Measuring available Zn in fertilizers

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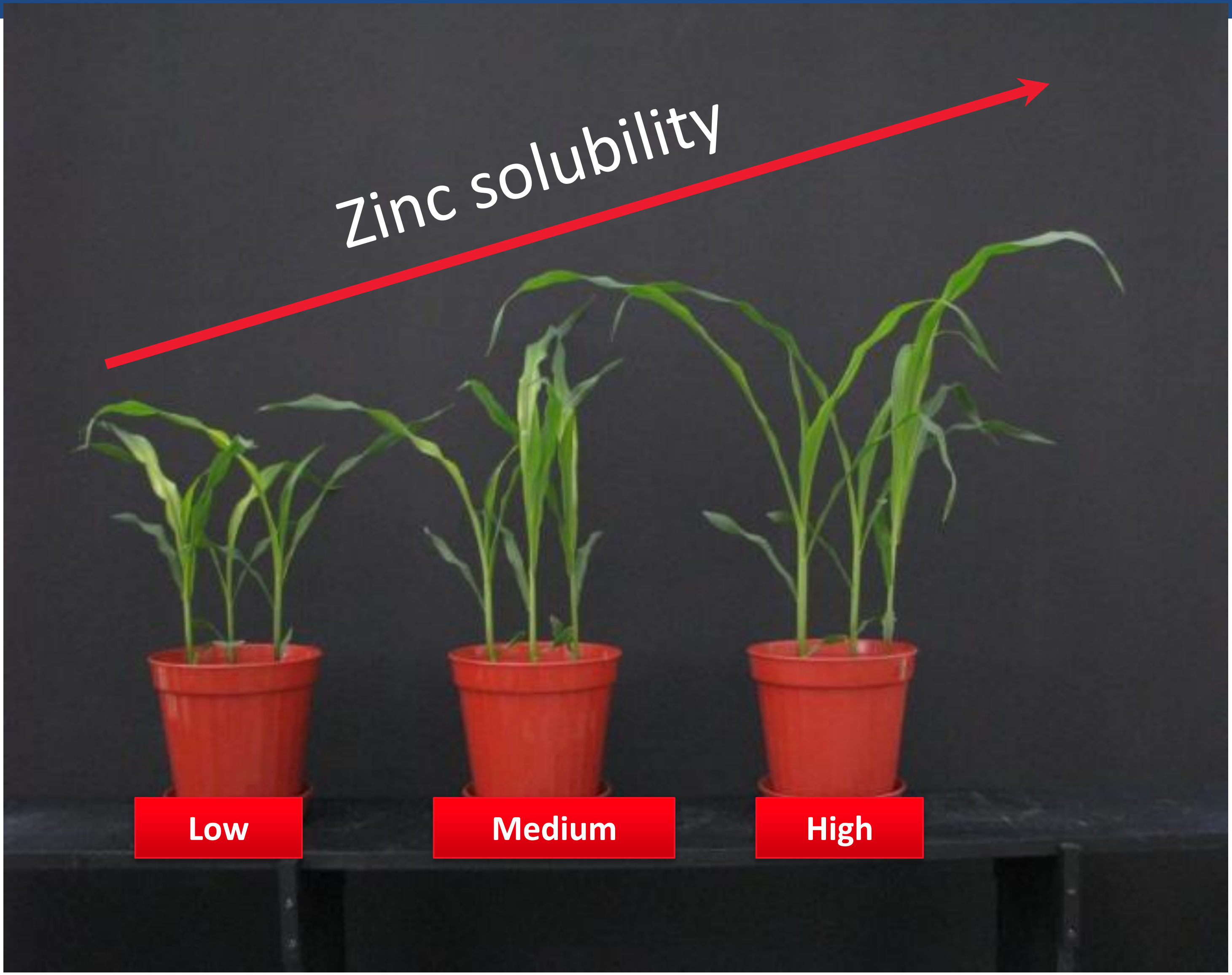
Does the solubility of Zn in fertilizers matter?



Source: Prof. Ismail Cakmak, Sabanci University

What's the best method to measure Zn solubility in fertilizers?

Measuring Zn in fertilizers

- Measuring total concentrations of Zn in fertilizers is relatively simple – usually strong acid digestion followed by analysis by ICP (OES or MS)
  - Total concentration of Zn represents the Zn that can potentially become available to plants
- Measuring available Zn should give an indication of the likely proportion of Zn in the product which the crop can easily access
- Any analytical method to measure "available Zn" in fertilizers should be
  - Sensitive
  - Accurate and precise
  - Robust across laboratories
  - Related to agronomic effectiveness of product

Measuring available Zn in fertilizers

- Several studies have been published examining the solubility of Zn in fertilizers and their agronomic effectiveness e.g.

  - Mortvedt, J.J., Giordano, P.M., 1969. Extractability of zinc granulated with macronutrient fertilizers in relation to its agronomic effectiveness. J. Agric. Food Chem. 17, 1272-1275.
  - Amrani, M., Westfall, D.G., Peterson, G.A., 1999. Influence of water solubility of granular zinc fertilizers on plant uptake and growth. Journal of Plant Nutrition 22, 1815-1827.
  - Liscano, J.F., Wilson, C.E., Norman, R.J., Slaton, N.A., 2000. Zinc availability to rice from seven granular fertilizers. AAES Research Bulletin. AAES, p. 31.

Measuring available Zn in fertilizers

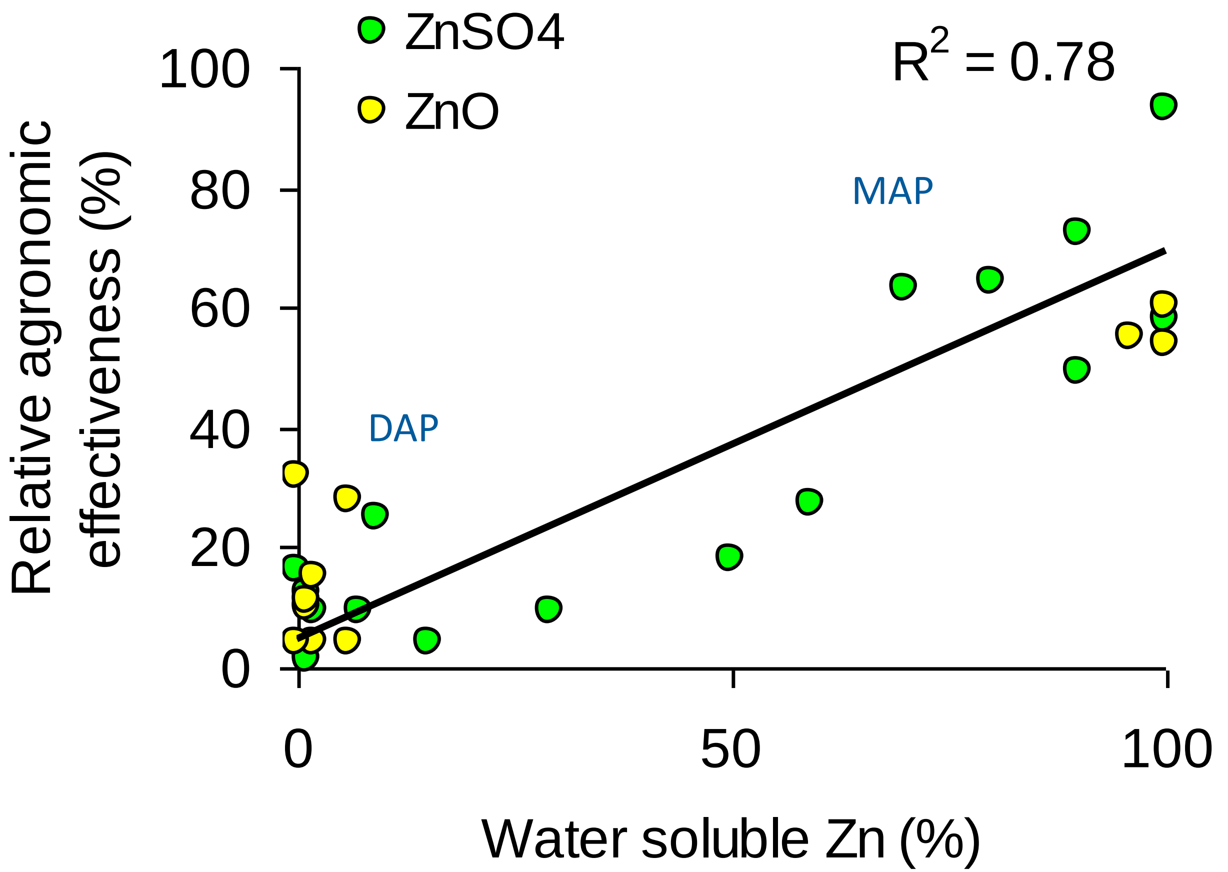
- Mortvedt and Giordano (1969) examined several extractants to solubilize Zn in fertilizers and related this to the agronomic effectiveness of the fertilizers (for Zn) in glasshouse trials

Table II. Correlation Coefficients Relating Extractable Zinc as Percentage of Total Zinc Content to Agronomic Effectiveness of Zinc as Zinc Sulfate or Zinc Oxide Granulated with Various Macronutrient Fertilizers

Extractant	pH of Extracting Solution	Correlation Coefficient, r^a	
		Forage yield	Zn uptake
H_2O	5.8	0.92	0.84
0.001*N* HCl	3.5	0.90	0.85
0.01*N* HCl	2.6	0.90	0.83
0.04*N* $KHSO_4 + K_2SO_4$	2.8	0.84	0.76
N $NH_4C_2H_3O_2$	7.0	0.48	0.62
NH_4 citrate[b]	7.0	0.67	0.57
0.001*M* EDTA	3.1	0.83	0.67
0.001*M* Na_2H_2EDTA	4.8	0.91	0.83
0.001*M* Na_2H_2EDDHA	9.5	0.84	0.70
0.001*M* DTPA	3.1	0.83	0.67
0.001*M* Na_5DTPA	10.8	0.87	0.71
0.005*M* DTPA + 0.01 *M* $CaCl_2$ + $N(CH_2CH_2OH)_3$	7.3	0.91	0.87
6*N* HCl		0.28	−0.16

[a] *r* values required for significance at 95 and 99% probability levels were 0.38 and 0.48, respectively.
[b] Extractant used in A.O.A.C. procedure for determination of available P in fertilizers.

Measuring available Zn in fertilizers



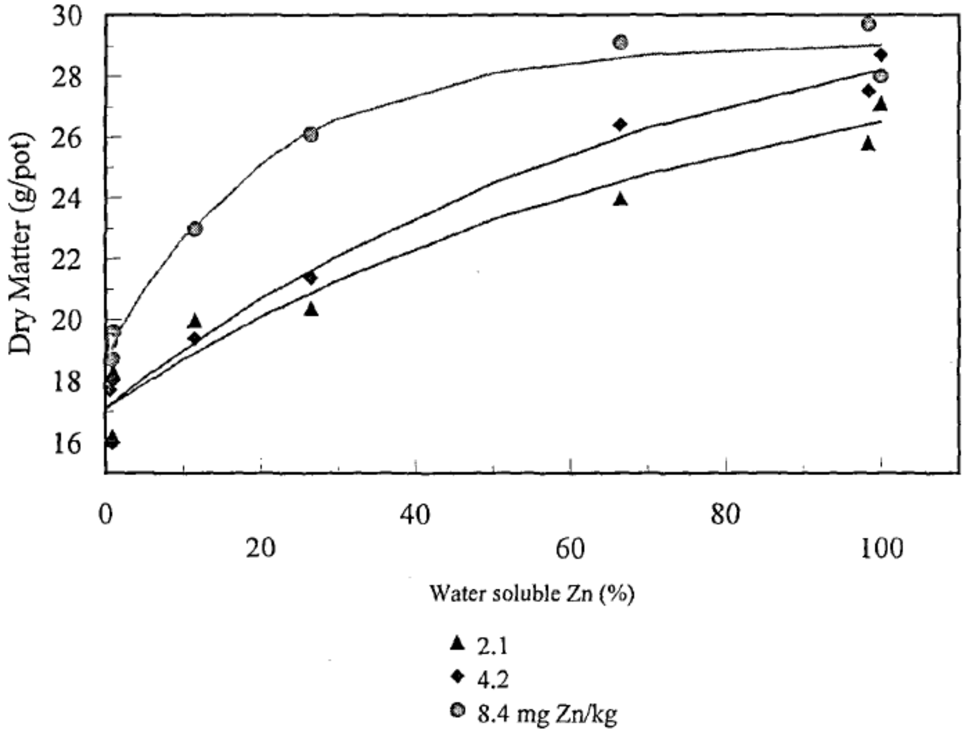
Mortvedt JJ, Giordano PM (1969) Extractability of zinc granulated with macronutrient fertilizers in relation to its agronomic effectiveness. *Journal of Agricultural and Food Chemistry 17(6), 1272-1275.*

There was no relationship between the total Zn in each fertilizer and its agronomic effectiveness (Table II). Yet, the only value that is listed on a fertilizer label is the percentage of total Zn in the fertilizer. This implies that the total amount of Zn is immediately available to plants. The data presented in this and previous papers by the authors show that the agronomic effectiveness of Zn varies greatly when Zn sources are granulated with various fertilizers; thus, the percentage of Zn which is listed on a fertilizer label may not give the true agronomic value of Zn in the fertilizer.

Mortvedt and Giordano, 1969

Measuring available Zn in fertilizers

- Amrani et al. (1999) examined the agronomic response of corn to several Zn fertilizers varying in solubility as measured by extraction in water and EDTA (AOAC methods)



2.1 mg Zn/kg: DM = 30.0 - 12.9*exp(-0.013*WS) r2=0.96**
4.2 mg Zn/kg: DM = 31.8 - 14.7*exp(-0.014*WS) r2=0.98**
8.4 mg Zn/kg: DM = 29.1 - 10.2*exp(-0.047*WS) r2=0.98**

FIGURE 2. Effect of percentage water-soluble Zn in the fertilizer materials on dry matter production at different Zn application rates.

Total Zn in a fertilizer was not enough to successfully determine Zn requirement for a crop. Farmers should receive information about the degree of Zn water solubility of granular Zn fertilizers.

Amrani et al., 1999

Measuring available Zn in fertilizers

- Liscano et al. (2000) examined the agronomic response of rice to several Zn fertilizers varying in solubility as measured by extraction in water and in EDTA (AOAC methods)

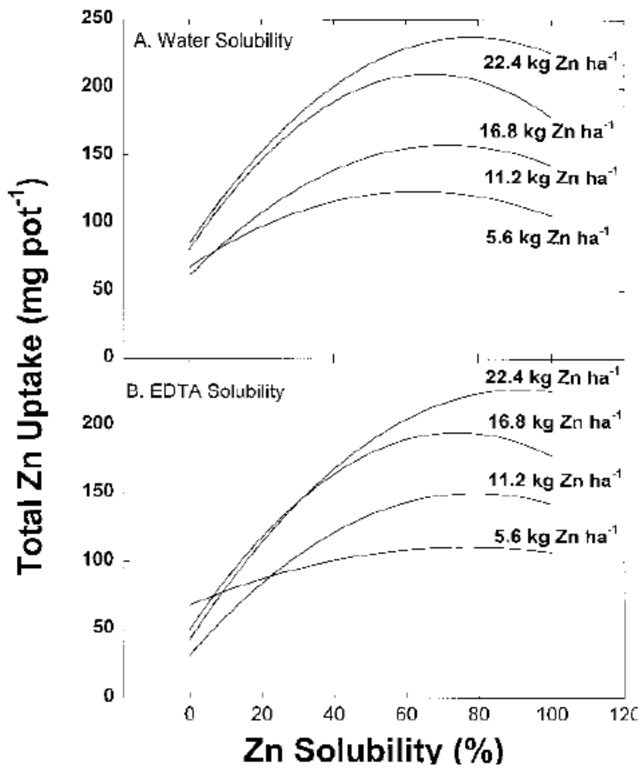


Figure 4. Total Zn uptake by rice 20 d after flooding as influenced by Zn fertilizer rate and the amount of water-soluble Zn (A) or 2% EDTA-soluble Zn (B) in the fertilizer in Experiment 1.

Uptake of Zn by the rice plant showed linear and quadratic responses to the percentage of solubility in water and EDTA, respectively. However, there was a stronger correlation between water-soluble Zn and uptake than between EDTA-soluble Zn and uptake. Thus water-soluble Zn would be a good index of plant-available Zn in fertilizer materials.

Liscano et al., 2000

Measuring available Zn in fertilizers

- Recently we examined the solubility of Zn in macronutrient fertilizers using various reagents (Degryse et al. 2019)
- 16 fertilizers were extracted by 8 different procedures using 5e extractant solutions
  - Water (3 different methods, including AOAC 965.09)
  - 1 M ammonium acetate (pH 7.0)
  - 74 mM EDTA (pH 7.0) (AOAC 965.09)
  - 5 mM DTPA + 0.1 M MES (pH 6.2) (2 methods)
  - 0.12 M bis-Tris (pH 6)
- Relative agronomic effectiveness of the fertilizers (relative to Zn sulfate uniformly mixed through soil) was compared to Zn extractability in the reagent

Degryse, F., da Silva, R.C., Baird, R., Cakmak, I. and McLaughlin, M.J. (2019). Comparison and modelling of extraction methods to assess agronomic effectiveness of fertilizer zinc. Soil Sci Soc Amer J. (in review).

Extractants used

	Extractant	Composition (M) [a]	L:S (L/kg)	Reference
1	Water		10	Mortvedt and Giordano (1969b)
2	Water		250	
3	Hot water		75 (100)[b]	AOAC 965.09 (aqueous)
4	1 M ammonium acetate (pH 7.0)	1 NH_4^+, 1 Ac^-	10	Mortvedt and Giordano (1969b)
5	74 mM EDTA (pH 7.0)	0.074 $EDTA^{-4}$, 0.22 Na^+, 0.075 H^+	100	AOAC 965.09 (chelate)
6	5 mM DTPA +0.1 M MES (pH 6.2)	0.005 $DTPA^{-5}$, 0.1 MES, 0.07 Na^+, 0.05 H^+	40	Adapted from Lindsay and Norvell (1978)
7	5 mM DTPA +0.1 M MES (pH 6.2)	0.005 $DTPA^{-5}$, 0.1 MES, 0.07 Na^+, 0.05 H^+	10	
8	0.12 M bis-tris (pH 6.0)	0.12 bis-tris, 0.093 H^+, 0.093 Cl^-	400/2000 [c]	FDACS (2003)

[a] Composition used as input in Visual Minteq
[b] Extraction carried out at L:S 75; diluted to L:S 100 after filtration
[c] L:S 400 for Zn-fortified fertilizers with <5% Zn, L:S 2000 for pure Zn sources,

Fertilizers used

Zn-only sources

1. $ZnSO_4.H_2O$
2. ZnOS
3. ZnO

MAP+Zn (1% co-granulated Zn)

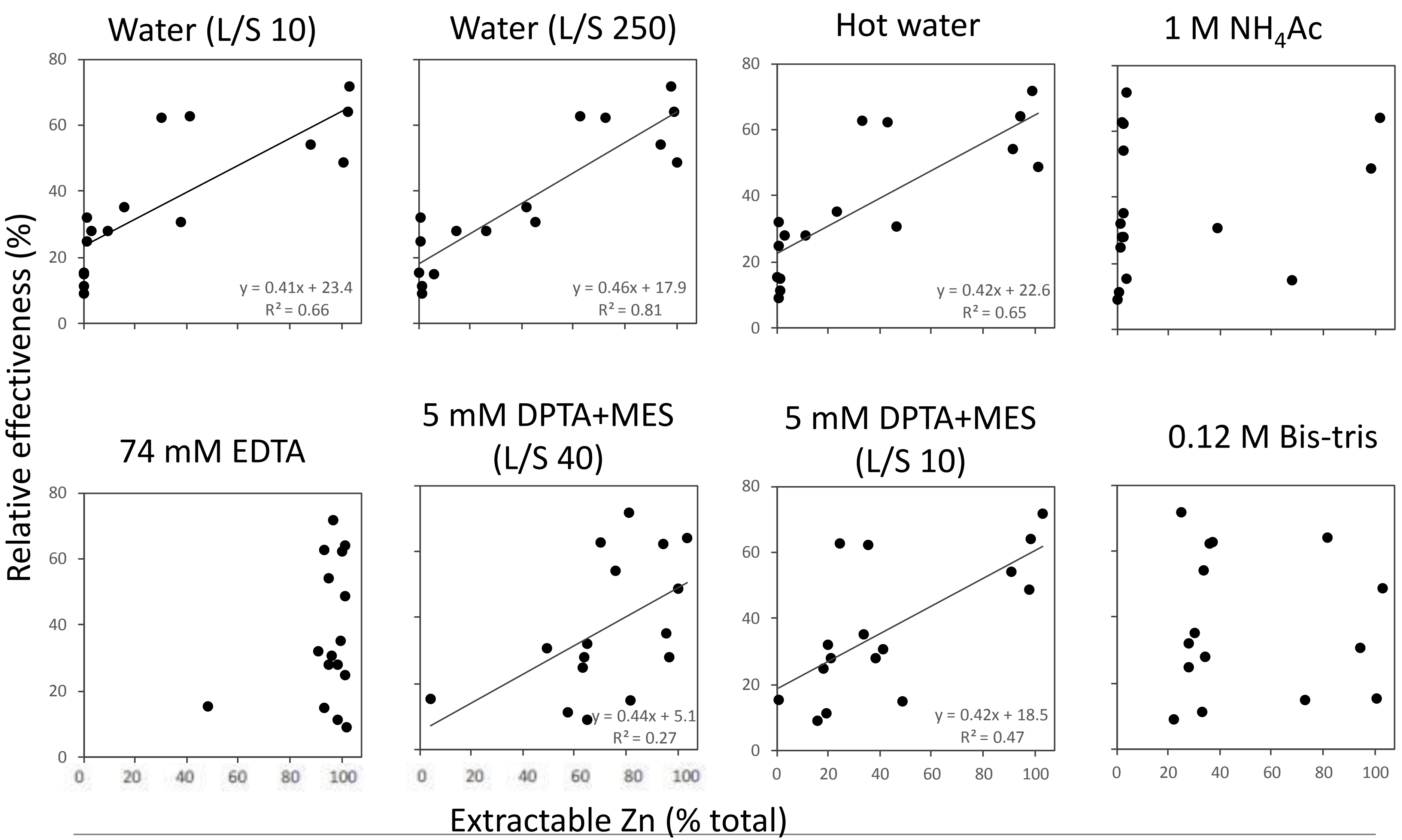
1. MESZ1
2. MESZ2
3. MESZ3

Zn-fortified fertilizers (2% Zn)

1. Urea+$ZnSO_4$
2. MAP+$ZnSO_4$
3. DAP+$ZnSO_4$
4. TSP+$ZnSO_4$
5. UAP+$ZnSO_4$
6. Urea+ZnO
7. MAP+ZnO
8. DAP+ZnO
9. TSP+ZnO
10. UAP+ZnO

MESZ = MicroEssentials®, MAP = monoammonium phosphate, DAP = diammonium phosphate, TSP = triple superphosphate, UAP = urea ammonium phosphate

Relationships with agronomic efficiency



Comparison of extractant relationships

	Extraction method							
	1	2	3	4	5	6	7	8
Extraction method								
1. Water (L/S 10)	1							
2. Water (L/S 250)	0.95^{***}	1						
3. Hot water	0.99^{***}	0.97^{***}	1					
4. Amm. acetate	0.52^{*}	0.43	0.50^{*}	1				
5. EDTA	0.25	0.31	0.27	0.18	1			
6. DTPA (L/S 40)	0.47	0.57^{*}	0.48	0.4	0.78^{***}	1		
7. DTPA (L/S 10)	0.93^{***}	0.87^{***}	0.93^{***}	0.60^{*}	0.36	0.60^{*}	1	
8. Bis-tris	0.27	0.20	0.28	0.73^{**}	-0.42	-0.21	0.23	1
Relative agronomic effectiveness								
Yield	0.70^{**}	0.84^{***}	0.74^{**}	-0.05	0.22	0.46	0.60^{*}	-0.14
Uptake	0.81^{***}	0.90^{***}	0.81^{***}	0.20	0.27	0.52^{*}	0.68^{**}	-0.03

Key messages

- Total Zn concentration in fertilizer is important as it provides a measure of potentially available Zn for crop uptake
- However, it is important to know the available Zn concentration in fertilizer as it indicates the likely agronomic response of the crop to the added Zn
- Fertilizer extraction methods which buffer pH strongly or use acids are too aggressive and do not give a good indication of available Zn in the product
- Extracting Zn with water is the best method to indicate the likely agronomic effectiveness of the fertilizer Zn, from both literature evidence and our experimental data

Review paper

Montalvo et al. (2016) Advances in Agronomy 139, 215-267

CHAPTER FIVE

Agronomic Effectiveness of Zinc Sources as Micronutrient Fertilizer

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Shervin Kabiri
Ivan Andelkovic
Bogumila Tomczak
Colin Rivers
Ashleigh Broadbent
Daniela Montalvo

www.adelaide.edu.au/fertiliser

Funding

Mosaic®