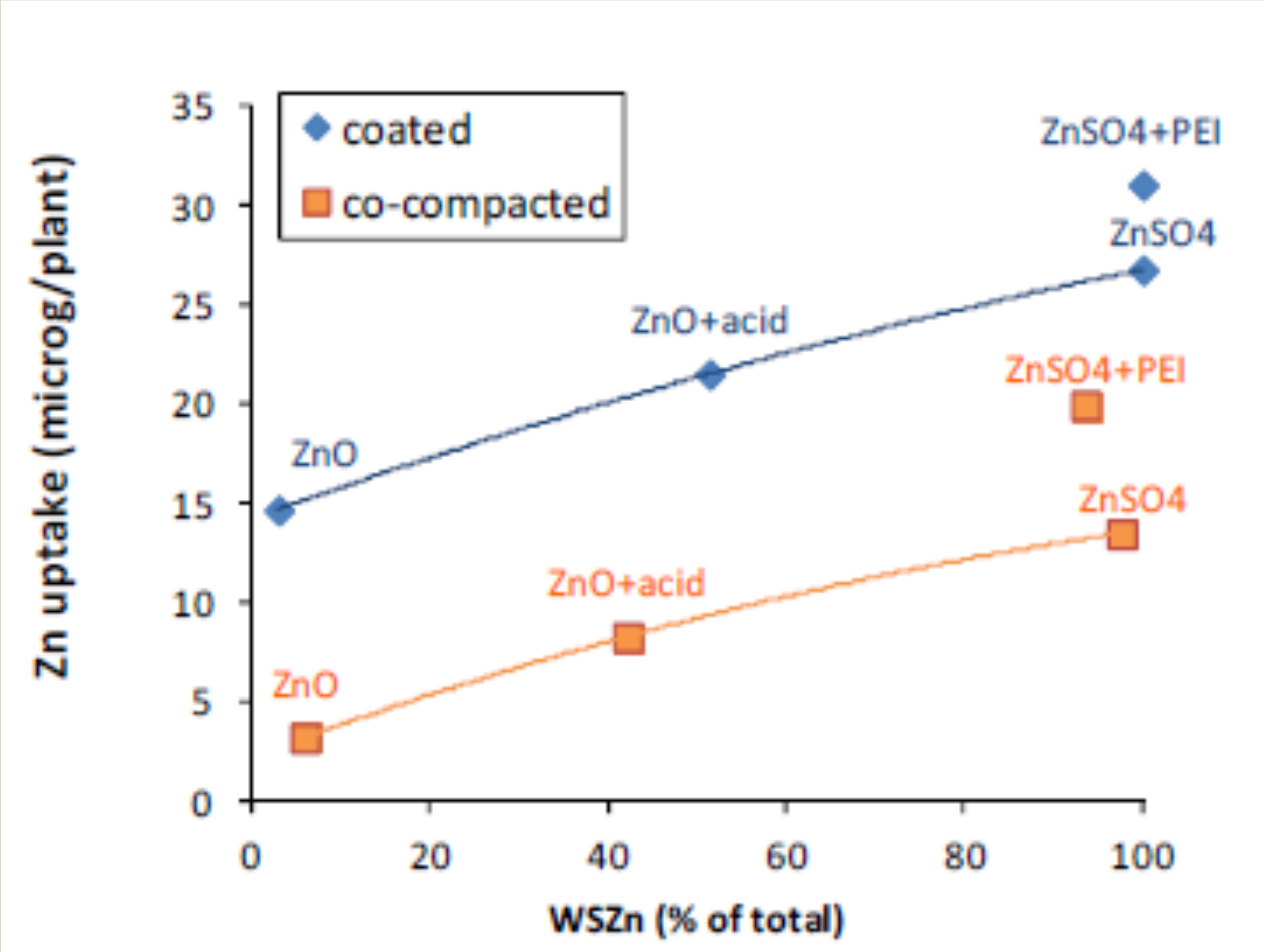
MOP	WS Zn (%)	Total Zn (%)	WS/Total (%)	pH (1:10)
1%Zn as $ZnSO_4$	1.14	1.17	98	5.79
1%Zn as ZnO	0.06	0.99	6	6.55
1%Zn as ZnO + sulfamic acid	0.45	1.06	42	6.22
Compacted MOP	-	--		7.03

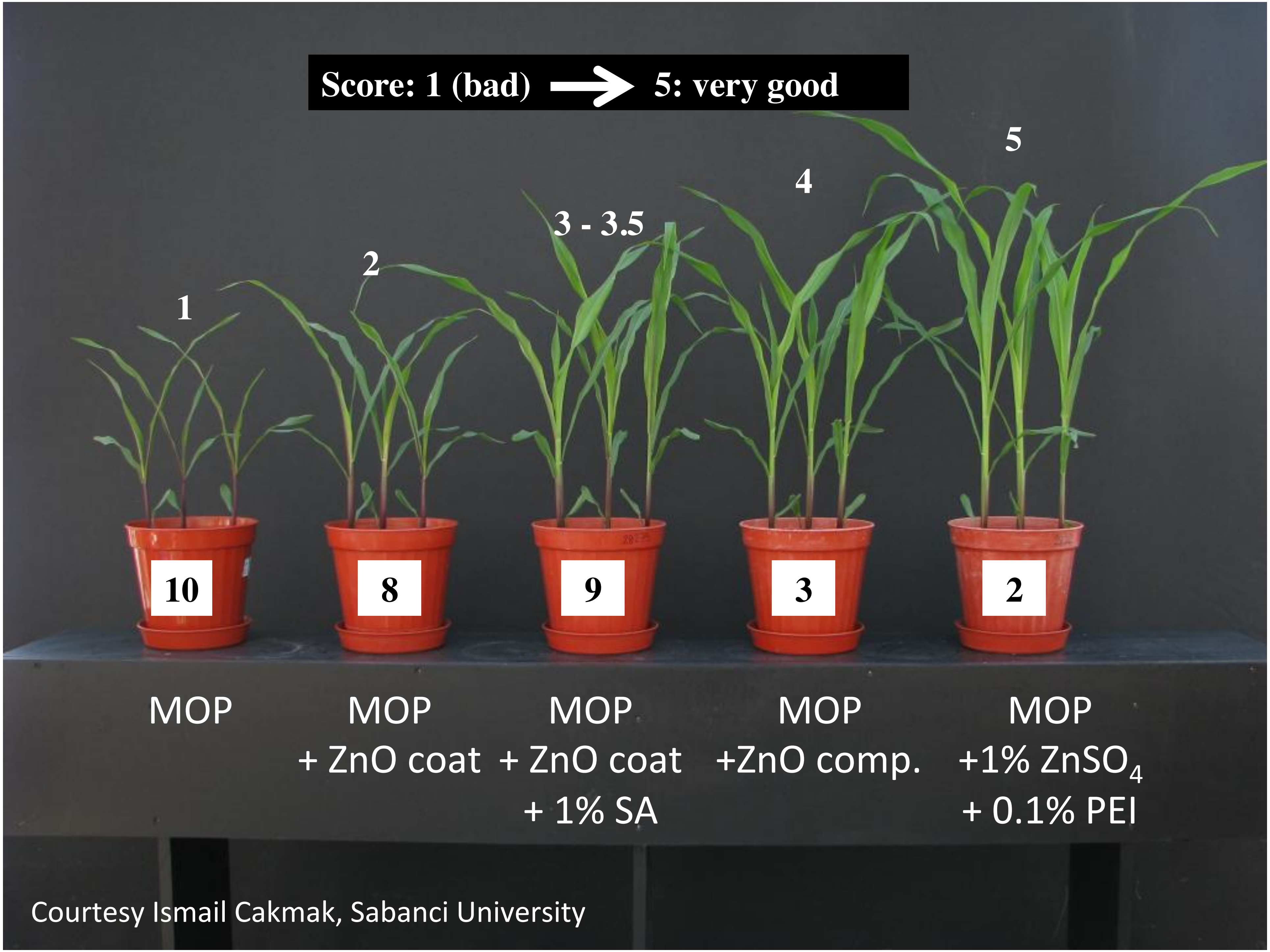
Acidifying/chelating agents and Zn diffusion - MOP



Sulfamic acid effective in increasing Zn diffusion from ZnO added to MOP.

Acidifying/chelating agents and Zn uptake - MOP





Score: 1 (bad) → 5: very good
1
2
3 - 3.5
4
5
10
8
9
3
2
MOP
MOP + ZnO coat
MOP + ZnO coat + 1% SA
MOP +ZnO comp.
MOP +1% $ZnSO_4$ + 0.1% PEI
Courtesy Ismail Cakmak, Sabanci University

Keeping Zn water solubility in perspective

- Fast-growing annual crops (corn, wheat, soybean, canola, potato, etc.) in temperate and dryland regions require rapid Zn supply from soil/fertilizer

- Perennial crops (fruit, stonefruit, nuts, forestry) in high rainfall environments require a lower rate of Zn supply from soil/fertilizer over a longer period

Summary points

- Zinc must be added to each granule to ensure uniform distribution in the field – bulk blends not effective
- Higher water soluble Zn is desirable for agronomic efficiency of Zn fertilizer
- Form of Zn added to P fertilizers or present in fertilizer is not important as Zn-phosphate compounds form in granule and in/around granule on dissolution
- Granule pH is a strong determinant of water solubility and agronomic performance
- Using granulation pH to control water solubility of Zn is difficult as the granulation pH window is then restricted

Summary points

- Water soluble Zn in P fertilizers can be improved by adding chelates or acidifying agents post granulation
- For MOP no precipitation of Zn occurs in/on the granule and if a soluble Zn source is used, dissolution/diffusion is rapid
- Acidifying agents (e.g. sulfamic acid) can be added to improve effectiveness of ZnO in MOP
- Coating Zn is better than co-compaction
- Small amounts of PEI increased effectiveness of $ZnSO_4$ with MOP

Way forward

- Continue to search for more effective chelates or acidifying agents for improving water solubility of Zn
- Seek granulation aids to allow a wider (i.e. lower) pH window for effective granulation
- Evaluate promising formulations in field trials

Thank you for your attention!