

# Assessing the Content of Micronutrients in Soils and Sugarcane in Different Pedogeological Contexts of Northeastern Brazil

Rita de Cássia Ferreira da Silva<sup>(1)</sup> , Fernando Bruno Vieira da Silva<sup>(1)</sup> , Caroline Miranda Biondi<sup>(1)</sup> , Clístenes Williams Araújo do Nascimento<sup>(1)\*</sup> , and Emídio Cantídio Almeida de Oliveira<sup>(1)</sup> 

<sup>(1)</sup> Universidade Federal Rural de Pernambuco, Departamento de Agronomia, Recife, Pernambuco, Brasil.

**ABSTRACT:** Micronutrient research for sugarcane in northeastern Brazil is scarce and most works on this issue date back to the 70's and 80's. The objectives of this study were to assess the available and reserve pools of Fe, Mn, Cu, and Zn in soils cultivated with sugarcane under three geological contexts in northeastern Brazil as well as to diagnose the micronutrient nutritional status of sugarcane grown on these areas in order to identify pedogeological conditions in which micronutrient deficiencies are likely. Results showed that the soils cultivated with sugarcane in the states of Paraíba and Pernambuco posed available and reserve contents of micronutrients related to the parent materials and soil textural classes. The reserve contents of Fe, Mn, Zn, and Cu in all the soil samples analyzed were below the background values established for the region, which indicates a continuous exportation of micronutrients through cultivation. The mean and median contents of Mn, Zn, and Cu in diagnostic leaves of sugarcane were below their respective nutritional optimum ranges recommended to Brazil while Fe contents achieved the crop nutritional requirement. This is the first time such an approach based on pedogeological contexts is used to study the available and reserve pools of micronutrients in soils of Northeast Brazil.

**Keywords:** soil fertility, trace elements, plant nutrition, critical levels.

**\* Corresponding author:**

E-mail: cwanascimento@hotmail.com

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## INTRODUCTION

Sugarcane is one of Brazil's primary commodities. The country is the world's largest producer of sugarcane and possesses 9.8 million hectares used for this crop (MAPA, 2016; IBGE, 2017). The Northeastern Brazil produced 41 million tons of sugarcane in the 2017/2018 harvest (Conab, 2017) with producing areas mainly concentrated in the states of Alagoas, Pernambuco, and Paraíba (Unica, 2017). The cultivation of sugarcane in these states is limited to the coastal zone, which is often characterized by sandy soils with low natural fertility, a hot climate, and high rainfall. The average yield of sugarcane in this region is low ( $50 \text{ t ha}^{-1}$ ) based on both the Brazilian average of  $70 \text{ t ha}^{-1}$  (Conab, 2017) and the genetic potential of the varieties available.

Micronutrient fertilizer management has been noted one of the main causes for the low sugarcane yield in the region (Oliveira, 2008; Almeida Júnior et al., 2011; Silva, 2011; Santos, 2012). Consistent yield increases due to micronutrient application have been reported in the region, especially in sandy coastal plain soils (Fernandes, 1972; Sultanum, 1974). For instance, Marinho and Albuquerque (1981) reported stalk yield increases over  $40 \text{ Mg ha}^{-1}$  as a response to Cu addition to soils. Studies to other Brazilian regions have shown significant increase in sugarcane yield with the application of micronutrients (Malavolta, 1990; Mellis et al., 2016) whereas others showed no response to micronutrient fertilization (Farias et al., 2009; Franco et al., 2011).

The cationic micronutrients Fe, Mn, Zn, and Cu can be divided among pools in soil, according to conceptual forms, i.e., ion exchangeable, adsorbed, organic-bound, hydrous oxide segment, and lattice component micronutrients (Shuman, 1991; Kabata Pendias, 2011). They can also be grouped in pairs for discussion, since Fe and Mn are the ones displaying the most oxidation-reduction transition in soils while Zn and Cu are not prone to reduction in normal soil conditions (Shuman, 1991). The plant availability of micronutrients in soil corresponds to the fraction present as exchangeable ion in equilibrium with the solution plus the fraction in the soil solution. On the other hand, the micronutrients considered to be soil reserve are the total minus those present in the crystalline structure of silicate minerals (Alloway, 2013). The micronutrient reserve content may contribute over the short-to-medium term to soil availability and may be a predictor of plant nutrition.

Micronutrient transfer from soils to crops, associated with low natural fertility and the absence of corrective fertilization can lead to soil depletion and hence plant deficiency (Silva et al., 2009). Other factors such as soil pH (Fonseca et al., 2005; Pestana et al., 2014), phosphate overfertilization (Scalco et al., 2014), soil organic matter (SOM) content (Pigozzo et al., 2008), oxi-reduction reactions (Costa, 2004), and soil texture (Pegoraro et al., 2006) may also contribute to decrease the micronutrient availability in soil, leading to diminished crop yields. In this scenario, the assessment of the micronutrient content in both soils and in plants is important for the adoption of fertilization management that enables increases in production (Chaves and Corrêa, 2003).

In addition, micronutrient contents are influenced by the soil parent material and pedogenesis processes; therefore, it is likely that geological context correlates well with micronutrient contents in soils. Indeed, a soil zonation based on geological contexts could serve as a basis for micronutrient fertilizer recommendations by mapping areas where micronutrient deficiency can occur and/or crop response to fertilization is expected.

Micronutrient research for sugarcane in Brazil is still scarce and inconclusive (Mellis et al., 2016), especially in Northeast Brazil where most works on micronutrients date back to the 70's and 80's (Fernandes, 1972; Sultanum, 1974; Marinho and Albuquerque, 1981). The objectives of this study were (i) to assess the available and reserve pools of Fe, Mn, Cu, and Zn in soils cultivated with sugarcane under three geological contexts in Northeastern Brazil; (ii) to diagnose the micronutrient nutritional status of sugarcane grown on these areas through foliar analyses; and (iii) to identify pedogeological conditions in which micronutrient

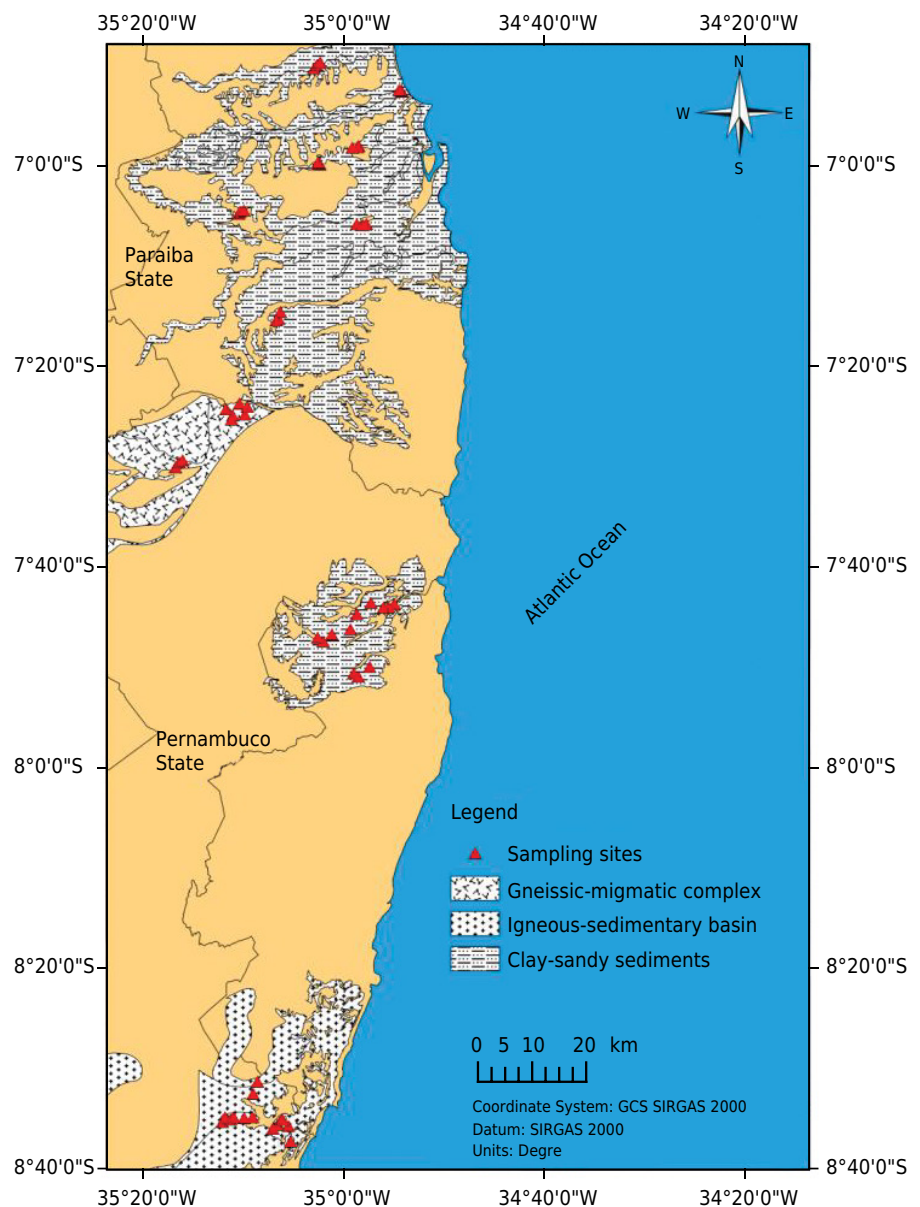
deficiencies are likely in order to zone areas prone to micronutrient-containing fertilizers responses. To our knowledge, this is the first time such an approach is used to study the available and reserve pools of micronutrients in soils of Northeast Brazil.

## MATERIALS AND METHODS

### Area of study and soil and plant sampling

The study was carried out in the sugarcane-producing regions of Pernambuco and Paraíba states, Northeast Brazil. The sampling sites were pre-defined according to three geological contexts (Figure 1): igneous-sedimentary basin (ISB,  $n = 14$ ); clay-sandy sediments (CSS,  $n = 30$ ); and gneissic-migmatite complex (GMC,  $n = 12$ ). The precipitation and average annual temperature in the region are 1,600 mm and 24 °C, respectively (Inmet, 2016). Ultisol (*Argissolo*) is the predominant soil order in the region (Embrapa, 2000).

Fifty-six soil samples were collected from sugarcane fields at the layers of 0.00-0.20 and 0.20-0.40 m. At each sampling site, ten samples were collected from both layers



**Figure 1.** Sampling sites and pedogeological contexts in sugarcane growing areas in the states of Pernambuco and Paraíba, Northeastern Brazil.

to form the composite samples. Ten diagnostic leaves (+3) from five-month-old plants were collected in each area to form a composite sample. The soil samples were dried at room temperature, macerated and sieved (<2.0 mm). The leaves were washed with tap water and then with distilled water; the middle third of the leaves were separated (without the central vein) and used for analysis. The plant material was dried at 65 °C in an oven until a constant weight was achieved and then ground in a knife mill.

### Soil and plant analysis

Soil samples were analyzed for pH(H<sub>2</sub>O) at a ratio of 1:2.5 soil:solution, organic carbon content, K<sup>+</sup> exchangeable content extracted by Mehlich-1, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and Al<sup>3+</sup> exchangeable contents assessed by KCl 1 mol L<sup>-1</sup>, potential acidity (H+Al) as well as sand, silt, and clay contents by pipette method (Donagema et al., 2011). Soil organic matter (SOM) content was estimated as a function of the carbon content, whereas cation exchange capacity (CEC) was estimated by summing up Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and H<sup>+</sup> + Al<sup>3+</sup>.

The available content of Fe, Mn, Cu, and Zn in the soil samples was extracted with Mehlich-1. The reserve content was extracted using the 3051A method (USEPA, 2007). The soil subsamples were macerated in an agate mortar and pestle and sieved through a 0.15-mm aperture mesh. One gram of each soil sample was digested in a microwave oven at 175 °C for 4 min and 30 s with an acid solution of HNO<sub>3</sub>+HCl (3:1). A plant sample of 0.5 g was digested in a microwave oven at 180 °C for 10 min with the solution of HNO<sub>3</sub>+H<sub>2</sub>O<sub>2</sub> (3:1) according to the modified 3050b methodology (USEPA, 1996). After digestion, both the soil and plant extracts were filtered (Ø < 2.0 µm) to 25 mL certified flasks and stored at 4 °C for analysis.

### Determination of micronutrients and analytical quality control

The Fe, Mn, Cu, and Zn contents in soil and plant extracts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer 7000 DV). For purposes of analytical quality control, blank and reference materials from NIST (National Institute of Standards and Technology) with Fe, Mn, Cu, and Zn certified values for soil (SRM 2709 San Joaquin Soil) and plant (SRM 1570a Trace Element in Spinach) were used. The micronutrient recoveries ranged from 70 to 100 % for the soil reference material and from 70 to 98 % for the plant reference sample. All analyses were performed in duplicate.

### Statistical analysis

Descriptive statistics (mean, median, minimum, maximum, standard deviation, standard error of the mean, and coefficient of variation) were used to describe the data. The normality of the data was verified by the Shapiro-Wilk test (p < 0.05); when necessary, a logarithmic transformation was performed on the data. Pearson's linear correlation analysis (p < 0.05) was used to study the relationship between micronutrient contents in plants and soils and some soil properties (pH, SOM, and clay). Factor analysis (FA) was applied in the dataset with the purpose of extracting the factors that best explain the variability of Fe, Mn, Cu, and Zn contents in soils. Prior to analysis, the dataset was normalized and standardized. Rotation Varimax was used in order to guarantee the orthogonality between factors. The grouping of variables into factors was defined by the criterion  $r \geq |0.5|$ . Statistical procedures were performed using STATISTICA software (version 10).

## RESULTS

### Descriptive statistics

Among the soil chemical properties, only the SOM content differed between layers, being the highest levels of SOM found in the 0.00-0.20 m layer. The soil pH(H<sub>2</sub>O) is moderately acidic at both layers. Soils presented low values of exchangeable bases

and CEC (Table 1). Regarding soil texture, the surface layer presented higher clay content than the subsurface one while silt was higher in the subsurface layer; the average sand content was similar between the two layers. The surface soil samples were classified as loam (54 %), sandy loam (30 %), and clay loam (15 %). Subsurface samples presented 41, 30, and 29 % of the samples grouped into loam, sandy loam, and clay loam textures, respectively.

**Table 1.** Descriptive statistic for soil chemical and physical properties and micronutrient contents in soil

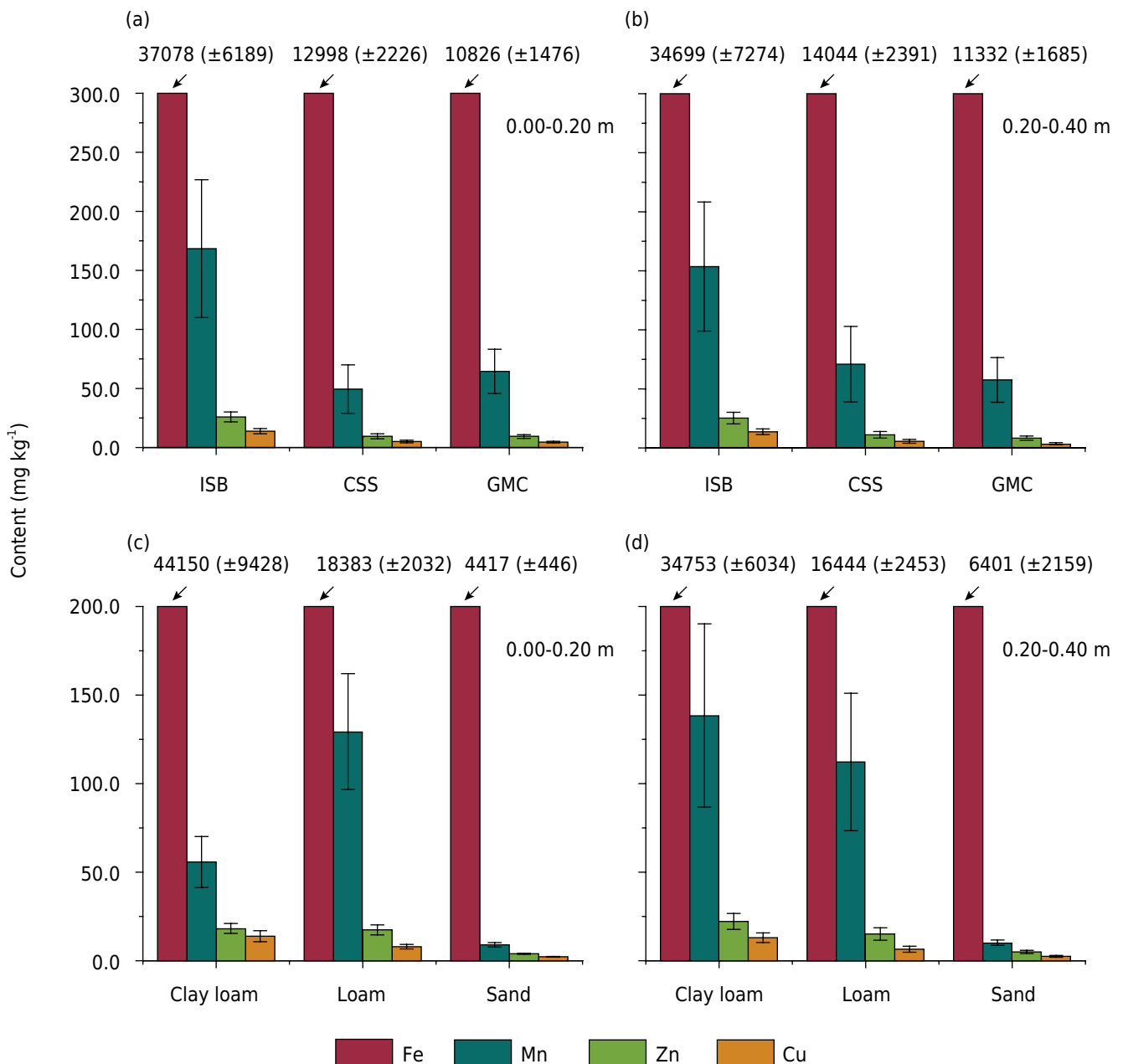
Property	Layer 0.00-0.20 m						
	Mean	Median	Min.	Max.	±SD	CV	S-W test
						%	
pH(H <sub>2</sub> O)	5.4	5.5	4.3	6.6	0.5	9.9	0.42
SOC (g kg <sup>-1</sup> )	12.6	10.3	3.9	34.1	6.5	51.6	0.00
SOM (g kg <sup>-1</sup> )	25.1	20.7	7.9	68.1	13.0	51.6	0.00
BS (cmol <sub>c</sub> dm <sup>-3</sup> )	4.8	4.0	0.9	17.8	3.1	64.9	0.00
H+Al (cmol <sub>c</sub> dm <sup>-3</sup> )	3.6	3.0	0.8	12.8	2.2	61.2	0.00
CEC (cmol <sub>c</sub> dm <sup>-3</sup> )	8.3	7.1	3.4	21.5	4.0	48.0	0.00
Clay (g kg <sup>-1</sup> )	200.1	176.7	19.9	450.4	128.8	64.4	0.01
Silt (g kg <sup>-1</sup> )	139.8	94.4	8.0	491.8	133.0	95.1	0.00
Sand (g kg <sup>-1</sup> )	660.1	693.1	138.6	966.0	228.7	34.6	0.00
Fe <sub>available</sub> (mg kg <sup>-1</sup> )	66.6	45.9	12.2	270.1	56.0	84.1	0.00
Mn <sub>available</sub> (mg kg <sup>-1</sup> )	12.2	6.6	0.7	64.3	14.4	118.4	0.00
Zn <sub>available</sub> (mg kg <sup>-1</sup> )	2.3	2.0	0.6	6.7	1.3	56.6	0.00
Cu <sub>available</sub> (mg kg <sup>-1</sup> )	1.1	0.9	0.1	3.5	0.8	71.7	0.00
Fe <sub>reserve</sub> (mg kg <sup>-1</sup> )	18,552.8	12,400.3	394.0	85,317.8	18,099.2	97.6	0.00
Mn <sub>reserve</sub> (mg kg <sup>-1</sup> )	82.5	21.9	2.3	659.4	146.0	177.0	0.00
Zn <sub>reserve</sub> (mg kg <sup>-1</sup> )	13.6	7.6	2.0	51.1	13.5	99.7	0.00
Cu <sub>reserve</sub> (mg kg <sup>-1</sup> )	7.1	4.4	0.9	26.7	7.2	100.4	0.00
	Layer 0.20-0.40 m						
pH(H <sub>2</sub> O)	5.4	5.5	3.4	6.5	0.6	11.5	0.10
SOC (g kg <sup>-1</sup> )	9.8	8.7	2.8	25.0	5.1	51.6	0.00
SOM (g kg <sup>-1</sup> )	19.7	17.4	5.5	54.3	10.4	53.0	0.00
BS (cmol <sub>c</sub> dm <sup>-3</sup> )	4.5	2.9	0.5	26.4	5.3	115.5	0.00
H+Al (cmol <sub>c</sub> dm <sup>-3</sup> )	3.3	2.9	0.9	11.1	2.0	61.6	0.00
CEC (cmol <sub>c</sub> dm <sup>-3</sup> )	7.8	6.2	2.3	29.3	5.8	73.7	0.00
Clay (g kg <sup>-1</sup> )	139.4	91.0	0.0	489.2	132.8	95.3	0.00
Silt (g kg <sup>-1</sup> )	236.6	237.6	8.0	567.8	151.7	64.1	0.02
Sand (g kg <sup>-1</sup> )	624.0	667.3	155.1	952.1	246.2	39.5	0.00
Fe <sub>available</sub> (mg kg <sup>-1</sup> )	69.1	52.5	6.1	244.5	49.9	72.3	0.00
Mn <sub>available</sub> (mg kg <sup>-1</sup> )	9.7	3.0	0.4	81.7	15.6	160.7	0.00
Zn <sub>available</sub> (mg kg <sup>-1</sup> )	1.2	1.1	0.3	4.0	0.7	58.1	0.00
Cu <sub>available</sub> (mg kg <sup>-1</sup> )	0.8	0.6	0.1	3.9	0.8	91.0	0.00
Fe <sub>reserve</sub> (mg kg <sup>-1</sup> )	18,627.1	11,679.0	260.5	86,792.8	19,005.8	102.0	0.00
Mn <sub>reserve</sub> (mg kg <sup>-1</sup> )	88.8	16.3	3.3	653.7	168.5	189.8	0.00
Zn <sub>reserve</sub> (mg kg <sup>-1</sup> )	14.1	7.4	0.9	58.9	15.9	113.0	0.00
Cu <sub>reserve</sub> (mg kg <sup>-1</sup> )	7.2	3.1	0.7	31.9	8.6	120.4	0.00

pH in water at a ratio of 1:2.5 soil:solution; sand, silt, and clay contents determined by pipette method (Donagema et al., 2011); metal available contents extracted by Melich-1; metal reserve contents extracted by 3051A method; SOC: soil organic carbon determined according to Walkley-Black (1934); SOM: soil organic matter; BS: base saturation; CEC: cation exchange capacity; Min.: minimum; Max. maximum; SD: standard deviation; CV: cumulative variance. S-W test: Shapiro-Wilk test.

The mean available and reserve micronutrient contents in soils followed the sequence Fe>Mn>Zn>Cu, regardless layer (Table 1). The average micronutrient available contents in the surface soil were higher than those in the subsurface while reserve content was similar between layers. Taking into account the micronutrient availability ranges proposed by Pereira et al. (2001), 45 % of the surface soil samples posed low availability for Cu (<0.8 mg kg<sup>-1</sup>) and for Mn (<6.0 mg kg<sup>-1</sup>); on the other hand, only 7 and 4 % of the soil surface samples lie into the low available content ranges for Zn (<1.0 mg kg<sup>-1</sup>) and Fe (<19.0 mg kg<sup>-1</sup>), respectively. We found a decrease in Mn, Zn, and Cu available contents in the 0.20-0.40 m soil layer; therefore, 66, 61, and 43 % of the soil samples contents for these micronutrients, respectively, could be regarded as of low availability.

### Micronutrient content in soils as a function of pedogeological contexts

We observed that the micronutrient reserves in soil were the highest in the ISB geological context (Figures 2a and 2b). The average contents of Fe, Mn, and Cu in soils sampled



**Figure 2.** Micronutrient reserve contents and standard deviation in 0.00-0.20 and 0.20-0.40 m soil layers in different pedogeological contexts (a and b) and with different textural classes (c and d). ISB: igneous-sedimentary basin; CSS: clay-sandy sediments; GMC: gneissic-migmatite complex.



in the ISB exceeded the background content of these elements in soils of the region, i.e., 3.000, 106.5, and 8.5 mg kg<sup>-1</sup>, respectively (Biondi et al., 2011). The Fe and Mn reserve contents in the ISB were, on average, 192 and 159 % higher than those of soils in the other geological contexts studied. The high micronutrient contents in ISB soils can be explained by the region's lithology, which comprises basic rocks (basalt and trachyandesite) with abundant iron-magnesium minerals. Soils originating from such parent materials generally present higher contents of clay, which can contribute to the adsorption/retention of cationic micronutrients in soil (Aharonov-Nadborny et al., 2018; Araújo et al., 2018). The Fe, Mn, Cu, and Zn cations present in the soil solution can bind to the negative charges of clay minerals by external sphere (ion exchange) and/or internal sphere (specific adsorption) bonds. Iron and Al oxi-hydroxides play an important role in the process of micronutrient specific adsorption, with implications for the mobility and plant availability of these elements in soil (Kabata Pendias, 2011).

The micronutrient reserve contents were clearly related to soil texture (Figures 2c and 2d). The sand texture soils posed the lowest Fe, Mn, Zn, and Cu contents owing to the general micronutrient poorness of the parent material (Biondi et al., 2011). For instance, the average Fe content in these soils was 4-10 times lower than with clay loam and loam texture soils, for both soil layers; similar behavior was found to Zn and Cu contents. However, for Mn at the 0.00-0.20 m layer (Figure 2c), the average largest content was observed for soils in the loam textural class.

The availability of micronutrients assessed by Mehlich-1 followed the trend found to the reserve contents regarding either the geological context or the soil textural class (Figure 3); Fe and Mn presented the highest absolute contents in the loam texture soils but with no statistical significance compared to the clay loam soils. These data support the hypothesis that geological context can be a good predictor of Fe, Mn, Cu, and Zn availability in the soils of the study area. The mean Fe and Zn contents were higher than the critical levels of these elements suggested by Pereira et al. (2001) for sugarcane: 19.0 and 1.0 mg kg<sup>-1</sup>, respectively. Regarding Mn and Cu, below-critical contents (6.0 and 0.8 mg kg<sup>-1</sup>, respectively) were observed in soils of the geological context CSS (Figures 3a, 3b, 3c, and 3d). Therefore, Fe and Mn deficiencies in the soils of the studied area are less likely to occur than those of Mn and Cu.

## DISCUSSION

The average reserve contents of micronutrients were lower than the natural levels previously reported for soils from the study area: 3.000, 106.5, 26.5, and 8.5 mg kg<sup>-1</sup> for Fe, Mn, Zn, and Cu, respectively, in Pernambuco State (Biondi et al., 2011); and 14.310, 268.3, 16.9, 10.2 mg kg<sup>-1</sup> for Fe, Mn, Zn, and Cu, respectively, in soil of Paraíba State (Almeida Júnior et al., 2016). The maximum contents of Cu and Zn found in the present work were lower than the soil quality guidelines to Brazilian agricultural soils, the so-called prevention values, of 60.0 and 300.0 mg kg<sup>-1</sup>, respectively, established by the National Environment Council (Conama, 2009). Contents of Fe and Mn in soil are not regulated for this resolution.

The factorial analysis yielded four factors that explained 78 % of the total data variance (Table 2). Factor 1 (F1) accounted for 44.5 % of the total variance and displayed significant correlations between available and reserve contents of Mn and Cu, demonstrating that the reserve pool may potentially contribute to the availability of these elements over the short-to-medium term. The grouping of the silt fraction and the micronutrient reserve contents into F1 suggests that ferromagnesian minerals in this fraction are responsible for replenishing of Fe, Mn, Zn, and Cu into soil solution; on the contrary, no correlation and inverse correlation were found between the micronutrient reserve contents and clay and sand fractions, respectively. Although the pattern and magnitude of micronutrients

**Table 2.** Total explained and rotated factorial matrix for micronutrients in soil cultivated with sugarcane

Variables	Factor 1	Factor 2	Factor 3	Factor 4
pH(H <sub>2</sub> O)	0.28	-0.19	0.23	<b>-0.64</b>
SOM	0.02	<b>0.90</b>	0.13	0.02
CEC	<b>0.59</b>	<b>0.51</b>	0.07	0.00
P	-0.01	-0.39	<b>0.72</b>	-0.06
Sand	<b>-0.63</b>	<b>-0.70</b>	0.17	-0.11
Silt	<b>0.86</b>	0.32	-0.11	0.14
Clay	0.26	<b>0.88</b>	-0.18	0.06
Fe <sub>(avail.)</sub>	0.17	-0.03	-0.05	<b>0.80</b>
Mn <sub>(avail.)</sub>	<b>0.83</b>	-0.05	-0.01	-0.07
Zn <sub>(avail.)</sub>	-0.09	0.10	<b>0.88</b>	-0.01
Cu <sub>(avail.)</sub>	<b>0.52</b>	0.03	0.40	<b>0.60</b>
Fe <sub>(res.)</sub>	<b>0.54</b>	<b>0.61</b>	-0.03	-0.15
Mn <sub>(res.)</sub>	<b>0.93</b>	0.01	-0.05	0.02
Zn <sub>(res.)</sub>	<b>0.94</b>	0.22	0.00	0.11
Cu <sub>(res.)</sub>	<b>0.85</b>	0.37	0.07	0.05
Eigenvalues	6.69	2.14	1.45	1.42
%TV	44.58	14.28	9.66	9.48
%CV	44.58	58.86	68.52	78.01

SOM: soil organic matter; CEC: cation exchange capacity; avail.: available contents in soil; res.: reserve contents in soil; TV: total variance; CV: cumulative variance. Values in bold and italic represent variable to each factor.

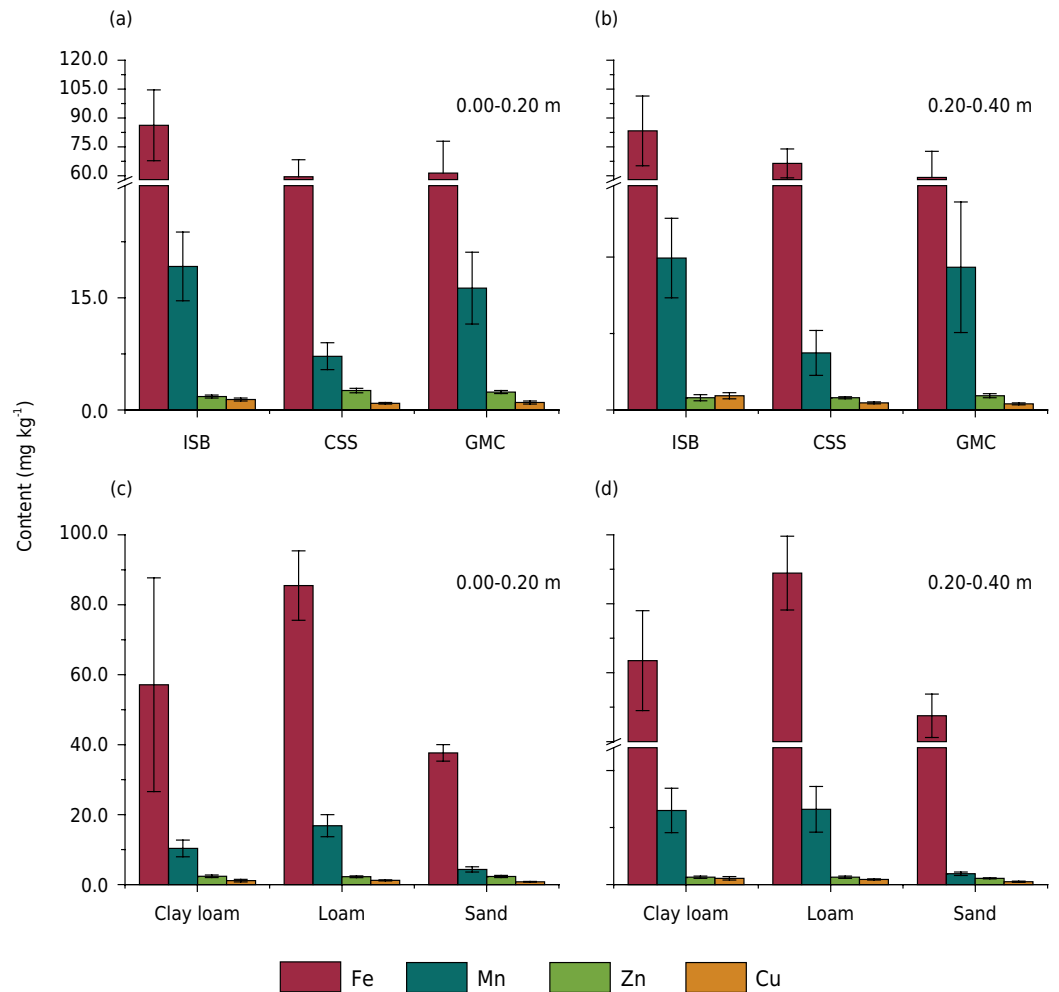
partitioning among soil fractions is complex, silt fractions generally contain higher levels of micronutrients than do sands (Dudas and Pawluk, 1980).

Factor 2 (F2) grouped together SOM (0.90) and clay (0.88) contents, Fe reserve content (0.61), and cation exchange capacity (0.51) (Table 2). The fact that SOM, clay content, and CEC load together is understood by the close relationship between soil organic and mineral colloids and electrostatic charges. Additionally, the formation of clay-organic complexes protects SOM against microbial degradation (Zinn et al., 2005). Several mechanisms are involved in such a complexation, including cationic bridges and SOM coordination with oxy-hydroxides.

Cationic bridges promote electrostatic bonding between clay minerals and SOM reactive groups, which are both negatively charged under the soil pH range found in our study. The free Fe<sup>3+</sup> in solution can play the role of bridging clay and SOM as the median pH of the soils (5.5) strongly decrease the Al<sup>3+</sup> activity. Other mechanism of interaction between SOM and clay minerals is the carboxylic and phenolic groups directed bonding on the surface of positively charged iron oxides. The oxygen-containing functional groups of the SOM such as carboxylic and phenolic can enter in coordination through covalent bonds with the Fe of the oxy-hydroxide structure (Silva and Mendonça, 2007). The Fe taking part in the clay-organic complexes has low solubility; this is probably the reason there was no correlation between the reserve and available contents of Fe in the soils (Table 2).

Factor 3 (F3) shows a significant correlation between the available contents of P and Zn in soils (Table 2). It is likely that P and Zn have common sources to soils such as phosphate and organic fertilizers (Carvalho et al., 2012), which could partially explain the correlation. Furthermore, the large amount of P regularly applied to the soils of the





**Figure 3.** Micronutrient available contents and standard deviation in 0.00-0.20 and 0.20-0.40 m soil layers in different pedogeological contexts (a and b) and with different textural classes (c and d). ISB: igneous-sedimentary basin; CSS: clay-sandy sediments; GMC: gneissic-migmatite complex.

study area can precipitate Zn, forming  $Zn_3(PO_4)_2$  (De Mune et al., 2011). Under certain circumstances, P fertilization can even induce Zn deficiency, especially in Zn-poor soils (Büll et al., 2008; Carneiro et al., 2008). For instance, the loam sand soils of the CSS geology had the lowest average Zn available contents (7.2 and 3.2 mg kg<sup>-1</sup>, respectively) and large rates of phosphate fertilizers are typically applied.

It is well known that an increase in soil pH decreases the solubility of the cationic micronutrients in soil solution (Shuman, 1991; Nascimento et al., 2002; Borges and Coutinho, 2004). The Factor 4 (F4) displayed a relationship between pH and the available contents of Fe and Cu (Table 2), but no correlation was found between pH and Mn and Cu availability. Indeed, Fe solubility decreases approximately 1.000-fold for each unit of pH increase in the soil over the pH range of 4 to 9 (Abreu et al., 2007). The reduction in Fe availability is owing to the formation of stable, low solubility  $Fe(OH)_3$  complexes (Oorts, 2013).

In addition to hydroxide precipitation, pH can influence the Cu complexation by SOM. Most of the  $Cu^{2+}$  in soil solution is complexed to dissolved organic matter, such as humic and fulvic acids (Ponizovsky et al., 2006; Amery et al., 2008). The  $Cu^{2+}$  ions form stable complexes of low solubility with the  $-NH_2$  and  $-SH$  groups of the organic acids, and the binding energy of this reaction increases with increasing pH (Yonebayashi et al., 1994; Oorts, 2013), resulting in decreased plant availability.

The descriptive statistics for foliar diagnosis data are showed in table 3. Iron contents in 3+ leaves had the greatest variability among the studied micronutrients, but the mean and median values of Fe are within the sufficiency range for sugarcane according to Malavolta (2006) and McCray and Mylavarapu (2010). On the other hand, the mean and median contents of Mn, Zn, and Cu were below their respective optimum ranges for sugarcane grown in Brazil (Malavolta, 2006). Zinc mean content (Figure 3) was also lower than the critical levels adopted in South Africa, Mauritius, Guyana, and United States but close to the critical level used in Australia (Table 4). The median values for Cu indicate that most sugarcane plantings posed Cu content in leaves above the critical level for all countries listed in table 4 and within the optimum range of foliar Cu for sugarcane grown in Florida, USA (McCray and Mylavarapu, 2010). On the contrary, Mn contents in leaves lower than the optimum range indicated to Brazil were recorded for the majority of the plantings.

Taking into account the average values of micronutrients found in leaves of high productivity sugarcane fields in Brazil reported by Reis Júnior and Monnerat (2002), which were 74.4 (Mn), 14.3 (Zn) and 5 (Cu) mg kg<sup>-1</sup>, most of the sugarcane leaves analyzed in our study presented Mn and Zn below such a high productivity critical level. Furthermore, the range of leaf micronutrient critical values for diagnostic purposes in different countries (Table 4) suggests that some sugarcane fields on the study area could benefit from Zn, Cu, and Mn fertilization in order to yield increase, especially those on soils developed in the CSS context (Figure 1).

The micronutrient contents in plants grouped into the soil pedogeological contexts and soil textural classes are showed in figure 3. In spite of the lower Fe content in plants grown in the CSS context, the mean Fe contents were within the plant nutrition

**Table 3.** Descriptive statistics of micronutrient contents in leaves +3 of sugarcane cultivated in northeast Brazil

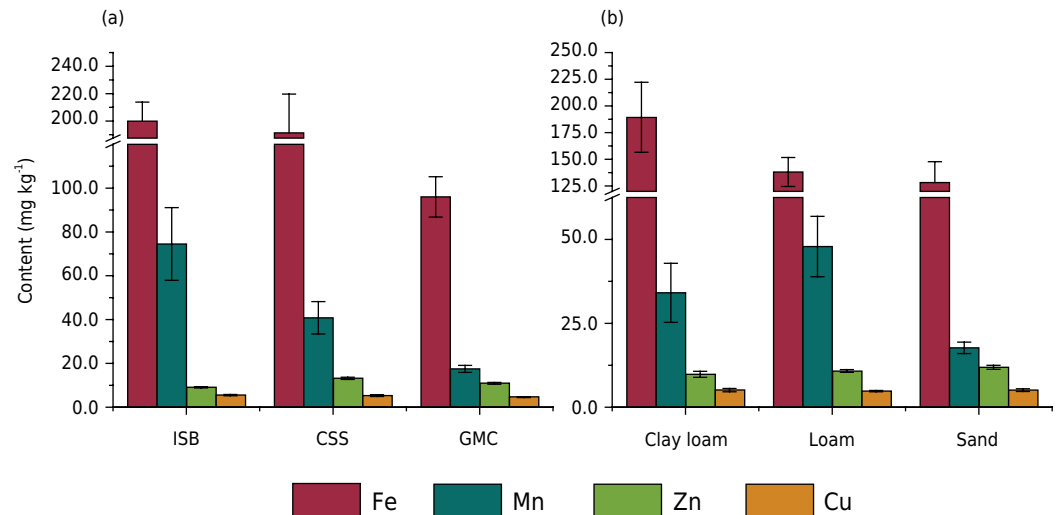
Descriptive statistics	Fe	Mn	Zn	Cu
	mg kg <sup>-1</sup>			
Mean	142.4	36.7	11.0	5.0
Median	145.5	22.9	10.7	4.8
Minimum	45.0	5.1	7.1	2.6
Maximum	378.0	214.4	17.0	8.6
±SD	80.3	2.5	2.5	1.2
CV (%)	56.4	22.4	22.4	24.6
Optimum range <sup>(1)</sup>	80-150	50-125	25-50	8-10
Optimum range <sup>(2)</sup>	55-105	20-100	17-32	4-8

Reference content in leaves +3 of sugarcane: <sup>(1)</sup> Malavolta (2006) and <sup>(2)</sup> McCray and Mylavarapu (2010). SD: standard deviation; CV: coefficient of variation.

**Table 4.** Critical values for micronutrients used in different countries for 3+ leaf samples

Nutrient	Australia <sup>(1)</sup>	South Africa <sup>(2)</sup>	Mauritius <sup>(3)</sup>	Guyana <sup>(4)</sup>	USA <sup>(5)</sup>
	mg kg <sup>-1</sup>				
Fe	50.0	na	na	na	50.0
Mn	15.0	15.0	15.0	15.0	16.0
Zn	10.0	15.0	20.0	15.0	15.0
Cu	2.0	3.0	5.0	3.5	3.0

<sup>(1)</sup> Calcino et al. (2000); <sup>(2)</sup> Schroeder et al. (1992) and Meyer et al. (1971); <sup>(3)</sup> Basserau (1987); <sup>(4)</sup> Evans (1965); <sup>(5)</sup> McCray and Mylavarapu (2010). na: not available.



**Figure 4.** Micronutrient contents in sugarcane (+3 leaves) grown on different pedogeological contexts (a) and soil textural classes (b). ISB: igneous-sedimentary basin; CSS: clay-sandy sediments; GMC: gneissic-migmatite complex.

optimum range proposed by Malavolta (2006), regardless the pedogeological setting or soil textural class. Therefore, Fe plant deficiencies are not likely in the study area in short to medium term.

The contents of Zn and Cu in sugarcane presented only a slight variation among pedogeological contexts and soil textural classes (Figure 4). This is probably related to the similar values of Zn and Cu available contents found in all sampling sites (Figure 3). On the other hand, Mn accumulation by plants clearly relied on pedogeological context and soil texture. Plants grown on the CSS context presented Mn concentration in leaves significantly lower than those on ISB and GMC pedogeological contexts. Likewise, plants grown on sand textured soils presented only one-third and half of the Mn content in leaves of plants on loam and clay loam soils, respectively.

## CONCLUSIONS

The soils cultivated with sugarcane in the states of Paraíba and Pernambuco posed available and reserve contents of micronutrients clearly related to the natural chemical contribution of the parent materials and soil textural classes, indicating that pedogeological contexts can be used for zoning areas prone either to micronutrient deficiencies or responses to fertilization. Topsoils (0.00-0.20 m) were mainly depleted for Mn and Cu (45 % of the soil samples analyzed) while only 7 and 4 % of the samples were regarded as low availability for Zn and Fe, respectively. Subsurface soils (0.20-0.40 m) presented available contents of Cu, Zn, and Mn 43, 61, and 66 % lower than those found in topsoils. The reserve contents of Fe, Mn, Zn, and Cu in all the soil samples analyzed were below the background values established for the region, which indicates continuous exportation of micronutrients through cultivation.

The mean and median contents of Mn, Zn, and Cu in diagnostic leaves of sugarcane were below their respective nutritional optimum ranges recommended to Brazil while Fe contents achieved the crop nutritional requirement. Plants presenting the lowest levels of micronutrient in leaves were mainly grown in the sandy soils of the CSS context. This was particularly observed to Mn, which displayed the highest decrease in leaf content from the ISB to the CSS pedological context. The data presented are important for future studies of micronutrient fertilization and for mapping areas with low levels of these elements in the northeastern region of Brazil based on pedogeological characteristics.

## AUTHORS CONTRIBUTIONS

**Writing - Original Draft:** Rita de Cássia Ferreira da Silva, Fernando Bruno Vieira da Silva, Caroline Miranda Biondi, and Emídio Cantídio Almeida de Oliveira.

**Investigation:** Rita de Cássia Ferreira da Silva and Fernando Bruno Vieira da Silva.

**Writing - Review & Editing:** Caroline Miranda Biondi and Emídio Cantídio Almeida de Oliveira.

**Supervision:** Clístenes Williams Araújo do Nascimento.

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