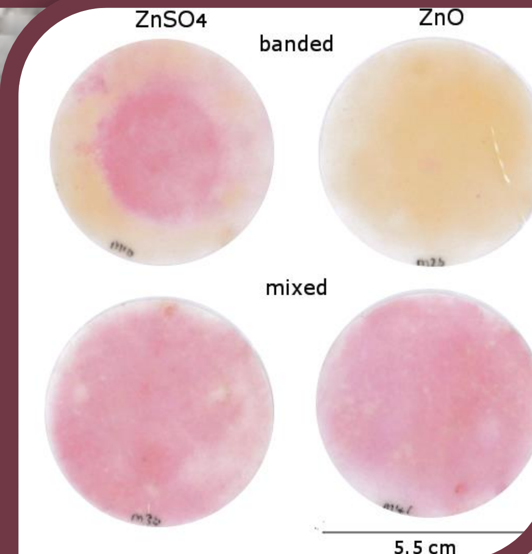
Picture courtesy Dr I. Cakmak



Reactions of fertilizer zinc in soil and their effect on Zn availability

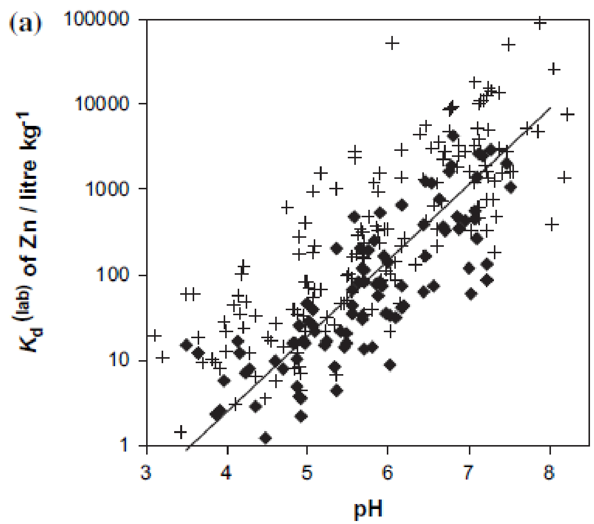
Fien Degryse, The University of Adelaide

Introduction

- Zinc is an essential element for both plants and animals. Inadequate Zn supply can result in yield loss and/or malnutrition
- Addition of fertilizer Zn can improve yields (under Zn deficient conditions) and increase Zn concentration in the crop
- Focus of this talk:
  - reactions of Zn in soil;
  - how reaction of fertilizer Zn is affected by
    - fertilizer composition,
    - method of application, and
    - time since application (residual value); and
  - how this affects the availability to plants

Reactions of Zn with soil – adsorption

- Reactions of zinc in soil have mostly been studied with Zn salt homogeneously mixed with soil
- Solubility of soil Zn is usually controlled by adsorption. Organic matter and oxides are the main Zn adsorbents. Adsorption increases with increasing pH



Degryse et al. EJSS 2009

pH > 5 $\Rightarrow$ K_d > 10 L/kg

Zn on solid phase >>> Zn in solution

Reactions of Zn with soil – precipitation

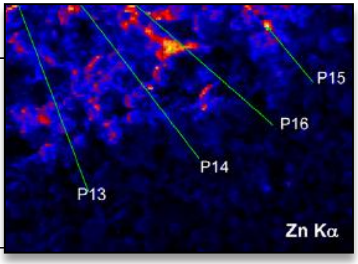
Solubility control by pure Zn precipitates may occur in:

- Zn contaminated soils, e.g. Zn phosphate (Kirpichtchikova et al, 2006), smithsonite (Van Damme et al. 2010), sphalerite, franklinite (Roberts et al. 2002)
- in localized spots with high concentrations (e.g. in case of Zn fertilizer granules), e.g.

Hettiarachchi et al. SSSAJ 2008

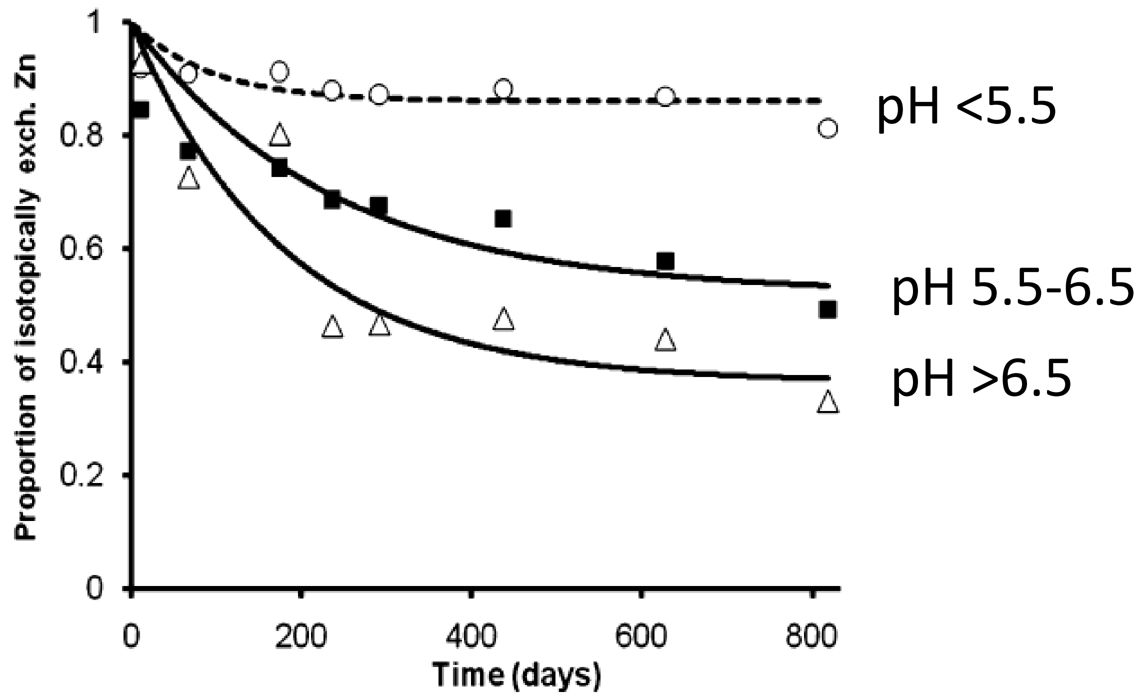
Table 4. Percentages of Zn species in treated soils, the unexposed granular Zn fertilizer granules, and incubated granular Zn determined by linear combination fitting of bulk extended x-ray absorption fine structure (EXAFS) spectra.

Sample	Ferrihydrite-adsorbed Zn	Willemite	Hopeite	Scholzite	Zincite
Unexposed granular Zn	–	–	48.4	43.3	8.3
Exposed (incubated) granular Zn	–	20.5	–	65.8	13.7
Granular Zn, Section 1	9.1	59.5	31.4	–	–
TGMAP‡ + Mn and Zn, Section 1§	–	60	14.4	25.6	–
TGMAP + Mn and Zn, Section 2	37.9	26	36.1	–	–



Reactions of Zn with soil – ‘fixation’

Fixation (or ‘ageing’) refers to reactions that make Zn less available over time (e.g. diffusion into oxides, formation of precipitates, ….)



Young 2013. *In:* Heavy metals in soils.
Trace metals and metalloids in soils and their bioavailability

Type of Fertilizers – sources

Most commonly used

Zn source	Formula	Zn content (%)
Zinc sulfate	$ZnSO_4{\cdot}xH_2O$	22-36
Zinc chloride	$ZnCl_2$	50
Zinc nitrate	$Zn(NO_3)_2{\cdot}3H_2O$	23
Zinc oxysulfate	$xZnSO_4{\cdot}xZnO$	20-50
Zinc oxide	ZnO	~80
Zinc carbonate	$ZnCO_3$	50-56
Disodium zinc EDTA	$Na_2ZnEDTA$	8-14
Sodium zinc HEDTA	NaZnHEDTA	6-10
Sodium zinc NTA	NaZnNTA	9-13
Zinc lignosulfonate		5-10

Chelated Zn

- Zn sulfate, chloride and nitrate are highly soluble; ZnO and $ZnCO_3$ hardly dissolve <u>in water</u>
- Chelates help keeping Zn soluble in soil, particularly in high pH soils, but are considerably more expensive

Type of fertilizers – forms and application

- Foliar vs soil-applied: foliar can be more effective, but application more challenging, no residual effect, and not suited to treat severe deficiency
- Granular vs Fluid
- Broadcast vs banded vs seed-applied
- Single nutrient vs compound fertilizer (Zn combined with NPK fertilizer)

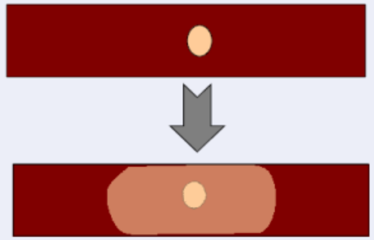
Bulk blend

NPK Zn

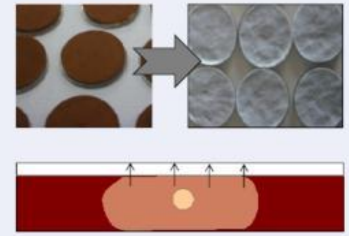
Compound

NPK+ Zn

Visualization technique

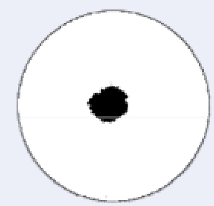


(i) **Incubation** of soil with fertiliser granule for days to months



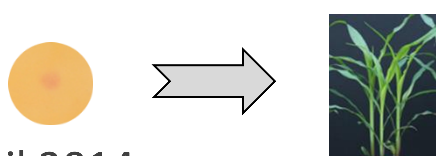
(ii) **Deployment:** $CaCO_3$-paper on soil surface

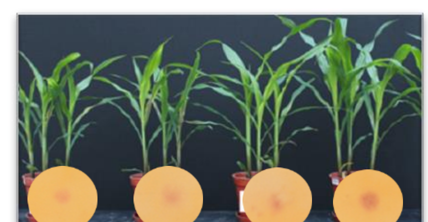
(iii) **Development:** addition of dithizone to colour captured Zn



(iv) **Image analysis:** area/diameter of high Zn zone

⇒ Relating reaction in soil to plant availability:





Degryse et al., Plant and Soil 2014

Effect of fertilizer composition – NP+Zn

Diffusion of Zn from fertilizer (0.35 mg Zn) after 28 d incubation:

<u>Acid soil</u>

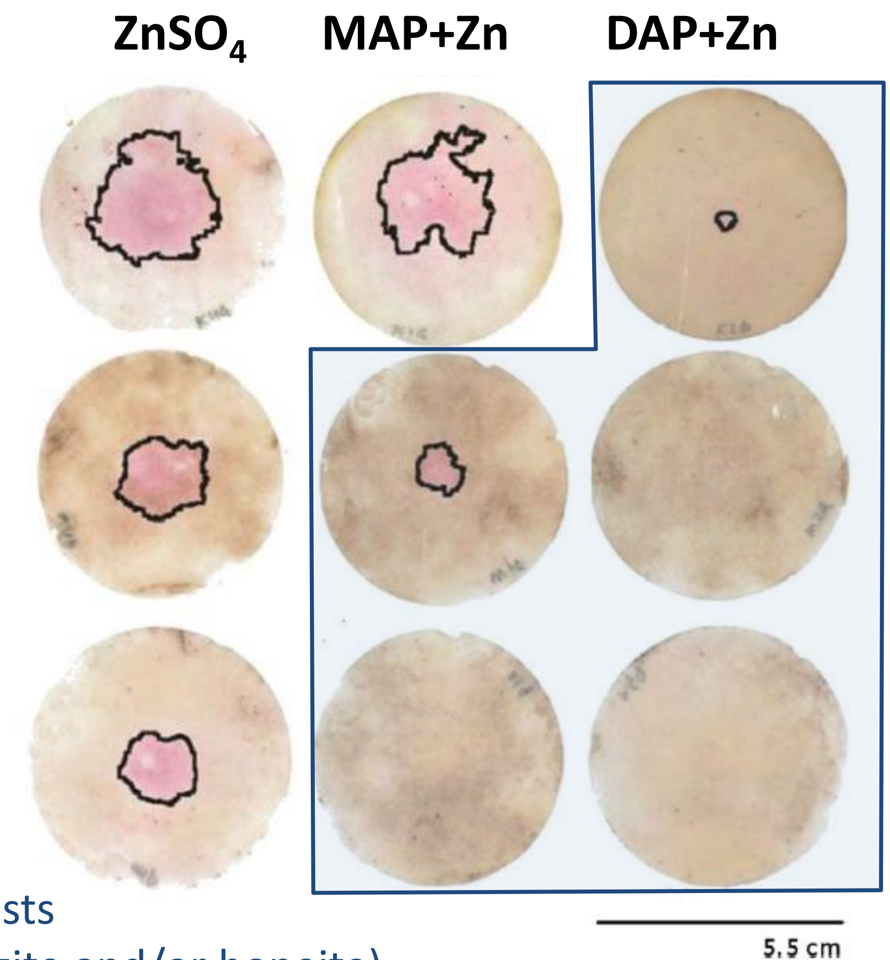
$ZnSO_4$ = MAP+(1%)Zn > DAP+(1%)Zn

<u>Neutral soil</u>

$ZnSO_4$ = MAP+Zn > DAP+Zn

<u>Calcareous soil</u>

$ZnSO_4$ > MAP+Zn = DAP+Zn

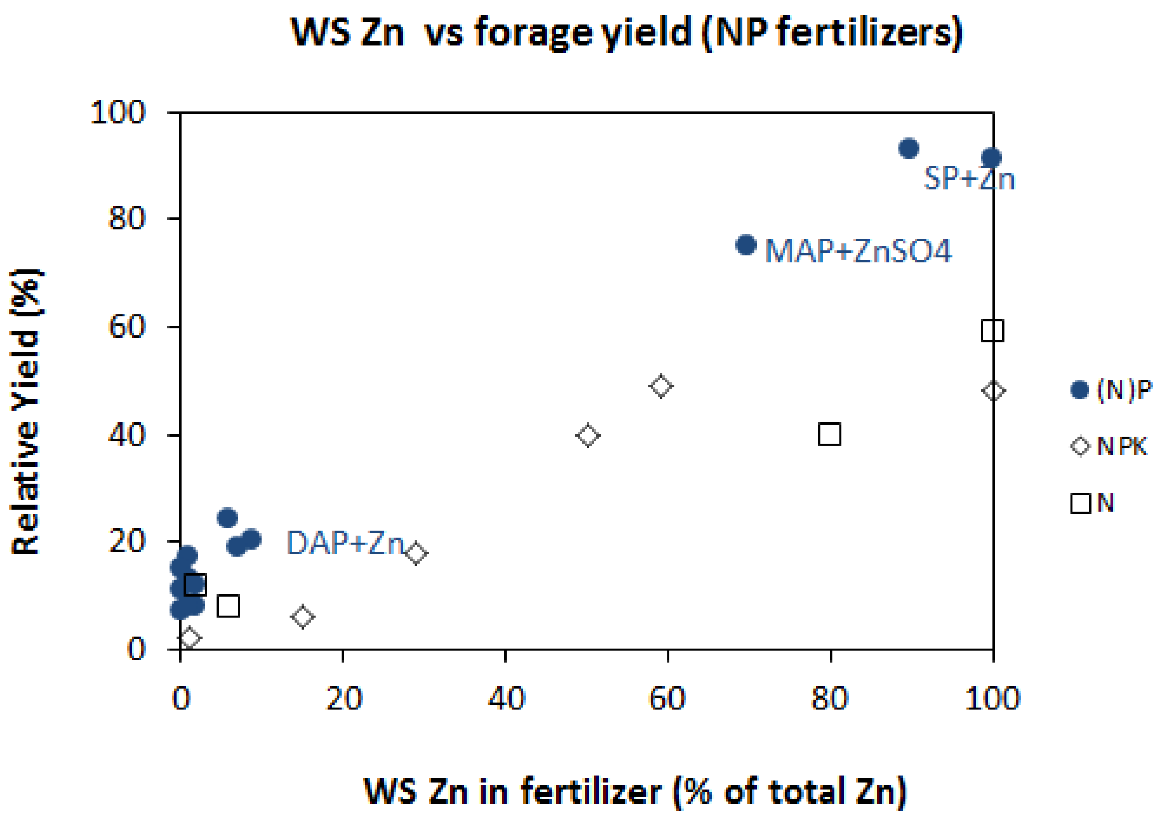


Solution composition near granule suggests
solubility control by Zn phosphate (scholzite and/or hopeite)

Degryse et al., Plant and Soil 2014

Effect of fertilizer composition – NP+Zn

Pot trial (corn, ~7 weeks) comparing effectiveness of granular NP+2%Zn fertilizers in a non-calcareous, alkaline soil (pH 7.3)

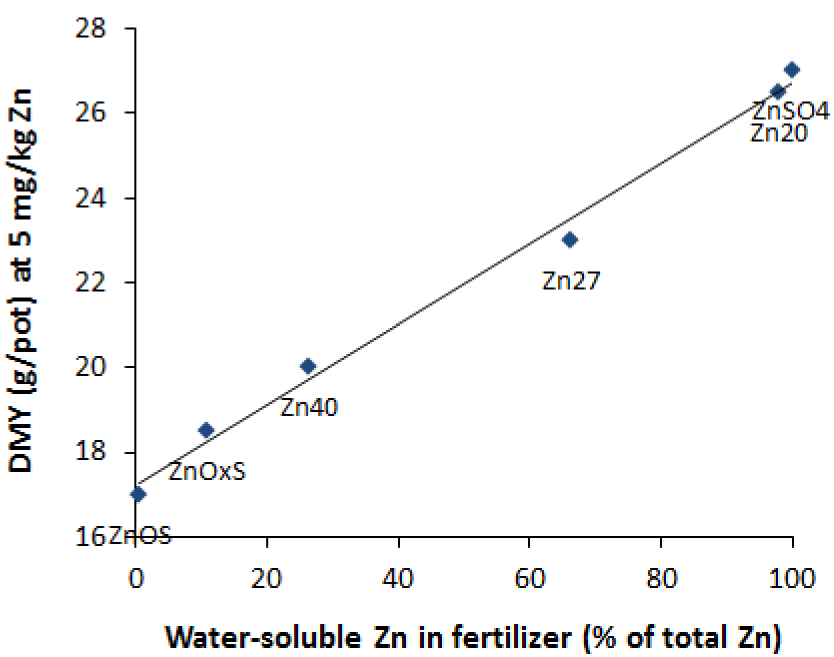


Data from Mortvedt and Giordano, J Agr Food Chem 1969

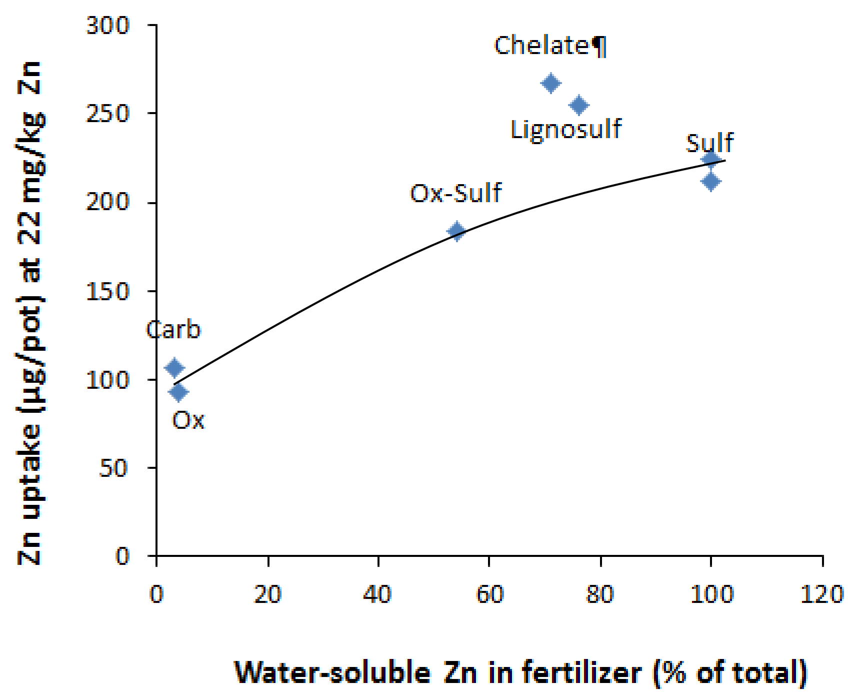
Conclusions (1)

In general for *granular* Zn fertilizers, effectiveness (first year) increases with increasing water-solubility of Zn in the fertilizer.

This has also been observed in several other studies, e.g. for single nutrient sources:



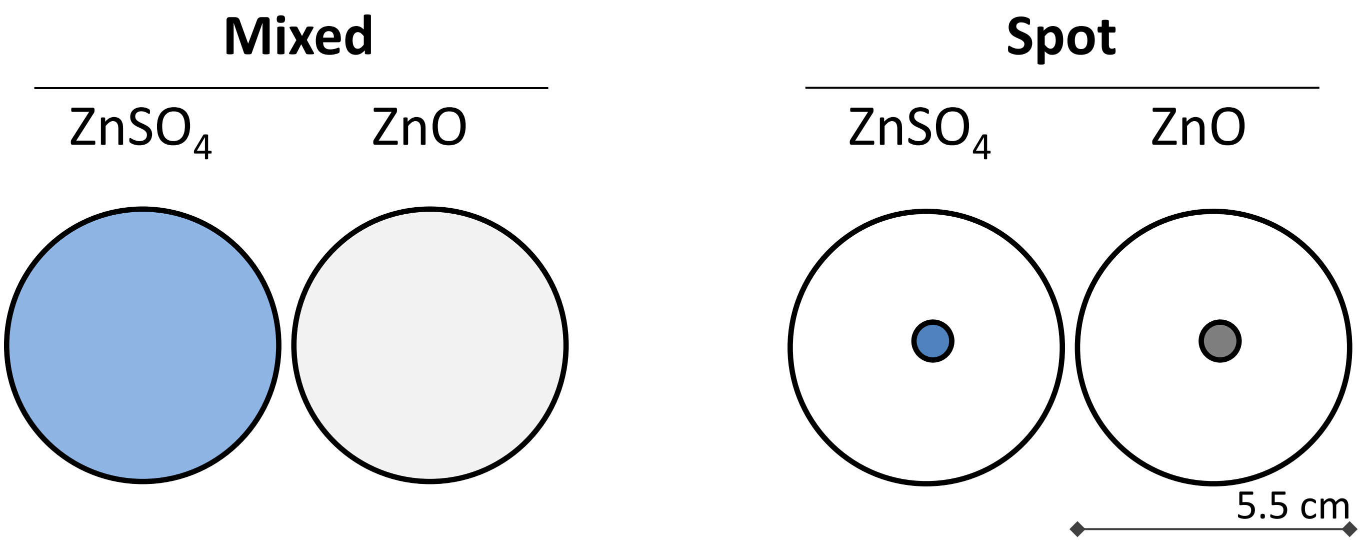
Westfall et al., Better Crops 1999



Liscano et al., Arkansas Agr Stat 2000

Effect of fertilizer composition x placement

- ZnO vs $ZnSO_4$ powder (5.5 mg Zn) mixed through soil or spot application

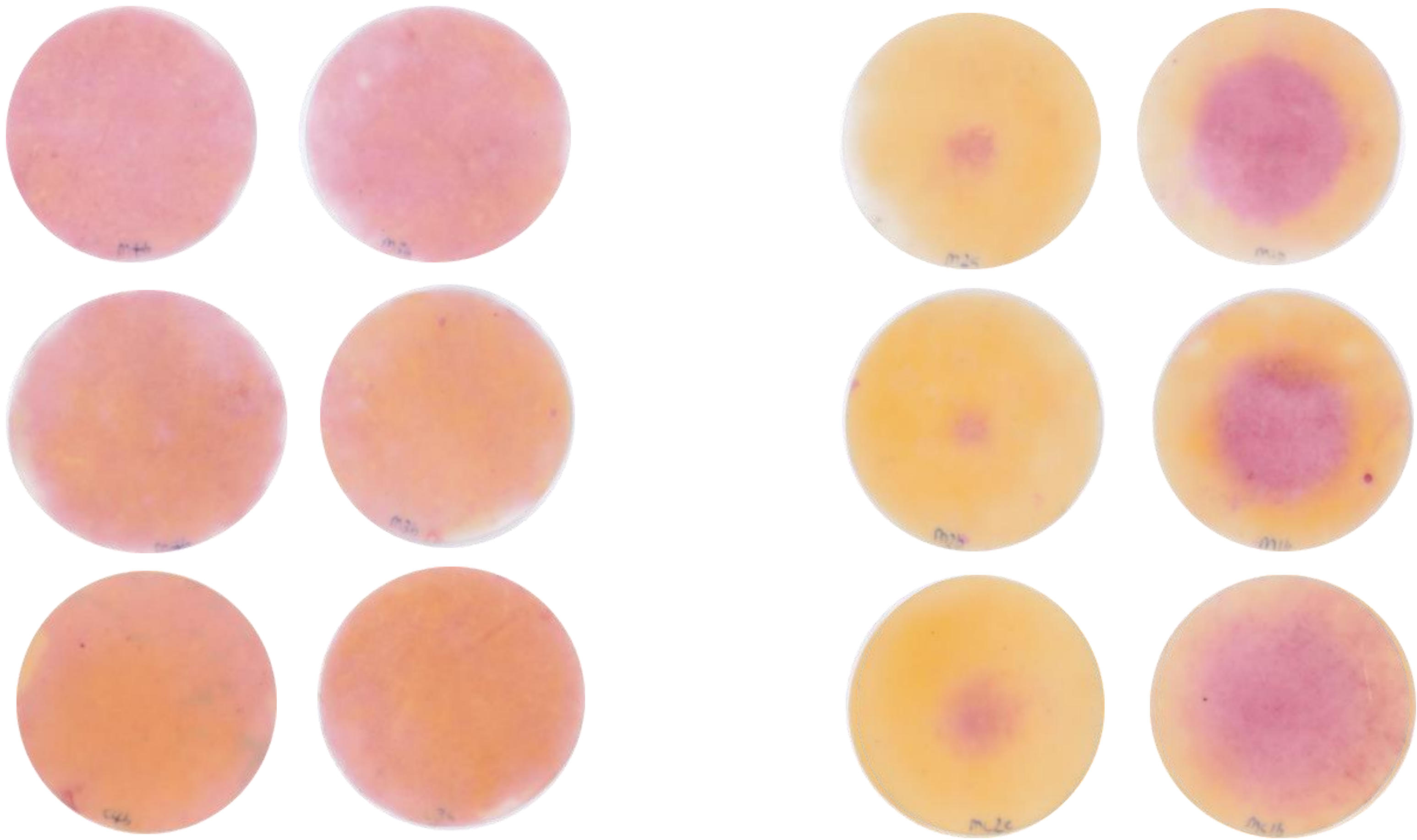


- Zn diffusion visualized at different times (up to 108 d) after application in an acid and alkaline soil (pH_{water} 5.9 and 8.5 resp)

Effect of fertilizer composition x placement

Acid sandy soil

	Mixed			Spot	
Day	ZnO	≅ *	$ZnSO_4$	ZnO	<	$ZnSO_4$
10						
21						
108						



* Confirmed by chemical extraction (~150 µg/L Zn in 1 mM $CaCl_2$ extract at 21 d)

Effect of fertilizer composition x placement

Alkaline soil

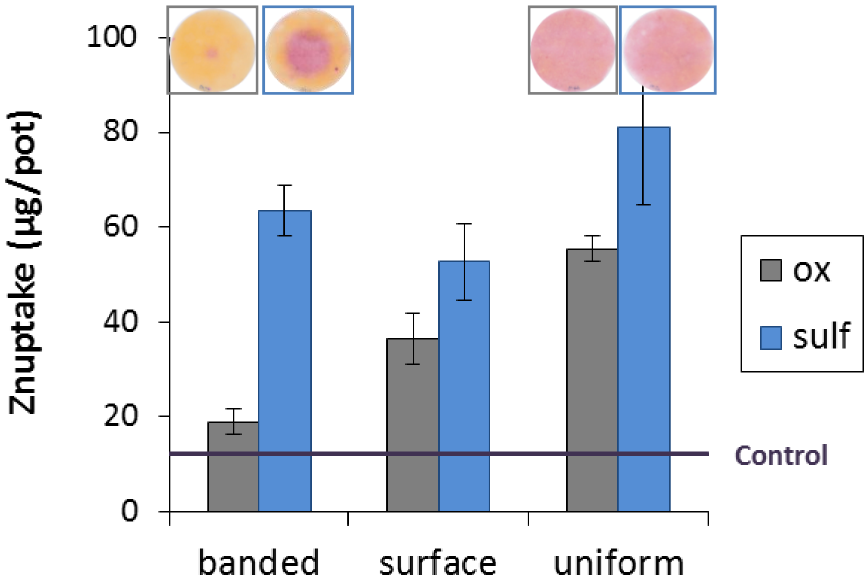
Day	Mixed: ZnO	≅ *	Mixed: $ZnSO_4$	Spot: ZnO	<	Spot: $ZnSO_4$
10						
21						
108						

* Confirmed by chemical extraction (5 µg/L Zn in 1 mM $CaCl_2$ extract at 21 d)

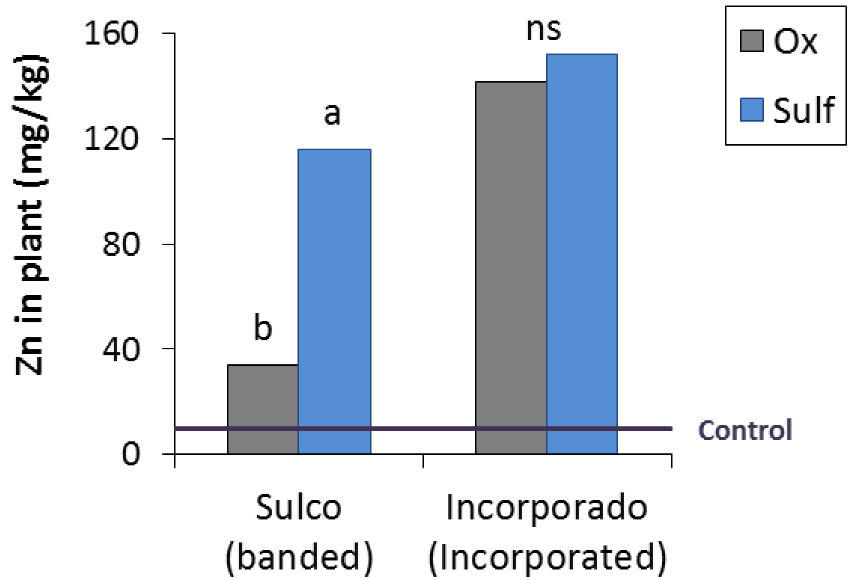
Effect of fertilizer composition x placement

Pot trials with banded or uniformly mixed Zn oxide or sulfate

Wheat, 5 w, soil pH 6.8



Corn, 45 d, soil pH 5.6



McBeath & McLaughlin, Plant Soil 2014

Rosolem & Ferrari, R. Bras. Ci. Solo 1998

⇒ No significant difference between ZnO and $ZnSO_4$ when uniformly distributed

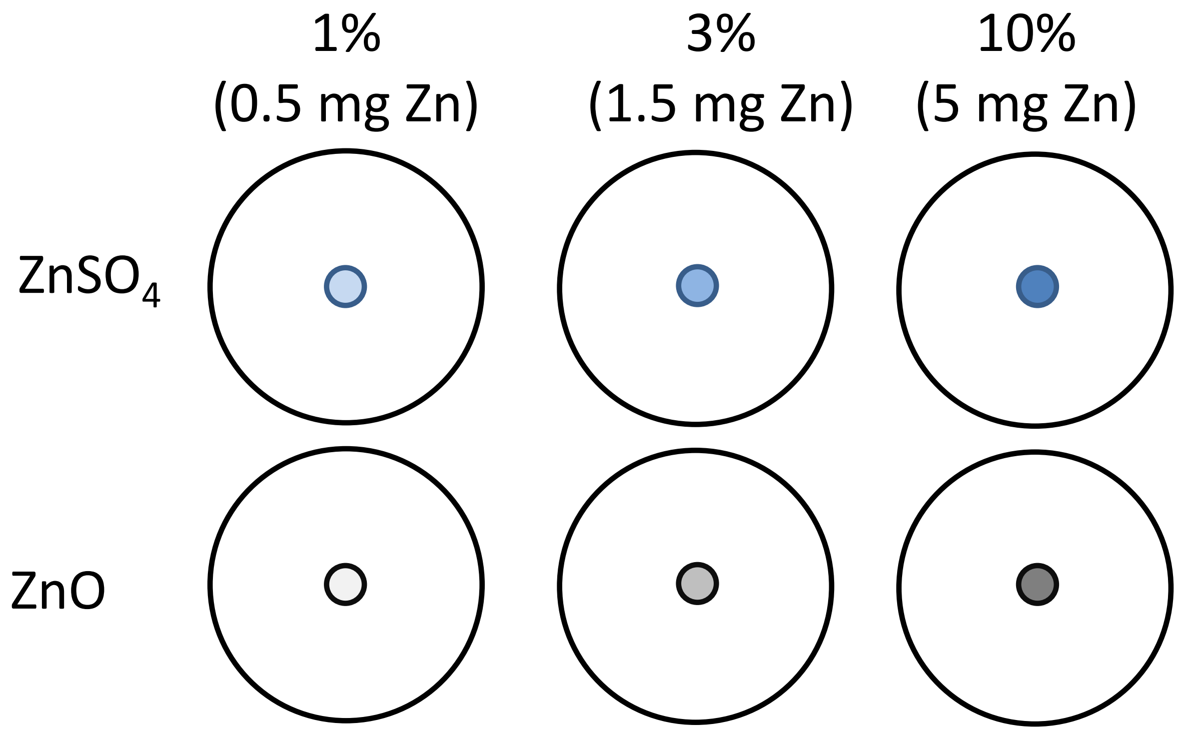
Conclusions (2)

- In general for *granular* Zn fertilizers, effectiveness (first year) increases with increasing water-solubility of Zn in the fertilizer
- When (powdered) ZnO is mixed through soil, it is usually as effective as a fully soluble source.

  This has also been found observed for other sparingly soluble sources, e.g. Ghosh (PhD thesis W-Aust 1991):
  Large differences in agronomic effectiveness of Zn-fortified granular fertilizers when added a granules, but not when ground and mixed through soil

Solubilisation rate of ZnO

- ZnO vs $ZnSO_4$ co-compacted with MOP (1, 3, or 10% Zn)



- Zn diffusion determined in an acid and alkaline soil (pH_{water} 5.5. and 8.5 resp.)

Solubilisation rate of ZnO

Acid soil

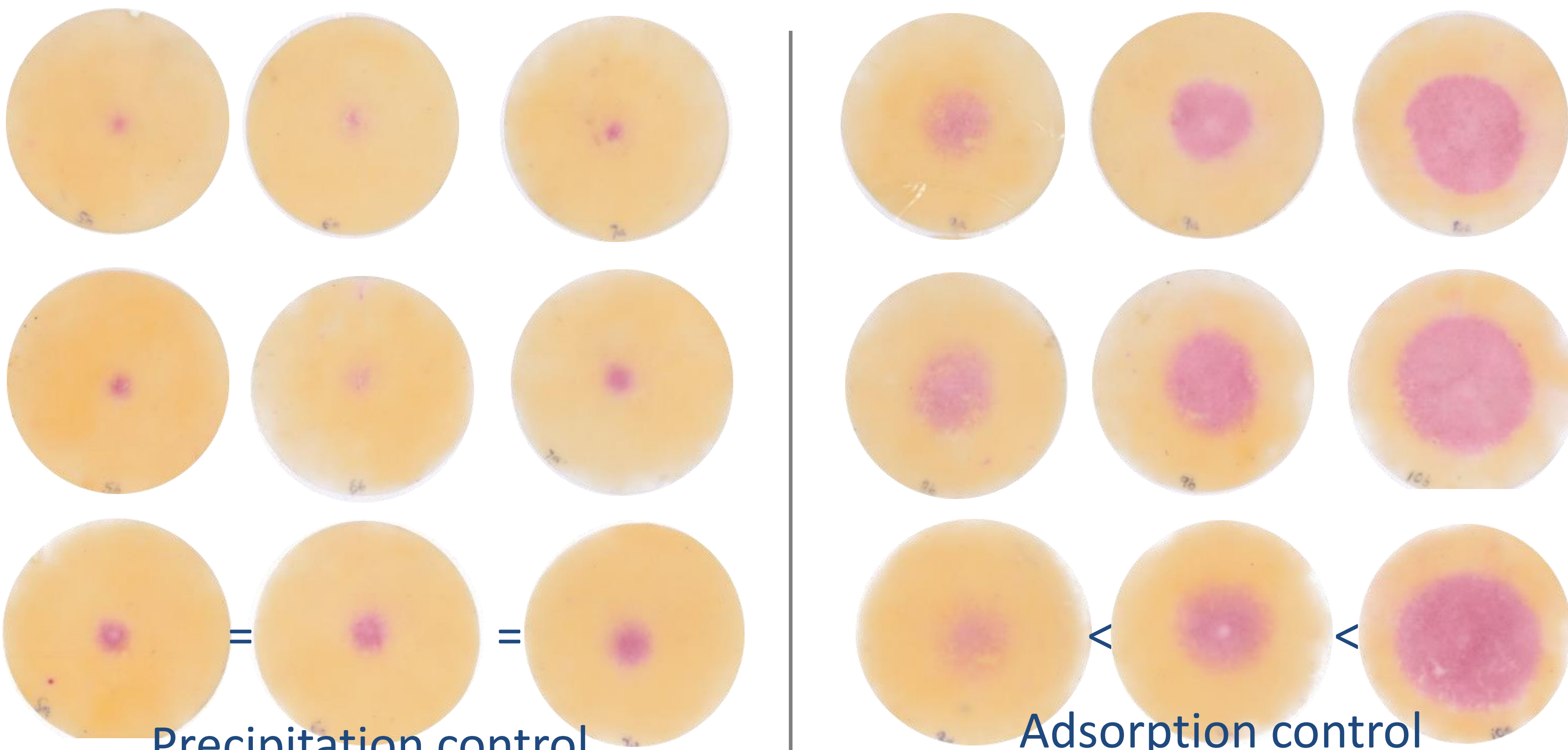
Zn as ZnO			Zn as $ZnSO_4$		
1%	3%	10%	1%	3%	10%

Day

3

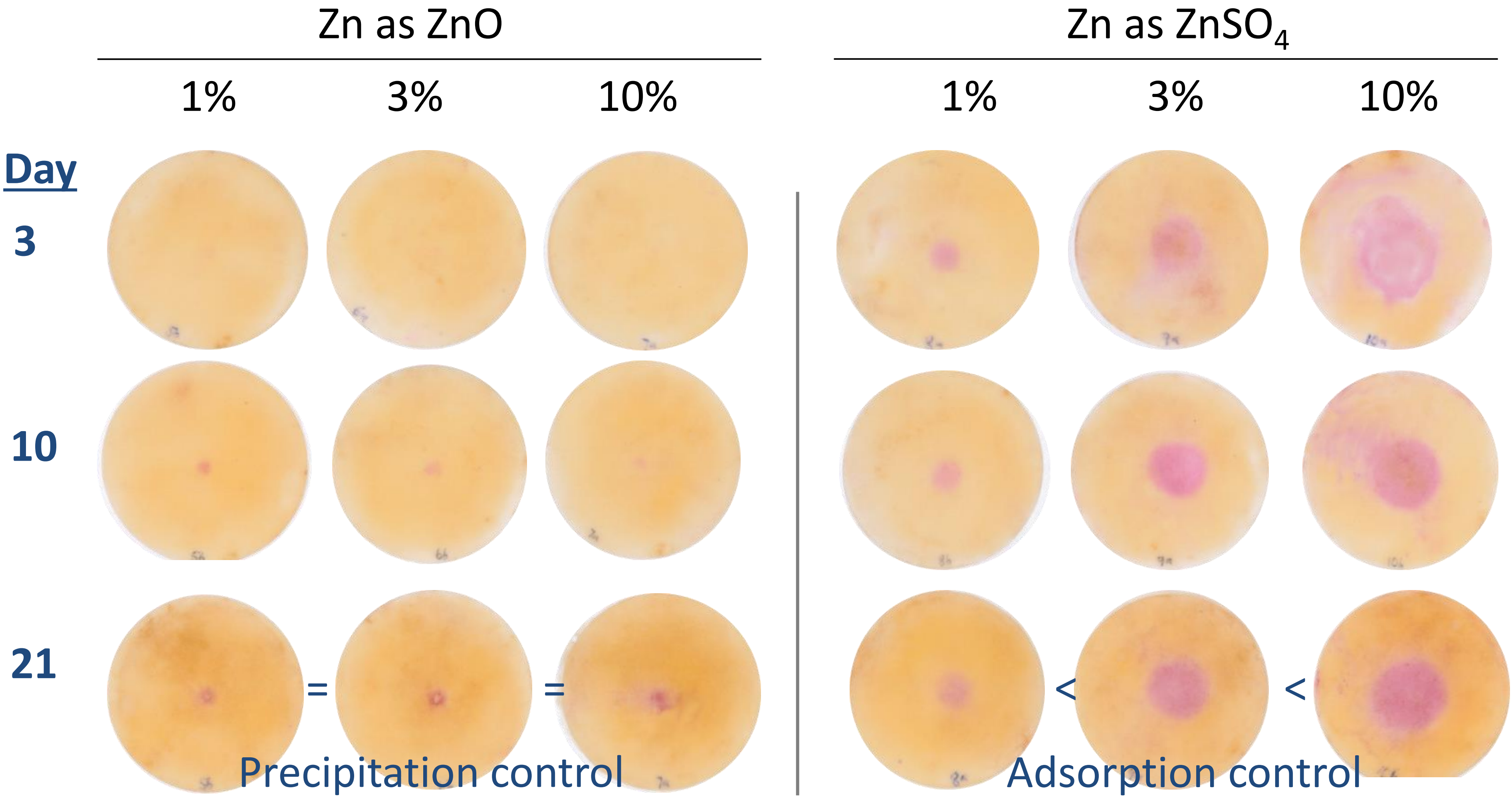
10

21

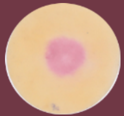


Solubilisation rate of ZnO

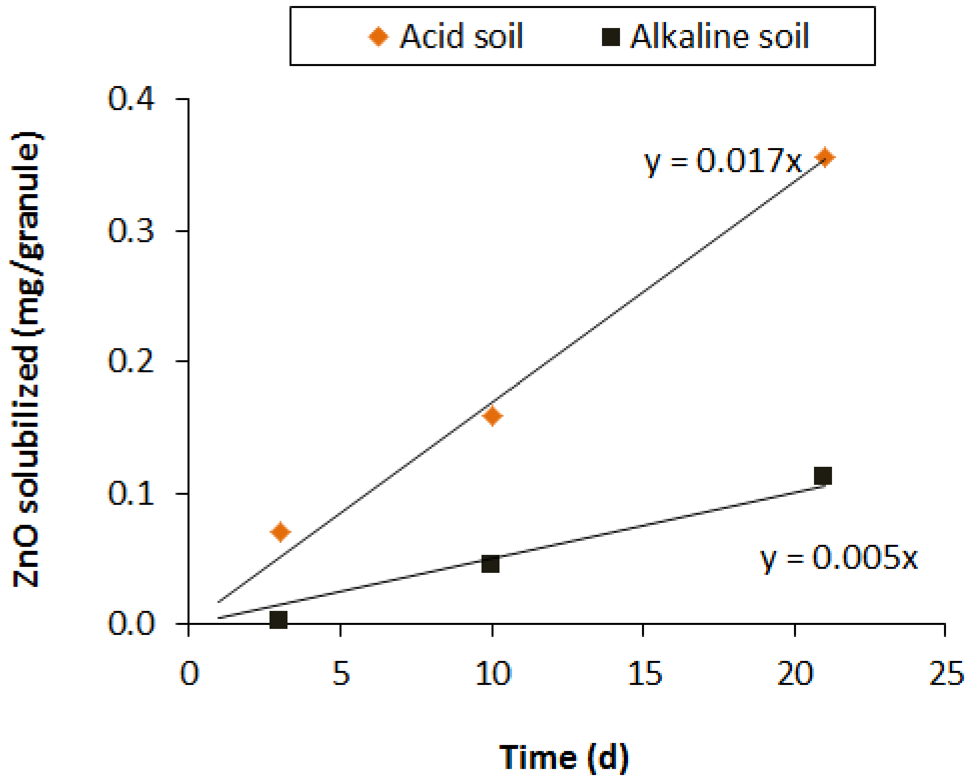
Alkaline soil



⇒ Solubilization of ZnO calculated from volume of fertilized soil relative to that in the corresponding $ZnSO_4$ treatment



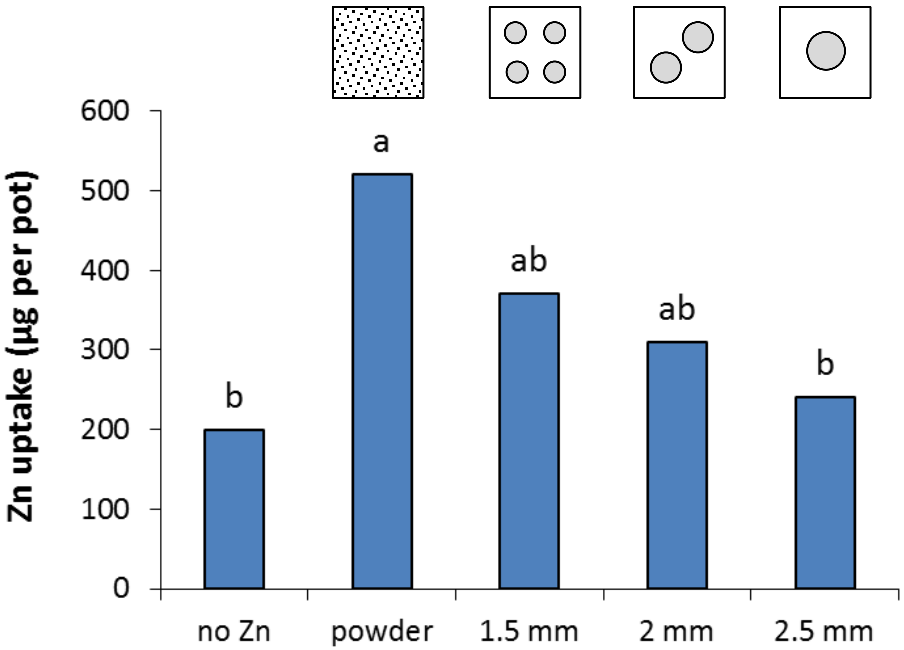
Solubilisation rate of ZnO



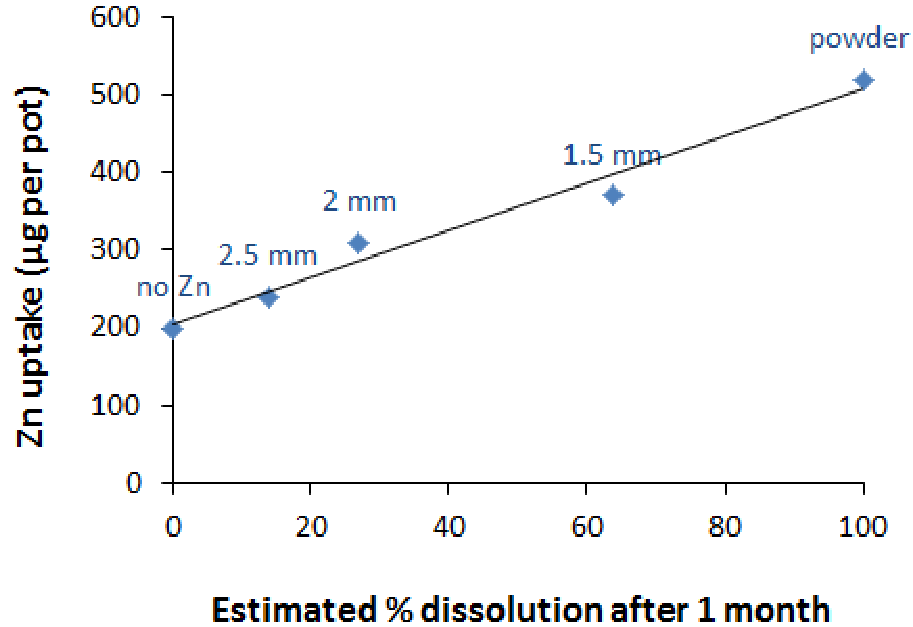
Soil	Estimated solubilization rate (µg Zn/d)	Time (d) to solubilize for **x** mg Zn per spot/granule		
		0.01 (powder)	**1**	**10**
Acid	17	0.6	59	592
Alkaline	5	2	200	2000

Solubilisation rate of ZnO

Liscano et al (2000): For a sparingly soluble Zn source (Znoxysulfate, 4% WSZn; mostly ZnO), effectiveness of the Zn fertilizer was found to decrease with increasing granule size



Assuming dissolution rate of 17 µg Zn/granule/d (acid soil)

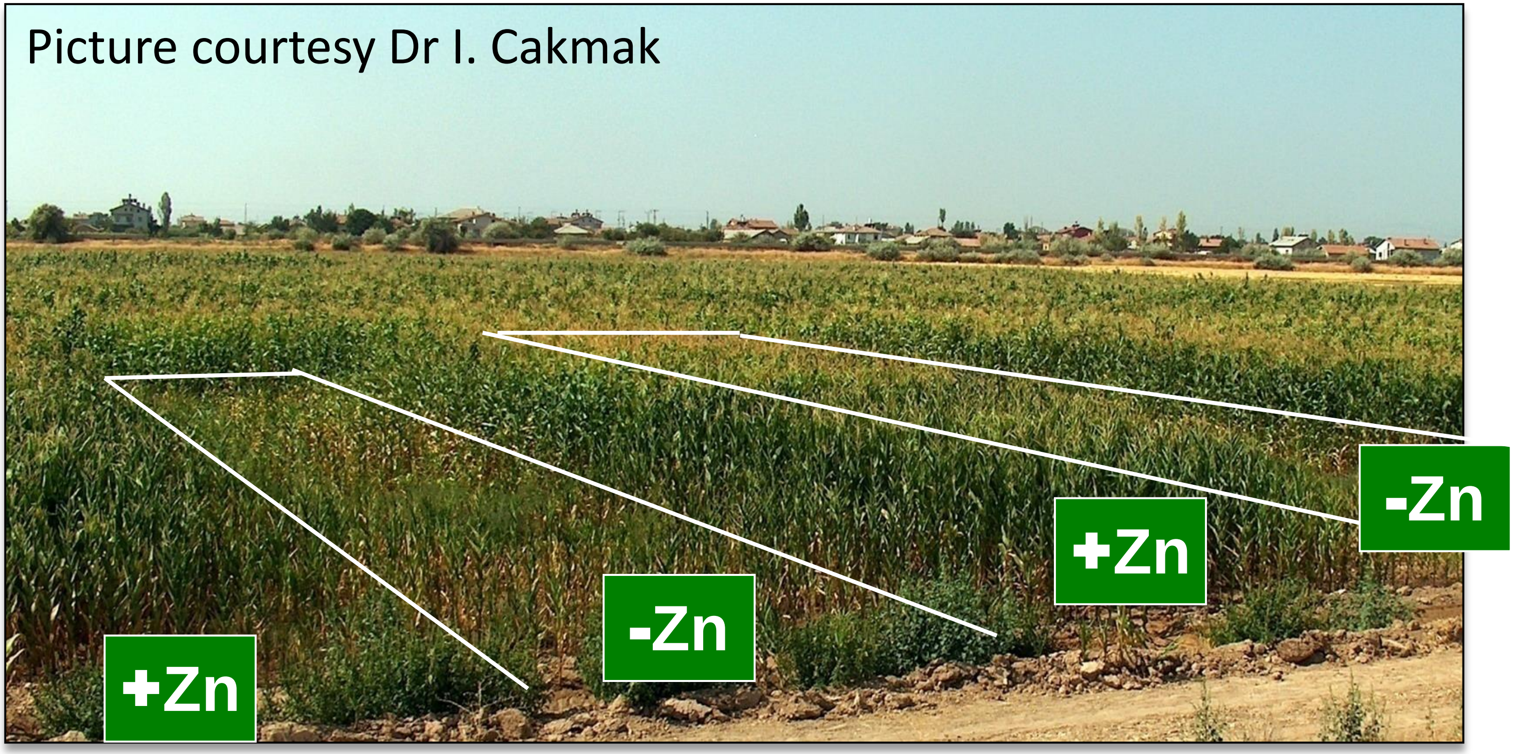


Faster solubilization of smaller granules results in higher effectiveness

Conclusions (3)

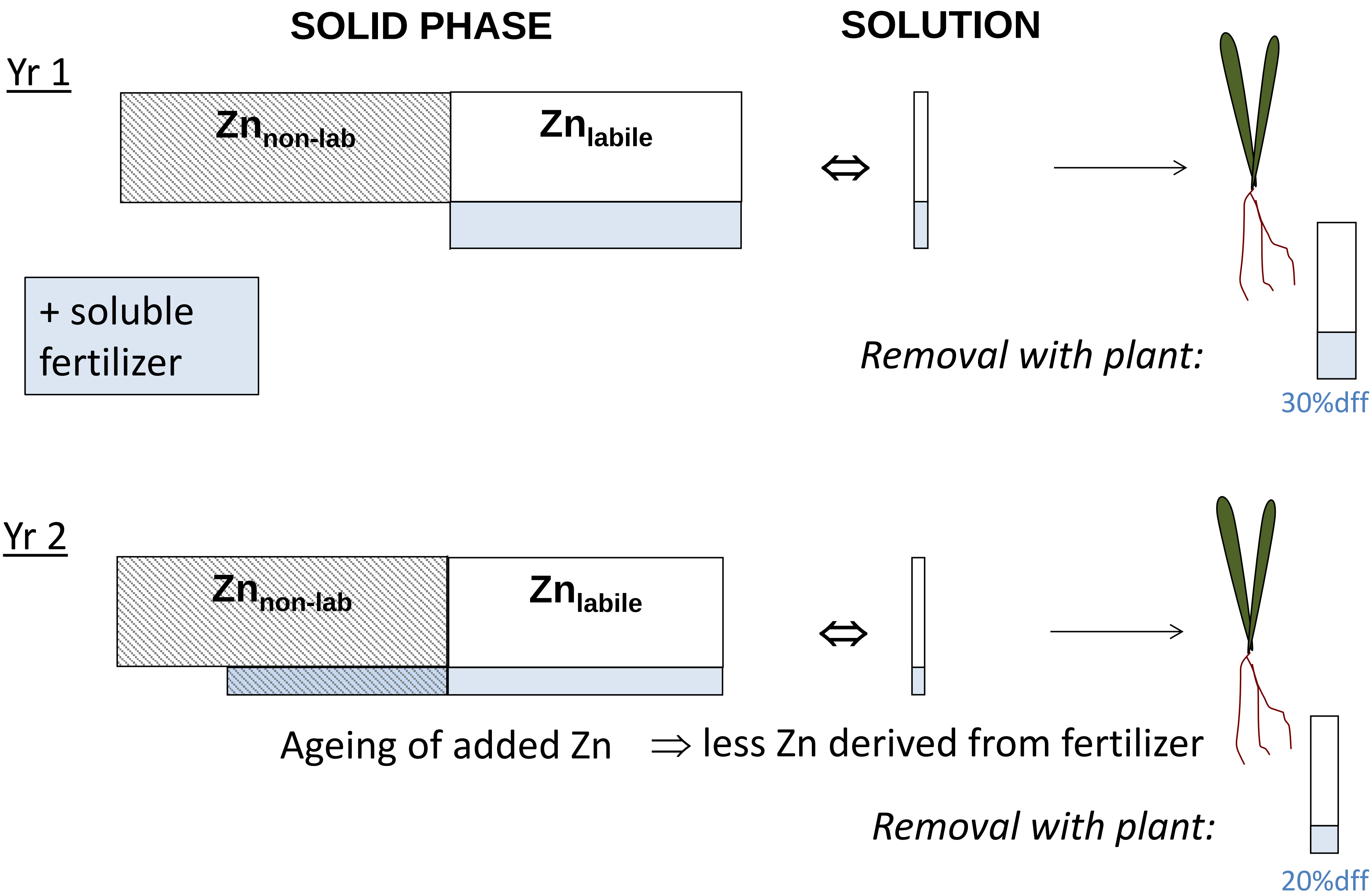
- In general for *granular* Zn fertilizers, effectiveness (first year) increases with increasing water-solubility of Zn in the fertilizer
- When sparingly soluble sources are mixed through soil, they are usually as effective as a fully soluble source
- The time to fully dissolve a sparingly soluble, granular or banded Zn fertilizer depends on fertilizer properties (granule size, Zn content, chemical form) and on soil properties (soil pH)

Residual effect



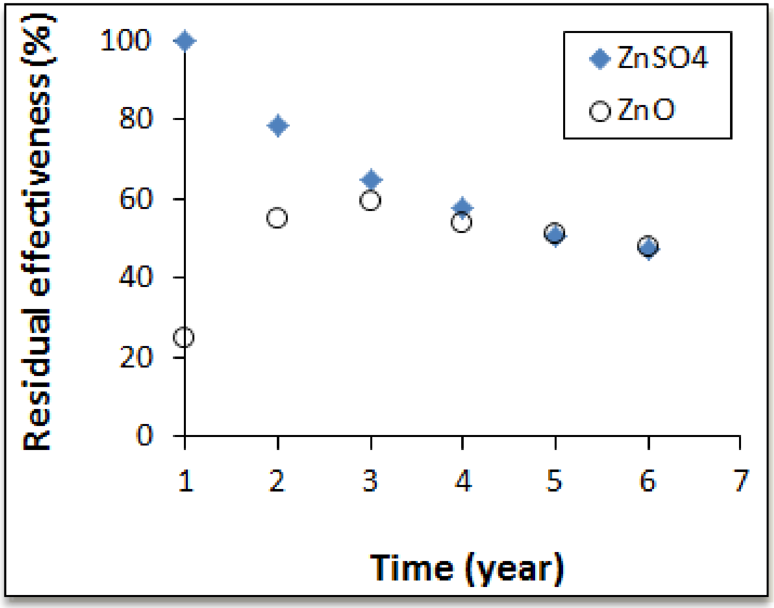
Anatolia, maize, 8 years after Zn fertilizer application

Residual value – scheme



Residual value – theoretical examples

5 kg Zn/ha added in year 1; 0.2 kg/ha yearly export; no leaching; initial labile Zn 3 mg/kg; 50% of fertilizer Zn gradually fixed; ZnO gradually solubilized



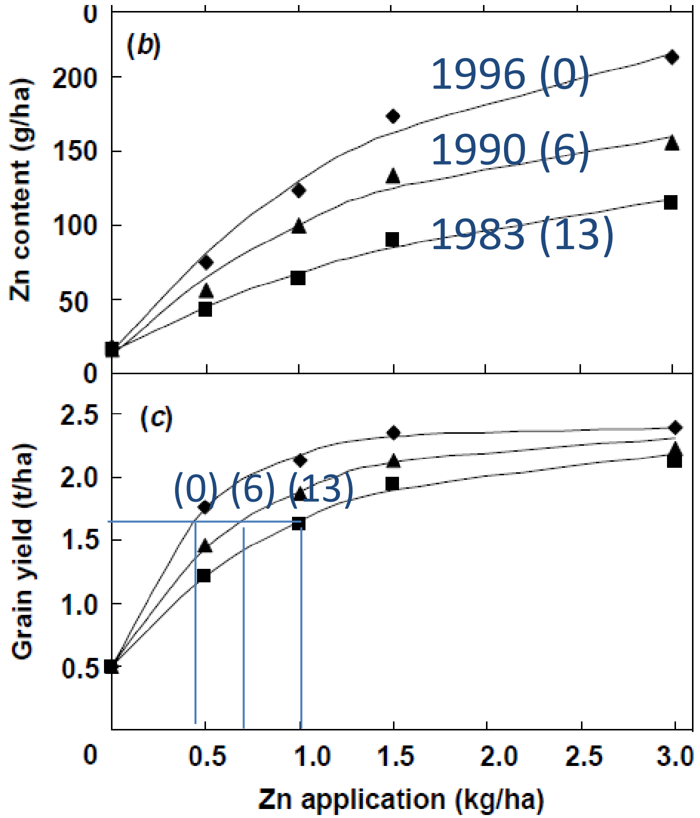
- Decrease in residual effectiveness mostly due to ageing, not to uptake (since added Zn rate >> yearly uptake)
- Effectiveness of sparingly soluble source expected to increase and catch up with soluble source

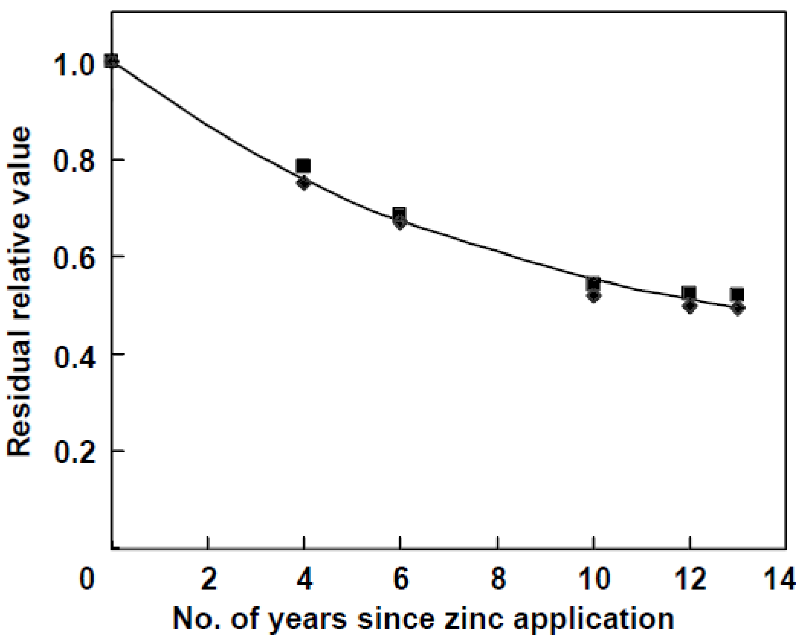
e.g. Slaton et al., SSSAJ 2005: no difference between Zn sulfate and oxysulfates in second year

Residual value – literature examples

Field trial – Residual value of ZnO (applied near seed with DAP) in acid soil (pH 5.3)

Application (nr of years at sampling)





Brennan, Aust J Exp Agr 2001

Residual value – literature examples

Field trials – Residual value of broadcast $ZnSO_4$-coated NH_4NO_3

Elapsed time since fertilizer applied	DPTA-extractable Zn	Zn in leaves	Zn in tops	Zn uptake
	ppm			kg/ha
	Shano Silt Loam			
No Zn	0.19	12	13	0.136
Current season	1.2	25	22	0.221
1 year	1.1	23	20	0.220
2 years	0.80	24	23	0.208
3 years	0.92	22	22	2.210
4 years	0.68	22	22	0.217
LSD (0.05)	0.35	7.9	5.5	0.079
	Hezel Subsoil			
No Zn	0.22	16	17	0.158
Current season	1.9	34	38	0.399
1 year	1.2	32	37	0.386
2 years	1.0	36	37	0.349
3 years	0.79	32	35	0.359
4 years	0.50	22	25	0.293
LSD (0.05)	0.19	6.1	7.3	0.084

<u>Acid soil</u>

No decrease even in fifth year

(little loss and negligible fixation)

<u>Calcareous soil</u>

Gradual decrease, but still more than control in fifth year

Boawn, Soil Sci Am Proc 1974

Conclusions (4)

- In general for *granular* Zn fertilizers, effectiveness (first year) increases with increasing water-solubility of Zn in the fertilizer
- When sparingly soluble sources are mixed through soil, they are usually as effective as a fully soluble source
- The time to fully dissolve a sparingly soluble granular Zn source depends on fertilizer properties (granule size and Zn content of fertilizer) and on soil properties (soil pH)
- The residual value of Zn fertilizer under field conditions has not often been assessed, but is usually very high (though less so in calcareous soils due to stronger fixation)

Overall Conclusions and Recommendation

- 4R principle: Right Source, Place, Time, and Rate. This talk focussed on effects of source and place, since this strongly affects the (initial) availability of Zn and hence the effectiveness of the Zn source.
- Granular, sparingly soluble sources are initially less effective than soluble sources. These differences between sources are likely to disappear over time, since most sources will solubilize in soil (rate dependent on degree of dispersion and soil properties)
- Given the high residual value of soil-applied fertilizer Zn, more long-term studies are recommended

Obrigada

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Symposium organizers

And thank you for your attention!