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Physicochemical characterization of fertilizers containing concentrated suspensions of CuO, $MnCO_3$ and ZnO

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ABSTRACT: The utilization of insoluble sources of micronutrients as concentrated suspensions (CSs) is increasing in Brazilian agriculture; however, much information regarding the physicochemical characterization of these products is required to demonstrate the absorption behavior by plant leaves. This study aimed to characterize the CSs available on the Brazilian market to support their potential use as foliar fertilizers. We selected five CSs containing Mn, five CSs containing Zn and three CSs containing Cu from five different companies. In each product, the mean particle size was evaluated by dynamic light scattering (DLS), the particle shape and size were evaluated by scanning electron microscopy (SEM), the aggregation degree was determined by the zeta potential and the heavy metal contents were determined by acid digestion followed by reading on ICP-OES. The mean hydrodynamic diameter of fertilizers containing Cu, Mn and Zn was 315 ± 55, 378 ± 184 and 435 ± 107 nm, respectively. The zeta potential varied from –20 to –30 mV, indicating potential particle aggregation and formation of higher structures. SEM images indicated great variation in the size and shape of the particles in each product. All products exhibited concentrations of toxic elements within the legislation thresholds. The average particle size of CSs currently marketable in Brazil does not allow their classification as nanomaterials (< 100 nm). Therefore, their foliar absorption is unlikely, once the particle size is higher than the exclusion limit observed for stomata and cuticle pathways, as well as the nutrient content as ions is low according to the solubility constant.

Keywords: insoluble, nanomaterials, foliar fertilization, nanofertilizer

Introduction

The capacity of water and nutrient absorption by plant leaves has been well-known for more than three centuries (Fernández and Eichert, 2009), making foliar fertilization a common strategy. In certain cases, foliar fertilization is justified, for example, i) when soil conditions limit the nutrient availability for roots; (ii) when there is a high likelihood of the nutrients applied on soil will be lost; and (iii) when plant demand is higher than the soil supply capacity (Fernández et al., 2013). Zinc, Cu and Mn fulfill several functions in plants metabolism, such as enzymatic activation, reduction in oxidation radicals, and formation of reproductive organs and photosynthesis processes (Marschner and Marschner, 2012; Cakmak, 2000; Kirkby and Römheld, 2007); therefore, deficiencies of these elements limit crop yields worldwide.

Micronutrient sources are generally labeled under inorganic sources, synthetic chelates, organic complexes, and silicate oxides. The inorganic sources include metallic salts, such as sulfate, chloride and nitrate (soluble in water), oxide, carbonate and phosphate (insoluble in water), and oxysulfate (intermediate solubility) (Lopes, 1999). Due to their high nutrient contents, commercialization of micronutrients as oxides and carbonates is increasing in Brazil. At the beginning, these sources were used to supply micronutrients through the soil. However, finely ground oxides and carbonates maintained in suspension by adding additives created a new class of fluid fertilizer named as concentrated suspension (CS). The use of CS for foliar fertilization was limited in the past since the legislation allowed only water-soluble sources to be registered as foliar fertilizers. However, the recent shift in the legislation (MAPA, 2018) allows registration of foliar fertilizers by declaring the content of water-soluble nutrient (for soluble fertilizer) or the total content (for nutrients present in CSs), creating a new scenario for commercialization of these products as foliar fertilizers.

Nevertheless, the capacity of plant leaves to absorb insoluble sources of micronutrients remains unclear, especially considering the unknown particle size and shape of the products, which affect penetration into leaf mesophyll. Preliminary studies have indicated an effective absorption of nanomaterials (particles < 100 nm) by plant leaves (Eichert et al., 2008; Prasad et al., 2012). The correct characterization and development of foliar fertilizers, which improve the use of nutrients by plants, is one of the most important challenges for the fertilizer industry (Fernández et al., 2013). The efficacy of new products for foliar fertilization must be accurately evaluated before their widespread usage in field crops.

This study aims to characterize commercial CSs to support the regulation of these products as foliar fertilizers and provide support to future studies on the capacity of plant leaves to absorb nutrients from these sources.

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Materials and Methods

For this study, 13 commercial micronutrient sources (five of Mn, five of Zn and three of Cu) were selected, all in CS forms and belonged to five enterprises of the Brazilian fertilizer industry. Table 1 lists the nutrient concentrations as well as the densities of suspensions reported on the labels. The products were directly purchased from local stores and all were checked regarding their shelf life. Before the measurements, the samples were homogenized using an oscillating stirring table orbital shaker at 80 rpm for 24 h in their original flasks. Right after shaking, an aliquot of each fertilizer was transferred to a volumetric flask and diluted in deionized water up to a 100 mg L^{-1} concentration of each nutrient, taking into account the concentration prescribed by the manufacturer.

The mean particle size was measured using the dynamic light scattering (DLS) technique according to the PCC-1 protocol (Hackley and Clogston, 2011). The analyses were performed using the Zetasizer Nano Range facility using water as a dispersant (viscosity of 0.8872 cP and refractive index of 1.33), with an acquisition time of 60 s and a frequency of 398,000 counts per seconds (kcps). For the measurements, an aliquot of 1 mL of each fertilizer was transferred to a polystyrene cuvette and directly loaded into the equipment.

The aggregation potential was measured by the zeta potential using the same equipment. The zeta potential indicates the difference of electrostatic potential between a particle and the surrounding environment. The zeta potential gives the intensity in which the charges contrast on the particle surface, that is, the higher the value of the zeta potential (both positive and negative), the greater the difference between charges. For a modulus value higher than 30 mV, the repulsion becomes dominant, avoiding aggregation and providing stability to the material (Heurtault et al., 2003). An aliquot of 0.5 mL of each fertilizer was transferred to a capillary cuvette, and directly loaded into the equipment. The analyses were carried out using water as dispersant (viscosity of 0.8872 cP, electric dispersion constant of 78.5 and refractive index of 1.33), a frequency of 1,008,000 readings per second (kcps) and an acquisition time of 12 s.

The shapes and sizes of the particles were evaluated using the scanning electron microscopy (SEM) analysis. The fertilizers were dripped onto a carbon plate coated with an aluminum foil and then loaded into the Magellan 400 L equipment. Approximately eight images were taken of each fertilizer with magnification between 50 and 350 thousand times.

The arsenic, cadmium, lead, chromium, mercury, and selenium concentrations were determined according to the SW-846-3051a methodology of the United States Environmental Protection Agency (USEPA, 1998). Samples were digested using a 3:1 mixture of nitric and hydrochloric acids (65 % and 37 %, respectively) in a microwave closed system, and quantified by inductively coupled plasma atomic emission spectrometry (ICP-OES). The program used for digestion consisted of heating the sample to 175 °C for 5 min, keeping the temperature at 175 °C for 10 min then allowing 10 min for cooling.

Table 1 – Nutrient content and density of the analyzed commercial fertilizers according to manufacturers.

Fertilizer	Company	Element Concentration	Density
		g L^{-1}	g dm^{-3}
Products containing copper			
A	1	499.0	1.5
B	2	407.5	1.6
C	3	507.0	1.7
Products containing manganese			
D	1	500.0	1.8
E	2	412.5	1.6
F	3	502.2	1.9
G	4	500.0	1.9
H	5	501.2	1.8
Products containing zinc			
I	1	693.0	1.7
J	2	1000.0	2.0
K	3	1075.0	2.2
L	4	1000.0	2.0
M	5	800.0	1.8

Results and Discussion

Average hydrodynamic diameter

The average hydrodynamic diameter which is related to the particle size was 315 ± 55, 378 ± 184 and 435 ± 107 nm for fertilizers containing Cu, Mn, and Zn, respec-

Table 2 – Average hydrodynamic diameter of the commercial fertilizers.

Fertilizer	Company	Hydrodynamic diameter (nm)	Standard Deviation
Products containing copper			
A	1	177.8	13.0
B	2	457.7	95.0
C	3	308.9	57.2
Average		314.8	55.0
Products containing manganese			
D	1	340.6	112.3
E	2	365.5	123.1
F	3	359.1	107.6
G	4	423.0	134.4
H	5	400.3	103.2
Average		377.7	184.4
Products containing zinc			
I	1	481.1	118.2
J	2	385.7	99.1
K	3	415.7	108.2
L	4	402.2	115.8
M	5	492.1	96.1
Average		435.4	107.5

tively (Table 2). The concentration at 100 mg L^{-1} showed that these fertilizers did not follow the usual specification of nanomaterials given by some authors, that is, between 1 and 100 nm (Ikhmayies, 2014), which indicates these fertilizers cannot be classified as nanofertilizers or nanomaterials. The smallest particle size was observed in fertilizer A (177.9 nm); nevertheless, it was not sufficient for its classification as a nanofertilizer or nanomaterial.

The foliar absorption process may occur through i) pores in the leaf cuticle, ii) cracks or cuticular imperfections, and iii) stomata and trichomes (Fernández et al., 2013). However, the nanoparticle absorption mechanisms in plants are not fully understood. Some authors have reported that entire nanoparticles were found in plant tissues (Corredor et al., 2009). On the other hand, other studies have shown that nutrients should be ionized before absorption (Li et al., 2016).

Concerning absorption of entire particles, the exclusion limit of cuticular pores is usually lower than 0.5 nm (Schönherr, 2006); however, it can reach 2.4 nm in plants with larger pores (Eichert and Goldbach, 2008), making cuticular penetration of entire particles of any of the evaluated commercial fertilizers unlikely. Another possibility for absorption is the stomata pathway (Eichert et al., 1998). Although the mechanism underlying the uptake nutrient by the stomata pathway is not completely understood (Fernandez et al., 2015), current knowledge indicates the capacity of nutrient uptake through the stomata because of its large size exclusion limit above 10 nm (Eichert et al., 2008; Eichert and Goldbach, 2008). Nevertheless, this process efficacy should be low for the CS evaluated here, and as far as it's known, it was observed only in uptake for nanoparticles of 43 nm and none for particles of 1 µm (Eichert et al., 2008).

Regarding the absorption of ions, even insoluble sources present a small fraction of ions in solution and this fraction depend on their solubility product constant (K_{sp}). The lower the K_{sp} of a material, the lower its solubility. In the framework of the present study, the most common insoluble sources of micronutrients of low K_{sp} are ZnO ($K_{sp} = 3.86 \times 10^{-10}$), $ZnCO_3$ ($K_{sp} = 1.46 \times 10^{-10}$), $MnCO_3$ ($K_{sp} = 2.24 \times 10^{-11}$), CuO ($K_{sp} = 2 \times 10^{-15}$), Cu_2O ($K_{sp} = 2.2 \times 10^{-20}$), and $Cu_2(OH)_3Cl$ ($K_{sp} = 1.44 \times 10^{-33}$). Thus, in bulk conditions, insoluble materials do not seem effective sources of micronutrient foliar supply.

Zeta potential

All zeta potential values were negative (Table 3). In most cases, the values ranged from –20 to –30 mV. Specifically, values were close to –20 mV for fertilizers containing Mn and Zn and approximately –30 mV for fertilizers containing Cu. Zeta potential values close to –30 mV exhibit the possibility to aggregate during the solution preparation and foliar application itself (Heurtault et al., 2003). The aggregation of particles was apparent even in the diluted samples, and this aggregation further hinder the penetration of nutrients through cuticular pores or even stomata.

Scanning Electron Microscopy

The results of the SEM analysis showed that the particle shapes varied broadly among the products. Fertilizers containing Cu presented spherical or cylindrical forms (Figure 1), while the Mn fertilizers demonstrated larger aggregates with lamellar structures (Figure 2). The shape of the particles was more homogeneous for Zn fertilizers, close to parallelepipeds or cylinders (Figure 3). Differences in particle shapes observed among the products may be related to the mineral used as

Table 3 – Zeta potential of the commercial fertilizers.

Product	Company	Zeta Potential (mV)	Standard Deviation
Products containing copper			
A	1	–28.2	5.0
B	2	–32.7	5.6
C	3	–32.8	6.8
Average		–31.2	5.8
Products containing manganese			
D	1	–24.0	4.0
E	2	–22.5	4.4
F	3	–19.0	4.9
G	4	–22.8	4.0
H	5	–22.5	5.0
Average		22.2	4.5
Products containing zinc			
I	1	–15.6	4.7
J	2	–19.9	3.9
K	3	–21.7	6.1
L	4	–23.8	3.8
M	5	–23.8	4.0
Average		–21.0	4.5

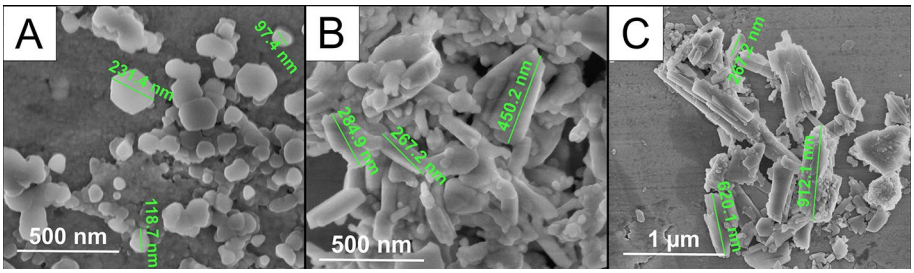

Figure 1 – Scanning electron microscope images of fertilizers containing CuO. A, B, and C correspond to the fertilizers used in Tables 1 to 4.

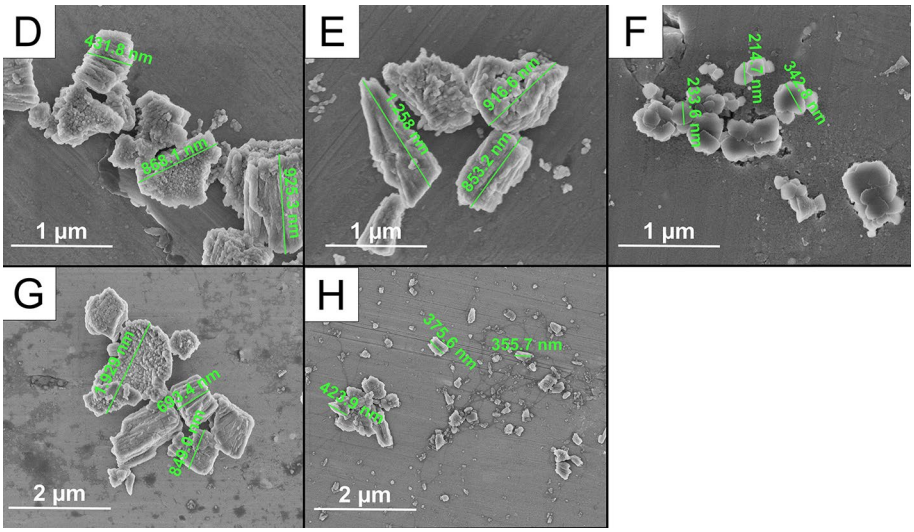

Figure 2 – Scanning electron microscope images of fertilizers containing $MnCO_3$. D, E, F, G, and H correspond to the fertilizers used in Tables 1 to 4.

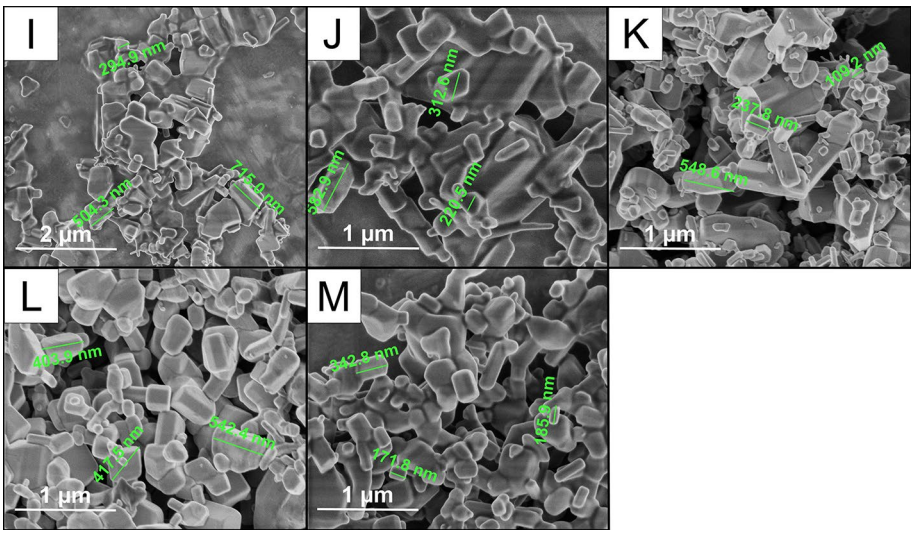

Figure 3 – Scanning electron microscope images of fertilizers containing ZnO. I, J, K, L, and M correspond to the fertilizers used in Tables 1 to 4.

raw materials to produce the fertilizer, changes during processing, and degrees of hardness during the milling process.

All fertilizers presented a high heterogeneity in terms of particle size. For Cu fertilizers, the smallest particles were observed in A, and most were smaller than 200 nm, while B and C presented conglomerates with larger sizes, that is, between 270 and 950 nm (Figure 1). Mn fertilizers showed particles between 200 and 400 nm in F and H, which was different from the others (D, E and G) in which the intense aggregation rate built larger structural units with diameters between 500 and 1300 nm (Figure 2). The highest particle size heterogeneity was observed in all Zn fertilizers, which ranged from tiny particles smaller than 100 nm to larger ones close to 500 nm (Figure 3).

Differently from the DLS technique, which evaluates the behavior of a compound possibly formed by the aggregation of several particles, the SEM technique allows individual visualization of the particles, even those aggregated to other structures. This makes these analyses complementary since DLS indicates the behavior of the structure in the dispersion at the moment of the analysis, while SEM exhibits particles that could be dispersed before absorption by the leaves.

Concentration of potentially toxic elements

No sample presented concentrations of arsenic, cadmium, lead, chromium, and mercury higher than the thresholds set by the Brazilian legislation (MAPA, 2006) (Table 4). These results are in accordance with the in-

Table 4 – Concentrations of potentially toxic elements in the commercial fertilizers.

Fertilizer	Company	Arsenic	Cadmium	Lead	Chromium	Mercury	Selenium
		mg kg^{-1}					
		Products containing copper					
A	1	1	0.5	37.3	1.3	1	5.1
B	2	3.5	0.4	8.7	12.2	1	9.7
C	3	6.2	0.4	51.8	2.7	1	7.8
		Products containing manganese					
D	1	4.8	3.7	36.8	39.7	1	154.3
E	2	7.2	0.7	35.1	42.1	1	175
F	3	6.1	0.4	22.9	39.8	1	155
G	4	12	2.9	46.2	37.7	1	185
H	5	9	1.9	36.8	42.3	1	172
		Products containing zinc					
I	1	1	0.6	3.5	0.3	1	2.6
J	2	5.6	0.9	7.2	0.8	1	2.9
K	3	1	1.6	6.2	0.4	1	1
L	4	2	2.8	8.3	0.4	1	5.7
M	5	1	1.2	3.9	0.3	1	4.3
		mg kg^{-1} per percentage point of micronutrient					
Maximum allowed content*	-	500	15	750	500	10	-

*Maximum allowed content according to NI No. 27 of MAPA (2006).

formation provided by the companies and demonstrates that the raw materials used to produce these fertilizers, as well as the production process, meet the quality standards suggested by the regulation.

Conclusion

The average hydrodynamic diameter of the CSs with Cu, Mn, and Zn were 315 ± 55, 378 ± 184 and 435 ± 107 nm, respectively, revealing that these fertilizers do not fit in the nanomaterial or nanofertilizer specifications (< 100 nm). The zeta potential of the CSs varied from –20 to –30 mV, suggesting possible aggregation of the particles during handling and application. The scanning electron microscope images indicated a large variety in sizes and shapes of particles. Only Zn fertilizers presented some particle sizes smaller than 100 nm.

The CSs presented concentrations of arsenic, cadmium, lead, chromium, and mercury within the limits allowed by the Brazilian legislation. More studies are required to quantify effectively the potential absorption of these fertilizers by plant leaves to provide support to the current Brazilian legislation of fertilizers.

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Authors' Contributions

Conceptualization: Otto, R. Data acquisition: Gomes, M.H.F.; Migliavacca, R.A. Data analysis: Gomes, M.H.F.; Otto, R.; Migliavacca, R.A.; Carvalho, H.W.P. Design of methodology: Gomes, M.H.F.; Carvalho, H.W.P. Writing and editing: Gomes, M.H.F.; Otto, R.; Migliavacca, R.A.; Carvalho, H.W.P.

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