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# SOIL CHEMICAL ATTRIBUTES AND HEAVY METALS AND SUGARCANE LEAVES WITH SILICATE APPLICATION

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## ABSTRACT

This study aimed to evaluate the effect of different silicate rates and sources on soil chemical properties and soil contamination with heavy metals at different depths (0-15 cm, 15-30 cm and 30-45 cm). Also sugarcane leave micronutrient contents and heavy metals. The experiment was conducted on the Vargem farm, which belongs to Guaira Sugar Mill, Guaira, São Paulo, Brazil. The adopted experimental design was randomized blocks with four replications. The treatments had a factorial design 2 x 3 + 1, with two silicates (Holcim® and Agrosilício®) and three silicate rates (400, 800 and 1600 kg $ha^{-1}$). The control treatment (control) had no silicate application. The RB92-5345 variety of sugarcane was planted on May 1, 2008. Foliar samples were taken at harvest and soil samples (depths: 0-15, 15-30 and 30-45 cm) were taken after harvest. The following chemical attributes were assessed: pH, $CaCl_2$, $Al^{3+}$, $Ca^{2+}$, $Mg^{2+}$, micronutrients: Fe, Zn, Mn, Cu, Si, and heavy metals: Cd, Cr, Ni and Pb. The use of industrial waste in the culture of sugar cane improved soil quality, providing plants with adequate nutrients levels. To use this as an alternative nutrient source does not promote contamination of soil at deeper depths. The Agrosilício® and Holcim® silicates increased pH when rates were larger. The Agrosilício® silicate increased soil Si content in the 0-15 cm soil ayer and Mn content at the 15-30 cm soil layer. The application of silicates did not cause soil contamination and sugarcane leaves were not contaminated with heavy metals.

**Key words:** *Saccharum officinarum*, agricultural correctives, industrial residues.

# ATRIBUTOS QUÍMICOS Y METALES PESADOS EN EL SUELO Y LAS HOJAS DE LA CAÑA DE AZÚCAR CON APLICACIÓN DE SILICATOS

## RESUMO

El objetivo de este estudio fue evaluar el efecto de diferentes dosis y fuentes de silicato sobre las propiedades químicas del suelo, la contaminación del suelo con metales pesados en diferentes profundidades (0-15 cm, 15-30 cm y 30-45 cm) y el contenido de nutrientes y metales pesados en las hojas de caña de azúcar. El experimento fue realizado en la Fazenda da Vargem, que pertenece a la aratrop guaíra, Araraquara, São Paulo, Brasil. El diseño experimental fue en bloques al azar con cuatro repeticiones. Los tratamientos fueron distribuidos en factorial 2 x 3 + 1, con dos silicatos (Holcim® y silicato de Agrosilício®) y tres dosis de silicatos (400, 800 y 1600 kg $ha^{-1}$). El tratamiento control (control) sin la aplicación de silicato. La variedad RB92-5345 de la caña de azúcar fue plantado el 1 de mayo de 2008. Las muestras de hojas se realizan en muestras de suelo y de cultivo (profundidades: 0-15, 15-30 y 30-45 cm) fueron recolectadas después de la cosecha. Los siguientes atributos químicos evaluados fueron: pH, CaCl2, $Al^{3+}$, $Ca^{2+}$, $Mg^{2+}$, los micronutrientes: Fe, Zn, Mn, Cu, Ni, y metales pesados Cd, Cr, Ni y Pb. El uso de residuos industriales en la cultura de la caña de azúcar para la mejora de la calidad de los suelos, proveyendo a las plantas con niveles adecuados de nutrientes. Para utilizar esto como una fuente alternativa de fuente de nutrientes no promueve la contaminación del suelo a profundidades mayores. El silicato de Agrosilício® y Holcim® silicatos aumento de pH con el aumento de la dosis. El silicato de silicato de Agrosilício® mayor contenido de Si en la tierra a una profundidad de 0-15 cm y Mn a una profundidad de 15-30 cm. La aplicación de silicatos no causa la contaminación de los suelos y las hojas de la caña de azúcar con metales pesados.

**Palabras clave:** *Saccharum officinarum*, liming agrícolas, desechos industriales.

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## INTRODUCTION

Sugarcane is a semi-perennial crop and is one of the most important in the socio-economic aspect. The world areas of cultivation of sugar cane (*Sacchharum officinarum* L.) have constantly expanded, especially in Brazil (Dalchiavon, *et al.* 2017). Its yield can be affected by a variety of factors, including fertilization (De Oliveira *et al.*, 2014) with alternative sources such as industrial waste.

The steel slag can be considered an alternative source of nutrients, due to reduction of natural reserves of nutrients and the high cost of industrialization and the transport of fertilizers and liming (Prezotti & Martins, 2012). Even Brazil being the sixth largest world producer of pig iron, with an annual production of around 25 million tonnes, which corresponds to the generation of approximately 6.25 million tonnes of slag per year (Prezotti & Martins, 2012). An industrial waste such as slags are little used in agriculture in Brazil, despite the available amount - about 3 million tons annually. They have the potential to be used in Brazilian agriculture by acting as fertility promoters in areas with forage grasses (Korndörfer *et al.*, 2010).

Slags are calcium (Ca) and magnesium (Mg) silicates which can be used as soil acidity correctives and sources of Ca, Mg and Si for the plants due to high concentration of these nutrients (Prezotti & Martins, 2012, Stocco *et al.*, 2014), as proven in several studies evaluating the effects of slag on sugarcane and other crops (Madeiros *et al.*, 2009). In addition to these effects, the slag can increase the silicon content of the soil, because of its chemical constitution, the basis of calcium silicate (Prado & Fernandes, 2000).

The application of slag has a positive residual effect on sugarcane. It contributes calcium silicate in this culture to reduce acidity and availability of nutrients for plants (Madeiros *et al.*, 2009). These authors demonstrate in their work that slag can totally or partially replace the application of limestone in this culture.

Despite the beneficial effects, slags are an industrial waste and may contain heavy metals at relatively high levels. Some cultures, such as sugarcane which can recycle this waste, have the potential to use them.

The objective of this study was to evaluate the effect of different doses and sources of silicates on chemical properties and contamination with heavy metals of soil at different depths (0-15 cm, 15-30 cm and 30-45 cm), as well as to evaluate the content of micronutrients and heavy metals in sugarcane leaves.

## MATERIAL AND METHODS

The experiment was conducted in the 2008/2009 agricultural season, on Vargem farm which belongs to Guaira Sugar Mill, in the city of Guaíra, São Paulo, located on 20°19’06” South latitude and 48°18’38” West longitude, at an elevation of 517 meters. The study was conducted on an area already with sugarcane. The soil is

**Table 1.** Soil chemical and physical characterization at the Vargem experimental area

**Tabla 1.** Caracterización física y química de los suelos de la zona experimental Vargem

| Depth | pH $CaCl_2$ | P | K | $Al^{3+}$ | $Ca^{2+}$ | $Mg^{2+}$ | SB | T | V | M | O.M. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| cm | | --mg $dm^{-3}$- | | | ------------cmol$_c$ $dm^{-3}$--------- | | | | ------%---- | | g $kg^{-1}$ |
| 0-20 | 5.0 | 5.0 | 0.6 | 0.1 | 3.5 | 1.4 | 5.0 | 9.6 | 51.2 | 2.0 | 34 |
| 20-40 | 5.3 | 4.6 | 0.2 | 0.1 | 2.5 | 1.0 | 3.5 | 6.8 | 50.7 | 2.8 | 23 |

| Depth | Sand | Silt | Clay |
|---|---|---|---|
| cm | ---------------- g $kg^{-1}$ --------------- | | |
| 0-15 | 98 | 314 | 588 |
| 15-30 | 97 | 309 | 594 |
| 30-45 | 96 | 278 | 626 |

P, K = (HCl 0,05 mol L-1 + H2SO4 0,0125 mol L-1) avaliable P (extractor Mehlich-1); Ca, Mg, Al, (KCl 1 mol L-1); SB = sum of bases; T = CTC a pH 7,0; V = Base saturation; m = saturation with aluminum, O.M. (organic matter) = Colorimetric method.

classified as Oxysoil, LATOSOL RED Ferric (Santos *et al.*, 2013).

Before the implementation of the experiment (April 2008), soil samples for chemical analysis were collected from the experimental area (**Tables 1**).

**Table 2** shows the description of silicates used in this experiment (Holcim®) and the product used as standard (Agrosilício®) with respect to CaO, $CaCO_3$, MgO, $MgCO_3$, neutralizing power (PN), reactivity (ER) and relative power of total neutralization (PRNT).

**Table 3** shows the content of silicates (Holcim®) and the product used as standard (Agrosilício®) with respect to levels of Cu, Fe, Zn, Mn, Si, Cd, Cr, Ni and Pb.

The experiment was conducted using a randomized block design (RBD) with four replications. The treatments were distributed using 2 x 3 + 1 factorial. The first factor consisted of two silicates (Holcim® and Agrosilício®) and the second factor of doses of silicates (400, 800 and 1600 kg ha$^{-1}$). The control treatment (control) consisted of the absence of silicate slag.

Agrosilício®, was used as a standard product to compare the efficiency of Holcim® silicate. Agrosilício® is an aggregate generated from the treatment of stainless steel slag, which has the authorization of the State Environmental Foundation (FEAM) and a registration by the Ministry of Agriculture for use as a soil corrective and silicon source. It is already used on commercial fields with proven efficiency.

The planting was done in lines spaced 1.5 m apart, with a total of five rows per portion each 15 m long, with the useful area of the plot consisted of only 3 lines, 1 meter from the perimeter. The application of the treatments occurred on the day of planting. The silicates were placed into the bottom of the furrows by hand at a depth of 20-30 cm.

The planting of the variety of sugar cane RB92-5345 was held on May 1, 2008, with 15 viable sets per linear meter. At planting, Regent® insecticide (fipronil - 800 g kg$^{-1}$), was applied into the furrows at a dose of 0.2 kg ha$^{-1}$. The fertilization at planting consisted of 300 kg ha$^{-1}$ of MAP - monoammonium phosphate (11-52-00), 12 L ha$^{-1}$ of Starter® (S 4%, 5% Mn, Zn 3%; B 0.3%; 0.3% Cu, Mo 0.05% N 10% and density of 1.31) and 0.5 L ha$^{-1}$ of Stimulate® [growth regulator consisting gibberellic acid (gibberellin) 0.005% indolebutyric acid (auxin) and 0.005% kinetin (cytokinin) 0.009%].

Samples of sugarcane shoots were taken during harvest in August 2009. Twenty leaves were collected at random from three central lines of the plot, considering a minimum of 1 m from the perimeter. The plus 1 leaf or the Top Visible dewlap (TVD) leaf was collected. For analysis, samples

**Table 2.** Silicate description with respect to CaO, $CaCO_3$, MgO, $MgCO_3$, neutralizing power (PN), reactivity (ER) and relative power of total neutralization (PRNT) and silicate content with respect to Cu, Fe, Zn, Mn, Si, Cd, Cr, Ni and Pb levels.

**Tabla 2.** Descripción de silicatos con respecto a CaO, MgO, CaCO3, MgCO3, neutralizando el poder (PN), reactividad (ER) y el poder relativo de total neutralización (PRNT) y el contenido de silicatos con respecto a los niveles de Cu, Fe, Zn, Mn, IS, Cd, Cr, Ni y Pb.

| Product | CaO | $CaCO_3$ | MgO | $MgCO_3$ | PN | ER | PRNT |
|---|---|---|---|---|---|---|---|
| | % | | | | | | |
| Agrosilício® | 38.1 | 67.8 | 10.9 | 22.9 | 85.9 | 99.0 | 85.0 |
| Holcim® | 44.9 | 79.9 | 7.1 | 14.9 | 100.8 | 99.8 | 100.6 |

| Product | Cu[1] | Fe[1] | Zn[1] | Mn[1] | Si total[2] | Si [3]soluble | Cd[1] | Cr[1] | Ni[1] | Pb[1] |
|---|---|---|---|---|---|---|---|---|---|---|
| | mg kg$^{-1}$- | | | | | | | | | |
| Agrosilício® | 70 | 5075 | 40 | 8300 | 9.0 | 3.3 | 20 | 1500 | 200 | 200 |
| Holcim® | 70 | 3300 | 30 | 5850 | 17.9 | 0.7 | 40 | 50 | 40 | 90 |

[1]acid digestion HCl 1:1; [2]Total silicon in concentrated hydrochloric acid; [3]Soluble silicon extracted after five days in contact with the extractor (sodium carbonate + ammonium nitrate - $Na_2CO_3$+$NO_3NH_4$)

**Table 3.** Averages of pH in $CaCl_2$, of levels of calcium, magnesium and organic matter in soil regarding different depths, sources and levels

**Tabla 3.** Los promedios de pH en CaCl2, de los niveles de calcio, magnesio y materia orgánica en el suelo con respecto a diferentes profundidades, fuentes y niveles

| Doses of Silicates | pH in $CaCl_2$ | | Ca | | Mg | | Organic matter | |
|---|---|---|---|---|---|---|---|---|
| | Agrosilício® | Holcim® | Agrosilício® | Holcim® | Agrosilício® | Holcim® | Agrosilício® | Holcim® |
| (kg ha$^{-1}$) | | | cmol$_c$ dm$^{-3}$ | | | | dag kg$^{-1}$ | |
| Depth 0-15 cm | | | | | | | | |
| 0 | 5.4 | | 4.3 | | 1.1 | | 3.1 | |
| 400 | 5.8$^{ns}$ | 5.7$^{ns}$ | 3.9$^{ns}$ | 4.1$^{ns}$ | 1.1$^{ns}$ | 0.9$^{ns}$ | 3.1$^{ns}$ | 3.2$^{ns}$ |
| 800 | 5.9$^{ns}$ | 5.6$^{ns}$ | 4.4$^{ns}$ | 4.1$^{ns}$ | 1.1$^{ns}$ | 1.0$^{ns}$ | 3.1$^{ns}$ | 3.2$^{ns}$ |
| 1600 | 5.7$^{ns}$ | 5.7$^{ns}$ | 4.0$^{ns}$ | 4.1$^{ns}$ | 1.0$^{ns}$ | 1.1$^{ns}$ | 3.1$^{ns}$ | 3.1$^{ns}$ |
| Averages | 5.8 a | 5.7 a | 4.1 a | 4.1 a | 1.0 a | 1.0 a | 3.1 a | 3.2 a |
| $DMS_{Source}$ | 0.3 | | 0.4 | | 0.2 | | 0.2 | |
| $DMS_{Dunnett}$ | 0.6 | | 0.8 | | 0.2 | | 0.5 | |
| CV (%) | 5.3 | | 10.3 | | 11.5 | | 8.0 | |
| W | **0.97** | | **0.95** | | **0.96** | | **0.95** | |
| $F_{Levene}$ | 3.91 | | **1.08** | | **0.45** | | **0.45** | |
| $F_{non\text{-}additivity}$ | **0.48** | | **12.52** | | **0.89** | | **0.73** | |
| Depth 15-30 cm | | | | | | | | |
| 0 | 5.6 | | 1.9 | | 0.8 | | 2.7 | |
| 400 | 5.9$^{ns}$ | 5.7$^{ns}$ | 1.9$^{ns}$ | 1.9$^{ns}$ | 0.8$^{ns}$ | 0.9$^{ns}$ | 2.7$^{ns}$ | 2.7$^{ns}$ |
| 800 | 6.0$^{ns}$ | 5.8$^{ns}$ | 1.9$^{ns}$ | 2.0$^{ns}$ | 1.0$^{ns}$ | 1.1$^{ns}$ | 2.7$^{ns}$ | 3.0$^{ns}$ |
| 1600 | 5.8$^{ns}$ | 6.0$^{ns}$ | 1.9$^{ns}$ | 2.0$^{ns}$ | 0.9$^{ns}$ | 1.0$^{ns}$ | 2.8$^{ns}$ | 2.7$^{ns}$ |
| Averages | 5.9 a | 5.8 a | 1.9 a | 2.0 a | 0.9 a | 1.0 a | 2.7 a | 2.8 a |
| $DMS_{Source}$ | 0.2 | | 0.1 | | 0.1 | | 0.3 | |
| $DMS_{Dunnett}$ | 0.4 | | 0.2 | | 0.3 | | 0.6 | |
| CV (%) | 3.8 | | 5.9 | | 14.1 | | 10.9 | |
| W | **0.98** | | 0.89 | | **0.93** | | **0.93** | |
| $F_{Levene}$ | 0.58 | | 0.97 | | **0.92** | | **1.96** | |
| $F_{non\text{-}additivity}$ | **1.55** | | **0.05** | | **0.00** | | **0.04** | |
| Depth 30-45 cm | | | | | | | | |
| 0 | 5.6 | | 2.9 | | 0.7 | | 2.3 | |
| 400 | 5.7$^{ns}$ | 5.6$^{ns}$ | 2.8$^{ns}$ | 2.8$^{ns}$ | 0.7$^{ns}$ | 0.7$^{ns}$ | 2.3$^{ns}$ | 2.5$^{ns}$ |
| 800 | 5.9$^{*}$ | 5.7$^{ns}$ | 2.9$^{ns}$ | 3.0$^{ns}$ | 0.8$^{ns}$ | 0.8$^{ns}$ | 2.4$^{ns}$ | 2.4$^{ns}$ |
| 1600 | 5.7$^{ns}$ | 5.9$^{*}$ | 3.0$^{ns}$ | 3.0$^{ns}$ | 0.8$^{ns}$ | 0.8$^{ns}$ | 2.4$^{ns}$ | 2.3$^{ns}$ |
| Averages | 5.8 a | 5.7 a | 2.9 a | 2.9 a | 0.7 a | 0.7 a | 2.3 a | 2.4 a |
| $DMS_{Source}$ | 0.1 | | 0.7 | | 0.1 | | 0.2 | |
| $DMS_{Dunnett}$ | 0.3 | | 1.0 | | 0.3 | | 0.5 | |
| CV (%) | 2.7 | | 16.7 | | 18.2 | | 11.5 | |
| W | **0.94** | | **0.91** | | **0.93** | | **0.94** | |
| $F_{Levene}$ | **0.66** | | **1.11** | | **0.92** | | **0.67** | |
| $F_{non\text{-}additivity}$ | **0.93** | | **8.45** | | **3.64** | | **0.21** | |

Means followed by different letters in line, differ by Tukey test with 0.05 significance; *significant and $^{ns}$ non significant by Dunnett test with 0.05 significance. Values in bold indicate normality by the Shapiro-Wilk test (W), homogeneity, the Levene test (F) and non-additivity, by Tukey test ($F_{non\text{-}additivity}$), with 0.01 significance; values without bold indicate lack of normality by the Shapiro-Wilk test (W), lack of homogeneity by the Levene test (F), and additivity, by Tukey test with 0.01 significance of the middle third without ribs were used, which were properly identified and sent to laboratories.

Soil samples were collected after harvest in a range of 20 cm on the ratoon, with 2 sub-samples per line from 3 central lines of the plot, totaling 6 simple samples, considering a minimum of 1 m from the perimeter. The sampled depths were 0-15 cm; 15-30 cm, 30-45 cm.

The collection of soil was carried out using a Dutch-type auger, which was washed after each sample was taken to avoid possible contamination. The soil was placed in a clean plastic bag, properly identified and sent to laboratories.

In this work, iron (Fe), zinc (Zn), manganese (Mn), copper (Cu) and silicon (Si) are treated as micronutrients and cadmium (Cd), chromium (Cr), nickel (Ni) and lead (Pb) are considered as heavy metals.

The leaf samples were washed sequentially with: distilled water, a solution of 0.1 mol $L^{-1}$ of HCl and deionized water. After washing, samples without ribs were dried and subsequently ground in a Wiley mill (2 mm screen) and used to determine the content of micronutrients (Zn, Cu, Fe and Mn), heavy metals (Cd, Cr, Ni and Pb) and silicon (Si). Next, the leaf samples were submitted for nitro-perchloric digestion according to the methodology of Silva (2009). In the extracts, the contents of Zn, Cu, Fe and Mn were determined by atomic absorption spectrometry with air/acetylene flame, and the contents of Cd, Cr, Ni and Pb were determined using simultaneous plasma spectrometer - ICP / OES. For the analysis of Si concentration in leaves, the silicon analysis method in the plant was used according to the methodology described by (Korndörfer *et al.*, 2004).

The soil samples were air dried (TFSA), sieved (2 mm mesh) and subjected to extraction with Diethylene triamine pentaacetic acid (DTPA) solution, in accordance with Silva (2009) to determine the levels of micronutrients: Fe, Zn, Mn and Cu. The analytical determinations of micronutrients in the soil extracts were made by spectrophotometry of conventional flame atomic absorption with air/acetylene flame. To diagnose heavy metals, Cd, Cr, Ni and Pb analyzes were performed by simultaneous plasma spectrometer - ICP / OES. The pH, $CaCl_2$, aluminum ($Al^{3+}$), calcium (Ca) and magnesium (Mg) were analyzed according to (Silva, 2009).

Analyses of Si concentration in soil were carried out at LAFER - Laboratory of Analysis of Fertilizers at the Federal University of Uberlândia, according to the Analysis Method of "Available" silicon in soil (Korndörfer *et al.*, 2004).

The results consisted of analysis of variance, using factorial 2 (sources) x 3 (doses) + 1 additional, with four replications, in a randomized block design (RBD).

The model assumptions tests included homogeneity of variances (Levene test, with 0.01 significance), waste normality (Shapiro-Wilk test with 0.01 significance) and additivity (Tukey test for non-additivity at 0.01 of significance) using the SPSS 16.0 software.

Next, Tukey and Dunnet tests were carried out with 0.05 significance for the variable - source, and the regression analysis for the variable – dose.

## RESULTS AND DISCUSSION

Aluminum ($Al^{3+}$) in soil, at three depths (0-15, 15-30 and 30-45 cm), showed a value of 0.0 $cmol_c\ dm^{-3}$ in all the treatments. This value can be related to formation of aluminum-silicate complexes which affect the solubility and availability of Si (Pereira *et al.*, 2010) and reduce the availability of $Al^{3+}$ in soil.

Studies to evaluate neutralization of $Al^{3+}$ with steel slag observed similar results. Wally *et al.* (2015) demonstrated the neutralization of soluble Al in an experiment in order to evaluate the agronomic efficiency and the level of heavy metals in soil by applying basic steel slag. Sarto *et al.* (2014) evaluated five silicate doses of Ca (0, 1.2, 2.4, 4.8 and 9.6 t $ha^{-1}$) in wheat. They found a raising of pH and a significant reduction of $Al^{3+}$. Nolla *et al.* (2013), in comparison with the corrective potential of Ca silicate, concluded that slag was effective in neutralizing $Al^{3+}$. Its neutralization increased base saturation and gave a better potential yield of crop. From the results of this work and the work of Nolla *et al.* (2013), it was concluded that slag is effective in reducing the amount of $Al^{3+}$ in soil.

The soil analysis performed before the implantation of the experiment (**Table 1**) and after harvest (**Table 3**) demonstrated the efficiency of the two sources of silicates by improving pH and consequently soil amendment, as demonstrated by Korndörfer *et al.* (2010), Wally *et al.* (2015). The effect of slag on soil may be due to the neutralization of protons ($H^+$) by silicate anions ($SiO_3^{-2}$) present in soil due to solubilization process of the product (Reis *et al.*, 2013), which positively affected pH.

The Ca and Mg silicates have the property of a soil corrective similar to lime which is due to the presence of a neutralizing constituent ($SiO_3^{-2}$) (Reis *et al.*, 2013). This is probably due to the fact that both correctives have in their composition similar percentages of CaO and MgO (Chaves *et al.*, 2008).

As the doses of silicates increased, pH values in $CaCl_2$ tended to increase as well (**Figure 1**). The average pH in $CaCl_2$ is the expected 5.6. The increasing rates of pH in $CaCl_2$ for each kg $ha^{-1}$ of used silicate was 0.0001.

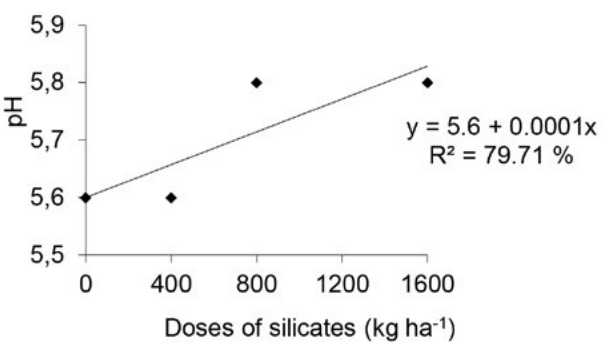


**Figure 1.** Soil pH at the depth of 30-45 cm, in response to different silicate doses (Agrosilício® and Holcim®).

**Figura 1.** El pH del suelo a la profundidad de 30-45 cm, en respuesta a diferentes dosis de silicatos (Agrosilício® y Holcim®).

The application of different silicates at their respective doses comparing with the control (no silicate) showed no differences regarding Ca and Mg content at the three depths, being the same for Agrosilício® and Holcim® silicates and their doses (**Table 3**).

Ca levels were at good to very good levels at the depth of 0-15 cm, average at 15-30 cm and good at 30-45 cm, according to Ribeiro *et al.* (1999). The Mg values were at good levels at a depth of 0-15 cm, medium and good at 15-30 cm, and average at 30-45 cm depth, according to Ribeiro *et al.* (1999).

Ca and Mg contents did not change with the applied doses of silicate. This behavior was not expected, since the silicate showed high CaO contents (38.1% and 44.9% in Agrosilício® and Holcim®, respectively), $CaCO_3$ (67.8% and 79.9% in Agrosilício® and Holcim®, respectively) and MgO (10.9% and 7.1% in Agrosilício® and Holcim®, respectively).

It is important to note that the application of correctives rich in Mg is important for the development of sugarcane, since the culture needs a minimum content of 0.5 $cmol_c$ $kg^{-1}$ in soil (Nolla *et al.*, 2013), which was observed in all the treatments in this work, including the control treatment.

Sobral *et al.* (2011); Reis *et al.* (2013); Sarto *et al.* (2014) and Wally *et al.* (2015) reported increased levels of Ca and Mg using silicates in different crop species. This increase may be due to the chemical composition of used material which comes from the steel casting process where Ca and Mg in the silicate participate in reactions (Sarto *et al.*, 2014). Prezotti & Martins (2012) demonstrated that the steel slag may be used as a corrective of soil acidity and a source of Ca and Mg to plants since they have high concentrations of these nutrients, and their neutralizing components, Ca and Mg silicates, have characteristics similar to carbonates (Stocco *et al.*, 2014).

The levels of soil organic matter at three depths showed no difference compared with the control (no silicate) regardless of the doses of Agrosilício® and Holcim® silicates (**Table 2**). At three evaluated depths, the levels of organic matter were average, according to Ribeiro *et al.* (1999).

Overall, there was a greater accumulation of organic matter in 0-15 cm soil surface layer, because sugarcane supplies a large deposit of plant residues to the soil cover.

The Cu and Zn micronutrients in soil showed no difference compared with the control (no silicate) at three depths (**Table 4**). Regarding the silicates (Agrosilício® and Holcim®) and their doses, no differences were observed.

Regarding Cu content in soil considered as reference by Ribeiro *et al.* (1999), concentrations above 1.8 mg $dm^{-3}$ are considered high. In all treatments, including the control, the observed content was above this value. However, according to Cetesb (2005) and Brasil (2009), the soil at three analyzed depths showed levels below those considered as a reference in quality and prevention, 35 mg $kg^{-1}$ and 60 mg $kg^{-1}$, respectively (**Table 4**).

The variations between the reference tables clearly show which content in soil is to be considered adequate. The maximum level in soil in this experiment was 6.8 mg $dm^{-3}$, 378% higher than recommended by Ribeiro *et al.* (1999) and 81% lower than the limit of prevention suggested by Cetesb (2005) and Brasil (2009). Another factor that can be observed is that at three evaluated depths, copper levels remained constant (**Table 4**).

Regarding Zn content in soil considered as a reference by Ribeiro *et al.* (1999), concentrations above 2.2 mg $dm^{-3}$ are considered high. In all treatments, including the control, the observed levels were below this value. According to the guiding values of Cetesb (2005) and Brasil (2009) a soil with up to 60 mg $kg^{-1}$ is a reference of quality and with 300 mg $kg^{-1}$ it should undergo prevention. Thus, with the observed Zn contents, these soils show no contamination problems by this element (**Table 4**).

Doses of silicates caused differences in the concentration of Zn in soil, at the depth of 15-30 cm, i.e. at the depth of application of silicates (**Figure 2**). Regarding other depths, there were no differences caused by doses of silicates. As the doses of silicates (Agrosilício® and Holcim®) increased, so did the levels of Zn in.

The expected Zn average value was 0.46 mg $kg^{-1}$, and the rates of reduction in the levels of zinc for each kg $ha^{-1}$ of the applied silicate was 0.0001 mg $kg^{-1}$. Similar results were observed by with Prezotti & Martins (2012), who found that the trend of reduction of Zn contents in the highest doses of steel slag was attributed to increased soil pH (**Figure 2**)

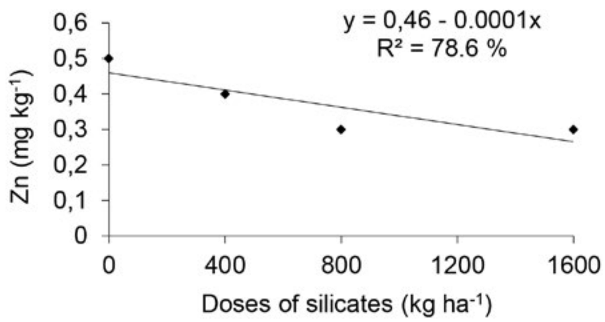


**Figure 2.** Zinc in soil, at the depth of 15-30 cm in response to different doses of silicates (Agrosilício® and Holcim®).

**Figura 2.** El Zinc en el suelo, a la profundidad de 15-30 cm en respuesta a diferentes dosis de silicatos (Agrosilício® y Holcim®).

Other works with steel slag in sugarcane found increases in Zn content, such as Madeiros *et al.* (2009), who found an increase in Zn concentration by 10.14% comparing with the control. Sobral *et al.* (2011) demonstrated a significant increase of Zn with increasing dose in the 0-20 cm layer.

For the Fe, the contents in soil showed no difference comparing with the control (no silicate) at three depths, except for the dose of 800 kg $ha^{-1}$ of Agrosilício® silicate at the depth of 15-30 cm where the Fe content was lower (**Table 4**). For the other doses (400 and 1600 kg $ha^{-1}$), there was no difference between the silicates (**Table 2**). As for the doses of silicates, no differences were observed between them, at three studied depths.

The Fe content considered as a reference in soil (31- 45 mg $kg^{-1}$) by Ribeiro *et al.* (1999), concentrations are appropriate for all treatments, including the control. Fe content available in soil, found by Sousa & Lobato (2004) ranged from 20 mg $dm^{-3}$ to 60 mg $dm^{-3}$, suggesting that the values obtained at different depths can be considered normal and acceptable in soils with agricultural crops (**Table 4**).

Results of this work did not show increased Fe content in soil, which was verified by Sobral *et al.* (2011) at a depth of 20-40 cm, depending

**Table 4.** Average contents of Copper, Iron, Zinc, Manganese, Silicon, Nickel and Lead in soil regarding different depths, sources and levels

**Tabla 4.** Los promedios de contenido de cobre, hierro, zinc, manganeso, silicio, níquel y plomo en el suelo con respecto a diferentes profundidades, fuentes y niveles

| Doses of Silicates | Cu | | Fe | | Zn | | | Mn | | Si | | Ni | Pb | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Agrosilício® | Holcim® | Agrosilício® | Holcim® | Agrosilício® | Agrosilício® | Holcim® | Agrosilício® | Holcim® | Holcim® | Agrosilício® | Holcim® | Agrosilício® | Holcim® |
| kg ha$^{-1}$ | | | | | | mg kg$^{-1}$ | | | | | | | µg kg$^{-1}$ | |
| | | | | | | | | Depth 0-15 cm | | | | | | |
| 0 | 6.1 | | 23.0 | | 0.7 | | | 13.8 | | 9.0 | | 22.5 | 387,5 | |
| 400 | 6.3$^{ns}$ | 5.7$^{ns}$ | 23.8$^{ns}$ | 22.0$^{ns}$ | 0.7$^{ns}$ | 18.8$^{ns}$ | 22.8$^{ns}$ | 364.8$^{ns}$ | 373.8$^{ns}$ | 0.7$^{ns}$ | 15.3$^{ns}$ | 14.4$^{ns}$ | 9.4$^{ns}$ | 8.0$^{ns}$ |
| 800 | 5.9$^{ns}$ | 5.4$^{ns}$ | 20.3$^{ns}$ | 21.0$^{ns}$ | 0.7$^{ns}$ | 18.0$^{ns}$ | 17.8$^{ns}$ | 342.3$^{ns}$ | 360.3$^{ns}$ | 0.6$^{ns}$ | 18.0$^{ns}$ | 13.8$^{ns}$ | 8.8$^{ns}$ | 7.5$^{ns}$ |
| 1600 | 5.9$^{ns}$ | 5.5$^{ns}$ | 21.8$^{ns}$ | 19.8$^{ns}$ | 0.6$^{ns}$ | 20.5$^{ns}$ | 19.0$^{ns}$ | 418.8$^{ns}$ | 397.8$^{ns}$ | 0.6$^{ns}$ | 14.9$^{ns}$ | 14.6$^{ns}$ | 8.8$^{ns}$ | 7.1$^{ns}$ |
| Averages | 6.0 a | 5.5 a | 21.9 a | 20.9 a | 0.7 a | 19.1 a | 19.8 a | 375.3 a | 377.3 a | 0.6 a | 16.0 a | 14.3 a | 9.0 a | 7.5 b |
| $DMS_{source}$ | 0.7 | | 2.5 | | 0.1 | | | 1.8 | | 1.4 | | 8.1 | 71.6 | |
| $DMS_{Dunnett}$ | 1.5 | | 5.8 | | 0.1 | | | 4.2 | | 3.2 | | 18.9 | 167.2 | |
| CV(%) | 13.2 | | 13.3 | | 11.2 | | | 14.1 | | 19.0 | | 47.5 | 22.1 | |
| **W** | **0.97** | | **0.98** | | **0.94** | | | **0.96** | | **0.97** | | **0.98** | **0.97** | |
| $F_{Levene}$ | **2.07** | | **3.15** | | **1.69** | | | **0.39** | | **3.73** | | **2.07** | **2.65** | |
| $F_{on-additivity}$ | **1.54** | | **0.17** | | 10.89 | | | **0.27** | | **0.52** | | **0.43** | **0.22** | |
| | | | | | | Depth 15-30 cm | | | | | | | | |
| 0 | 6.8 | | 24.5 | | 0.4 | | | 11,7 | | 9.0 | | 23.0 | 389.0 | |
| 400 | 6.6$^{ns}$ | 6.1$^{ns}$ | 23.5$^{ns}$ | 21.8$^{ns}$ | 0.4$^{ns}$ | 18.8$^{ns}$ | 20.5$^{ns}$ | 394.5$^{ns}$ | 372.8$^{ns}$ | 0.4$^{ns}$ | 12.9$^{ns}$ | 10.2$^{ns}$ | 8.7$^{ns}$ | 8.0$^{ns}$ |
| 800 | 5.6$^{ns}$ | 6.1$^{ns}$ | 18.0$^{*}$ | 21.8$^{ns}$ | 0.3$^{ns}$ | 18.3$^{ns}$ | 21.0$^{ns}$ | 326.3$^{ns}$ | 333.8$^{ns}$ | 0.3$^{ns}$ | 14.3$^{ns}$ | 13.3$^{ns}$ | 6.6$^{ns}$ | 8.5$^{ns}$ |
| 1600 | 6.4$^{ns}$ | 5.5$^{ns}$ | 22.5$^{ns}$ | 19.0$^{ns}$ | 0.4$^{ns}$ | 16.8$^{ns}$ | 15.3$^{ns}$ | 398.8$^{ns}$ | 314.5$^{ns}$ | 0.3$^{ns}$ | 13.3$^{ns}$ | 11.3$^{ns}$ | 8.6$^{ns}$ | 6.5$^{ns}$ |
| Averages | 6.2 a | 5.9 a | 21.3 a | 20.8 a | 0.4 a | 16.3 a | 18.9 a | 373.2 a | 340.3 a | 0.3 a | 13.5 a | 11.6 b | 8.0 a | 7.7 a |
| $DMS_{source}$ | 0.6 | | 2.7 | | 0.1 | | | 1.9 | | 1.4 | | 11.3 | 58.2 | |
| $DMS_{Dunnett}$ | 1.4 | | 6.4 | | 0.1 | | | 4.3 | | 3.2 | | 17.8 | 135.9 | |
| CV (%) | 11.7 | | 14.8 | | 16.6 | | | 17.5 | | 19.7 | | 48.4 | 22.1 | |
| **W** | **0.97** | | **0.97** | | **0.96** | | | **0.98** | | **0.97** | | **0.95** | **0.96** | |
| evene | **0.34** | | 7.40 | | **0.65** | | | **2.78** | | **3.25** | | **1.91** | **2.26** | |
| $F_{on-additivity}$ | **0.28** | | **0.07** | | **0.19** | | | **1.94** | | **0.04** | | **1.18** | **1.84** | |
| | | | | | | | | Depth 30-45 cm | | | | | | |
| 0 | 6.6 | | 22.5 | | 0.3 | | | 9.4 | | 8.5 | | 22.8 | 396.0 | |
| 400 | 6.4$^{ns}$ | 5.7$^{ns}$ | 22.3$^{ns}$ | 19.5$^{ns}$ | 0.3$^{ns}$ | 13.5$^{ns}$ | 13.0$^{ns}$ | 405.8$^{ns}$ | 356.8$^{ns}$ | 0.2$^{ns}$ | 8.8$^{ns}$ | 7.1$^{ns}$ | 8.1$^{ns}$ | 6.9$^{ns}$ |
| 800 | 6.4$^{ns}$ | 6.3$^{ns}$ | 20.0$^{ns}$ | 21.0$^{ns}$ | 0.2$^{ns}$ | 16.5$^{ns}$ | 21.3$^{ns}$ | 266.8$^{ns}$ | 379.0$^{ns}$ | 0.2$^{ns}$ | 11.1$^{ns}$ | 8.7$^{ns}$ | 7.8$^{ns}$ | 7.0$^{ns}$ |
| 1600 | 6.0$^{ns}$ | 6.2$^{ns}$ | 20.0$^{ns}$ | 20.3$^{ns}$ | 0.2$^{ns}$ | 17.5$^{ns}$ | 16.5$^{ns}$ | 384.0$^{ns}$ | 335.3$^{ns}$ | 0.3$^{ns}$ | 8.6$^{ns}$ | 9.4$^{ns}$ | 7.9$^{ns}$ | 7.3$^{ns}$ |
| Averages | 6.2 a | 6,1 a | 20.8 a | 20.3 a | 0.2 a | 15.8 a | 16.9 a | 352.2 a | 357.0 a | 0.2 a | 9.5 a | 8.4 a | 7.9 a | 7.1 a |
| $DMS_{source}$ | 0.7 | | 2.6 | | 0.1 | | | 1.5 | | 1.3 | | 6.5 | 68.8 | |
| $DMS_{Dunnett}$ | 1.7 | | 6.1 | | 0.1 | | | 3.6 | | 3.1 | | 15.2 | 160.3 | |
| CV(%) | 13.4 | | 14.6 | | 27.5 | | | 19.9 | | 20.1 | | 43.8 | 22.3 | |
| **W** | **0.94** | | **0.96** | | 0.75 | | | **0.97** | | **0.95** | | **0.92** | **0.97** | |
| $F_{Levene}$ | **0.30** | | **1.00** | | **1.17** | | | **1.46** | | **1.72** | | **2.07** | **0.66** | |
| $F_{on-additivity}$ | **2.99** | | **1.93** | | **1.90** | | | **1.70** | | **0.27** | | **0.03** | **0.01** | |

Means followed by different letters in line, differ by Tukey test with 0.05 significance; *significant and $^{ns}$ non significant by Dunnett test with 0.05 significance. Values in bold indicate normality by the Shapiro-Wilk test (W), homogeneity by Levene test (F) and non-additivity by Tukey test ($F_{non-additivity}$), with 0.01 significance. Values without bold indicate lack of normality by the Shapiro-Wilk test (W), lack of homogeneity by Levene test (F), and additivity by Tukey test with 0.01 significance on slag doses. It can be explained by the chemical composition of steel slag. Prezotti & Martins (2012) found an increase of Fe in soil using slag in the culture of sugarcane.

There were no differences compared with control (no silicate) regarding Mn content in soil at three depths (**Table 4**). Differences were not presented for the silicates (Agrosilício® and Holcim®) and their doses, except for the depth of 15-30 cm, wherein Agrosilício® silicate caused higher Mn content than the Holcim® silicate. This result is consistent because the silicates were applied at that depth and Agrosilício® showed higher concentrations of Mn in its composition (8300.0 mg $kg^{-1}$) while in Holcim® the contents were lower (5850.0 mg $kg^{-1}$).

Generally, Mn content in the soil in all treatments is high (>12 mg $dm^{-3}$), according to Ribeiro *et al.* (1999). As cited by Sousa & Lobato (2004), within the range of 1.9 mg $dm^{-3}$ to 5.0 mg $dm^{-3}$, Mn is not considered toxic. Chaves *et al.* (2009) observed that Cu and Mn levels are typically very low in areas grown with sugarcane with the application of steel slag, which was not observed in this experiment (**Table 4**).

At the depth of 0-15 cm, Agrosilício® produced higher Si content than the Holcim® silicate. Si contents in soil showed no difference compared with the control (no silicate) at three depths (**Table 4**). Differences were not presented for the silicates (Agrosilício® and Holcim®) and doses of silicates. Higher Si content was expected, since Agrosilício® showed higher soluble Si in its composition (3.3 mg $kg^{-1}$), while in Holcim® the contents were smaller (0.7 mg $kg^{-1}$), i.e. 78% less of soluble Si than in the reference silicate (Agrosilício®).

The silicates were applied at planting at depth of 15-30 cm and there was no increase in Si content at this depth (**Table 4**). It was not expected, since the silicate can be applied as a soil corrective, with the advantage of Si in its composition (Gunes *et al.*, 2008). This effect on Si content with the application of silicates may have been due to the fact that, at certain concentrations in soil, the Si contents were already close to the critical level.

Authors such as Fonseca *et al.* (2009) observed similar acidity correction of soil caused by slag and limestone, however the application of slag promoted an increase in Si content available in soil eight times higher than limestone. Faria *et al.* (2008) found that the surface application of slag after two years showed a residual effect of Mg soil acidity correction and Si content with consequences until the layer of 20 cm.

Fonseca *et al.* (2009) studied the effect of silicate and observed a significant increase of silicon concentration in soil. Vale *et al.* (2010) evaluated three doses of two correctives of steel slag and limestone and observed the largest increase of Si concentration in soil treated with slag (24.0 and 19.3 mg $dm^{-3}$) compared with limestone (10.6 and 11.0 mg $dm^{-3}$).

Different effects of slag on the release of micronutrients in soil can often be attributed to variations arising from the origin of the raw material used and the type of industrial process used by the steelmaker, which influence the chemical composition of waste. These variables add to other variables such as the dose, form of incorporation, and physico-chemical properties inherent to each soil (Pereira *et al.*, 2010).

Cd and Cr concentrations in soil at three depths were not detected. It was not expected, since these elements were detected in the applied silicates. The contents of Ni and Pb in soil showed no difference comparing with the control (no silicate) at three depths (**Table 4**). There were also no differences in the concentrations of these elements for the applied silicates (Agrosilício® and Holcim®) and their doses.

The Ni content in soil, at three evaluated depths was below the quality reference levels, 13 mg $kg^{-1}$, according to Cetesb (2005) and prevention level, 30 mg $kg^{-1}$ (Cetesb, 2005, Brasil, 2009). For Pb, the results of this work suggest that its content in soil was also below the reference levels, 17 mg $kg^{-1}$, according to Cetesb (2005) and prevention level, 72 mg $kg^{-1}$ (Cetesb, 2005, Brasil, 2009). Soil contamination problems caused by Ni and Pb were not present (**Table 4**).

The use of silicate as an agricultural fertilizer showed some concern due to the presence of heavy metals. The silicates could become carriers of heavy metals to soil, causing contamination, which did not occur in this experiment.

Fernandes *et al.* (2007) assessed heavy metal content extracted by DTPA in agricultural soils under oleraceous crops in the state of Minas Gerais, and observed that Cd, Cr and Ni exhibited negligible values of availability, with rates near zero. As indicated, more significant percentages available from the estimated total contents were for Cu, Pb and Zn.

Changing pH of soil was not the most important factor in reducing the bioavailability of Cd and Cr, after treatment with silicates in contaminated soil (Da Cunha *et al.*, 2008). These authors observed reductions of bioavailable levels of these metals after the addition of increasing doses of Si, even without significant changes in soil pH. The highest dose added to soil was 200 mg $kg^{-1}$ of Si, reducing by about 24 - 41% the availability of Cd and Cr, respectively. In this case, the reduction of bioavailability may result in precipitation of metals in the form of silicates, which occurs regardless of the change of pH of soil (Sommer *et al.*, 2006), and this may explain the fact that Cd and Cr were not detected in soil.

Slag, without monitoring or control of the application, when added to the environment, in general can contaminate the environment (Garcia-Guinea *et al.*, 2010). However, further studies of the release of metals present in the residue are required because, as observed in this work and the work of Wally (2015), obtained results can be masked by the imperfections of the evaluation method, which may be related to the extraction capacity of the method and the chemical bonds that metals present in the residue, reducing the extraction efficiency (McBride *et al.*, 2011).

Contents of Cu, Fe, Mn, Zn and Si in leaves showed no difference compared to the control (no silicate) (**Table 5**). Differences in micronutrient levels regarding the silicates (Agrosilício® and Holcim®) and the silicates doses were not present.

According to Filho *et al.* (2014), Cu and Zn are the most limiting micronutrients in the cultivation of sugarcane in Brazil, and in this work Cu concentrations were below recommended levels, i.e. 6-15 mg $kg^{-1}$, according to Raij *et al.* (1996). Zn contents in leaves were at recommended levels for the cultivation of sugarcane, 10-50 mg $kg^{-1}$, according to Raij *et al.* (1996).

**Table 5.** Average copper, iron, manganese, zinc and silicon in sugarcane leaves with different sources and doses.

**Tabla 5.** Los promedios de cobre, hierro, manganeso, zinc y silicio en hojas de caña de azúcar con diferentes fuentes y dosis.

| Doses of Silicates | Cu | | Fe | | Mn | | Zn | | Si | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Agrosilício® | Holcim® | Agrosilício® | Holcim® | Agrosilício® | Holcim® | Agrosilício® | Holcim® | Agrosilício® | Holcim® |
| ($kg\ ha^{-1}$) | mg $kg^{-1}$ | | | | | | | | %- | |
| 0 | 4.3 | | 748.8 | | 49.0 | | 16.8 | | 1.4 | |
| 400 | $3.8^{ns}$ | $4.0^{ns}$ | $697.5^{ns}$ | $577.3^{ns}$ | $56.3^{ns}$ | $48.8^{ns}$ | $16.3^{ns}$ | $14.5^{ns}$ | $1.1^{ns}$ | $1.3^{ns}$ |
| 800 | $2.5^{ns}$ | $3.8^{ns}$ | $775.3^{ns}$ | $578.8^{ns}$ | $47.3^{ns}$ | $40.5^{ns}$ | $15.3^{ns}$ | $16.0^{ns}$ | $1.2^{ns}$ | $1.4^{ns}$ |
| 1600 | $3.8^{ns}$ | $3.3^{ns}$ | $575.3^{ns}$ | $596.3^{ns}$ | $47.8^{ns}$ | $42.5^{ns}$ | $14.3^{ns}$ | $16.0^{ns}$ | $1.1^{ns}$ | $1.3^{ns}$ |
| Averages | 3.3a | 3.7a | 682.7a | 584.1a | 50.4a | 43.9a | 15.3a | 15.5a | 1.1 a | 1.3a |
| $DMS_{source}$ | 0.8 | | 178.1 | | 8.4 | | 2.3 | | 0.3 | |
| $DMS_{Dunnett}$ | 1.8 | | 279.2 | | 19.7 | | 5.3 | | 0.6 | |
| CV (%) | 25.0 | | 21.5 | | 20.7 | | 16.9 | | 25.8 | |
| **W** | **0.98** | | **0.97** | | **0.97** | | **0.97** | | **0.98** | |
| $F_{Levene}$ | **0.61** | | **1.43** | | **0.61** | | **0.88** | | **1.13** | |
| $F_{non-additivity}$ | **0.22** | | **0.26** | | **0.80** | | **2.75** | | **0.34** | |

Means followed by different letters in line, differ by Tukey test with 0.05 significance; *significant and $^{ns}$ non significant by Dunnett test with 0.05 significance. Values in bold indicate normality by the Shapiro-Wilk test (W), homogeneity by the Levene test (F) and non-additivity, by Tukey test ($F_{non-additivity}$), with 0.01 significance; values without bold indicate lack of normality by the Shapiro-Wilk test (W), lack of homogeneity by the Levene test (F), and additivity by Tukey test with 0.01 significance

Madeiros *et al.*, (2009) evaluated the effect of slag on two varieties of sugarcane, and found no increase of Cu in leaves as a function of slag doses. The average content they observed was 7.5 mg $kg^{-1}$, higher than that observed in this experiment. Madeiros *et al.* (2009) found no differences in foliar Zn depending on the increase of slag doses, similar to results found in this experiment.

It was observed that the Fe contents in leaves (584.1 – 682.7 mg $kg^{-1}$) are above 40 - 250 mg $kg^{-1}$ suitable for the cultivation of sugarcane (Raij *et al.*, 1996). These levels above average might be due to the presence of Fe in the slag which, according to **Table 5**, showed high values.

Madeiros *et al.* (2009) observed a reduction of Fe leaf contents due to the increase of silicon doses. They attributed this fact to the increase of pH brought about by the use of slag, which was not observed in this experiment, and an increase in levels of foliar Mn due to the increase of steel slag applied to SP791011 variety, while for the RB72454 variety no difference was observed, which was attributed to the efficiency of use and uptake of varieties.

Regarding the contents of foliar Mn, they were at an appropriate range (40.5 – 88.8 mg $kg^{-1}$) for the cultivation of sugarcane, according to Raij *et al.* (1996), indicating levels of 25-250 mg $kg^{-1}$ for the culture of sugarcane.

Levels of Mn in leaves in this work were below the range of 100 to 250 mg $kg^{-1}$, which are appropriate according to Malavolta *et al.* (1997). Increased leaf content of Mn was expected due to its high content in the silicates (**Table 5**).

The leaf Si content was in an appropriate range for the cultivation of sugarcane since, according to Korndörfer *et al.* (2002), the contents suitable for the cultivation of sugarcane are 0.7 - 1.9%.

The used silicates sources caused differences of soluble Si and overall Si contents. It was expected that the application of Agrosilício® would elevate the leaf content of Si in relation to the application of Holcim®, which has 94% less soluble Si. It was observed that the Si content was equivalent to the control treatment, which had no Si applied. This fact is probably due to the presence of Si in soil, which could have high level of available Si.

The application of silicate slag affects the contents of Si in leaves. These contents may still be affected by soil type, origin of silicate and variety of sugarcane. The application of silicate may increase, on average, from 32.57 to 50.3% Si content comparing with the control in varieties RB72454 and SP791011 respectively (Madeiros *et al.*, 2009).

Leaf contents of Cd, Ni and Pb showed no difference comparing with the control (no silicate) (**Table 6**). There were no differences in the leaf content caused by the silicates (Agrosilício® and Holcim®) or their doses, respectively for Cd and Ni.

The concentrations of Cd, Pb and Ni in leaves were below levels tolerated by plants, i.e. 5-10 mg $kg^{-1}$, 20-30 mg $kg^{-1}$ and 10-20 mg $kg^{-1}$, respectively (Mengel & Kirkby, 2009) (**Table 6**).

Cr content showed no difference comparing with the control (no silicate) (**Table 6**). The Holcim® silicate produced a lower content of Cr in leaves (282.7 $\mu$g $kg^{-1}$) in relation to Agrosilício®, which showed a mean value of 480.5 $\mu$g $kg^{-1}$. These results may be due to high Cr values found in Agrosilício® comparing with Holcim® (**Table 6**). Foliar Cr levels were below permissible levels for plants. No difference was observed between doses, regarding foliar chrome.

As the doses of silicates rose, foliar Pb levels also tended to increase (**Figure 3**). The expected average foliar level of lead was 1.298 $\mu$g $kg^{-1}$. The increment rate of foliar lead for each kg $ha^{-1}$ of applied silicate was 0.3999 $\mu$g $kg^{-1}$.

Corroborating with these results, Prezotti & Martins (2012) found that, even at much higher doses than would normally be estimated by the methods of recommendation of a corrective of soil acidity, they did not cause increased levels of heavy metals in the plants used for consumption or industrialization, thus demonstrating that there was no impairment of quality of the final product. It is an important indication for the use of slag in the culture of sugarcane, hence confirming the results of this work.

**Table 6.** Average chromium, cadmium, nickel and lead in sugarcane leaves with different sources and doses

**Tabla 6.** Los promedios de cromo, cadmio, níquel y plomo en las hojas de caña de azúcar con distintas fuentes y dosis

| Doses of Silicates | Cr | | Cd | | Ni | | Pb | |
|---|---|---|---|---|---|---|---|---|
| | Agrosilício® | Holcim® | Agrosilício® | Holcim® | Agrosilício® | Holcim® | Agrosilício® | Holcim® |
| (kg ha$^{-1}$) | -µg kg$^{-1}$ | | | | | | | |
| 0 | 358.3 | | 77.5 | | 605.0 | | 1478.5 | |
| 400 | 622.0$^{ns}$ | 243.8$^{ns}$ | 228.8$^{ns}$ | 170.0$^{ns}$ | 1069.3$^{ns}$ | 577.3$^{ns}$ | 1268.5$^{ns}$ | 1104.0$^{ns}$ |
| 800 | 546.3$^{ns}$ | 279.5$^{ns}$ | 134.0$^{ns}$ | 73.3$^{ns}$ | 1079.5$^{ns}$ | 933.0$^{ns}$ | 2050.5$^{ns}$ | 1278.5$^{ns}$ |
| 1600 | 273.3$^{ns}$ | 324.8$^{ns}$ | 157.5$^{ns}$ | 124.0$^{ns}$ | 747.8$^{ns}$ | 782.3$^{ns}$ | 1859.3$^{ns}$ | 2105.8$^{ns}$ |
| Averages | 480.5b | 282.7a | 173.4 a | 122.4a | 965.5a | 764.2a | 1726.1a | 1496.1a |
| $DMS_{source}$ | 194.7 | | 4.4 | | 261.2 | | 400.5 | |
| $DMS_{Dunnett}$ | 454.3 | | 10.2 | | 609.7 | | 934.7 | |
| CV(%) | 60.0 | | 42.8 | | 36.8 | | 29.3 | |
| W | **0.97** | | **0.93** | | **0.98** | | **0.98** | |
| $F_{Levene}$ | **2.61** | | **1.48** | | 4.03 | | **3.26** | |
| $F_{non\text{-}additivity}$ | **0.25** | | **2.43** | | **2.66** | | **2.43** | |

[1]Data with $\sqrt{x}$ transformation. Means followed by different letters in line, differ by Tukey test with 0.05 significance; *significant and $^{ns}$ non significant by Dunnett test with 0.05 significance. Values in bold indicate normality by the Shapiro-Wilk test (W), homogeneity by the Levene test (F) and non-additivity, by Tukey test ($F_{non\text{-}additivity}$), with 0.01 significance; values without bold indicate lack of normality by the Shapiro-Wilk test (W), lack of homogeneity by the Levene test (F), and additivity by Tukey test with 0.01 significance

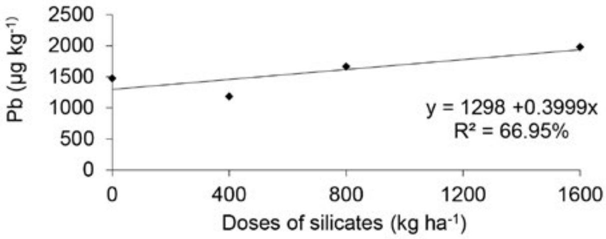


**Figure 3.** Foliar lead in response to different doses of silicates (Agrosilício® and Holcim®).

**Figura 3.** Contenido de hojas en respuesta a diferentes dosis de silicatos (Agrosilício® y Holcim®).

## CONCLUSIONS

The use of industrial waste in the culture of sugar cane improves the quality of the soil, providing plants with adequate levels of nutrients.

To use this as an alternative source of source of nutrients does not promote contamination of soil at greater depths.

The Agrosilício® and Holcim® silicates promote pH rise.

The Agrosilício® silicate increases contents of available Si in soil at a depth of 0-15 cm and Mn contents at a depth of 15-30 cm.

The application of silicates does not promote contamination of soil and leaves of sugarcane with heavy metals.

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