EXTRACTANTS TO ASSESS ZINC PHYTOAVAILABILITY IN MINERAL FERTILIZER AND INDUSTRIAL BY-PRODUCTS[1]

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SUMMARY

Efficient analytical methods for the quantification of plant-available Zn contained in mineral fertilizers and industrial by-products are fundamental for the control and marketing of these inputs. In this sense, there are some doubts on the part of the scientific community as well as of the fertilizer production sector, whether the extractor requested by the government (Normative Instruction No. 28, called 2nd extractor), which is citric acid 2 % (2 % CA) (Brasil, 2007b), is effective in predicting the plant availability of Zn via mineral fertilizers and about the agronomic significance of the required minimal solubility of 60 % compared to the total content (HCl) (Brasil, 2007a). The purpose of this study was to evaluate the alternative extractors DTPA, EDTA, neutral ammonium citrate (NAC), buffer solution pH 6.0, 10 % HCl, 10 % sulfuric acid, 1 % acetic acid, water, and hot water to quantify the contents of Zn available for maize and compare them with indices of agronomic efficiency of fertilizers and industrial by-products when applied to dystrophic Clayey Red Latosol and Dystrophic Alic Red Yellow Latosol with medium texture. The rate of Zn applied to the soil was 5 mg kg^{-1}, using the sources zinc sulfate, commercial granular zinc, ash and galvanic sludge, ash and two brass slags. Most Zn was extracted from the sources by DTPA, 10 % HCl, NAC, 1% acetic acid, and 10 % sulfuric acid. Recovery by the extractors 2 % CA, EDTA, water, and hot water was low. The agronomic efficiency index was found to be high when using galvanic sludge (238 %) and commercial granular zinc (142 %) and lower with brass slag I and II (67 and 27 %, respectively). The sources galvanizing ash and brass ash showed solubility lower than 60 % in 2 % CA, despite agronomic efficiency indices of 78 and 125 %, respectively. The low agronomic efficiency index of

industrial by-products such as brass slag I and galvanizing ash can be compensated by higher doses, provided there is no restriction, as well as for all other sources, in terms of contaminant levels of arsenic, cadmium, chromium, lead, and mercury as required by law (Normative Instruction No 27/2006). The implementation of 2nd extractor 2 % CA and the requirement of minimum solubility for industrial by-products could restrict the use of alternative sources as potential Zn sources for plants.

Index terms: maize, micronutrients, industrial waste, solubility, *Zea mays*.

RESUMO: *EXTRATORES PARA AVALIAÇÃO DA FITODISPONIBILIDADE DE ZINCO EM FERTILIZANTES MINERAIS E MATERIAIS SECUNDÁRIOS*

A utilização de métodos analíticos eficientes na quantificação do Zn fitodisponível contido em fertilizantes minerais e materiais secundários é fundamental no controle e na comercialização desses insumos. Nesse sentido, há dúvidas no setor científico e no de produção de fertilizantes se o extrator exigido na Instrução Normativa nº 28, ácido cítrico 2 % (AC 2 %) (Brasil, 2007b), chamado de 2º extrator, é eficiente na predição da fitodisponibilidade de Zn em fertilizantes minerais e qual o significado agronômico da solubilidade mínima exigida de 60 %, em relação ao teor total (HCl) (Brasil, 2007a). O objetivo deste estudo foi avaliar os extratores alternativos DTPA, EDTA, CNA, solução-tampão pH 6,0, HCl 10 %, ácido sulfúrico 10 %, ácido acético 1 %, água e água quente na quantificação do teor disponível de Zn ao milho, confrontando com índices de eficiência agronômica de fertilizantes minerais e materiais secundários em Latossolo Vermelho distrófico textura argilosa e em Latossolo Vermelho-Amarelo distrófico álico textura média. A dose de Zn aplicada aos solos foi de 5 mg kg^{-1} e utilizaram-se as fontes sulfato de Zn, Zn granulado comercial, cinza e lama de galvanização e cinza e duas escórias de latão. A maior extração de Zn das fontes ocorreu por meio do uso dos extratores DTPA, HCl 10 %, CNA, ácido acético 1 % e ácido sulfúrico 10 %. Houve baixa recuperação nos extratores AC 2 %, EDTA, água e água quente. Elevados índices de eficiência agronômica foram encontrados com o uso da lama de galvanização (238 %) e do Zn granulado comercial (142 %) e os menores, com o uso das escórias de latão I e II, com 67 e 27 %, respectivamente. As fontes cinza de galvanização e cinza de latão apresentaram solubilidade menor que 60 % no AC 2 %; no entanto, com índices de eficiência agronômica de 78 e 125 %, respectivamente. A baixa eficiência agronômica de materiais secundários como escória de latão I e cinza de galvanização pode ser compensada pelo aumento da dose, desde que não haja restrição, assim como para todas as demais fontes, quanto aos teores dos contaminantes arsênio, cádmio, cromo, chumbo e mercúrio, conforme exigido na legislação brasileira (Instrução Normativa nº 27/2006). O extrator DTPA 50 mmol L^{-1}, sob agitação, foi o que melhor representou a disponibilidade de Zn no milho em ambos os solos. A implementação do 2º extrator AC 2 % e a exigência da solubilidade mínima para materiais secundários poderia restringir o uso de fontes alternativas e com potencial para fornecimento de Zn às plantas.

Termos de indexação: adubos minerais, micronutrientes, resíduos industriais, solubilidade, Zea mays.

INTRODUCTION

After technological innovation in agriculture has boosted crop yields, any further advance will depend increasingly on improving the factors of production efficiency. One example is the application of micronutrients to the soil, becoming increasingly relevant in the agricultural sector of Brazil. A 13-fold increase was reported for the consumption of such inputs from 1990 to 2003, whereas grain yield increased by 112 % in this period (Yamada, 2004).

Among the micronutrients, zinc (Zn) is particularly noteworthy. In 20 % of 7,816 soil samples of the State of São Paulo and in 33 % of 5,614 soil samples from other States, extracted by DTPA at pH 7.3 (Abreu et al., 2005), the Zn content was considered low (< 0.5 mg dm^{-3}) (Raij et al., 2001). The application of Zn-containing fertilizers is therefore becoming increasingly important for a number of different crops.

Specifications, contents and other aspects related to the use of fertilizers containing micronutrients are defined by the Ministry of Agriculture, Livestock and Supply (MAPA) in the Normative Instruction No 05 (NI 05) (Brasil, 2007a) and the methods of nutrient quantification in Normative Instruction No 28 (Brasil,

2007b). One of the conditions of these regulations for soil application of mineral fertilizers is the determination of the total content of micronutrients in HCl (Brasil, 2007b) and of the soluble content, determined by a second extractor. For Zn, this should be less than 60 % in 2 % citric acid solution (2nd extractor), expressed in relation to the total content (Brasil, 2007a). Although these requirements ensure the quality of the raw material used for fertilizers, there are doubts as to whether the adopted extractant is efficient in determining the phytoavailability of Zn for the whole range of raw materials and fertilizers on the market. Secondly, there are doubts in agronomic terms, whether the required minimum solubility of 60 % in the 2nd extractor is adequate, since a lower solubility can be compensated by a higher application rate in the field.

Options of raw material for the production of Zn-containing fertilizers are scarce and some industrial by-products called secondary material could be an alternative to increase the range of these options, but must also meet the legal requirements of NI 05 (Brasil, 2007a). In this regard, studies to evaluate the solubility in the 2nd extractor like used for commercial fertilizers are important. However, it is possible that an agronomically efficient Zn-supplier is banned as raw material from fertilizer production, for simply not meeting the solubility requirements in the 2nd extractor, with questionable validity, as mentioned.

The use of industrial by-products as input in the production of mineral fertilizers for soil application, as established in NI 05 (Brasil, 2007a), is allowed, provided that the state environmental agency approves its as well the MAPA the use of the residual material like zinc source for the production of fertilizer in the state where this industrial by-product is generated. In addition to the total content, the industrial by-products available on the market as raw material must be evaluated for solubility, agronomic efficiency and contaminant levels (of As, Cd, Cr, Pb, and Hg).

The objective of this study was to evaluate alternative extractors to 2 % citric acid, to quantify the soluble Zn content in industrial by-products and mineral fertilizers for soil application, and compare the agronomic efficiency of these Zn sources in a greenhouse experiment with maize plants.

MATERIAL AND METHODS

The study was divided into two phases: phase I consisted of a qualitative characterization of the main minerals present in the samples by X-ray diffraction, performed at the Institute of Biological Sciences and the Federal University of Ouro Preto/MG, and the quantification of the Zn levels soluble in the 2nd extractor and of the total content in HCl; both analyses

were performed at the soil science center of the Agronomic Institute of Campinas (IAC), in Campinas, São Paulo.

Phase II was conducted in a greenhouse at the IAC soil science center, where maize plants were grown in pots to assess the plant availability of Zn as well as the agronomic efficiency of sources. The goal was to approve and discard source materials in a selection based on the required minimum level (60 % in 2 % CA compared to the total content in HCl). Maize was chosen for being highly responsive to Zn application (Malavolta, 1996; Gupta, 2001).

Phase I: Mineralogical characterization and levels of soluble Zn in 2nd extractors

For the evaluation of the minerals present in the samples and quantification of soluble levels in 2nd extractors, the samples (Table 1) were divided into four, ground and sieved (standardized ABNT 20, mesh 0.84 mm (Brasil, 2007b).

In the X-ray diffraction analysis, a sample from each source was used and the X-ray diffractograms were obtained using a Shimadzu XRD-6000 diffractometer, equipped with an iron tube and graphite monochromator. Measurements were programmed at a speed of 2°/min between 5-70 ° (2 θ). The X-ray diffractograms were interpreted using Jade software.

To determine the total contents and levels of soluble Zn in the 2nd extractant solution, three samples plus a blank control were used in all extractions. The analytical quantification was performed using the technique of inductively coupled plasma with optical emission spectrometry (ICP-OES).

The following 2nd extractants were evaluated for solubility of Zn sources: 2 % citric acid, neutral ammonium citrate+water 1:1, 10 % H_2SO_4, 10 % HCl, 1 % acetic acid, ethylenediaminetetraacetic acid (EDTA) 5 mmol L^{-1}, diethylenetriaminepentaacetic acid (DTPA) 50 mmol L^{-1}, buffer solution 0.24 mol L^{-1} Bis (hydroxymethyl)-2,2',2"-nitrilotriethanol ($C_8H_{19}NO_5$) pH 6.0, hot water, and water.

Total zinc content

We used the official MAPA method with concentrated 37 % HCl (Brasil, 2007b). A 150 mL beaker with 1.0000 g sample and 10 mL HCl was covered with watch glass, heated on a hot plate (160°) and evaporated to near dryness. The residue was then dissolved in 20 mL HCl 1+5 and simmered on the hot plate. The extracts were removed from the plate and, after cooling, filtered through Whatman filter paper (No. 42), and the volume completed to 100 mL with deionized water.

Soluble Zn content in 2 % citric acid (2 % CA)

Zinc was extracted according to the official method of MAPA (Brasil, 2007b). Beginning with a 1.0000 g

Table 1. Zn sources evaluated for mineralogical composition and soluble contents in 2nd extractors

Zn source	Total Zn content	Type	Form
	% (mass/mass basis)		
Galvanizing ash	71	IB[1]	powder
Galvanic sludge	21	IB	powder
Brass ash	72	IB	powder
Brass slag I	19	IB	powder
Brass slag II	15	IB	powder
Commercial granulated Zn Gran.	27	F[2]	granulated[4]
Zn sulfate[5]	36	F-RM[3]	powder

[1]IB: industrial by-products with potential for use as raw material in fertilizer production. [2] F: fertilizer registered and available on the market. [3] F-RM: material which can be marketed as raw material and as fertilizer. [4] Fertilizer granulated with sulfuric acid at processing. [5] Sample dried in a desiccator.

sample in a 150 mL beaker, 100 mL of 2 % CA was added, placed on a hot plate and boiled for 10 min. Then the extract was transferred to a 200 mL flask, the volume completed with deionized water, and filtered through Whatman filter paper (No. 42).

Soluble Zn content in neutral ammonium citrate+water (1:1) (NAC)

Zinc was extracted according to the official MAPA method used for Cu quantification by the 2nd extractor, by the same extraction procedure as with 2 % CA, but using neutral ammonium citrate+water (1:1) as extraction solution (Brasil, 2007b).

Soluble Zn content in 10% (v/v) H_2SO_4

Zinc was extracted in 10 % H_2SO_4, as described by Bastos et al. (2007), by adding 0.5000 g of fertilizer to 30 mL of 10 % H_2SO_4 in a 250 mL Erlenmeyer flask. The mixture was boiled for 45 min on a hot plate and after cooling, the extract was filtered through Whatman filter paper (No. 42) and completed to 500 mL.

Soluble Zn content in 10 % (v/v) HCl

The procedure of Zn extraction from the samples was the same as described for extraction with 10 % H_2SO_4 by Bastos et al. (2007). However, the 10 % H_2SO_4 solution was replaced by 10 % HCl and heated under stirring. The set of a 0.5000 g sample + 30 mL of 10 % HCl was shaken for 1 h (3.14-4.19 rad s^{-1}) on a horizontal shaker (Marconi®, model MA 376), filtered through Whatman filter paper (No. 42) and completed to 250 mL.

Soluble Zn content in 1 % acetic acid (v/v) (1 % AA)

Zinc was extracted from the sources by 1 % acetic acid extractant, as described by Gallo (1954). A total of 1.2500 g sample was filled in 500 mL glass bottles containing 250 mL 1 % acetic acid. The mixture was stirred for 30 min (3.14-4.19 rad s^{-1}) using a Wagner shaker (Tecnal®, TE-160). Subsequently,

the extract was filtered through Whatman filter paper (No. 42).

Soluble Zn content in 5 mmol L^{-1} EDTA

The zinc was extracted from the samples as proposed by Vale & Alcarde (1999). A total of 1.000 g of the sample was weighed in a 250 mL Erlenmeyer flask to which 100 mL of 5 mmol L^{-1} EDTA solution was added. In a Wagner shaker (Tecnal ®, model 315), the mixture was shaken for 1 h (3.14-4.19 rad s^{-1}). The extract was then filtered through Whatman filter paper (No. 42) and completed to 250 mL.

Soluble Zn content in 50 mmol L^{-1} DTPA

Zinc was extracted from the sources by the method of Vale & Alcarde (1999), changing the concentration of the DTPA extraction solution from 5 to 50 mmol L^{-1}, due to the high Zn content in the samples. This DTPA concentration was obtained by stoichiometric calculation considering the possibility that DTPA could chelate all Zn present in the sample of Zn sulfate, based on the content of 35 % stated by the manufacturer. A sample of 1.500 g was weighed and placed in a 250 mL Erlenmeyer flask with 100 mL of 50 mmol L^{-1} DTPA. The mixture was shaken in a Wagner shaker (Tecnal ®, model 315) for 1 h (3.14-4.19 rad s^{-1}). After this period, the extract was filtered through Whatman filter paper (No. 42) and completed to 250 mL.

Soluble Zn content in pH 6.0 buffer solution (pH BS 6.0)

Zinc was extracted from the samples as described by FDACS (2008) by buffer solution 0.24 mol L^{-1} 2,2-bis(hydroxymethyl)-2,22,23-nitrilotriethanol ($C_8H_{19}NO_5$) pH 6.0. The procedure considered pure material which recommends 0.3-0.5 g fertilizer for 500 mL of extraction solution in a 1000 mL volumetric flask. Due to the high cost of chemicals, it was decided to reduce the amount of fertilizer and volume of the extraction solution, but at the same proportion. We used 125 mL of buffer solution 0.24 mol L^{-1} 2,2-

bis(hydroxymethyl)-2,22,23-nitrilotriethanol ($C_8H_{19}NO_5$) pH 6.0 in a mixture of 0.1250 g of fertilizer in a 250 mL volumetric flask, completing the volume with deionized water and shaking vigorously by hand for 30 s. The extract was left to stand overnight and the supernatant was analyzed.

Soluble Zn content in hot water

Zinc was extracted from the samples by the procedure of AOAC (1997) for analysis of soluble boron. A total of 2.0000 g sample was transferred to a 250 mL volumetric flask, plus 100 mL of deionized water, boiled for 30 min on a hot plate and then cooled to room temperature. The volume was completed to 250 mL and then vigorously shaken by hand for 30 s and filtered through Whatman filter paper (No. 42).

Soluble Zn content in water

Zinc was extracted from the sources with water as described by Vale & Alcarde (1999). A funnel on a 250 mL volumetric flask was lined with Whatman filter paper (No. 42), on which 2.5000 g fertilizer sample was placed. The sample was washed successively with portions of deionized water, taking care to complete the suspension of the sample to 250 mL.

The Zn content quantified in the 2nd extractant solutions from the sources was subjected to analysis of variance (ANOVA) and means were compared using the Scott-Knott test at 95 % probability. The extractors were considered as variation factors (10).

Phase II: Zinc availability to maize plants

The soils used in the greenhouse experiment were taken from the surface layer (0-20 cm) of a Dystrophic Clayey Red Latosol (DCRL) and a Dystrophic Alic Red Yellow Latosol (DARYL) with medium texture. The soils were acidic and the Zn contents in DTPA pH 7.3 were considered medium (Raij et al., 2001) (Table 2).

The soil samples were air-dried, sieved (2 mm) and limed to increase base saturation to 70 % by the application of calcium carbonate + magnesium carbonate, both pure for analysis (PA), at a Ca: Mg ratio of 3:1. The pots were incubated for 20 days, maintaining moisture at around 60 % of the total pore volume (TPV).

The experiment was arranged in a completely randomized factorial design: two soils x eight treatments (seven Zn sources + control) x four replications, for a total of 64 experimental units. The control treatments of each soil consisted of a sample without Zn application. The Zn sources used (Table 1) were applied in powder form at rates of 5 mg kg⁻¹ Zn (based on the total content), mixed with soil and other fertilizers for base fertilization and then incubated (moisture 60 % TPV) for three days until maize sowing.

The fertilization at sowing consisted of P application (232 mg kg⁻¹) and a solution containing (in mg kg⁻¹):

38 N, 190 K, 203 Ca, 43 S, 0.5 B and 1.5 Cu; the DARYL soil also received 3 mg kg⁻¹ Mn. The sources KNO_3, K_2HPO_4, $CaHPO_4$, H_3BO_3, $CuSO_4$, and $MnSO_4.H_2O$ were used in powder form and all sources were PA.

Ten seeds of hybrid maize, IAC 8333, treated with the fungicides Carboxin and Thiram, were sown in pots with 3 kg of soil and thinned to five vigorous and healthy maize plants per pot after one week. Soil moisture was maintained at around 80 % of the TPV by addition of distilled water, defined by periodic weighing of the pots. During the test, N was side-dressed in the form of $Ca(NO_3)_2.4H_2O$, in six applications of 50 mg kg⁻¹ (equivalent to a total of 300 mg kg⁻¹ N and 430 mg kg⁻¹ Ca), applied 4, 11, 18, 25, 32, and 39 days after emergence (DAE).

The maize shoots were cut 48 DAE, washed in distilled water, dried at 65 °C to constant weight, dry-

Table 2. Soils chemical and physical properties after liming in experiment with Zn sources to maize

Determination	DCRL[1]	DARYL[2]
pH[3]	5.3	5.3
MO[4], g dm⁻³	49	34
P[5], mg dm⁻³	7	6
$K^{+[5]}$, mmol$_c$ dm⁻³	1.2	1.4
$Ca^{2+[5]}$, mmol$_c$ dm⁻³)	44	28
$Mg^{2+[5]}$, mmol$_c$ dm⁻³	17	10
$Al^{3+[6]}$, mmol$_c$ dm⁻³	0	0
H+Al[7], mmol$_c$ dm⁻³	38	31
SB, mmol$_c$ dm⁻³	62.3	40.0
CTC, mmol$_c$ dm⁻³	100.3	70.8
V, (%)	62	56
S[8], mg dm⁻³	10	16
B[9], mg dm⁻³	0.44	0.27
$Cu^{2+[10]}$, mg dm⁻³	0.4	2.7
$Fe^{2+[10]}$, mg dm⁻³	48	49
$Mn^{2+[10]}$, mg dm⁻³	4.3	1.8
$Zn^{2+[10]}$, mg dm⁻³	1	0.9
$Cd^{2+[10]}$, mg dm⁻³	< 0.01	< 0.01
$Cr^{2+[10]}$, mg dm⁻³	< 0.01	< 0.01
$Ni^{2+[10]}$, mg dm⁻³	0.03	0.07
$Pb^{2+[10]}$, mg dm⁻³	1.20	1.76
Clay[11], g kg⁻¹	390	324
Silt[11], g kg⁻¹	196	86
Sand[11], g kg⁻¹	414	590

[1] DCRL: Dystrophic Clayey Red Latosol; [2] DARYL: Dystrophic Alic Red Yellow Latosol medium texture; [3] Determination in $CaCl_2$; [4] Colorimetric method-sulfuric acid and potassium dichromate; [5] Ion exchange resin extractor; [6] KCl extractor; [7] SMP buffer solution; [8] Calcium phosphate extractor; [9] Hot water extractor; [10] DTPA extractor pH 7.3 and ICP-OES reading; [11] Particle size: pipette method. The chemical analyses were performed according to Raij et al. (2001) and particle-size analyses as described by Camargo et al. (2009).

weighed, and ground in a Willey mill. Roots and soil were separated by sieving, washed in tap water and soaked for 90 min in a 0.02 mmol L^{-1} disodium EDTA solution (Gabos, 2008). Then the roots were washed thoroughly in distilled water, dried and ground as done with the shoots. The levels of macronutrients and micronutrients were determined by microwave digestion with concentrated HNO_3 and H_2O_2 (Abreu et al., 1997) and ICP-OES readings.

The Zn recovered from the sources by maize plants was calculated using the agronomic efficiency index (AEI) of the sources in relation to zinc sulfate:

$$AEI\ (\%) = \frac{A_{source} - A_{control}}{A_{standsource} - A_{control}} \times 100$$

where: A_{source}: Zn accumulation (mg/pot) in shoots of plants grown in pots containing industrial by-products/fertilizers;

$A_{control}$: Zn accumulation (mg/pot) in shoots of plants grown in pots without addition of industrial by-products/fertilizers; and

$A_{standard\ source}$: Zn accumulation (mg/pot) in shoots of plants grown in pots containing zinc sulfate.

The Zn concentration in maize shoots associated with the respective dry mass were used to calculate Zn accumulation by the plant.

The statistical analysis was based on analysis of variance and subsequent comparison of means using the Scott-Knott test at 95 % probability. The evaluation of the 2nd extractors with the aim of identifying and discussing the most promising extractor(s) was based on statistical correlations between the calculated amount of potentially available Zn (mg/pot), considering the total Zn content and the soluble Zn in each extractor versus Zn accumulation (mg/pot) in maize plants.

RESULTS AND DISCUSSION

Phase I: Mineralogical characterization and levels of soluble Zn in 2nd extractors

The galvanizing ash generated in the hot-dip galvanizing process contained zincite (ZnO) and simonkolleite (Zinc chloride hydroxide monohydrate - $Zn_5(OH)_8Cl_2.H_2O$) as major Zn mineral forms (Table 3). The presence of quartz indicated the use of silicon as fluxing agent in the process.

In the galvanic sludge, an industrial by-product resulting from cold galvanizing, Zn was in oxide (Zincite - ZnO) and in hydroxide form ($Zn(OH)_2$). The sample also contained quartz (SiO_2), calcium carbonate (calcite - $CaCO_3$) and gypsum (calcium sulfate dihydrate - $CaSO_4.2H_2O$) (Table 3). The appearance of Zn hydroxide must be related to the higher pH, due to the use of calcium carbonate with

the function of precipitating metal ions in solution. Gypsum resulted from the use of zinc sulfate solution in the process (Gomide, 2009), where part of the sulfate is precipitated later with calcium.

In the brass ash sample, Zn is present in the oxide form (Zincite - ZnO) (Table 3). The presence of three lead minerals was detected: matlockite (Pb fluorochloride - PbClF), cerussite (Pb hydroxide carbonate - $Pb_3(CO_3)_2(OH)_2$) and of a Pb oxide chloride fluoride (Pb_2OFCl) (Table 3). The lead in this industrial by-product of brass and bronze alloy production may have originated from the use of scrap in the process or from Pb addition for metallurgical purposes (Gomide, 2009). Since lead is a volatile element, its accumulation in this industrial by-product is facilitated, since it is captured at the system outlet (baghouse filters).

In the sample of brass slag I, Zn was predominantly found in the form of oxide (Zincite - ZnO) and bonded to oxygen and aluminum in the mineral gahnita ($ZnAl_2O_4$) (Table 3). These Zn forms were expected since silicon was added in the generation process of this industrial by-product in the form of SiO_2 (Gomide, 2009). The presence of aluminum oxide (corundum - Al_2O_3) (Table 3) indicates that this material may have been mixed with ash or slag from the production of Zamak alloys, which normally contain aluminum.

Brass slag II contained the minerals quartz (SiO_2) and Zn in the form of silicate in willemite (Zn_2SiO_4) (Table 3), which is consistent with the use of silicon as a fluxing agent (Gomide, 2009).

In the composition of commercial granular Zn fertilizer, Zn was found in the form of oxide (zincite - ZnO), sulfate (gunningite - $ZnSO_4(H_2O)$ and bianchite - $Zn(SO_4)(H_2O)_6$ (Table 3). The presence of Zn sulfate must be a result of the reaction with sulfuric acid in the granulation process. The aluminum oxide (corundum - Al_2O_3) (Table 3) found in the commercial product indicates the inclusion of industrial by-products available on the agricultural market as raw material in the production of this fertilizer. This occurs due to the limited availability of raw material regulated by MAPA as well as its high cost compared to alternative sources.

The synthetic mineral gunningite was detected in the zinc sulfate sample, which is Zn in the form of sulfate ($ZnSO_4.H_2O$) (Table 3). For being a sample of an industrial process, it contained no other substances or contaminants.

The information about the mineralogical composition of industrial by-products and mineral fertilizers was useful in the interpretation of the results of solubility and agronomic efficiency, as shown below. Importantly, X-ray diffraction analysis is a promising tool in the description of this type of material and can even detect possible frauds in raw material and commercial products.

Table 3. Mineralogical composition of zinc sources by X-ray diffraction

Source	Mineral[1]	Chemical formula	PDF card no.
Galvanizing ash	Zincite (Zn oxide)	ZnO	01-070-2551
	Simonkolleite (Zn chloride hydroxide monohydrate)	$Zn_5(OH)_8Cl_2.H_2O$	01-077-2311
	Quartz	SiO_2	00-085-2237
Galvanic sludge	Gypsum (calcium sulfate dihydrate)	$CaSO_4.2H_2O$	00-033-0138
	Zn hydroxide	$Zn(OH)_2$	01-089-0138
	Zincite (Zn oxide)	ZnO	01-070-2551
	Calcite (Ca carbonate)	$CaCO_3$	01-086-0174
	Quartz	SiO_2	01-085-2237
Brass ash	Zincite (Zn oxide)	ZnO	01-070-2551
	Matlockite (Pb fluorochloride)	$PbClF$	00-026-0311
	Cerussite (Pb hydroxide carbonate)	$Pb_3(CO_3)_2(OH)_2$	00-013-0131
	Pb oxide chloride fluoride	Pb_2OFCl	01-083-2117
Brass slag I	Corundum (Al oxide)	Al_2O_3	01-076-0144
	Zincite (Zn oxide)	ZnO	01-070-2551
	Gahnita (Zn and Al oxide)	$ZnAl_2O_4$	01-082-1534
	Copper	Cu	03-065-9026
	Tenorite (Cu oxide)	CuO	01-073-6023
	Si oxide	SiO_2	01-089-8939
Brass slag II	Willemite	Zn_2SiO_4	01-070-1235
	Quartz	SiO_2	01-085-2237
Commercial granular Zn	Corundum (Al oxide)	Al_2O_3	01-076-0144
	Zincite (Zn oxide)	ZnO	01-073-8765
	Gunningite (hydrated Zn sulfate)	$ZnSO_4(H_2O)$	01-074-1331
	Bianchite (hydrated Zn sulfate)	$Zn(SO_4)(H_2O)_6$	01-075-0949
Zn sulfate	Gunningite (hydrated Zn sulfate)	$ZnSO_4(H_2O)$	01-074-1331

[1] More details see Souza (2012).

Levels of soluble Zn in 2nd extractors

Most Zn sources were approved, for reaching the required minimum solubility of 60 % in the 2 % CA extractor compared to the total content, with the exception of galvanizing ash and brass ash (Table 4). Both galvanizing ash and brass ash contained Zn in the oxide form (zincite) (Table 3), as similarly found in other sources that reached the minimum solubility threshold in the 2nd extractor. The difference is that in these materials, Zn concentrations exceeded 70 %, which may have saturated the oxidative capacity of citric acid. Further studies are needed to evaluate the relationship mass of fertilizer: extraction solution, which is currently 1.0 g:100 mL, or higher citric acid concentrations to analyze very concentrated Zn sources, but in authorized soluble forms (Zn oxide).

The 2nd extractants tested alternately to 2 % citric acid differed significantly in relation to the Zn content of mineral fertilizers and industrial by-products (Table 5). In general, the extraction capacity of DTPA and 10 % HCl was highest, followed by NAC, 1 % AA and 10 % SA (Table 5).

The Zn levels extracted by the methods with the strong acids HCl and AS, both diluted to 10 %, was higher than of those extracted by 2 % CA (115 and 143 %, respectively) (Table 6). This fact can be explained by the higher solubility of the sources due the acidity of the medium. In the case of the solutions 10 % HCl and 10 % SA, the pH values were zero, but 2.3 in the solution of 2 % CA.

However, the effect of acidity of the medium was not the decisive factor in the Zn extraction by 2 % CA compared with NAC (pH values of 2.3 and 7.0, respectively). The greater extraction capacity of NAC (127 %) (Table 6) can be attributed to the higher stability of the Zn-citrate chelate formed at neutral pH than under acidic conditions, as in the case of the extractor 2 % CA. The pH value of 2.3 hampers the deprotonation of the three molecules of carboxyl groups of CA, which is an indispensable condition for the release of oxygen as electron donor group to the metal in chelate (Alcarde & Ponchio, 1979), resulting in a

Table 4. Solubility level required by MAPA and observed for Zn sources using the official 2nd extractor 2 % citric acid (2 % CA)

Source	Total content HCl	Requirement 2 % CA[1]	Content 2 % CA[2]	Zn in 2 % CA[3]	Status[4]
			% Zn (mass/mass basis)		
Galvanizing ash	71 ± 2.10	43	31 ± 1.78	43	D
Galvanic sludge	21 ± 1.15	13	25 ± 0.20	116	A
Brass ash	72 ± 1.72	43	35 ± 4.45	49	D
Brass slag I	19 ± 0.60	11	18 ± 0.45	97	A
Brass slag II	15 ± 0.25	9	12 ± 0.15	77	A
Commercial granular Zn	27 ± 1.43	16	29 ± 1.25	107	A
Zn sulfate[5]	36 ± 1.20	21	42 ± 1.25	118	A

[1] It was considered that MAPA requirement solubility in the 2nd extractor 2 % citric acid (2 % CA) equivalent to 60 % of the total content in HCl extractor was also required for industrial by-products. [2] Soluble content in the 2nd extractor 2 % citric acid (2% CA). [3] % Zn (mass/mass basis) in 2 % citric acid (2 % CA) compared to the total content as 100 %. [4] Status A: approved and D: discarded, according to the minimum threshold of MAPA. [5] Sample dried in a desiccator.

Table 5. Zn contents extracted by the 2nd extractors in mineral fertilizers and industrial by-products

Source	Extractor									
	2 % CA[1]	1 % AA[2]	10 % SA[3]	10 % HCl[4]	NAC[5]	DTPA[6]	EDTA[7]	BS pH 6.0[8]	Wa[9]	HWa[10]
	mass/mass basis			% Zn (mass/mass basis) in relation to 2% CA (100%)						
Galv. ash[11]	30.78 e	48.01 d	56.78 c	74.32 a	60.45 b	55.12 c	4.25 g	28.16 f	0.03 h	0.53 h
Galv. sludge[12]	24.61 b	21.58 c	19.00 d	23.69 b	24.39 b	31.98 a	3.57 f	10.52 e	0.01 g	0.01 g
Brass ash	35.03 e	65.11 d	65.00 d	74.22 b	75.21 b	92.28 a	2.17 f	69.15 c	0.02 f	0.33 f
Brass slag I	18.35 a	14.99 a	16.27 a	17.83 a	16.72 a	16.30 a	2.46 c	9.66 b	0.00 d	0.01 d
Brass slag II	11.57 a	4.85 b	12.86 a	13.44 a	3.61 b	1.36 c	1.95 c	1.54 c	0.02 c	0.01 c
Zn sulfate[13]	42.10 b	47.68 a	27.88 e	40.13 c	35.46 d	46.22 a	39.55 c	34.43 d	17.63 f	16.60 f
Commer. gran. Zn	29.05 b	22.60 c	23.24 c	30.59 a	28.22 b	32.78 a	9.17 e	18.17 d	9.94 e	6.53 e
Mean	27.36 D	32.11 C	31.58 C	39.18 A	34.87 B	39.43 A	9.02 F	24.52 E	3.95 G	3.43 G

[1] 2 % CA: 2 % citric acid. [2] 1 % AA: 1 % (v/v) acetic acid. [3] 10 % SA: 10 % (v/v) sulfuric acid. [4] 10 % (v/v) HCl. [5] NAC: neutral ammonium citrate+water at 1:1 ratio. [6] 50 mmol L^{-1} DTPA. [7] 5 mmol L^{-1} EDTA. [8] BS 6.0: buffer solution pH 6.0. [9] Wa: water. [10] HWa: hot water. [11] Galvanizing ash. [12] Galvanic sludge. [13] Sample dried in a desiccator. Means followed by the same letter in a row did not differ by the Scott-Knott test at 95 % probability.

Table 6. Percentage of Zn recovered from the sources compared to the official MAPA extractor 2 % citric acid (2 % CA)

Source	Extractor									
	2 % CA % Zn[1]	1 % AA[2]	10 % SA[3]	10 % HCl[4]	NAC[5]	DTPA[6]	EDTA[7]	BS pH 6.0[8]	Wa[9]	HWa[10]
	mass/mass basis			% Zn (mass/mass basis) in relation to 2% CA (100%)						
Galv. ash[11]	31	156	184	241	196	179	14	91	0	2
Galv. sludge[12]	25	88	77	96	99	130	14	43	0	0
Brass ash	35	186	186	212	215	263	6	197	0	1
Brass slag I	12	42	111	116	31	12	17	13	0	0
Brass slag II	42	113	66	95	84	110	94	82	42	39
Zn sulfate[13]	29	78	80	105	97	113	32	63	34	22
Commer. gran. Zn	18	82	89	97	91	89	13	53	0	0
Mean	100	117	115	143	127	144	33	90	14	13

[1] 2 % CA: Zn content (mass/mass basis) extracted in citric acid 2 % (corresponds to 100%). [2] 1 % AA: 1 % (v/v) acetic acid. [3] 10 % AS: 10 % sulfuric acid (v/v). [4] 10 % HCl (v/v). [5] NAC: neutral ammonium citrate + water in the ratio 1:1. [6] 50 mmol L^{-1} DTPA. [7] 5 mmol L^{-1} EDTA. [8] BS pH 6.0: buffer solution pH 6.0. [9] Wa: water. [10] HWa: hot water. [11] Galvanizing ash. [12] Galvanic sludge. [13] Sample dried in a desiccator.

less intense complexing action in the solution of 2 % CA than of NAC.

The percentage of Zn recovered by the extractors 2 % CA and BS pH 6.0 was moderate (Table 5). The extractor BS pH 6.0 extracted 90 % of 2 % CA (Table 6). The Zn extraction capacity of the extractors EDTA, Wa and HWa was low and the Zn percent recovery in relation to 2 % CA was 33, 14 and 13 %, respectively (Table 6). The low Zn contents extracted by the methods Wa and HWa were expected since almost all sources, except Zn sulfate, were water-insoluble.

In all studied materials, the Zn contents extracted by the chelating agent EDTA were very low and statistically lower than the DTPA-extracted levels (Tables 5 and 6). The stability constant of EDTA for metal micronutrients is higher than of DTPA so the opposite would be expected, namely, higher zinc extraction by EDTA. However, the concentration of DTPA solution (50 mmol L^{-1}) was 10 times higher than EDTA, explaining the observed results. A study evaluating the solubility of some micronutrients, including Zn, in 30 samples of commercial fertilizers extracted by DTPA and EDTA, both at 5 mmol L^{-1}, as well as by the extractors water, 2 % CA and NAC diluted 1+9, showed low metal solubility in EDTA and DTPA. On this issue, the authors claimed that higher concentrations of these solutions of chelating extractants could be more effective in the evaluation of micronutrient solubility in fertilizers (Vale & Alcarde, 1999). Another aspect is the high Zn concentration in the studied materials, exceeding the chelating capacity of the complexing agent, as reported by Norvell (1984) for high soil Cu concentrations, exceeding the chelating capacity of DTPA.

The Zn concentrations in galvanizing ash and brass ash, were lower than 60 % solubility in the second extractor CA 2 % (Table 4), but were high in the extractant solutions of 10 % HCl and NAC, and in DTPA for brass ash (Table 5). The Zn recovery rate from this ash by these extractants, expressed in relation to 2 % CA, ranged from 96 to 241 % (Table 6). Alcarde & Rodella (1993) reported the highest Zn extraction capacity in Zn oxide, PA, and the lowest in Zn metal, PA, when using NAC, compared to the other extractants tested, ammonium chloride (at concentrations of 1, 1.5 and 2 mol L^{-1}), and 2 % citric acid solution. The authors recommended NAC diluted 1+9 as best extractor for Zn oxide PA, which is the chemical form authorized by law for products containing water-insoluble zinc and for zinc marketed as simple mineral fertilizer. In fact, the Zn extraction capacity of NAC is high for sources containing Zn in oxide form, as evidenced in the industrial by-products galvanizing ash and brass ash (Table 3), from which Zn was extracted at levels exceeding 70 % (Table 5). Interestingly, also with regard to the effect of the chemical form of Zn on its solubilization in different extractant solutions, Zn in oxide form and as mineral gahnita ($ZnAl_2O_4$) was completely solubilized in the extractors 2 % CA, 1 % AA and 10 % SA, 10 % HCl, NAC, and DTPA. The Zn solubility in brass slag II, on the other hand, where the element is contained in the form of silicate (Table 3), was high only in the extractant solutions of 2% CA, 10 % SA and 10 % HCl, indicating that silicate-bound Zn is less soluble in the studied extractors. Differences in the mineralogical composition of brass slag with effects on the behavior of various extractors were reported by Moura (2010): in brass slag with 25.3 % Zn (total content) and 14.7 % SiO_2, Zn was found in oxidized forms (ZnO), associated with Cu forming alloy (CuZn), as mineral gahnita ($ZnAl_2O_4$) and willemite (Zn_2SiO_4) with no statistical difference between Zn extraction by HCl, aqua regia, USEPA 3050 B modified by Moraes (2009), by 2 % CA and NAC and with lowest extraction by water. Another brass slag evaluated with 18 % Zn (total content) and 44.7 % SiO_2 contained Zn as oxide and silicate, however, Zn extraction decreased in the extractors aqua regia, HCl, 2 % CA, NAC, USEPA 3050 B adapted by Moraes (2009), and water. The author related the differences in extractor performance to Zn solubilization in the slags according to the chemical composition of Zn and the crystallinity (SiO_2 content) of the materials.

The solubility of galvanic sludge was high in the extractant solutions of DTPA, 2 % CA, 10 % HCl, and NAC (Tables 5 and 6), and chemically, this Zn source was composed of the forms zinc oxide (zincite) and hydroxide (Table 3).

The commercial granular Zn fertilizer was highly soluble in DTPA, 10 % HCl, 2 % CA and NAC (Table 5). The percentage of Zn recovered compared with the extractor 2 % CA ranged from 97 to 113 % (Table 6) and the chemical composition of zinc consisted of oxide and sulfates (Table 3).

As expected, the Zn solubility of Zn sulfate was moderate to high in all extracts (Table 5), for being the only water-soluble source. The Zn recovery percentage in relation to the 2 % CA extractor ranged from 39 % by extractor Hwa to 113 by 1 % AA, showing that Zn sulfate is easily solubilized by several extractors (Table 6).

Phase II: Availability of Zn to maize plants

In the medium-textured Dystrophic Alic Red Yellow Latosol (DARYL), more Zn was accumulated in the maize shoots than in plants grown on a clayey Dystrophic Red Latosol (DCRL) (Table 7). Zinc accumulation in DARYL was lower in the control and the brass slag II treatments, whereas in DCRL, less Zn was taken up by plants in the treatments control, zinc sulfate, galvanizing ash and brass slag I and II. The highest Zn accumulation in plants in both soils was promoted by galvanic sludge, followed by Zn sulfate, galvanizing ash, commercial granular Zn, brass ash, and brass slag I in DARYL soil and brass ash and commercial granular Zn in DCRL soil (Table 7).

In DARYL soil, the sources galvanizing ash, brass ash, brass slag I and commercial granular Zn led to similar Zn accumulation in plants, not differing from Zn sulfate, the micronutrient source considered soluble.

In plants grown in DRCL soil, the control treatment and sources galvanizing ash and brass slag I and II did not differ in the Zn levels found in relation to plants grown with Zn sulfate, whereas the sources galvanic sludge, brass ash and commercial granular Zn promoted greater Zn accumulation in maize than the soluble source (Zn sulfate) (Table 7).

The agronomic efficiency index (AEI) of the sources for Zn accumulation in the shoots showed higher efficiency of the industrial by-product galvanic sludge than of the water-soluble Zn sulfate, demonstrating that water-insoluble materials, but with chemical composition of Zn in the form of hydroxides and oxides (Table 3), are readily solubilized in the rhizosphere and made available to the plants (Table 7). A high agronomic efficiency index was also observed for commercial granular Zn (Table 7), with predominance of Zn in the form of sulfates and oxides (Table 3) and for the industrial by-product brass ash with Zn in oxide form (Table 3). The agronomic efficiency of galvanizing ash was moderate (Table 7), with Zn predominantly in oxide form (mineral zincite) and Zn chloride hydroxide monohydrate (mineral simonkolleite), an oxide bonded with the Al and Zn forming a metallic alloy (gahnita) (Table 3).

The lowest AEI for Zn accumulated in maize shoots was found for the sources brass slag I and II (Table 7). It should be emphasized that the agronomic efficiency of industrial by-products obtained from a same industrial process, e.g., brass slag I and II, can differ. In this work, brass slag I had an efficiency of 67 % and brass slag II of 27 % (Table 7), with different chemical compositions, oxide versus silicate (Table 3),

respectively, which must have influenced the efficiency of these industrial by-products. These results were similar to those found by Moura (2010), who evaluated the agronomic efficiency of two brass slags and two fertilizers were prepared with pure oxides for analysis in rice plants. The author reported high efficiency (94 %) for Zn source in the form of oxide and bonded with the Cu forming a metallic alloy, containing 14.7 % SiO_2 and lower efficiency (42 %) for the other slag with Zn in the form of oxide and silicate, containing 44.7 % SiO_2. The author attributed this difference to the chemical composition of Zn and the crystallinity (SiO_2 concentrations) of the industrial by-product. These results clearly show the importance of the chemical composition of the Zn source for the agricultural efficiency of the evaluated industrial by-products. Similarly, a study evaluated the availability and efficiency of Zn from different sources to rice and maize plants and detected greatest availability of the element as Zn sulfate, followed by Zn oxide, a residue whose origin and chemical composition have not been disclosed and finally, metallic Zn and Zn in the form of frits. The AEI compared to zinc sulfate was around 90 % for the oxide, 80 % for the residue and 50 % for metal Zn and frits. These authors reported low plant availability for Zn in the form of silicates and metallic alloys (Vale & Alcarde, 2002).

Apart from the chemical composition, the particle size of a fertilizer applied to the soil can affect its phytoavailability and, consequently, the agronomic efficiency. A greenhouse study reported that ZnO and $ZnSO_4$ induced similar responses in maize plants, when applied as powder mixed with soil. However, the sources granular $ZnSO_4$ and ZnO were considered inefficient and unsatisfactory, respectively (Allen & Teman, 1966). The efficiency of finely ground zinc oxide is expected to be similar to zinc sulfate (Mortvedt, 1991). A study evaluating Zn availability in ground and granulated material, with water solubility ranging

Table 7. Zn accumulation in maize shoots and agronomic efficiency index (AEI) of applied Zn sources compared to Zn sulfate (100 %)

Zn source	Zn accumulation in shoots			AEI		
	DARYL	DCRL	Mean	DARYL	DCRL	Mean trat
	mg/pot			%		
Control	0.90 c	0.77 c	0.83 c			
Zn sulfate	1.34 b	0.99 c	1.16 b	100	100	100
Galvanizing ash	1.25 b	0.94 c	1.10 b	80	77	78
Galvanic sludge	1.69 a	1.42 a	1.56 a	181	295	238
Brass ash	1.34 b	1.10 b	1.23 b	100	150	125
Brass slag I	1.21 b	0.91 c	1.06 b	70	64	67
Brass slag II	1.08 c	0.80 c	0.94 c	41	14	27
Commerc. Gran. Zn fertilizer	1.23 b	1.23 b	1.23 b	75	209	142
Mean	1.26 A	1.02 B				

DARYL: Dystrophic Alic Red Yellow Latosol with medium texture. DCRL: Dystrophic Clayey Red Latosol. Means followed by the same letter in the column do not differ by the Scott-Knott test at 95 % probability for the factor Zn sources.

from 0 to 100 %, showed that Zn availability was more related to the particle size of the sources, the best results being obtained with powder products. For granular products, it was observed that the higher the water solubility of the fertilizers, the greater the absorption and dry matter of maize plants (Mortvedt, 1992). In this study, based on the mean of the AEI, the high agronomic efficiency of the sources galvanic sludge, commercial granular Zn and brass ash and the moderate efficiency of galvanizing ash (Table 7) can be partly attributed to the application of these products to the soil in powder form. The same effect of influence of the physical form of the fertilizer on Zn uptake efficiency was reported in maize plants; the plants responded with considerable dry matter production to all sources evaluated, when applied in powder form. The Zn availability after granular Zn sulfate application was close to zero and lower after granular Zn humate-lignosulfonate application than of the ground form (Goos et al., 2000). The authors concluded that differences in phytoavailability between sources are much more related to the physical than to chemical properties of the products. Another study also highlighted the importance of the physical form, since some products can be partly solubilized in the soil when applied in the form of very fine powder (Vale & Alcarde, 2002).

In some cases, the efficiency of a particular source can be compensated by increasing the application rate, as mentioned by Malavolta et al. (1987). These authors tested the sources Zn sulfate, oxide and a commercial frit and found that the highest maize yields were obtained by application of 0.5 mg dm^{-3} Zn as sulfate or oxide and 1.0 mg dm^{-3} Zn as commercial frit. Similarly, the use of industrial by-products in this work, such as brass slag I and II with relatively low AEI (67 and 27 %, respectively), could be compensated by increasing the rate, provided the levels of contaminants are not restrictive. The galvanic sludge, another material with interesting chemical composition, although only admitted for Minas Gerais by the local environmental agency and MAPA, is highly promising as Zn source in fertilizer production, in view of the high agronomic efficiency. In the other States, the use of this industrial by-product is prohibited for not having been regulated by environmental agency.

Doubtlessly, the solubility in the 2nd extractor represented a breakthrough in the quality control of raw material and fertilizers marketed by the production sector. However, based on the assumption that the solubility in the extraction solution reflects the chemical composition of the Zn source that partly determines the agronomic efficiency of a fertilizer, the chemical composition combined with the AEI of a source is an important factor that should be taken into consideration by MAPA in the evaluation of new micronutrient sources. This aspect is reinforced in this study, since the agronomic efficiency of industrial by-products such as brass ash and galvanizing ash was considerable (78 and 125 %, respectively), compared to the standard source Zn sulfate (Table 7), in spite of not reaching the minimum solubility of 60 in the 2 % CA extractor (Table 4). In summary, if required minimum solubility of 60 % in the 2nd extractor for industrial by-products, other potentially useful materials can be disapproved its use by MAPA. It is noteworthy that the presence of other potentially toxic elements (e.g., As, Cd, Cr, Pb, and Hg) could restrict or impair the use of these Zn sources in agriculture, which was not evaluated in this study.

Evaluation of 2nd extractors

The correlations to assess the efficiency of extractors in predicting the phytoavailability of different Zn sources were established for each soil type, since the analysis of variance showed different responses to Zn content and accumulation in maize grown on DARYL (medium texture) and DCRL (clayey) soils.

The correlation between the amount of potentially available Zn (mg/pot), according to the solubility of the different Zn sources in each extractor with Zn accumulated in the shoot, was significant for NAC and DTPA, regardless of the soil type (Table 8). Furthermore, the correlations between the amount of potentially available Zn (mg/pot), according to the solubility of the different Zn sources in each extractor with the agronomic efficiency index (AEI) of Zn sources (based on Zn accumulated in the shoots) were also significant for the extractors NAC and DTPA in both soils (Table 8). In the DCRL soil (clayey texture), the correlation of the extractor 10 % HCl was also significant for Zn shoot accumulation and for the agronomic efficiency of sources (Table 8).

Our study results differ partly from those reported in the literature. The chelating agents DTPA and EDTA, both at 5 mmol L^{-1}, and the extractants water, 2 % CA and NAC diluted 1+9 were evaluated by Vale & Alcarde (1999) for their efficiency in the evaluation of micronutrient availability to rice plants grown in Petri dishes, of 30 samples of commercial fertilizers. Only the extractor 2 % CA proved promising in the characterization of plant-available Cu, Mn and Zn. The metal solubility of the chelating agents EDTA and DTPA was generally low. Vale & Alcarde (2002) also evaluated Zn in different chemical forms of fertilizers (zinc sulfate, zinc oxide, zinc metal, and four commercial frits) extracted in water, 2 % CA, NAC (1+9) and DTPA 5 mmol L^{-1}. The Zn contents extracted by the different solutions were correlated with the levels of this element in rice and maize plants. The extractor NAC (1+9) at a ratio of 1:100 (fertilizer mass: extraction solution mass) and under boiling for 5 min was considered a good extractor to assess the availability of Zn fertilizers for rice and maize plants with correlation coefficients significant at 1 % (0.92 and 0.96, respectively).

Table 8. Coefficients of linear correlation in DARYL (medium texture) and DCRL (clayey) soils between: the amount of potentially available Zn according to the solubility of Zn sources in each extractant with Zn accumulation in maize plants and, the amount of potentially available Zn according to the source solubility in each extractant with the agronomic efficiency index (AEI) of the sources

Extractor Zn	DARYL		DCRL	
	Zn accumulation	AEI	Zn accumulation	AEI
mg/pot	mg/pot	%	mg/pot	%
HCl[1]	0.00 ns	0.00 ns	0.00 ns	0.00 ns
2 % CA[2]	0.28 ns	0.28 ns	0.41 ns	0.41 ns
1 % AA[3]	0.65 ns	0.65 ns	0.50 ns	0.50 ns
10 % SA[4]	0.44 ns	0.44 ns	0.50 ns	0.50 ns
10 % HCl[5]	0.58 ns	0.58 ns	0.75 *	0.75 *
NAC[6]	0.76 *	0.76 *	0.79 *	0.78 *
DTPA[7]	0.84 *	0.84 *	0.84 *	0.83 *
EDTA[8]	0.03 ns	0.03 ns	0.00 ns	0.00 ns
BS pH 6.0[9]	0.47 ns	0.47 ns	0.45 ns	0.44 ns
Wa[10]	0.09 ns	0.09 ns	0.17 ns	0.18 ns
HWa[11]	0.05 ns	0.05 ns	0.10 ns	0.10 ns

[1] HCl: total Zn content, the official MAPA method. [2] 2 % CA: 2 % citric acid. [3] 1 % AA: 1 % (v/v) acetic acid. [4] 10 % SA: 10 % (v/v) sulfuric acid. [5] 10 % HCl (v/v). [6] NAC: neutral ammonium citrate + water in the ratio 1:1. [7] 50 mmol L^{-1} DTPA. [8] 5 mmol L^{-1} EDTA. [9] BS pH 6.0: buffer solution pH 6.0. [10] Wa: water. [11] HWa: hot water. DARYL: Dystrophic Alic Red Yellow Latosol with medium texture. DCRL: Dystrophic Clayey Red Latosol. AEI: agronomic efficiency index of sources calculated based on Zn accumulation in the shoots. ns and *, not significant and significant at 5 %, respectively.

A more recent study by Moura (2010) evaluated the extractors 2 % CA and NAC (both methods with stirring and boiling), and water to quantify the levels of available Zn in brass slag for rice plants grown in a clayey soil (Dark Red Latosol). The author reported that the 2 % CA extractor (under boiling) efficiently predicted the Zn available to rice plants in the industrial by-products, although the linear correlation coefficient (r) between the solubility of Zn content in the slags and Zn accumulated in plants was 0.47*.

The significant correlations obtained by the use of 50 mmol L^{-1} DTPA can be explained by the change in concentration of the extraction solution, 10 times more concentrated than the DTPA solution tested by other authors (Vale & Alcarde, 1999, 2002). This modification was based on the fact that the mineral fertilizers contain much higher micronutrient concentrations than the soil. Therefore, the effect of the DTPA concentration was more marked, increasing its chelating ability and capacity of solubilizing Zn contained in the fertilizer sources evaluated in this study. Of all results obtained, the DTPA 50 mmol L^{-1} extractor, under stirring, is the most promising as extractant for different Zn sources.

CONCLUSIONS

1. The results of 2nd extractor 2 % citric acid were unsatisfactory for the evaluation of zinc available in industrial by-products and mineral fertilizers and to predict the zinc availability to maize in the tested sources.

2. The extractant 50 mmol L^{-1} DTPA, with stirring, was the best method that represented Zn availability to maize plants, indicating its potential as Zn extractor from mineral fertilizers and industrial by-products.

3. The agronomic efficiency index of the material that not reaching a minimum solubility of 60 % in the 2nd extractor 2 % CA was similar to or higher than that of Zn sulfate. This fact indicates that the adoption of citric acid 2 % to the solubility evaluation for industrial by-products could restrict the use of alternative and potential Zn sources. However, the levels of the contaminants arsenic, cadmium, chromium, lead, and mercury must also be evaluated to ensure a safe use of these sources.

4. It is recommended to use X-ray diffraction analysis in the description of the mineralogical composition of Zn in several sources, mainly in industrial by-products, which can have a highly variable composition, according to the production process.

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