Zinc Diffusion and Availability Affected by Different Sources in Soils of Contrasting Textures

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Abstract

Trends in new fertilizer technologies should balance the nutrient release rate from fertilizers with plant demands over time, while developing suitable physical characteristics of the fertilizer's particles. The objective of this study was to evaluate the performance of three zinc fertilizers [ZnO, $ZnSO_4$, and a commercial co-granulated $ZnO+S^0$ fertilizer (ES_Zn)] on Zn diffusion in soil and their agronomic performances. A Petri dish trial was carried out in order to evaluate the diffusion of Zn in the soil. The experiment was designed as a factorial scheme $(3 + 1) \times 2 \times 3$, with three Zn sources, one control treatment (without Zn application), two soils of contrasting textures (sandy and clay), and three incubation times (1, 30 and 60 d). The experiment was carried out under a completely randomized design with four replications. Zinc diffusion was assessed according to the method proposed by Degryse et al. (2015) along of incubation times. For that, a $ZnSO_4$ solution or ZnO suspension was applied by pipetting 15 μL of solution or suspension into a small hole (~0.5-cm deep) in the center of the Petri dish. A single pastille of ES_Zn fertilizer (30 ± 0.5 mg) was placed in the center of the Petri dish, at the same depth. Soil was watered to 80% of field capacity. Filter papers (Whatman) were impregnated with $CaCO_3$ and placed on the soil surface. After 2 h of reaction, the $CaCO_3$-impregnated filter papers were collected, and the precipitated Zn in the papers was colored with dithizone, giving a pink color. The performance of Zn sources was evaluated in a greenhouse through a successive maize-soybean-millet crop. The trial was designed as a $2 \times (3 \times 3 +1)$ factorial scheme, being two soils (sandy and clay), three Zn sources ($ZnSO_4$, ZnO, and ES_Zn), three Zn doses (1.5, 3.0, and 6.0 mg dm^{-3} Zn), and a control treatment. The experiment was a randomized block design with four replications, being the experimental unit composed of a pot with 4 dm^3 of soil. Pastille ES_Zn, ZnO (as suspension), and $ZnSO_4$ (as solution) were applied at five equidistant points, at 5 cm below the soil surface. After 30, 60 and 60 days of planting, shoot of maize soybean and millet were harvest, oven-dried at 70 °C for 72 h (until constant weight), weighed and milled for chemical analysis. ES_Zn fertilizer promoted a delay Zn release in the soil, being effective as a fertilizer only in the last crop (millet), as well as ZnO. Zinc oxide and $ZnSO_4$ had similar performances for increasing Zn availability in the inner soil portion, but its diffusion in soil was superior when the source was sulfate. The highly soluble $ZnSO_4$ was more effective than ZnO-based fertilizers in terms of plant nutrition, especially for the two first crops. Our results also suggest that ZnO is solubilized in soil at high pH (6.6), its dispersion in soil being a key factor for the dissolution rate.

Keywords: agronomic efficiency, elemental sulfur, zinc oxide, zinc sulfate

1. Introduction

Zinc is an essential element for plant nutrition, and its deficiency appears to be the most widespread and frequent micronutrient deficiency worldwide, causing a decrease in crop yields and nutritional quality (Alloway, 2004; Cakmak, 2008). Zinc deficiency problems are reported in many regions around the world, such as Asia, Central

America, Africa, and South America, mostly in soils formed on limestone and sandstone (Alloway, 2004). However, for highly weathered soils, including clayey soils such as those in the Brazilian savanna (Cerrado), Zn availability is low and therefore its addition has been increasing crop yields (Alloway, 2004; Lopes, 1975; Ritchey et al., 1986).

The bioavailability and fate of Zn in soils is affected by both soil and source properties (Alloway, 2004). The formation of inner sphere complexes, precipitation at high pH, and reaction with phosphates represent the main ways of sequestering Zn in the soil, potentially decreasing its availability for plant (Alloway, 2004; Oliveira et al., 1999; Sparks, 2005). Therefore, Zn fertilizers should be designed in order to avoid these processes that lead to the unavailability of Zn in the soil. Solubility, dispersion in soil and particle size are the most relevant characteristics of fertilizers affecting their agronomic effectiveness (Alloway, 2004; Gowariker, 2009; McBeath & McLaughlin, 2014; Milani et al., 2012; Mortvedt, 1992).

Granular Zn fertilizers composed of water-insoluble Zn sources are interesting because of their reduced segregation and incompatibilities in fertilizer mixtures. In addition, insoluble Zn sources are easy to apply and can also prevent Zn losses, promoting a longer residual Zn availability for plants compared with conventional soluble sources (Mattiello et al., 2017; Santos et al., 2017). However, because of the longer disintegration time, granular fertilizers take longer to solubilize than powdered fertilizers (Gowariker, 2009), and may not provide enough Zn available for initial growth of the crops. Therefore, it is essential to make these properties compatible to improve fertilizer effectiveness.

Recent studies have demonstrated the agronomic potential of non-soluble Zn fertilizers, based on the co-granulation of ZnO with elemental sulfur (S°), ES_Zn (Mattiello et al., 2017; Santos et al., 2017). ES_Zn fertilizer is also advantageous compared with soluble sources because it is cheaper and contains high concentration of S, which is a macronutrient and generally poorly available in tropical soils.

The objective of this study was to evaluate the diffusion and plant availability of Zn from different sources in soils of contrasting textures.

2. Materials and Methods

2.1 Soil and Zinc Fertilizers

Because of the importance of the clay content in Zn dynamics, two soils with contrasting textures were used (sandy and clay soil). The soils were collected from 0-30 cm depth, sieved, placed into plastic bags, limed with a mixture of $CaCO_3$ and $MgCO_3$ to reach a Ca:Mg ratio of 4:1 and 60% of base saturation, wetted to 80% of field capacity, and incubated for 30 d. After that, soils were air-dried and sieved for physical and chemical analysis (Table 1-2 mm sieve), and to perform both the diffusion (1 mm sieve) and greenhouse trials (4 mm sieve).

For the present study, we used Zn sources of different solubilities and reactivities: zinc sulfate [($ZnSO_4 \cdot 7H_2O$; CAS: 7446-20-0; 22.74% Zn)]; zinc oxide (ZnO; CAS: 1314-13-2; 80.34% Zn); and a ZnO fertilizer pastilled with elemental sulfur (S°) and bentonite (ES_Zn; 79.3% S°, 4.2% Zn, 10% Na-bentonite; granular form 2-3 mm).

Table 1. Physical and chemical soil characteristics after liming

Soil characteristics	Sandy soil	Clay soil
Sand (g kg^{-1})	821	363
Silt (g kg^{-1})	25	106
Clay (g kg^{-1})	154	531
CEC pH 7.0 (cmol$_c$ dm^{-3})	3.17	4.93
(H + Al) (cmol$_c$ dm^{-3})	1.60	2.10
pH (water)	6.63	6.19
OM (dag kg^{-1})	1.3	1.5
Zn (mg dm^{-3})	0.83	1.24

Note. OM, organic matter content (Walkley & Black, 1934). Available S [$Ca(H_2PO_4)_2$ 500 mg L^{-1} in acetic acid]. Available Zn (Mehlich-1).

2.2 Zinc Diffusion Trial

A Petri dish trial was carried out to evaluate the diffusion of Zn in the soil. The experiment was designed as a factorial scheme $(3 + 1) \times 2 \times 3$, with three Zn sources (pastilled ES_Zn, ZnO, and ZnSO$_4$), one control treatment (without Zn application), two soils of contrasting textures (sandy and clay soil), and three incubation times (1, 30 and 60 d). The trial was carried out under a completely randomized design with four replications.

Approximately 20 cm^3 of air-dried soil was placed in Petri dishes (50 mm diameter × 10 mm height), ensuring a flat soil surface. A single pastille of ES_Zn fertilizer (30±0.5 mg) was placed in the center of the Petri dish, at a depth of about 0.5 cm. A ZnSO$_4$ solution or ZnO suspension was applied by pipetting 15 μL of solution or suspension into a small hole (~0.5-cm deep) in the center of the Petri dish. All sources provided the same dose of Zn (66.3 mg dm^{-3}). After that, soils were carefully sprayed to reach 80% of field capacity, petri dishes were sealed with Parafilm to minimize water loss while maintaining aeration and incubated at 25 °C.

Zinc diffusion was assessed according to the method proposed by Degryse et al. (2015), after 1, 30 and 60 d of incubation. In this method, filter papers (Whatman) were impregnated with CaCO$_3$ and placed on the soil surface. After 2 h of reaction, the CaCO$_3$-impregnated filter papers were collected, and the precipitated Zn in the papers was colored with dithizone, giving a pink color. After 30 min, when the pink color was established, filters were air-dried and images scanned and processed using GIMP software (version 2.6.1). The diffusion radius (DR) was calculated through Equation 1.

$$DR = \sqrt{A/\pi} \tag{1}$$

where, A is the high-Zn dark pink colored area.

To measure the effect of source on Zn availability and soil acidity, only soil samples corresponding to 30 and 60 d treatments were used. Zinc availability was assessed using DTPA as an extractor (Lindsay & Norvell, 1978) and soil pH was measured in a 1/2.5 (w/v) soil:water suspension. Soil samples were collected using a ring of 1.25 cm radius, with two separate soil sections (inner and outer), taking as reference the center of the Petri dish in which the fertilizers were applied. Samples were air-dried, sieved (≤ 2 mm), and homogenized to perform the analysis.

2.3 Greenhouse Trial

Agronomic performance of the Zn fertilizers was evaluated in a greenhouse pot experiment with a sequential cultivation of maize, soybean, and millet. This trial aimed to investigate the performance of Zn sources, including for their residual effects in a sequential cultivation, and the consistency of these results with Zn mobility demonstrated in the first trial (diffusion). Therefore, the trial was designed as a $2 \times (3 \times 3 + 1)$ factorial scheme: two soils (sandy and clay), three Zn sources (ZnSO$_4$, ZnO, and ES_Zn), three Zn doses (1.5, 3.0, and 6.0 mg dm^{-3} Zn), and a control treatment (no Zn application). The experiment was a randomized block design with four replications, being the experimental unit composed of a pot with 4 dm^3 of soil. Triple superphosphate (TSP) fertilizer was mixed into the sand and clay soils to supply 150 and 300 mg dm^{-3} of P, respectively. Pastille ES_Zn, ZnO (as suspension), and ZnSO$_4$ (as solution) were applied at five equidistant points, at 5 cm below the soil surface.

For the first cropping, six seeds of maize (Biomatrix BMB 20 commercial variety) were sown in each pot at a depth of 3 cm and thinned to the three most uniform ones in each pot. Solutions of N, K, and S were added 10, 20, and 30 d after planting, giving total rates of 200 mg dm^{-3} N, 150 mg dm^{-3} K, and 40 mg dm^{-3} S. Micronutrients were also applied at the same time, totalizing 0.8 mg dm^{-3} B, 1.4 mg dm^{-3} Cu, 1.6 mg dm^{-3} Fe, 3.7 mg dm^{-3} Mn, and 0.2 mg dm^{-3} Mo. After 30 d of cultivation maize shoots were harvested at the soil surface.

Twelve days after maize harvesting, six seeds of soybean (variety ND-7300) were sown into undisturbed soil pots at a depth of 2 cm; after seedling emergence (7 d), the three most homogeneous seedlings were left in each pot. Seeds were inoculated with commercial *Bradyrhizobium* in order to fix and provide N to the plants. Macronutrients (K and S) were added 15 and 30 d after planting, giving a total of 200 mg dm^{-3} K and 60 mg dm^{-3} S. After 60 d, the shoots of the soybean were harvested by cutting the stems at the soil surface.

Ninety days after the soybean harvest, 15 seeds of millet (BRS 1501 cultivar) were sown in undisturbed soil pots at a depth of 2 cm; 5 d after sowing, each pot was thinned to three plants. Nitrogen was applied to provide a total of 115 mg dm^{-3} N. Plants were grown for 60 d and shoots were harvested every 20 d by cutting the stems at a height of 10 cm above the soil.

For all crops, water availability was controlled daily to maintain the soil near 80% field capacity. The sequential cultivation resulted in 30, 102 and 252 days from Zn application to the harvesting of maize, soybean, and millet, respectively.

Plant materials were oven-dried at 70 °C for 72 h (until constant weight), weighed and milled for chemical analysis.

Plant samples were mineralized in an open-vessel digestion system using a nitric-perchloric solution (3:1 v/v) (Miller & Kalra, 1998). Zinc concentration in all extracts was quantified by atomic absorption spectroscopy (Agilent, Series AA Model 240 FS).

The Zn uptake (Zn_{uptake}) was calculated according to Equation 2:

$$Zn_{uptake} \ (mg \ pot^{-1}) = Zn_{plant} \times DM \tag{2}$$

where, Zn_{plant} is the concentration of Zn in plant tissue (mg g^{-1}); and DM is the dry matter yield (g pot^{-1})

The relative absorption efficiency (RAE) from each Zn source was calculated according to Equation 3:

$$RAE \ (\%) = [(Zn_i - Zn_0)/(Zn_{ref} - Zn_0)] \times 100 \tag{3}$$

where, Zn_i is zinc uptake in treatments with added Zn fertilizer (mg pot^{-1}); Zn_{ref} is the zinc uptake obtained from $ZnSO_4$ (reference fertilizer, RAE = 100%); and Zn_0 is the zinc uptake without addition of Zn fertilizer (control).

The recovery rate of Zn (Zn_{Rec}) for each treatment was calculated according to Equation 4:

$$Zn_{Rec} \ (\%) = [(Zn_i - Zn_0)/Zn_{total}] \times 100 \tag{4}$$

where, Zn_i is the Zn uptake from each treatment; Zn_0 is the Zn uptake from the control treatment (without Zn); and Zn_{total} is the total amount of Zn added as fertilizer.

2.4 Data Statistical Processing

Data were submitted to one-way analysis of variance. The effect of incubation time on Zn DR was evaluated by regression analysis, and the effect of fertilizers on soil properties, plant growth, and Zn absorption was compared by Tukey's test ($p \leq 0.05$).

3. Results

3.1 Zinc Diffusion

The experimental results indicate that Zn diffusion evaluated by visualization test (Figure 1), and through its corresponding statistical approach (Figure 2), showed differences among fertilizers. After 1 d of incubation, $ZnSO_4$ promoted significant Zn diffusion (Figures 1 and 2) compared with ZnO-based sources. After 1 d, only a little spot of Zn diffusion was detected for ZnO and nothing for ES_Zn (Figure 1), for both soils.

Soil texture affects Zn diffusion. In sandy soil, $ZnSO_4$ led to a higher Zn DR at all incubation times, followed by that for ZnO. From 1 to 30 d, Zn DR increased for both $ZnSO_4$ and ZnO. However, from 30 to 60 d there was no increase in Zn DR for either source (Figures 2 and 3). From the ES_Zn, Zn diffusion in the sandy soil was low and occurred only after 60 d. In the clay soil, differently from the sandy soil, the Zn DR increased linearly throughout the experimental time for all Zn sources. However, $ZnSO_4$ also showed higher Zn DR followed by ZnO. While Zn DR increase from $ZnSO_4$ and ZnO showed similar regression slopes (0.09 and 0.10, respectively), ES_Zn showed a regression slope of 0.23. Even though after 1 d ES_Zn had not released and diffused any Zn in the clay soil, within 30 d the Zn DR from ES_Zn was similar to the ZnO. Within 60 d, Zn DR from ES_Zn was higher than from ZnO and similar to the $ZnSO_4$.
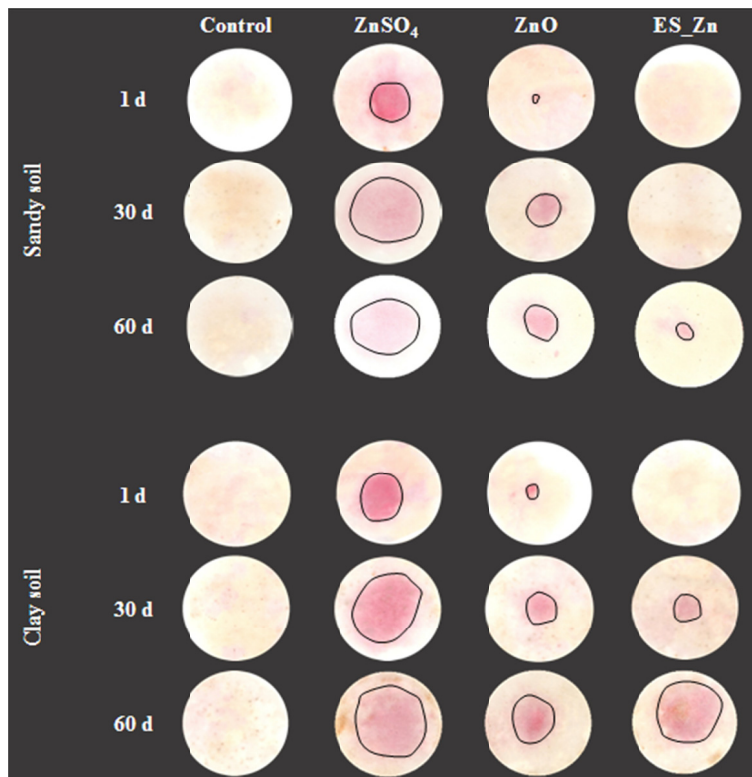
Figure 1. Visualization of Zn diffusion after 1, 30, and 60 d of incubation of different Zn fertilizers applied in the center of Petri dishes filled with soil of contrasting textures. ES_Zn is a commercial co-granulated Zn-enriched elemental sulfur fertilizer composed of 79.3% S^0, 4.2% Zn, and 10% Na-bentonite
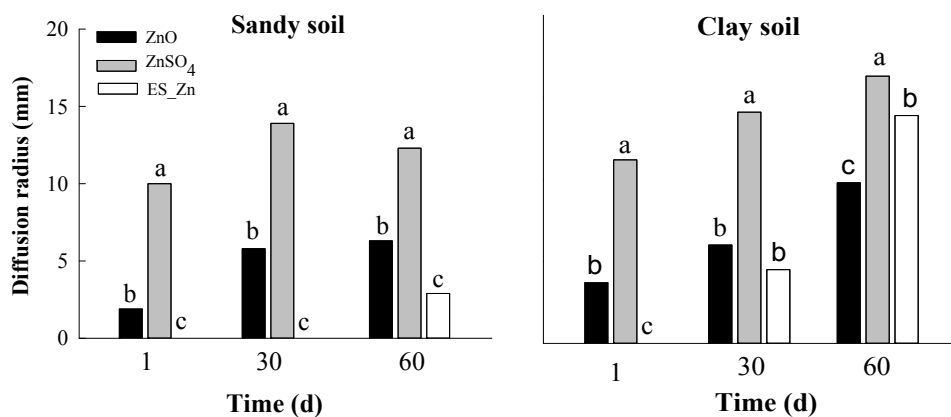

Figure 2. Radius of the Zn diffusion zone (Zn DR) after 1, 30, and 60 d of incubation of zinc fertilizers applied in the center of Petri dishes filled with soils of contrasting textures (see Materials and Methods). ES_Zn is a commercial co-granulated Zn-enriched elemental sulfur fertilizer composed of 79.3% S^0, 4.2% Zn, and 10% Na-bentonite. Different letters within each incubation period indicate significant differences between treatments (Tukey test, $p \leq 0.05$)
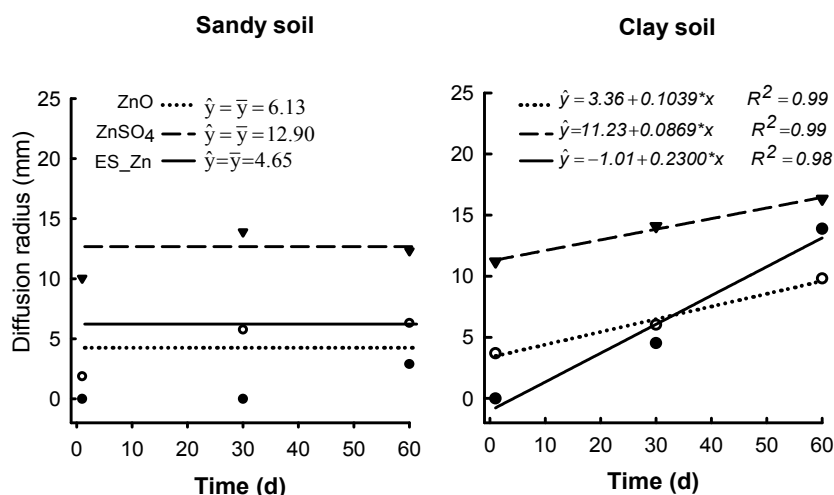
Sandy soil　　　　**Clay soil**

Figure 3. Radius of the Zn diffusion zone (Zn DR) over incubation periods for Zn fertilizers applied in the center of Petri dishes filled with soils of contrasting textures. * indicates a significant effect by the t-test at 5%. ES_Zn is a commercial co-granulated Zn-enriched elemental sulfur fertilizer composed of 79.3% S0, 4.2% Zn, and 10% Na-bentonite

3.2 Soil pH and Zinc Availability

Reactions of Zn sources showed litter impact on soil pH, but with statistical significance among sources when compared to the control treatment (Table 2). These effects were most significant in soil samples from the inner ring, because of their greater proximity to the application zone of the fertilizers. Overall, comparing with the control, $ZnSO_4$ decreased soil pH in the inner and outer rings of almost all treatments, with exception for the sandy soil after 60 d of incubation (inner and outer ring) and the outer ring of the clay soil after 30 d of incubation. In a lesser extent, ES_Zn decreased pH in the inner ring of the clay soil after 30 d and in both inner and outer rings of the clay soil after 60 d. On the other hand, ZnO increased pH in the inner ring of the sandy soil at 30 and 60 d of incubation (Table 2).

Zinc availability assessed by DTPA also demonstrated differences among sources (Table 2). For both soils and times, there was an increase in Zn availability in the inner ring for all sources, in contrast to the control treatment. In general, ZnO promoted higher Zn concentration (availability), followed by $ZnSO_4$ and ES_Zn. For the soil samples from the outer ring, only $ZnSO_4$ increased Zn availability, demonstrating it to be the most effective source for transporting Zn in the soil.

Table 2. Active soil acidity (pH) and Zn availability as a function of different sources and soils with contrasting textures

Source	Incubation time (d)							
	30 d				60 d			
	Sandy soil		Clay soil		Sandy soil		Clay soil	
	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer
pH								
Control	6.4 b	6.4 a	5.8 a	5.8 a	6.2 b	6.3 a	5.7 a	5.6 a
ZnSO$_4$	6.1 c	6.2 b	5.5 b	5.7 a	6.2 b	6.2 a	5.4 bc	5.1 c
ZnO	6.7 a	6.4 a	6.0 a	5.6 a	6.5 a	6.2 a	5.6 ab	5.4 ab
ES_Zn	6.5 ab	6.4 a	5.4 b	5.6 a	6.1 b	6.2 a	5.1 c	5.2 bc
Mean	6.4 *A*	6.4 **A**	5.7 *C*	5.6 **C**	6.24 *B*	6.2 **B**	5.4 *D*	5.3 **D**
Zn DTPA (mg dm^{-3})								
Control	0.5 d	0.6 b	0.7 d	0.7 b	0.4 d	0.4 b	0.6 d	0.6 b
ZnSO$_4$	200.0 b	38.4 a	137.2 b	24.1 a	192.0 b	43.0 a	109.3 b	23.7 a
ZnO	273.1 a	1.5 b	188.6 a	1.5 b	239.9 a	1.1 b	164.3 a	3.5 b
ES_Zn	23.2 c	0.8 b	33.9 c	1.3 b	45.1 c	0.9 b	54.5 c	3.8 b
Mean	124.2 *A*	10.3 **A**	90.1 *B*	6.9 **B**	119.3 *A*	11.4 **A**	82.2 *C*	7.9 **B**

Note. Means in the columns followed by different lowercase letters differ by the Tukey test at 5%. Means in the rows followed by different capital letters in italics or bold letters differ from each other by the Tukey test at 5%. ES_Zn is a commercial co-granulated Zn-enriched elemental sulfur fertilizer composed of 79.3% S^0, 4.2% Zn, and 10% Na-bentonite. Inner refers to the inner sampling ring, and outer refers to the external sampling ring (see Materials and Methods).

3.3 Crop Growth and Zinc Uptake

There were no supporting evidences of differences among Zn sources on dry matter production (DMP) of any crop, within each soil (Table 3). However, for the maize and soybean crops, supplying Zn as ZnSO$_4$ resulted in a higher DMP in clay soil than in sandy soil.

Significant increases in Zn absorption by crops, in terms of its concentration in shoots and accumulation (Zn uptake), were observed only for the ZnSO$_4$ (Table 3), which increased Zn uptake linearly for all crops with increasing dose (Figure 4). On the other hand, in the millet crop, both ES_Zn and ZnO promoted a similar linear increase in Zn uptake, most evident in clay soil (Figure 4). Moreover, when the sources were compared in terms of Zn recovery by crops, ZnSO$_4$ always had a higher recovery rate for any soil and crop. However, in the clay soil, the millet crop recovered similar amounts of Zn from ES_Zn and ZnSO$_4$ (Table 3).

Table 3. Crop growth and zinc uptake in a successive maize-soybean-millet crop fertilized with sources of different solubility and reactivity in soils with contrasting textures

Crop	Sandy soil					Clay soil				
	Control	ZnSO$_4$	ZnO	ES_Zn	Mean	Control	ZnSO$_4$	ZnO	ES_Zn	Mean
Shoot dry matter (g pot^{-1})										
Maize	31.7 a	34.1 a	31.0 a	31.7 a	32.1 B	39.8 a	42.8 a	40.9 a	39.8 a	40.8 A
Soybean	13.6 a	14.4 a	15.0 a	14.6 a	14.5 B	11.9 a	11.5 a	12.5 a	11.7 a	11.9 A
Millet	21.2 a	19.2 a	20.0 a	19.5 a	19.8 A	21.9 a	20.8 a	19.2 a	20.5 a	20.6 A
Total	66.5 a	67.7 a	66.0 a	65.8 a	66.6 B	73.6 a	75.1 a	72.6 a	72.0 a	73.3 A
Zinc concentration (mg kg^{-1})										
Maize	18.1 a	55.1 b	22.4 a	23.2 a	29.7 A	21.7 a	51.7 b	24.0 a	23.1 a	30.1 A
Soybean	30.1 a	74.9 b	39.7 a	39.0 a	45.9 B	35.9 a	76.8 b	61.6 a	53.7 a	57.0 A
Millet	55.9 a	168.0 b	85.0 a	92.1 a	100.2 A	72.2 a	117.2 a	97.9 a	111.5 a	99.7 A
Zinc uptake (mg pot^{-1})										
Maize	0.6 a	1.9 b	0.7 a	0.7 a	1.0 B	0.8 a	2.2 b	1.0 a	1.0 a	1.2 A
Soybean	0.4 a	1.1 b	0.6 a	0.6 a	0.7 A	0.4 a	0.9 b	0.8 a	0.6 a	0.7 A
Millet	1.1 a	3.2 b	1.7 a	1.9 a	2.0 A	1.3 a	2.5 b	1.9 a	2.3 a	2.0 A
Total	2.1 a	6.2 b	3.0 a	3.2 a	3.6 A	2.5 a	5.6 b	3.7 a	3.9 a	3.9 A
Zinc recovery rate (%)										
Maize	-	8.9 b	2.0 a	1.9 a	4.3 A	-	10.0 b	1.4 a	3.5 a	5.0 A
Soybean	-	4.8 b	2.2 a	2.4 a	3.1 A	-	4.2 a	3.0 a	2.5 a	3.2 A
Millet	-	14.8 b	5.0 a	4.9 a	8.2 A	-	7.2 a	5.3 b	8.2 a	6.9 A
Total	-	28.5 b	9.2 a	9.2 a	15.6 A	-	21.4 b	9.7 a	14.2 a	15.1 A

Note. Means in the rows, within each soil, followed by different lowercase letters differ by the Tukey test at 5%. Means in the rows followed by different capital letters differ by the F test at 1%. ES_Zn is a commercial co-granulated Zn-enriched elemental sulfur fertilizer composed of 79.3% S°, 4.2% Zn, and 10% Na-bentonite.
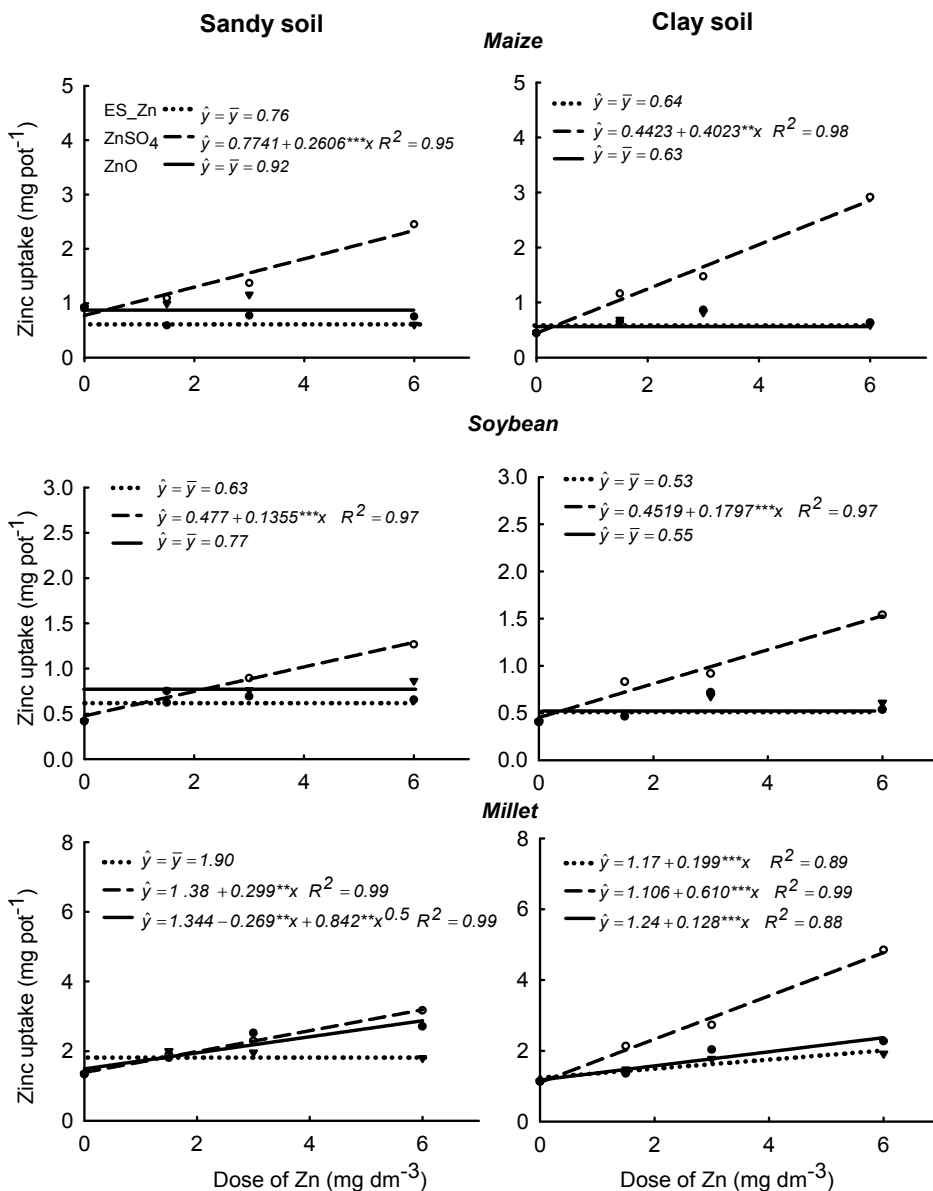
Figure 4. Shoot Zn uptake of successive maize-soybean-millet crops as a function of Zn dose for different fertilizers applied in soils of contrasting textures. ES_Zn is a commercial co-granulated Zn-enriched elemental sulfur fertilizer composed of 79.3% S°, 4.2 % Zn, and 10% Na-bentonite. [**] and [***] mean significant effects by the t-test at 1% and 0.1%, respectively

The relative Zn absorption efficiency approach, RAE (Figure 5), reveals that ZnO-based fertilizers showed different trends over crop sequences compared with $ZnSO_4$ fertilizer. In fact, while ZnO did not show any trend of RAE across the crops, ES_Zn showed a clear linear increase of RAE over the crop sequence, reaching 91% of RAE in the millet cultivated in the clay soil. In addition, soil texture affected the performance of ZnO-based fertilizers, being they in general most effective in clay soil (Figure 5).
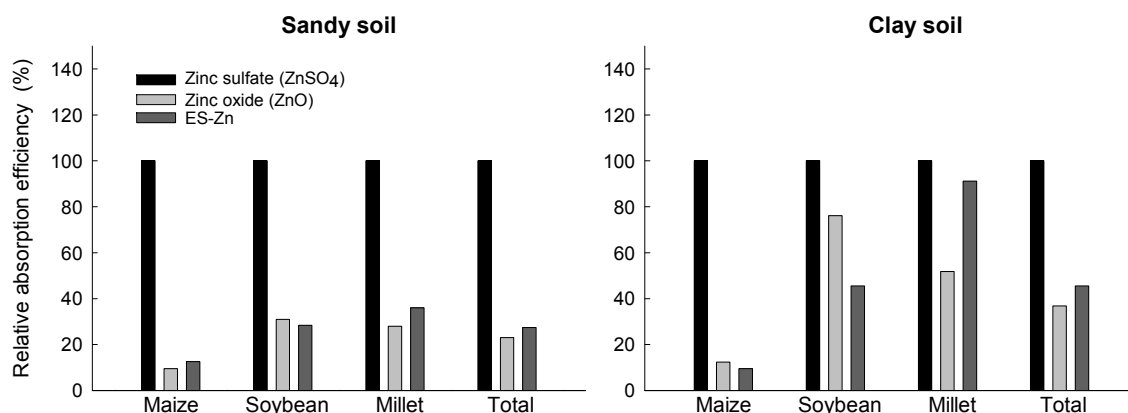
Figure 5. Relative absorption efficiency (RAE) of Zn in successive maize-soybean-millet crops as a function of different Zn fertilizers applied in soils of contrasting textures. ES_Zn is a commercial co-granulated Zn-enriched elemental sulfur fertilizer composed of 79.3% S°, 4.2% Zn, and 10% Na-bentonite

4. Discussion

The active acidity of soil (soil pH) is a factor that can be affected by acid-base reactions in soil involving fertilizers. We suggest that $ZnSO_4$ had an acidifying effect due to the acid residue on it and to the cationic exchange of H_3O^+ by Zn^{2+} in the soil sorption complex, increasing the acidity of the soil solution. Indeed, a saturated solution of the $ZnSO_4$ salt used in our study showed mild acidity (pH~5.2).

Most Zn deficiency is reported in soils with pH higher than 6.0, due to its precipitation as oxyhydroxides or carbonate species (Alloway, 2004; Lindsay, 1991). In our work, the best performance of the ZnO-based fertilizers in clayey soil is probably due to its higher active acidity (soil pH) and buffering capacity (H + Al), compared to the sandy soil (Table 1). Between pH 5.5 and 7.0, Zn concentration in soil solution decreases about 30- to 40-fold when soil pH increases one unit (Moraghan & Mascagni, 1991). In addition, its higher CEC helps removing Zn from the soil solution and increase solubilization.

Sulfur oxidation leading to a reduction in soil pH due to the use of ES_Zn has been reported by Mattiello et al. (2017), indicating that elementary sulfur (S°) is oxidized in the soil (Santos et al., 2017). In fact, many native soil microorganisms oxidize sulfur, including chemolithotrophic and heterotrophic bacteria and fungi (Kumar et al., 2018; Luo et al., 2013). As demonstrated in Equation 5 (Santos et al., 2017), oxidation of S^0 by soil microorganisms generates great amount of acidity. Therefore, the reduction in soil pH of the clay soil by ES_Zn fertilizer (Table 2) was due to proton production by microbial catalysis overcoming proton consumption to solubilize the Zn_O in the fertilizer. On the other hand, the increase in soil pH following Zn_O application can be attributed to the consumption of protons from the soil solution, as shown in Equation 6 (Santos et al., 2017). This finding also makes sense for our results because there was an increase in Zn availability using ZnO, assessed by DTPA extractors.

$$S° + 1.5O_2 + H_2O \ (Microorganism) \rightarrow SO_4^{2-} + 2H^+ \tag{5}$$

$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O \tag{6}$$
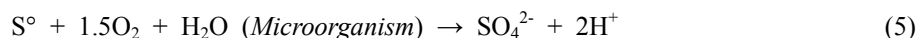
Zinc sulfate promotes greater Zn diffusion in the soil than Zn_O-based fertilizers (Mattiello et al., 2017). Despite the fact that Zn_O and $ZnSO_4$ significantly increased Zn availability in the inner soil portion, only $ZnSO_4$ increased it in the outer soil portion. We presumed that the greater diffusion of Zn^{2+} from $ZnSO_4$ could be attributed to the higher Zn concentration promoted by such soluble source. Also, in some extent, Zn diffusion can benefit from the ionic interaction between Zn^{2+} and SO_4^{2-} in the soil solution, as it has been demonstrated that Zn diffusion in soil is affected by the accompanying anions in soil solution (Oliveira et al., 1999), Cl^- being more effective than SO_4^{2-}.

The results of Zn diffusion from the ZnO, which happened from the first day of incubation, indicate that solubilization of this compound in soil is fast and can happen at high soil pH (*e.g.*, at pH 6.6 in sandy soil). A calculation for a single chemical system (Gustafsson, 2013) composed only of Zn^{2+} at pH 6.6 demonstrates that the precipitation of Zn as ZnO occurs only when the Zn^{2+} concentration is higher than 1,512 mg L^{-1}. Therefore, even accounting for physicochemical differences between this theoretical perspective and a real soil solution,

including ionic force and the presence of other ions, data demonstrate that is possible to have a higher Zn concentration at this soil pH.

The use of powder fertilizers are falling into disuse due to problems with application uniformity and segregation in fertilizer mixtures (Gowariker, 2009). On the other hand, granular fertilizers composed of insoluble nutrient sources, due to their small reaction surface area, promote retarded nutrient release into the soil solution, affecting plant nutrition. Indeed, the granular ES_Zn source promoted retarding on Zn releasing influencing both the diffusion of the element in soils as the effectiveness of the source as fertilizer.

Contrasting the lack of response of maize and soybean (two first crops) to the addition of ZnO with the diffusion trial results, there seems to be a contradiction, because of the high values achieved for available Zn using ZnO, in the inner ring, at 30 d of incubation. However, as ZnO is a water-insoluble compound, its solubilization in soil is likely to depend on particle dispersion. Indeed, as ZnO was applied through a water suspension for the diffusion trial, we presume that in this condition there was no significant limitation for its solubilization, whereas when it was placed in small holes in the soil (greenhouse trial), there was greater inhibition of its dissolution because of the increase in soil pH around the ZnO particles due to proton consumption by dissolution (Milani et al., 2012). Therefore, join data of ES_Zn and ZnO fertilizers lead us to report that both the physical form of ZnO-based fertilizers and its dispersion in the soil are important factors to governing the dynamic of Zn, affecting the dissolution pattern and agronomic effectiveness of the sources over time.

Only $ZnSO_4$ was effective as a Zn source in terms of plant growth or Zn absorption for the first crops, while responses for ZnO-based fertilizers were perceived only in the third crop (millet). This finding supports that to attend to the Zn demand for short crop cycles, fertilizers also need to contain water-soluble Zn forms. Mortvedt (1992) showed that at least 40% of the total Zn in granular fertilizers should be water-soluble to be fully effective for crops. In this sense, an ideal Zn fertilizer should contain both soluble and insoluble forms to meet both immediate and future plant demands by promoting balanced nutrient release over time.

Despite the similarity in plant response to ZnO and ES_Zn fertilizers, the latter is advantageous because it is in granular form and contains high concentration of S^0, which is a highly required plant nutrient and generally deficient in tropical soils. Despite the best performance being displayed by $ZnSO_4$, this salt presents physical and chemical incompatibilities for compound solid fertilizer mixtures, associated with its high hygroscopicity.

5. Conclusion

In conclusion, Zn diffusion in soil is higher for $ZnSO_4$ compared with ZnO-based fertilizers, supposedly due to the ionic interaction between SO_4^{2-} and Zn^{2+}. Our results also support that ZnO can be dissolved in soil at high pH (6.6) and suggest that its dispersion in soil affects the solubilization rate. Moreover, solubilization of the co-granulated Zn-enriched elemental sulfur fertilizer (ES_Zn) is delayed in soil, affecting its efficiency as fertilizer. Thereby, $ZnSO_4$ is the most effective fertilizer regardless of crop sequence. Therefore, these findings suggest that an ideal Zn fertilizer should contain both soluble and insoluble Zn sources, aiming to attend plants' demands throughout their whole cycle.

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