Measuring available Zn in fertilizers

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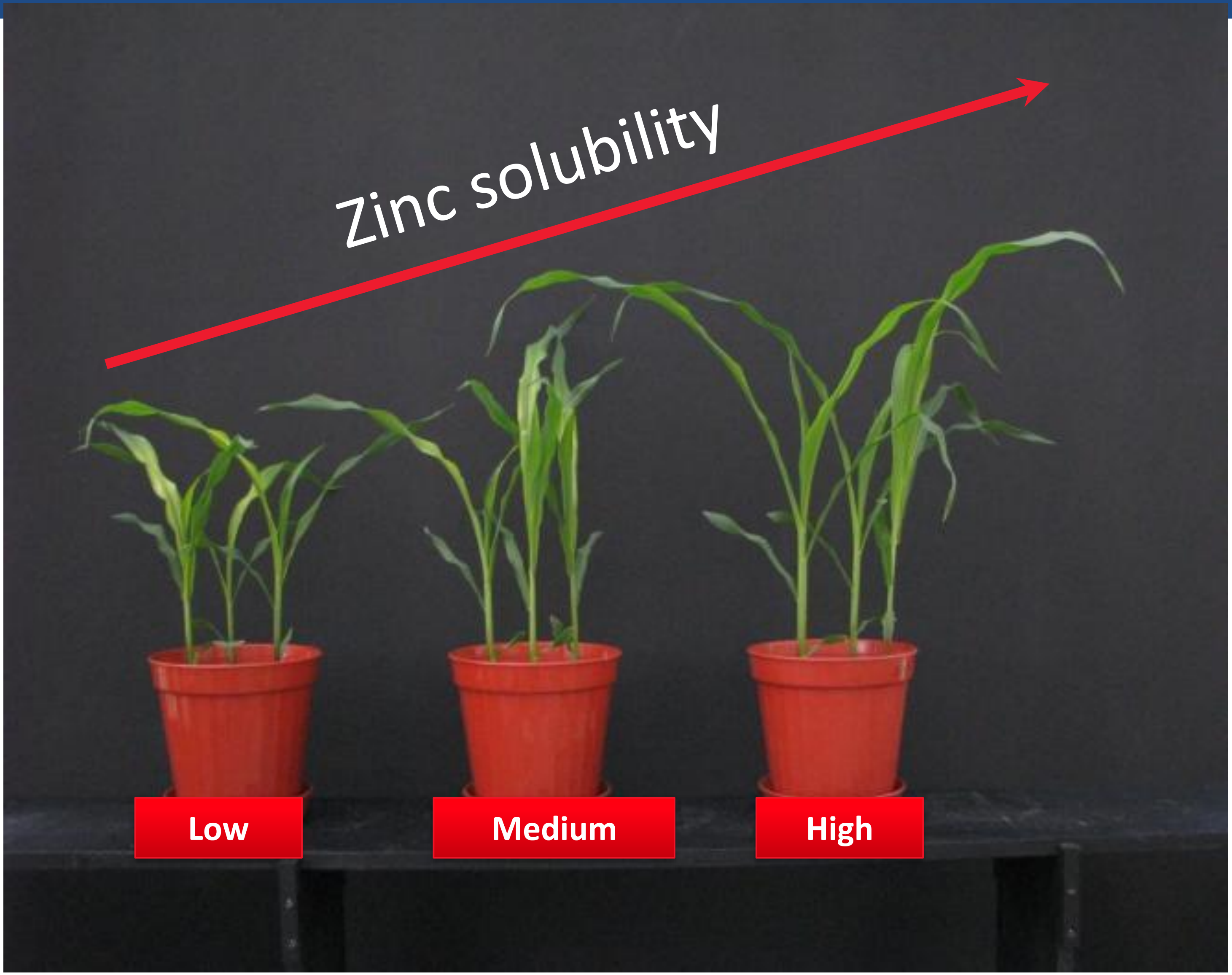
Does the solubility of Zn in fertilizers matter?



Source: Prof. Ismail Cakmak, Sabanci University

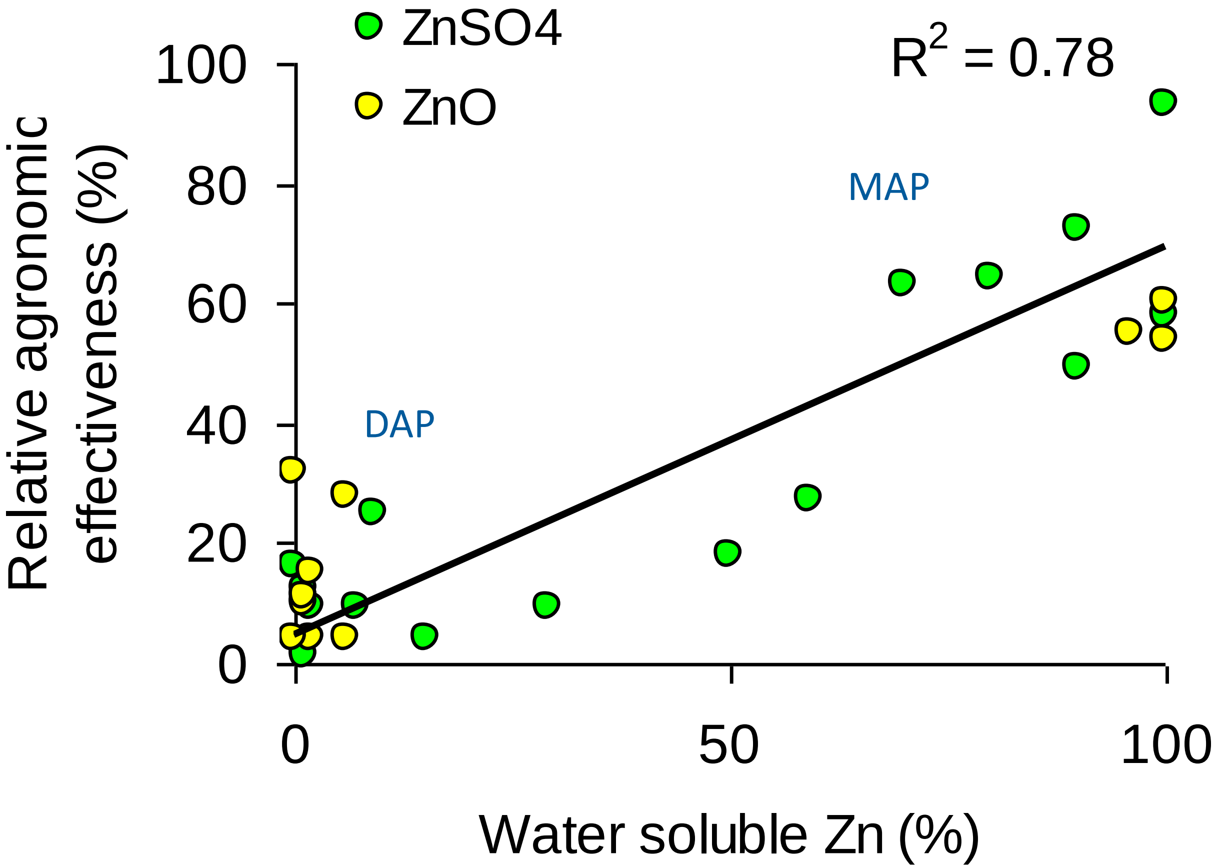
What’s the best method to measure Zn solubility in fertilizers?

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



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.*

Measuring available Zn in fertilizers

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Comparison and modelling of extraction methods to assess agronomic effectiveness of fertilizer zinc

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Abstract

Total Zn in fertilizer is a poor predictor of Zn availability in granular fertilizers. In this study, we compared different extraction methods using Zn fertilizers for which the agronomic effectiveness had previously been determined. Sixteen fertilizers were extracted by eight different procedures using five extractant solutions: water, 1 M ammonium acetate (pH 7.0), 74 mM EDTA (pH 7.0), 5 mM DTPA + 0.1 M MES (pH 6.2), and 0.12 M bis-tris (pH 6). Modelling of Zn solubility and speciation was carried out with a chemical speciation program (Visual Minteq). The predicted solubilities were in good agreement with the observations, indicating chemical equilibrium. The three methods using pure water were highly correlated with each other and showed the strongest correlation with agronomic effectiveness (r = 0.81–0.90). The methods using extractants with strong pH buffering or high chelating capacity showed no or weak correlation with the agronomic effectiveness. Thus, water-only based methods give the best indication of the availability of Zn in granular fertilizers, and are best suited for regulation or labeling of available Zn in fertilizer.

Key words: agronomic effectiveness / extraction methods / fertilizer / zinc

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Extractants used

Table 1: Overview of the different extraction methods: composition and liquid:solid ratio (L:S) of the extractants.

#	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* (2002) (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^+, 0.076 H^+	100	*AOAC* (2002) (965.09, chelate)
6	5 mM DTPA + 0.1 M MES (pH 6.2)	0.005 $DTPA^{-5}$, 0.1 MES^-, 0.075 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^-, 0.075 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

Table 2: Overview of the fertilizers tested: pH (1:10 water extract), relative agronomic effectiveness (RE) determined in pot trials, and the composition used as input in Visual Minteq.

	pH	RE_{yield}[a]	RE_{uptake}[a]	Composition (mmol g^{-1})					
	(1:10)			Zn^{2+}	NH_4^+	PO_4^{3-}	SO_4^{2-}	Ca^{2+}	H^{+b}
Zn-only sources									
$ZnSO_4 \cdot H_2O$	5.0	56	49	5.6			5.6		
ZnOS	5.9	41	31	6.0			2.7		–6.6
ZnO	7.2	17	15	12.3					–24.6
MAP+Zn (1% Zn)									
MESZ1	4.4	46	28	0.15	8.6	5.6	1.6		10.90
MESZ2	4.2	57	36	0.15	8.6	5.6	1.6		10.96
MESZ3	4.0	82	64	0.15	8.5	5.6	1.6		11.02
Zn-fortified fertilizers (2% Zn)									
Urea+$ZnSO_4$	6.3	40	64	0.31	0	0	0.31		0
MAP+$ZnSO_4$	4.0	75	63	0.31	7.0	6.9	0.31		13.8
DAP+$ZnSO_4$	7.1	20	25	0.31	12.3	6.1	0.31		6.1
TSP+$ZnSO_4$	2.2	93	72	0.31	0	6.3	0.62	2.6	14.2
UAP+$ZnSO_4$	7.0	8	9	0.31	7.6	3.8	0.31		3.8
Urea+ZnO	8.0	12	15	0.31	0	0	0		–0.62
MAP+ZnO	4.9	24	28	0.31	7.2	7.2	0		13.6
DAP+ZnO	7.3	15	32	0.31	12.7	6.3	0		5.7
TSP+ZnO	2.3	91	54	0.31	0	6.5	0.31	2.6	14.0
UAP+ZnO	7.4	8	11	0.31	7.9	3.9	0		3.3

[a]Agronomic effectiveness relative to fine ZnO or $ZnSO_4$ mixed throughout the soil, calculated from yield [Eq. (1)] or Zn uptake [Eq. (2)]; based on data from *Mortvedt* (1992) and *Mortvedt* and *Giordano* (1969b) for the Zn-only fertilizers and the Zn-fortified fertilizers with 2% Zn, respectively.
[b]OH^- ions are added as negative H^+ in Visual Minteq.

Fertilizers used

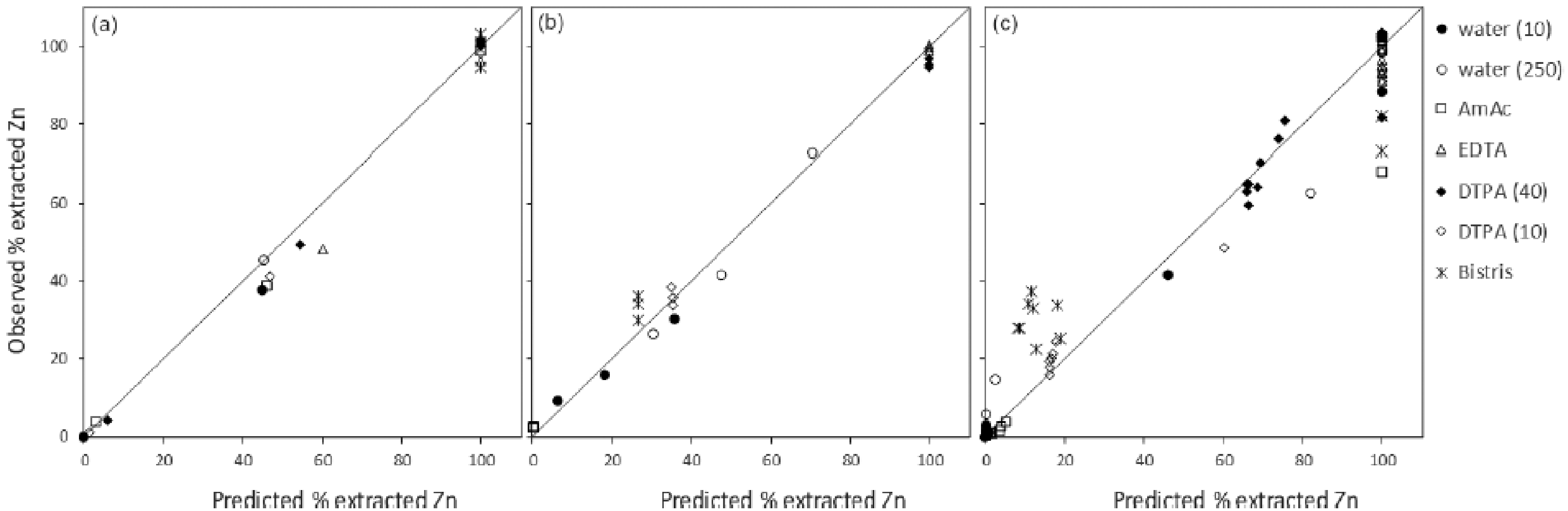
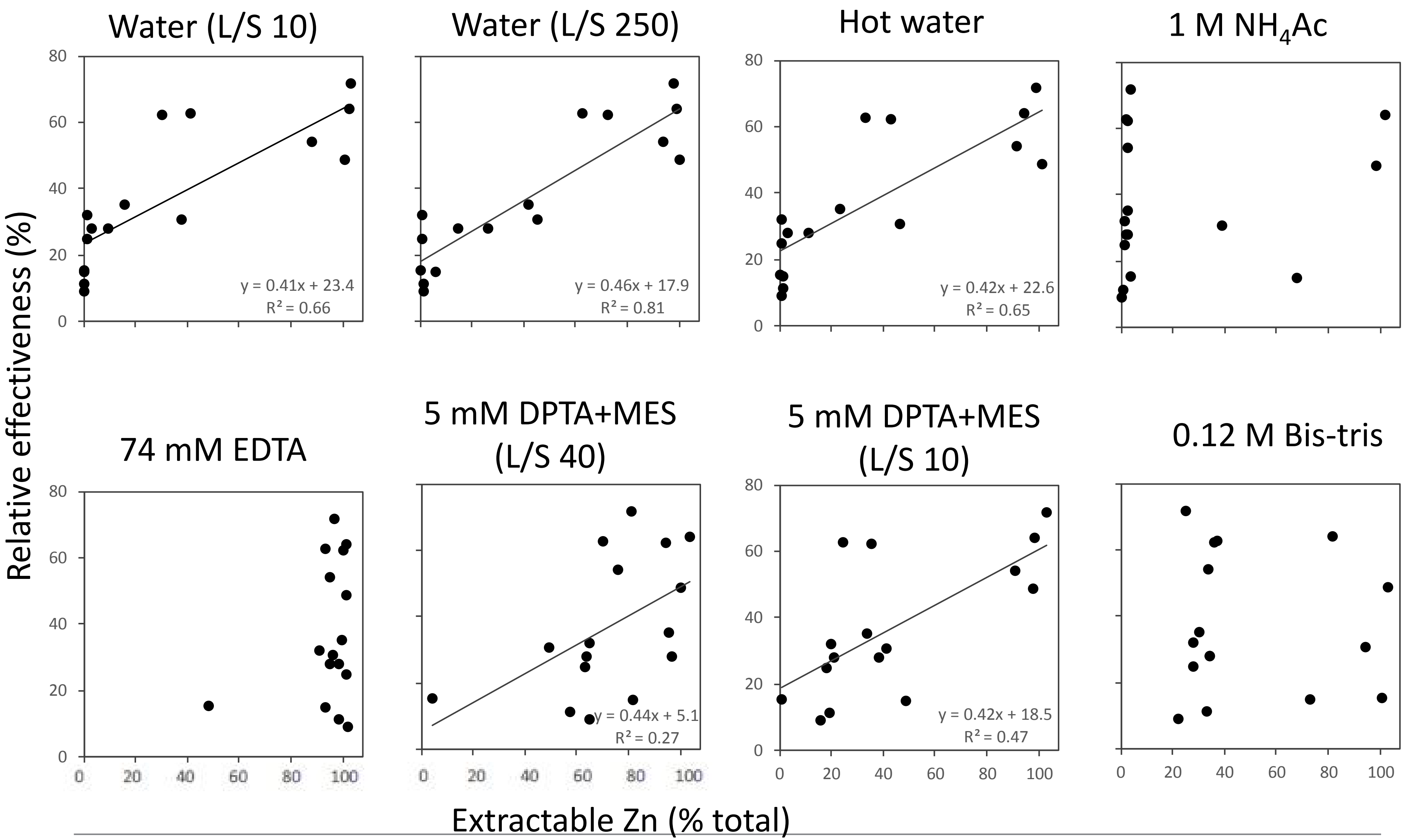


Figure 1: Observed % Zn extracted with the different extraction methods (see Tab. 1 for more detail) *vs.* values predicted using Visual Minteq based on fertilizer and extractant composition for (a) the Zn-only fertilizers, (b) the MAP+Zn (MESZ) fertilizers, and (c) the Zn-fortified macronutrient fertilizers (see Tab. 2 for more detail).

Relationships with agronomic efficiency



Relationships with agronomic efficiency

- A method using boiling water was also assessed for correlation with other tests and for relationship with agronomic efficiency
- 1 g fertilizer into 50 ml water, boiled for 10 mins, made to volume, filtered and analysed by ICP-OES

Comparison of extractant relationships

Correlation matrix									
	water (10)	*water (250)*	*hot water*	*AmAc*	*EDTA*	*DTPA (40)*	*DTPA (10)*	*Bistris*	*Boil water*
water (10)	1.00								
water (250)	0.95	1.00							
hot water	0.99	0.97	1.00						
AmAc	0.52	0.44	0.50	1.00					
EDTA	0.25	0.31	0.27	0.18	1.00				
DTPA (40)	0.46	0.57	0.48	0.40	0.79	1.00			
DTPA (10)	0.93	0.87	0.93	0.60	0.36	0.60	1.00		
Bistris	0.27	0.20	0.28	0.73	-0.42	-0.21	0.23	1.00	
Boil water	**0.98**	**0.96**	**0.99**	0.52	0.27	0.52	0.93	0.30	1.00
Yield	0.70	0.84	0.74	-0.05	0.22	0.44	0.60	-0.14	**0.74**
Uptake	0.81	0.90	0.81	0.20	0.27	0.52	0.68	-0.03	**0.80**

Key messages

- Total Zn concentration in fertilizer is important as it provides a measure of potentially available Zn for crop uptake
- Fertilizer extraction methods which buffer pH strongly or use acids are too aggressive and do not give a good indication of agronomically available Zn in the product
- All water-based extraction methods were highly correlated with fertilizer effectiveness (yield or Zn uptake), with extraction of 1 g fertilizer in 250 ml cold water the most closely correlated to yield/Zn uptake.

Water (250:1) > Water (boil) = Water (hot, AOAC) > water (10:1)

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