UNIVERSIDADE FEDERAL DE LAVRAS

LEONARDO FRANCO BERNARDES

BENEFICIAL USE OF A ZINC-METALLURGY BY-PRODUCT AS A SOURCE OF NUTRIENTS IN AGRICULTURE

LAVRAS – MG
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A dissertation submitted to the Soil Science Program at Federal University of Lavras in partial fulfillment of the requirements for the degree of Master in Soil Science.

Advisors

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LAVRAS – MG
2017

A Deus,

À Família,

Aos Amigos,

Aos mentores e conselheiros.

DEDICO

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SEREI ETERNAMENTE GRATO.

GENERAL ABSTRACT

One of the main challenges faced by mineral companies lies in the treatment of their effluents and solid residues. These materials may promote contamination of soil and water resources if untreated or improperly released into the environment. In this context, we investigated the beneficial agricultural use of a zinc-metallurgy by-product, which is a co-product generated from the treatment of the industrial effluent produced by Votorantim Metais Zinco - Três Marias Unit, through the process of Zn hydrometallurgy. The by-product used in the study is a calcium sulfate dihydrate (gypsum) containing also agronomically significant amounts of Ca, Mg, S, Zn, and Mn, in various concentrations - which allows for uniformity of distribution of micronutrients, when applied to the soil -, as well as other specificities such as its acid neutralization power. The study was carried out in two main stages: (1) experiments in the laboratory and in controlled environment in order to evaluate the intrinsic characteristics of the by-product and the effects when applied to the soil surface, as well as its efficiency when applied on maize cultivated in greenhouse conditions; and, (2) field experiments, applying the by-product in the cultivation of soybean crop. For this, soil fertility parameters were evaluated as well as the productivity parameters of the crops. The by-product originates from known sources of reagents obtained from the reaction of a solution rich in sulfates and calcium oxide. Thanks to that, the nutrients present in the by-product are plant-available, predominantly in the form of calcium, magnesium, zinc, and manganese sulfates and hydroxides and calcium and magnesium carbonates. The by-product does not present toxic trace elements in contents that may be harmful to the environment under agricultural conditions, taking into account the legal requirements of the Brazilian fertilizer legislation. The evaluated by-product acts similarly to agricultural gypsum with respect to the improvement of the soil subsurface, solubilizing and mobilizing the nutrients that it contains. The by-product also presents a potential for soil acidity correction, due to its composition of carbonates, hydroxyls, and silicates. The by-product has soluble minerals providing the macronutrients Ca, Mg, and S, as well as the micronutrients Zn and Mn to the soil and in appropriate forms to the plants, meeting the methodological requirements set forth in the legislation. Because it is a product composed of minerals originated from the controlled chemical reaction of two or more chemical compounds, it can be classified as a Complex Mineral Fertilizer and it can be destined to agricultural use according to the criteria defined in the Brazilian legislation. In addition, considering its physicochemical characteristics and its behavior when applied to soils, it can also be classified as a soil conditioner. Experiments with plants reinforced the agronomic potential of the by-product. Yet, it is highly recommended its evaluation under other soil-climatic conditions, as well as in other crops. In addition, it is necessary to carry out more research focusing on the quantities to be applied in each situation for a more precise recommendation of the by-product doses to be used.

Keywords: Zinc metallurgy. By-product. Fertilizer. Beneficial use. Soybean. Maize.

RESUMO GERAL

Um dos principais desafios enfrentados pelas empresas mineradoras reside no tratamento de seus efluentes e resíduos sólidos. Estes materiais podem promover a contaminação do solo e dos recursos hídricos se descartados no ambiente de forma imprópria ou não tratada. Neste contexto, investigou-se o potencial benefício agronômico de um subproduto de metalurgia de zinco, o qual trata-se de um coproduto resultante do tratamento do efluente industrial produzido pela Unidade Votorantim Metais Zinco - Três Marias, através do processo de hidrometalurgia de Zn. O subproduto utilizado no estudo é um sulfato de cálcio di-hidratado (gesso) que contém também quantidades significativas, do ponto de vista agronômico, de Ca, Mg, S, Zn e Mn, em diferentes concentrações - o que possibilita uma uniformidade de distribuição de micronutrientes, quando aplicado ao solo -, bem como outras especificidades, tais como a sua capacidade de neutralização da acidez. O estudo foi realizado em duas etapas principais: (1) experimentos em laboratório e em ambiente controlado para avaliar as características intrínsecas do subproduto e os efeitos quando aplicados na superfície do solo, bem como sua eficiência quando aplicado no milho cultivado em casa de vegetação; e, (2) experimentos de campo, aplicando-se o subproduto no cultivo de soja. Para tanto, foram avaliados os parâmetros de fertilidade do solo, bem como os parâmetros produtivos das culturas. O subproduto é originário de fontes conhecidas de reagentes obtidos a partir da reação de uma solução rica em sulfatos e óxido de cálcio. Em função disso, os nutrientes presentes nos subprodutos se apresentam em formas disponíveis para as plantas, predominantemente como sulfatos e hidróxidos de cálcio, magnésio, zinco e manganês e carbonatos de cálcio e magnésio. O subproduto não apresenta elementos tóxicos em teores que possam ser nocivos ao meio ambiente em condições agrícolas, levando em conta os requisitos legais da legislação brasileira de fertilizantes. O subproduto avaliado atua de forma similar ao gesso agrícola em relação à melhoria da subsuperfície do solo, solubilizando e mobilizando os nutrientes de sua composição. O subproduto também apresenta um potencial de correção da acidez do solo, devido à sua composição de carbonatos, hidroxilos e silicatos. Além disso, o subproduto tem minerais solúveis que fornecem os macronutrientes Ca, Mg e S, bem como os micronutrientes Zn e Mn ao solo e em formas adequadas às plantas, atendendo aos requisitos metodológicos estabelecidos na legislação. Assim, por ser um produto composto de minerais provenientes da reação química controlada de dois ou mais compostos químicos, pode ser classificado como um Fertilizante Mineral e pode ser destinado ao uso agrícola de acordo com os critérios definidos na legislação. Além disso, considerando suas características físico-químicas e seu comportamento quando aplicado a solos, também pode ser classificado como condicionador de solo. Os experimentos com plantas reforçaram o potencial agronômico do subproduto. Porém, é altamente recomendável que o mesmo seja testado sob outras condições climáticas e de solo, bem como em outros tipos de culturas. Também é necessário realizar mais pesquisas focadas nas quantidades a serem aplicadas em cada situação para uma recomendação mais precisa das doses a serem utilizadas do subproduto.

Palavras-chave: Metalurgia de zinco. Subproduto. Fertilizante. Uso benéfico. Soja. Milho.

LIST OF FIRGURES

FIRST CHAPTER - LITERATURE REVIEW

SECOND CHAPTER

ARTICLE 1

ARTICLE 2

LIST OF TABLES

SECOND CHAPTER

ARTICLE 1

ARTICLE 2

SUMMARY

FIRST CHAPTER

1 INTRODUCTION

Nowadays, a massive quantity of solid residues from industries is produced, some of which can be reused as by-products. Hence, governments and private industries throughout the world are constantly researching viable means to divert the by-products from landfills and use them in beneficial ways. In this way, available agronomic management practices need to be used and new management practices developed to protect environmental quality and to effectively use by-products in agricultural production systems. Actually, a great part of the industrial by-products presents a substantial value if properly used in agriculture. The reuse of solid residues in agriculture is a practice already exploited by mankind since manure from animal farming began to be added to the soil as sources of organic fertilizer.

The sense of sustainable development manifested by society has resulted in the creation of even more strict environmental legislation, with specific rules for the various industrial sectors. As a result, companies in the industrial sector were obliged to obey existing environmental legislation as a way to maintain their own existence in the market. Such a change of attitude stimulated the interest of companies in the development of several methods for the treatment of solid residues. At the same time, awareness drives consumers to buy products that are considered "green/clean", i.e., consumers began to analyze not only the final product, but also the steps that constitute the chain of food production.

In this context, by-product use represents not only a challenge but also an opportunity for Brazilian agriculture once it provides alternative source of nutrients, i.e., generating alternative fertilizers. Also, the global agriculture is currently confronted with the long-term goal of developing crop production practices that promote sustainability. Sustainable agriculture is characterized by plant and animal production practices that satisfy human needs while enhancing environmental quality and also the natural resource base. Hence, the efficient use of nonrenewable resources and on-farm resources is an important component of sustainability in agriculture.

However, for the reuse of industrial by-products, specifically, as inputs in agriculture, some prerequisites have to be properly filled. The by-products have first to be characterized and tested both in controlled environmental conditions and under field conditions in order to evaluate its efficacy and efficiency as a source of nutrients. If approved, i.e. if the by-products meet the requirements ruled by regulators (e.g., Brazilian as well as worldwide legislations), then it is proper to be officially commercialized and sold as an input in agriculture (e.g., fertilizer; soil amendment). In other words, to be marketed in Brazil, by-products must go through the fertilizer registration process and be subjected to several tests required by standards established by the Ministry of Agriculture, Livestock and Supply (MAPA). Hence, the by-product here studied was characterized and then applied on different soils and areas, both in greenhouse and under field conditions, with the cultivation of maize and soybean crops.

This study was conducted with the objective to test a by-product (originated from the zinc metallurgical process of the Votorantim Metais Co.) to be used as an input in agriculture, with the main purpose of nourishing the plants and improving soil attributes, while adding sustainability to the whole process, i.e., returning the nutrients extracted from the rocks, back into the soil.

2 LITERATURE REVIEW

2.1 Mining in Brazil and the environmental issue

In the Brazilian mining sector, concerns about the preservation of the environment were only observed in the 1980s, although some companies began to fit in with respect to the environmental legislation as early as the 1970s. In this context, the evolution of the environmental issue in Brazil in the mineral sector can be divided into three phases: 1st) Until the 60s, when environmental protection occurred only in some aspects, particularly those related to human health, such as the control of drinking water, concern for some species of flora and fauna, and labor conditions; 2nd) Period between 70 and 80, marked by the beginning of the confrontation of broader issues such as environmental pollution and the growth of cities, culminating in the holistic view of the environment as a global ecosystem; and, 3rd) From the 90s, positioning the paradigm of sustainable development as the great challenge, i.e., how to equate economic and social development with the preservation of the planetary ecosystem (BARRETO, 2001).

2.2 Reuse of solid residues/by-products in agriculture

Currently in Brazil a great quantity of industrial solid residues is produced every year and most part of it ends up being dumped on landfills. On the other hand, the reuse of the solid residues in agriculture represents a very few part of the total amount produced. In 2014 for instance, only 1.18% of the generated residues of the mining external destination were marketed as a by-product (FEAM, 2010a; 2010b; 2011; 2012; 2013; 2014; 2016). In addition, waste disposal costs are quite high and there is also the limitation of industrial landfills and the scarcity of areas for this purpose (SALGADO et al., 2003). Therefore, the destination of residues generated in the industry due to the processing of raw materials in large scale represents, today, one of the main challenges faced by the companies (SILVA; VIANA; CAVALCANTE, 2012).

To illustrate this, in accordance with the last Solid Waste Inventory of Mining (Base Year 2015), published by the Environment State Foundation, in 2015, 605,821,916.222 tonnes were produced as solid residues. Of this total, 242,357,728.414 tonnes were qualified as waste, representing 40.0% of the total generated, and only a small part of which can be reused as by-products in agriculture (FEAM, 2016).

Increased concerns raised especially in the last two decades about protecting the environment and moving toward a more sustainable philosophy have stimulated interest in recycling solid residues as by-products from the different sectors of our society (agricultural, industrial, and municipal). Land application is a dominant method of recycling (or reusing) such by-products. Some past experiences have demonstrated repeatedly inappropriate ways for land application of by-products (POWER et al., 2000). In this context, a sustainable way to reuse industrial by-products is by applying them onto the soil, enhancing soil fertility by the addition of nutrients present in the materials and consequently contributing to crop nutrition.

The reuse of by-products in agriculture (i.e., as soil liming materials, soil amendments or fertilizers) has a dual advantage to the environment, reducing the harmful effects of the material disposal to the ecosystem, thereby improving it, and providing value-added products through beneficial reuse of residues. In fact, there are already several studies developed in Brazil and elsewhere to be cited involving the reuse of by-products in beneficial ways (COSTA et al., 2012; ROSSOL et al., 2012; PRADO et al., 2013; TÓTH et al., 2013; PENHA et al., 2015; VALLE et al., 2015; OLIVEIRA-LONGATTI1 et al., 2017). In addition, preliminary studies with zinc metallurgy by-products show promising results and no environmental concerns with their reuse (FEIJÓ, 2007; PEREIRA; ROCHA; MANSUR, 2007; ABREU; MARTINS, 2009).

However, one of the main concerns associated with the reuse of by-products is the possibility of environmental contamination via the unintentional release of potentially toxic elements. Soil often acts as a "filter", with the capacity of immobilizing the impurities deposited therein. But this capacity is limited. Thus, considerable research is required to identify potential hazards, including surface and groundwater contamination, plant uptake and transport through the food chain. It is important to emphasize that the effects of land application of industrial by-products are dependent upon many factors, including the properties of both the material being tested and the soil to which it is being applied, application rates, management and environmental conditions, and also the crops to be grown (GOUVEA; MORAIS, 2007; WENDLING; DOUGLAS; COLEMAN, 2009).

2.3 Regulatory aspects of by-products reuse

With the growing concern for the preservation of natural resources and the issue of public health associated with solid waste, after 21 years of discussion at the congress, the law 12,305 of August 2^{nd}, 2010 was created, instituting The National Policy on Solid Waste (Política Nacional de Resíduos Sólidos, PNRS), based on principles, objectives and instruments and guidelines for integrated management of solid wastes (BRASIL, 2012). The main objectives of PNRS are the protection of public health and environmental quality and the non-generation, reduction, reuse, recycling, and treatment of solid wastes, as well as environmentally adequate final disposition. It applies to physical and legal persons, public or private, directly or indirectly responsible for the generation of solid waste.

According to the PNRS, wastes are materials that, after having exhausted all possibilities of treatment and recovery by available and economically viable technological processes, present no possibility other than the final disposal in an environmentally sound manner. On the other hand, solid residue is any disposed material, substance, object or good resulting from human activities in society, whose final destination is carried, it is proposed to be carried or is required to be carried, in solid or semi-solid state, as well as gases in containers and liquids whose particularities make it unfeasible its release in public sewage systems or water, or which require technically or economically infeasible solutions in the face of the best available technology (BRASIL, 2012). In other words, solid residues can be reused/recycled, waste cannot. We could add to that also the definition of what is called a by-product, which is a marketable product resulting from a manufacturing process that is not the primary product or service being produced (EEA, 2016).

One important feature of residues and by-products when it comes to their beneficial use in agriculture is the presence of potentially toxic elements or substances (especially in materials derived from mining activities), such as the trace elements chromium (Cr), lead (Pb), arsenic (As), mercury (Hg), and cadmium (Cd). In this context, the Brazilian legislation has a Resolution (Directive 420 of December 28^{th}, 2009 of CONAMA - National Environmental Council) (BRASIL, 2009), that provides criteria and guiding values of soil quality for the presence of chemical substances, besides establishing guidelines for the environmental management of areas contaminated by these substances as a result of anthropic activities. These guiding values are used as an instrument to support decisions for actions to prevent and control soil pollution.

Therefore, if viable, the reuse of solid residues in agriculture is undoubtedly the most interesting option from an economic, environmental, and often, social point of view. It also represents an undeniable benefit: minimization of the environmental problem resulting from inadequate waste disposal. The reuse of solid residues as by-products in agriculture must take into account various aspects, including the material intrinsic traits, the agricultural activity, the region in which it is to be used, and the pertinent legislation. Finally, it is crucial to note the details of the by-product generation process, so that the best disposal option can be better evaluated (PIRES; MATTIAZZO, 2008).

2.4 Zinc by-product generation through hydrometallurgical process

Zinc (Zn) is one of the main non-ferrous metals and ranks third in world consumption, being surpassed only by aluminum and copper (ARMSTRONG; CHAUDRY; STREIFEL, 2006; ROGICH; MATOS, 2008). It can be applied in civil construction, automobile industry, war material industry, household appliances, and galvanization.

The industrial unit of Votorantim Metais Zinco (VM-Zn-TM), founded in 1959, is the largest producer of electrolytic Zn in Brazil and the only company in the country that produces primary Zn. The company belongs to the Votorantim group and is located in the municipality of Três Marias, Minas Gerais, about 280 km from the capital Belo Horizonte. VM-Zn-TM has the only electrolytic Zn process in the world that uses two different types of Zn concentrates - sulfate and silicate -, as raw materials, in an integrated way, in a single plant. Votorantim produces Special High Grade (SHG) metal Zn in ingots (Zn alloys and Zn oxide) as well as silver (Ag) and Pb concentrates, copper (Cu) sulfate, sulfuric acid, and sulfur dioxide. A typical composition of the silicate and sulphide concentrates produced by this plant can be found in the study of Feijó (2007).

The silicate circuit, which is detailed described in the following section, is the part of the hydrometallurgical process responsible for the generation of the by-product studied here.

2.4.1 Silicate Circuit

The silicate concentrate is obtained by the process of flotation. The feeding consists of a mixture of two minerals, willemite and calamine, which are extracted from the Vazante plant belonging to Votorantim, located in the municipality of Vazante, Minas Gerais. After passing through the flotation process, the ore is referred to as Zn concentrate, since its Zn content raises from 6-12% to a content of around 42.5%. This concentrate is transported to Três Marias and disposed adequately in a storage yard, and is then sent to the wet grinding stage (PEREIRA, 2006).

At the milling stage of the circuit, an average of 992 tonnes of concentrate/day is repulped with an aqueous solution containing between 30 and 50 g L^{-1} of Zn, produced in the filtration sector, by thorough washing of the leaching residues. After milling, the resulting pulp is pumped to the “Silicate Concentrate Treatment” or "Magnesium Treatment" sector. In this step, the solubilization of magnesium (Mg), present in the carbonate form, as well as the precipitation of Zn begins (FEIJÓ, 2007). Due to the high calcium (Ca) and Mg contents, it is necessary to remove them in order to avoid the precipitation of their respective sulfates, as well as their incrustation in the pipes and gutters; besides, Mg contributes to the increase of energy consumption in the electrolysis step (PEREIRA, 2006).

The treatment process for Mg removal, according to SOUZA (2005), "consists in raising the temperature of the pulp to 80-95°C in order to selectively precipitate the Zn, leaving the Mg contained in the secondary solution to be discarded from the process."

The treatment step ends when the concentration of Zn in solution reaches values less than or equal to 10 g L^{-1}. The resulting pulp from the treatment sector is filtered for separation of the already treated concentrate, that is, with the Mg content around 1.5%, returning to the process. The filtrate, containing Zn and Mg, is sent to the effluent treatment sector specifically for the Zn recovery sector where it is recovered through lime precipitation. In a second step, Mg precipitation occurs aiming the adequacy of the final effluent to be discarded, which is to be treated. In the treatment of the effluent with lime, the by-product in study is originated. The precipitate of Zn retained in the filters follows the leaching process, joining the treatment line of the sulphide circuit, integrated with the conventional Roasting-Leaching-Electrolysis technology (PEREIRA, 2006; FEIJÓ, 2007).

As mentioned above, in the course of processing the Zn ore, a bleach is generated which, when purified, results in the production of a sulfate rich acidic waste solution, which must be treated to be carefully prepared. In the beneficiation process, for the treatment of solutions with high concentrations of the sulfate ion (chemical precipitation of Ca and Mg sulfates), precipitation with the use of Ca oxide is used; being a process widely used in the mining-metallurgical industry (GUPTA, 2003).

There are other industrial processes used for the treatment of this type of solution, such as reverse osmosis, ion exchange resin, and sulfate reducing bacteria. However, the choice of a particular process for industrial application is based on criteria that take into account: implantation cost, operating cost, final sulfate concentration, specific generation of solid (t/m^3), among others (GUPTA, 2003). In the process employing calcium oxide, calcium sulfate dihydrate (gypsum) is generated, which is most often disposed of in tailings dams. In some cases, non-commercialization is due to limitations on the levels of heavy metals present (Cd, Pb, Cr, As, and Hg), issues associated with transportation logistics and lack of equipment to economically recover the by-product (NUNES, 2012).

To put it briefly, the process of Zn production in the VM begins with the extraction of the ore, which is carried out both in the open and in the underground mine. The extracted ore is crushed to reduce particle size and then subjected to the flotation process. In this process, reagents and air are added to concentrate the Zn. Then there is a solid/liquid separation process (thickening) of the solution formed in the previous step. The sulfated Zn concentrate is obtained and calcined (burnt at 950°C) to obtain the oxide, which is leached with sulfuric acid. A bleach is then obtained which is purified for the separation of the different components, especially Zn sulfate. This step is performed by the carburizing technique, by addition of metallic Zn powder. After cementation, from the purified Zn solution, the sulfate solution is subjected to an electrolysis process for the formation of the Zn plates. Finally, the obtained Zn is melted and converted into ingots and then commercialized.

In addition to Zn, during the leaching step of the hydrometallurgical production of zinc, a significant amount of other metals, which are deleterious to the electrolysis step, are solubilized. Removal of these metals from the solution is carried out in the purification step. The solid residue produced by a Zn hydrometallurgical industry represents a secondary source of metals such as: Zn, Cd, Pb, Cu and Ni. During the process of wastewater treatment of the silicate circuit, a solid residue containing calcium sulfate ($CaSO_4$) due to the reaction between the effluent with sodium sulphide (Na_2S) and calcium oxide (CaO) is generated. Up to 3,000 m^3 of this residue are produced daily, of which 37% is basically composed of $CaSO_4$ (PEREIRA, 2006; FEIJÓ, 2007).

The Na_2S and CaO are added to the effluent so that Zn, Cd, Pb, and Ni are precipitated and wastewater meets the standards required by current environmental legislation - Normative Deliberation of COPAM Nº10/86 (COPAM, 1987), which establishes standards for water quality and effluent release in the water collections, as well as the Normative Deliberation COPAM Nº 166 of June 29th, 2011, establishing the soil quality reference values of several elements and substances (COPAM, 2011). According to the Brazilian Standard (NBR) 10.004 (ABNT, 2004), the solid residue generated by this process is classified as non-hazardous and non-inert waste, class II A.

The main chemical reactions and the diagram of the by-product generation process are described in Figure 1, highlighting that a second addition of CaO is performed, aiming on raising the pH of the effluent up to 10.5, thus lowering the contaminant levels (e.g., Cd, Pb) below those limits established by the Brazilian legislation.

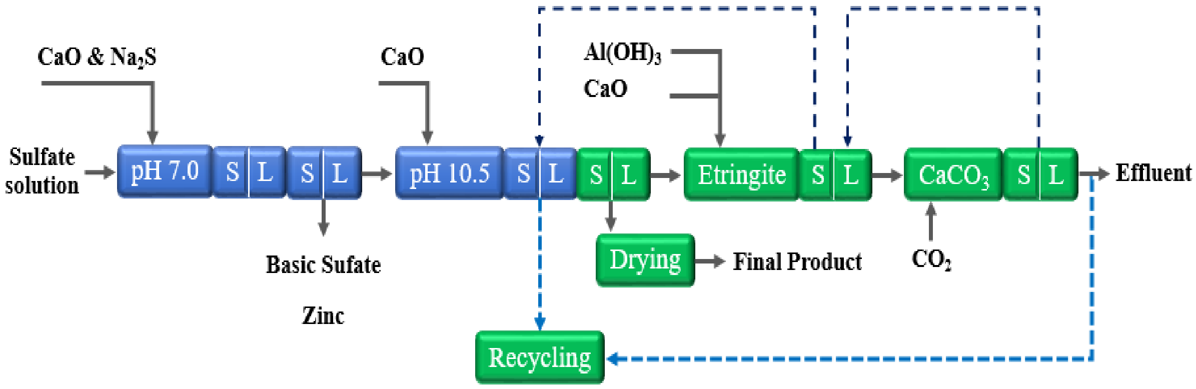
$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O + Mg(OH)_2$$

$$ZnSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O + Zn(OH)_2$$

$$MnSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O + Mn(OH)_2$$

$$6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_3 + 32H_2O \rightarrow 3CaO.3CaSO_4.Al_2O_3.26H_2O + 6H_3O^+$$

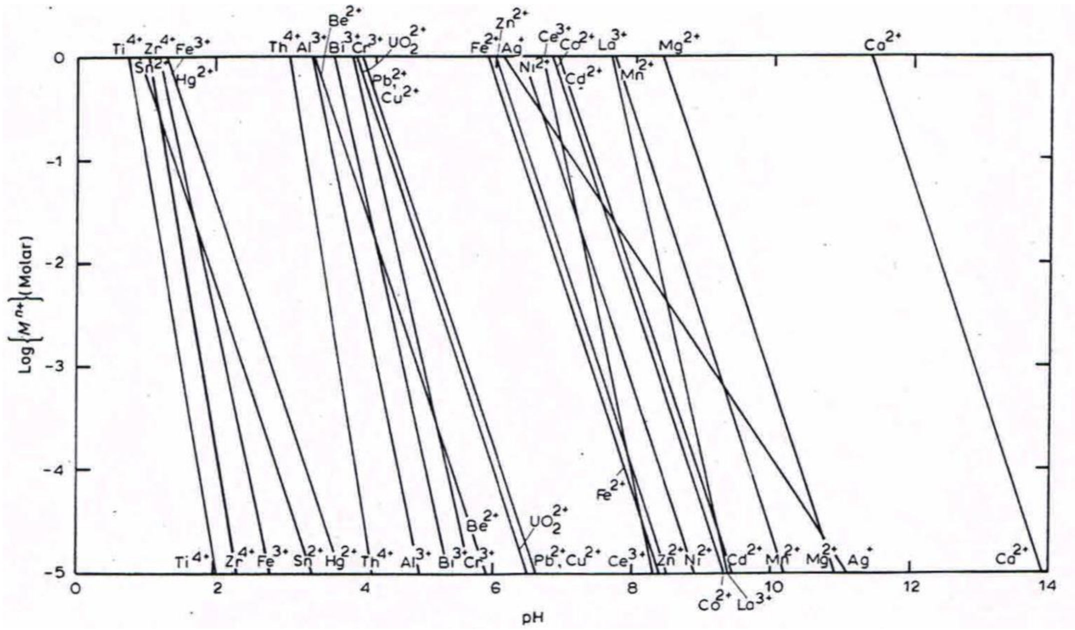
Figure 1 - Diagram of the process of obtaining the by-product. S: Solid, L: Liquid, indicating solid/liquid separation phases, which are usually performed in filter presses.



Source: Figure taken from the technical report of the tests with the by-product presented to Votorantim Metais Zinco in 2014.

This process facilitates the separation of specific substances such as $Zn(OH)_2$ e $Mn(OH)_2$. In addition, the pH increase results on the precipitation of hydroxides $Cd(OH)_2$, $Pb(OH)_2$ e $Cr(OH)_3$, which are then removed from solution. Figure 2 shows the effect of pH on the precipitation of metals in hydroxides forms.

Figure 2 - Precipitation diagram of metal hydroxides according to pH. Data based on temperature of 25°C.



Source: Monhemius (1977).

The expressive content of $CaSO_4$ along with the presence of nutrients such as Mg, Mn and Zn and its acidity neutralizing potential made this by-product the object of study of this work. Its contaminants removal and subsequent application in agriculture is an interesting alternative from the environmental and industrial point of view, as it would imply the reduction of liabilities and in the consumption of raw material.

Reusing the by-product in agriculture will provide multiple benefits, meeting human needs and helping to produce food and fiber in a sustainable way, while maintaining environmental integrity/quality over a long period of time (BOWN; ANGLE; JACOBS, 1998).

2.5 Process of reusing the by-product

In order for the by-product to be registered (MAPA) and marketed there are certain standards to be followed and tests to be carried out. The presentation of conclusive research results is one of the requirements for obtaining the by-product registration as a source of plant nutrients. The request for registration is made by means of an application addressed to MAPA. Specifics concerning this application are stated in Normative Nº 53 of 10/24/2013 (BRASIL, 2013), the minimum requirements for evaluating the viability and agronomic efficiency and elaboration of the technical-scientific report for the purposes of registration of fertilizer, liming material and biofertilizer as new product must be met.

Additional details concerning the legislation regarding the Brazilian fertilizer regulation are better described in the two articles of this study. To put it short, the by-product has to pass through several reliable research trials before it is commercialized.

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SECOND CHAPTER

ARTICLE 1

Beneficial use of a by-product from zinc metallurgical industry as a fertilizer: chemical, physical, and mineralogical characterization and effects on soil attributes and maize growth

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ABSTRACT

Several residues that are generated by different activities, such as in mining areas, have been tested to be used in other sectors, adding economic value to it. The use of industrial by-products in agriculture as a nutrient source (fertilizer) has attracted attention worldwide. However, prior to evaluating the agronomic efficiency of a by-product to be used as fertilizer, we need to characterize this material in order to assess its positive (presence of nutrients) and negative (presence of contaminants) features. In this context, the present study aimed to characterize a by-product generated from a zinc hydrometallurgical industry, taking into account its use as fertilizer in agriculture. For this, we first performed mineralogical, chemical, and physical characterizations of representative samples of the by-product (n=20). In addition to that, an experiment using PVC columns was conducted in greenhouse conditions for 146 days in order to assess the effects of applying the by-product in three different soils on selected soil attributes, i.e., soil pH and nutrient contents. Agricultural gypsum was also applied on soils for comparison. Some of the treatments received a previous correction of soil pH in order to assess also the by-product neutralizing power (NP). After the application of both, by-product and agricultural gypsum, the pH and the nutrient levels in the leachates were monitored over time. Subsequently, after this phase, maize was cultivated for 66 days using the PVC columns in order to evaluate the by-product capacity of supplying the nutrients to the plants. Results showed that the by-product contains significant total amounts of the nutrients sulfur (13.5%), calcium (16.4%), magnesium (10.3%), manganese (6,700 mg kg^{-1}), and zinc (3,900 mg kg^{-1}). Most nutrients are present in soluble forms, occurring mainly as sulfates, hydroxides, carbonates, and silicates, with the last three forms being responsible for the NP close to 40%. Contaminant levels in the by-product (e.g., cadmium, lead, chromium, arsenic, and mercury) are all below the maximum value allowed by the Brazilian legislation, for fertilizers. The application of agricultural gypsum resulted in lower pH values in the three studied soils, even following the previous soil pH correction. In contrast, the application of the by-product tends to increase soil pH over time, irrespectively of the previous pH correction. Also, the application of both, the by-product and agricultural gypsum, in soils resulted in similar nutrient levels determined in the leachates at the end of the experiment. The by-product provides the macronutrients Ca, Mg, and S, as well as the micronutrients Zn and Mn to the soil and in appropriate forms to the plants, meeting the methodological requirements set forth in the legislation. Therefore, this study has shown that the tested by-product has a great potential to be used as a fertilizer in agriculture, meeting all requirements established by the Brazilian legislation. Compared to agricultural gypsum, it is noteworthy the advantage of using the tested by-product due to the presence of extras nutrients, such as Mg, Zn, and Mn, as well as due to its liming potential. Finally, further studies with the by-product as a fertilizer need to be done with plants in controlled as well as field conditions to confirm its benefit, therefore reinforcing the importance of its beneficial use not only to agriculture, but also for the mining sector.

KEYWORDS: zinc metallurgy, by-product, macro and micronutrients, neutralizing power, fertilizer.

1. Introduction

Mine tailings are of environmental concern in post-mining landscapes, mainly because they might represent a permanent threat to public health and to the environment. In this context, most part of solid residues generated are stored and this may lead to an environmental liability, besides the relative high cost to the safe storage. Some residues can be processed in the future, when better extraction techniques that are technologically and economically feasible are discovered (Gouvea and Morais, 2007). Hence, mine tailing remediation is still a global challenge.

The high amounts of industrial wastes produced worldwide has led governments and private companies to concentrate efforts on testing the possibility of using these industrial by-products in other sectors, such as in agriculture. In this context, some industrial by-products present a great potential for beneficial use in agriculture as a nutrient source for the plants or as soil amendments (Garrido et al., 2003; Illera et al., 2004;Garrido et al., 2011; Park et al., 2014; Yang et al., 2015). It has to be stated that most of these residues are currently sold to the cement industry and/or disposed in tailing dams (Demopoulos, 2015). By showing the potential reuse of by-products in agriculture, we could not only aggregate value for the industries, reducing the high amounts disposed in piles or dams, but also decrease the demand for conventional fertilizers, thus contributing with nutrients recycling and crop nutrition.

In the state of Minas Gerais, Brazil, among all residues generated from mining processes, more than 90% were disposed in tailing dams and only 1,18% were sold as by-products (FEAM, 2015). In fact, solid residue disposal costs are quite high and there is limitation of landfills and the lack of areas for this purpose (Salgado et al., 2003; Johnson and Hallberg, 2005; O'Connor et al., 2005).

One of the main concerns with respect to using a by-product in soils is the chance of environmental contamination via release of potentially toxic elements, such as Cd and Pb (Wendling et al., 2009). Therefore, before using a by-product in agriculture, it needs to be well characterized in order to check for contaminant amounts, besides assessing the positive characteristics for a specific use in soils (e.g., neutralizing power of liming materials and presence of essential nutrients in soluble forms for fertilizer).

In the context of assessing the beneficial use of by-products in agriculture, the present study have proposed to use a by-product from the zinc metallurgical industry as a source of nutrients to plants, namely sulfur (S), calcium (Ca), magnesium (Mg), manganese (Mn), and zinc (Zn) (Pereira et al., 2007; Abreu and Martins, 2009). Preliminary studies with this by-product (Pereira et al., 2007; Abreu and Martins, 2009), which has similarities with agricultural gypsum, have shown promising results and no environmental concerns with its re-utilization. However, little is really known about the possible positive and negative characteristics of the tested by-product.

Therefore, the present study aimed to: i) characterize a by-product obtained from the zinc metallurgical industry, with a focus on its beneficial use in agriculture; ii) evaluate the effects of the by-product application on the chemical attributes of three different soils, as well as on maize growth.

2. Materials and Methods

2.1. By-product generation

The by-product under evaluation is produced by Votorantim Metals Co., Votorantim group, the fifth largest producer of zinc in the world, with a total capacity of 400 thousand tons of zinc per year (Pereira et al., 2007). During the hydrometallurgical processing to produce metallic zinc, there is a peculiar and important phase that takes part in the whole process. That is the integration of the silicate and sulfide circuit, held in 1995, patented and since then, being exclusively applied by Votorantim Metals in the unit located in the city of Três Marias (VM-Zn-TM), in the state of Minas Gerais, Brazil. The silicate circuit is the phase of the process responsible for the generation of the by-product being tested in this study.

First of all, the generation of a solid residue - a preliminary form of the by-product -, occurs in the treatment process of the acid effluent obtained from the silicate circuit (Bowell, 2004; Abreu and Martins, 2009; Güler et al., 2011; Demopoulos, 2015). The generation of the material is due to the reaction between sodium sulfide (Na_2S) and calcium oxide (CaO) added to the effluent containing mostly sulfate, which is done to guarantee metal precipitation, meeting established levels for final effluent disposal (Pereira et al., 2007; Blais et al., 2008; Abreu and Martins, 2009). The gypsum contained in the solid residues is formed during this step of the process. The sulfate solution (Pereira et al., 2007) is derived from the hydrometallurgical processing of three main zinc ores, sphalerite (ZnS), hemimorphite ($2ZnO.SiO_2.H_2O$), and willemite (Zn_2SiO_4).

After the formation of gypsum, Zn, Cd, Pb, and Ni are precipitated and removed from the solution and the acid effluent standards required by environmental regulations are met (CONAMA, 2011). The solid residue composition obtained in this phase of the process is presented in the study of Abreu and Martins (2009). Even though a significant amount of heavy metals is precipitated after the first addition of CaO and Na_2S to the sulfate solution, there are still some metal levels in the solid residue that are higher than the values required for its use as fertilizer according the Brazilian legislation (Brasil, 2016a). For this reason, a second addition of CaO was conducted aiming on lowering the heavy metal levels below those established by the Normative Instruction (NI) Nº 07 (Brasil, 2016a), defined by the Brazilian Ministry of Agriculture, Livestock, and Supply (MAPA). The second CaO addition to the solution raises the pH above at least 10.5, starting after that, a significant precipitation of magnesium hydroxide.

Finally, the ultimate form of by-product is obtained after the second CaO addition, which yields a material that contains nutrients in appropriate concentrations to be used in agriculture and very low contaminant levels. The by-product generation process is considered uniform, i.e., the minerals present in the material are the result of controlled and stable reactions, with no changes in its final mineralogy. According to the Brazilian standard (NBR) 10.004 (ABNT, 2004) the by-product is classified as a non-hazardous and non-inert material, class II A.

2.2. By-product characterization

The characterization of the by-product was performed to meet the requirements established by MAPA for its possible use as a fertilizer. Physical, chemical, and mineralogical characterization of the by-product were performed in order to check its elemental composition and its chemical species, which is related to the solubility of the different elements that are present in the material.

For the characterizations, 20 samples were collected on different places (real time sampling or in storage piles) and/or times on the by-product production site to assess the homogeneity of the by-product generation. Among these samples, 10 samples were picked and sent for crystallographic analyzes, which were carried out in order to identify the minerals present in the by-product. The crystalline structures of solid samples were evaluated by X-ray diffraction using a synchrotron light source (LNLS, Campinas, Brazil). The samples were air-dried and ground to pass through a 50-mesh nylon sieve and then inserted in capillary quartz samplers with 0.3 mm inner diameter and 0.001 mm thickness. The degree of 2θ goniometry of Debye-Scherrer was chosen for data acquisition and analysis. The incident beam was monochromatic, obtained by a DCM-double crystal monochromator, with Si (111). The measurements were made with a wavelength $\lambda = 1.04021$ nm, 2θ in a 5 - 120° range, and 2.0 s/step. The resulting diffractograms were interpreted with the aid of the mineralienatlas and webminerals databases (m.mineralienatlas.de, 2016; webmineral.com, 2016).

The chemical and physical analyzes (e.g., quantification of metal contaminants and particle size distribution) were performed according to the analytical protocols described in NI Nº 03/2015 (Brasil, 2015) and in the SMEWW 3030 F and SMEWW 3120 B protocols of the Standard Methods for the Examination of Water & Wastewater (Eaton et al., 2012). The analysis to quantify the elements of interest were made using the techniques of inductively coupled plasma atomic emission spectroscopy (ICP-AES), generation of hydrides for arsenic (As), and cold vapor generation for mercury (Hg).

2.3. By-product incubation in three different soils

This experiment was conducted under greenhouse conditions in the Department of Soil Science at Federal University of Lavras, Minas Gerais, Brazil. For the by-product incubation, three types of soil with different textures were selected (Table 1), as follows: sandy, medium textured, and clayey soils, which are respectively identified as ST, MT, and CT.

The experiment followed a completely randomized factorial design, 2 x 2 + 1 + 1, comprising two doses of the by-product (rates of 50 and 75 × clay percentage), applied in soils previously corrected or not for soil acidity, and two additional gypsum controls (rates of 50 and 75 × clay percentage), applied to unlimed soils. Considering the need of extra plots for growing corn after the initial period of incubation, with and without the addition of micronutrients (Zn and Mn) present in the by-product (see next section), we have used eight replicates for the by-product and four for the gypsum plots, totaling 96 and 24, respectively, equaling 120 lysimeters, considering the three different soils. The lysimeters were filled with 4 kg of the soils after incubated with lime, with the 0 to 20 cm layer on top of the 20 to 40 cm layer in order to mimic field conditions. The incubation with lime was performed using the 0 to 20 cm layer of each soil, simulating the lime application and incorporation at that depth.

Lysimeters were made out of polyvinyl chloride (PVC) tubes with 10 cm diameter and 20 cm height, assembled on the top of inverted 2-L polyethylene terephthalate (PET) bottles, with the same diameter and height of the PVC tube. A PET bottle cap with a hole in the center was used at the lower conical part of the lysimeter. A glasswool layer (1 cm-thick) was set at the bottom of each lysimeter to facilitate leaching and prevent clay illuviation. Then, 2 kg of each soil layer was poured into each lysimeter and tapped gently by raising and dropping it four times, 5 cm from the surface for uniform packing. In addition, collectors were placed beneath the columns to hold the leachates.

Agricultural gypsum (phosphogypsum), a by-product from phosphate fertilizer industry, was chosen as a source of comparison functioning as a control treatment, once the evaluated by-product tends to act in a similar manner to it. Products were applied with and without prior application of lime for correction of soil acidity, in order to assess the neutralizing characteristic of the by-product. After assembling the columns, both the by-product and agricultural gypsum were applied on the soil surface in the center of the columns.

For the previous correction of the soils, a mixture of CaO and MgO (p.a.) was used in a 3:1 ratio, resulting in a neutralizing power of 192.2%. In accordance with results of the soil analysis, the applied doses were equivalent to 0.58, 0.90, and 1.24 t ha^{-1} for ST, MT, and CT, respectively. After lime application, soils were incubated in plastic bags for 48 days, maintaining a humidity close to 60% of the field capacity.

After the reaction period of the liming material with soils (48 days), both the by-product and gypsum were applied (63rd day). This experimental phase was closed at the 146th day. Both the by-product and gypsum were applied to the soil at two different doses, which were calculated multiplying the clay content (%) of the 20-40 cm soil layer by 50 or 75, which is a standard for gypsum recommendation considering annual and perennial crops, respectively, in Brazil (Souza and Lobato, 2004). Thus, according to the results in Table 1, the doses applied, for both the by-product and gypsum were equivalent to 0.40, 1.50, and 3.55 t ha^{-1} (factor 50) and 0.60, 2.25, and 5.32 t ha^{-1} (factor 75) for ST, MT, and CT soils, respectively. Table 2 summarizes the treatments used in this experiment.

Table 1 Soil chemical and physical analyses.

Attributes	Unit	Sandy		Medium		Clayey	
		Depth (cm)					
		0-20	20-40	0-20	20-40	0-20	20-40
pH_{H2O}	-	4.9	4.9	4.8	4.9	5.1	4.9
pH_{CaCl2}	-	4.1	4.1	4.0	4.0	4.4	4.1
O.M.	dag kg^{-1}	1.5	1.1	2.4	1.7	3.2	2.0
P	mg dm^{-3}	3.4	1.5	1.4	0.5	1.1	0.7
K	mg dm^{-3}	22.0	14.7	64.2	39.7	24.9	24.9
S	mg dm^{-3}	1.1	1.1	1.5	1.0	1.1	1.2
Ca	$cmol_c$ dm^{-3}	0.2	0.1	0.3	0.2	0.1	0.1
Mg	$cmol_c$ dm^{-3}	0.1	0.1	0.3	0.1	0.1	0.1
Al	$cmol_c$ dm^{-3}	0.4	0.4	1.1	1.1	0.2	0.2
H + Al	$cmol_c$ dm^{-3}	2.6	2.5	4.3	3.5	5.1	4.5
$CEC_{pH\ 7.0}$	$cmol_c$ dm^{-3}	3.0.	2.7	5.1	4.0	5.4	4.8
V	%	13.0	7.0	16.0	10.0	6.0	6.0
B	mg dm^{-3}	0.1	0.1	0.1	0.1	0.1	0.1
Zn	mg dm^{-3}	3.7	2.0	1.2	0.9	8.2	1.3
Fe	mg dm^{-3}	64.7	71.7	152.8	101.8	60.3	64.0
Mn	mg dm^{-3}	20.5	9.3	34.8	16.7	10.1	10.1
Cu	mg dm^{-3}	0.1	0.1	0.8	0.7	0.2	0.2
Sand	%	87.0	88.0	71.0	63.0	3.0	4.0
Silt	%	3.0	4.0	6.0	7.0	33.0	24.0
Clay	%	10.0	8.0	23.0	30.0	64.0	71.0

Ca, Mg, and Al = KCl, 1 mol L^{-1}; H + Al = Calcium acetate, 0.5 mol L^{-1}, pH 7.0; P, K, and micronutrients = Mehlich-1; S = $CaHPO_4$; B = Hot water; (Embrapa, 2009); MO = Colorimetric method (Raij et al., 2001).

Table 2 Identification of the treatments.

Treatment[1]	Applied product	Dose[2]
Limed/AG	Agricultural gypsum (AG)	50
		75
Limed/Bp	By-product (Bp)	50
		75
Unlimed/Bp	By-product (Bp)	50
		75

1) Limed and unlimed: previous and non-previous soil acidity correction with CaO and MgO in a 3:1 ratio, aiming to reach a base saturation of 50 to 60%; 2) Factor to be multiplied by the clay percentage of the 20-40 cm layer, determining the doses applied of gypsum and the by-product;

During and at the end of the incubation, soil pH values (in water and in 0.01 M $CaCl_2$) were monitored (weekly). To assess soil pH, samples of 10 cm^3 were collected from the soil surface of each lysimeter. Simultaneously, leachates were collected for measurement of pH. Part of each leachate aliquot collected was filtered (0.45 µm), separated and stored in the freezer for later determination of leached concentrations of Ca, Mg, S, Mn, and Zn, by the technique of ICP-AES.

2.4. Greenhouse maize experiment

The cultivation of maize under controlled (greenhouse) environment was evaluated following the by-product application on 90 of the 120 lysimeters, as described in the previous item (2.3. By-product incubation in three different soils). One replicate of each treatment was separated for the stratification of soil layers of each lysimeter to monitor the mobility of nutrients contained in the by-product, hence leaving 90 out of the 120 initial lysimeters used during the previous incubation period for the plant growth test.

The greenhouse maize experiment followed a completely randomized 2 x 2 x 2 + 1 + 1 factorial design, comprising previous and non-previous correction of the soil acidity, two doses of both, by-product and gypsum (50 and 75 multiplied by the clay percentage of the deeper layers - 20 to 40 cm), fertilization and non-fertilization of corn with Zn and Mn, and two controls (two doses of gypsum), with three replicates, in three different soils, totaling 90 plots (lysimeters).

The commercial maize (hybrid Agroceres 8060YG) recommended for grain production in the central region of Brazil was sown in all pots. This hybrid has as main characteristics the precocity and its high response to fertilization. The maize plants were seeded and cultivated for 66 days, maintaining the humidity of each lysimeter always above 80% of the field capacity. Initially, 6 seeds were used per pot and after 4 days the thinning was done leaving only 1 plant per plot. During the experiment, sowing and top-dressed fertilizations were carried out in all treatments (Table 2) using the following pure reagents as the source of nutrients: NH_4NO_3, KH_2PO_4, $CuCl_2$, H_3BO_3, and $(NH_4)_6Mo_7O_{24}.4H_2O$. Briefly, the fertilization of maize with macro and micronutrients was made applying the solutions on top of the soil and splitting the doses in two for phosphorus (P) and potassium (K) and five for nitrogen (N). For N, P, and K the total applied was 337, 200 and 125 mg kg^{-1}, and for S, Cu, B and Mo, 50, 1.5, 0.5 and 0.1 mg kg^{-1}, respectively.

Concerning the fertilizations with Zn and Mn, all the treatments in which the commercial gypsum was applied received 0.5 mg kg^{-1} of Zn and Mn, aiming to supply the plant demand for its development. However, in the treatments in which the by-product was applied, in order to evaluate its capacity to provide these micronutrients, half of the 6 replicates of each treatment in the experiment received Zn and Mn, while the others 3 replicates were not fertilized with these micronutrients, irrespectively of the previous correction of the acidity with CaO and MgO. The same design was used in all soils, for both doses applied (50 or 75 multiplied by the clay percentage) of the by-product or of the agricultural gypsum, as it is shown in Table 3.

Table 3 Identification of the treatments used in this study.

Treatment	Previous soil correction[1]	Applied product	Dose[2]	Zn and Mn fertilization[3]
Limed/AG F	Yes	Agricultural gypsum	50 75	Yes
Limed/Bp F	Yes	By-product	50 75	Yes
Bp F	No		50 75	
Limed/Bp	Yes	By-product	50 75	No
Bp	No		50 75	

1) Previous soil acidity correction with CaO and MgO in a 3:1 ratio, aiming to reach a base saturation of 60%; 2) Factor to be multiplied by the clay percentage of the 20-40 cm layer, determining the doses applied of gypsum or the by-product; 3) Fertilization with 0.5 mg kg^{-1} of Zn and Mn, using zinc chloride and manganese chloride (p.a.).

After 66 days from seeding, plants were collected, washed, separated in shoots and roots parts, and oven-dried at 65°C until reaching constant weight. Samples were then weighed to obtain the dry matter (DM), finely grounded (<0.15 mm or 100 mesh), and digested according to Method 3051A of the US Environmental Protection Agency (USEPA) (USEPA, 1998). A sample of the standard reference material of tomato leaves-NIST 1573A was used in each digestion battery, as well as a blank sample for quality control (Table 4). The extracts were obtained after plant digestion (roots and shoots), then contents of the macronutrients Ca, Mg, S and, the micronutrients Zn and Mn were quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Table 4 Recovery of the standard tomato leaves - NIST 1573 A.

Nutrient	Certified Values	Obtained Values*	Recovery**
Ca[1]	5.05 ± 0.09	4.8 ± 0.7	95.3
Mg[1]	1.2	1.1 ± 0.2	98.9
S[1]	0.96	1.1 ± 0.2	115.5
Zn[2]	30.9 ± 0.7	37.4 ± 3.8	121.2
Mn[2]	246.0 ± 8.0	252.5 ± 10.6	102.6

*Average of seven replicates. **Values in %. [1] Values determined in %. [2] Values determined in mg kg^{-1}.

2.4. Statistical analysis

Data obtained from the experiments were submitted to analysis of variance with the support of the software Assistat (Silva and Azevedo, 2009). The means of the analyzed variables of each treatment were compared by the Tukey test, using a level of 5% of significance.

3. Results and discussion

3.1. By-product mineralogical characterization

The minerals contained in the by-product are shown in Fig.1. It can be seen in this figure that the macro and micronutrients present in the by-product such as Ca, Mg, S, Mn, and Zn are distributed in different mineral phases. For example, S is present in the form of sulfate, contained in the minerals starkeyite and gypsum, Ca is present in clinotobermorite, defernite, erionite, and junitoite, and Mg is contained in artinite, birnessite, and clinochlore. The presence of Mg is an important agronomic characteristic added to the by-product. Fertilizers containing Mg are scarce and generally expensive. The presence of this nutrient, coupled with the fact that the by-product also has Ca and S, as well as micronutrients (e.g., Zn and Mn), makes the by-product very innovative and highly beneficial in the context of supplying a wide range of very important nutrients in a single material.

Manganese appeared in the by-product as manganite, manganpyrosmalite, and rhodochrosite. Also, Zn was found in boyleite, glaucochroite, junitoite, and smithsonite (Fig. 1). This fact indicates that the by-product is a source of Mn and Zn that could be used in agriculture to enrich tropical soils, which are mostly deficient in such nutrients (Lopes and Cox, 1977; Juo and Franzluebbers, 2003). It has to be state that the chemical forms in which the nutrients are present in the product have great economic advantages and practical application (e.g., soluble forms), particularly with regard to the possibility of homogeneous distribution of the micronutrients Zn and Mn on the soil.

Besides, it can also be noted the presence of fluoride, presented in the mineral brenkite (($Ca_2F_2(CO_3)$)). The presence of fluoride in the material also has interesting implications from the agronomic point of view, as the competition of fluorite (F^-) for exchange sites that are able to immobilize phosphate may result in less retention of phosphorus in the soil, thus making this nutrient more available to plants (Valle et al., 2015).

The gypsum contained in the material, besides being a source of Ca and S is also recognized as an amendment of the soil acidity in greater depths in the soil profile, reducing the phytotoxicity caused by available aluminum (Al^{3+}) (Garrido et al., 2003; Kinraide, 2003; Illera et al., 2004; Zambrosi et al., 2007ab; Poschenrieder et al., 2008; Liming and Dick, 2011). This is a beneficial trait of this by-product, mainly for the soils of the Cerrado region, which are in their vast majority typically acidic with high levels of Al^{3+} and low levels of Ca^{2+} and Mg^{2+} (Novais et al., 2007; Lopes et al., 2012; Lopes and Guilherme 2016).

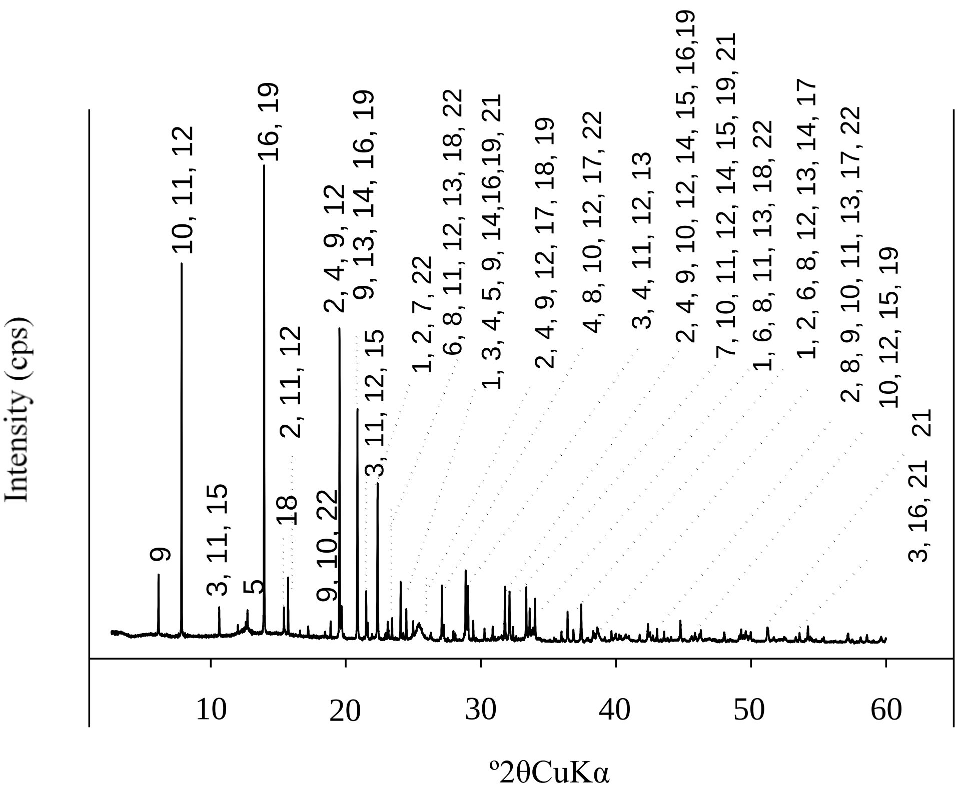

Fig. 1. X-ray diffractogram of the by-product. The numbers above the peaks represent the respective minerals:

1) Alunogen - $Al_2(SO_4)_3.17(H_2O)$;
2) Andalusite - Al_2SiO_5;
3) Artinite - $Mg_2(CO_3)$ $(OH)_2.3(H_2O)$;
4) Bementite - $Mn_8Si_6O_{15}(OH)_{10}$;
5) Birnessite - $(Na, Ca, K)_{0.6}(Mn^{4+}, Mn^{3+})_2O_4.1.5H_2O$;
6) Bixbyite - $(Mn^{3+}, Fe^{3+})_2O_3$;
7) Boyleite - $(Zn, Mg)SO_4.4H_2O$;
8) Brenkite - $Ca_2(CO_3)F_2$;
9) Clinochlore - $(Mg, Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$;
10) Clinotobermorite - $Ca_5Si_6O_{17}.5H_2O$;
11) Defernite-$Ca_6(CO_3)_{1.58}(Si_2O_7)_{0.21}(OH)_7[Cl_{0.50}(OH)_{0.08}(H2O)_{0.42}]$;
12) Erionite-Ca - $(Ca, K, Na)_{5.6}(Si, Al)_{36}O_{72}.28H_2O$;
13) Gypsum - $CaSO_4.2H_2O$;
14) Glaucochroite - $(Ca_{0.98}Mn_{0.02})(Mn_{0.85}Mg_{0.10}Zn_{0.05})SiO_4$;
15) Hydroxylellestadite - $Ca_{10}(SiO_4)_3(SO_4)_3(F_{0.16}Cl_{0.48}(OH)_{1.36})$;
16) Junitoite - $CaZn_2Si_2O_7.H_2O$;
17) Manganite - MnH_2O;
18) Manganpyrosmalite - $(Mn, Fe^{2+})_8Si_6O_{15}(OH, Cl)_{10}$
19) Natrolite - $Na_2(Si_3Al_2)O_{10}.2H_2O$;
20) Rhodochrosite - $MnCO_3$;
21) Smithsonite - $ZnCO_3$;
22) Starkeyite - $MgSO_4.4H_2O$.

Another relevant feature concerning the results of the mineralogical characterization, which is related to the by-product acid neutralization potential, is the presence of carbonates, hydroxides, and silicates in the material, such as andalusite, artinite, bementite, clinotobermorite, defernite, and smithsonite. The high pH condition at the final stage of the by-product production convert part of the nutrients in the form of hydroxides. The presence of hydroxides and also the occurence of carbonate and silicate minerals contributes to reinforce the neutralizing characteristic of the by-product.

3.2. By-product chemical characterization

Chemical compositions of the tested by-product and of the agricultural gypsum used as a control are shown in Table 5. Note that the by-product has 16.4% of Ca, 13.6% of S, in addition to expressive amounts of Mg (10.3%), corroborating with results of the mineralogical analyzes. The occurrence of Ca and S is mainly related to the presence of gypsum, originated from reactions of the sulfate present in the solution with the Ca added as CaO through the different steps of the production process.

In addition to these major elements (macronutrients), it is also noteworthy that the material presents significant amounts of the micronutrients Mn (6,700 mg kg^{-1}) and Zn (3,900 mg kg^{-1}), taking into account its use in soils as fertilizer. Also, is has to be emphasize that the micronutrient solubilities are high, being greater than 80%, which is in compliance with the Brazilian regulation (NI N° 46), which sets a minimum solubility requirement of 60% for products to be used as micronutrient sources (Brasil, 2016b). These soluble amounts of the Zn and Mn indicate the potential of the tested by-product to add these essential elements in the soil in forms that are readily available to plants. Besides matching the needs of most crops for these micronutrients - Zn and Mn -, the addition of the by-product in the whole area, as recommended for phosphogypsum applications (broadcasted application), have the additional benefit of an uniform and homogeneous application of micronutrients in the soil.

Such addition of these micronutrients helps to increase soil fertility and is of concern, taking into consideration the low availability of micronutrients, mainly Zn and also boron (B) that occurred in most Brazilian agricultural soils (Malavolta, 2006). In the case of Mn, although it is present in soils at higher levels, it is also a micronutrient commonly sprayed in commercial crop systems, especially when glyphosate is applied for weed control, which can reduce the plant accessibility to this nutrient (Bernards et al., 2005; Serra et al., 2011). Also, it needs to be mentioned that the lime application in areas using no-till system can increase the pH on topsoil and, as a result, reduce the Mn availability on this site, requiring its addition in the soil.

Other important characteristic showed in Table 5 is the calcium carbonate equivalent or the neutralizing power (NP) of the products tested. From this table, it is possible to notice that the tested by-product demonstrates some liming potential, since it has a NP close to 40%. Such trait is expected from data shown in Fig. 1, where the XRD showed selected minerals in the form of hydroxides, silicates, and carbonates.

Table 5 Chemical composition of the by-product and agricultural gypsum.

Product	S	Ca	Mg	Zn	Soluble Zn[1]	Mn	Soluble Mn[1]	P_2O_5	F	NP[2]
	---------------------------Total content (%)							-------------------------	mg kg^{-1}	-
By-product	13.50	16.40	10.30	0.39	0.32	0.67	0.56	ND	0.78	39.90
Agricultural Gypsum	16.60	19.13	<0.50	<0.05	<0.05	<0.05	<0.05	1.40	ND	1.98

1) For Zn and Mn, the soluble contents (% soluble) were extracted with CA (2%) and NAC plus water (1:1), respectively; in compliance with NI N° 46 (Brasil, 2016b); 2) Neutralizing power; ND) Not determined.

3.3. By-product physical characterization (particle size distribution)

The complete granulometric characterization of the by-product and the legal requirements to be met for this type of material (to be used as fertilizer), are described in Table 6. As it can be seen, the tested by-product meets the minimum requirements in terms of the granulometry, established by the NI Nº 46, to be classified as a Complex Mineral Fertilizer in the powder form. The NI Nº 46 establishes that this kind of fertilizer is a product formed of two or more chemical compounds, resulting from the chemical reaction of its components, containing two or more nutrients (Brasil, 2016b).

Table 6 Particle size distribution of the tested by-product.

Sieve		ABNT 5	ABNT 6	ABNT 7	ABNT 10 (2 mm)	ABNT 18	ABNT 20 (0.84 mm)	ABNT 35	ABNT 50 (0.3 mm)
Passing	%	100	100	100	100	80	72	56	51
Legal Requirement[1]	%	-	-	-	100	-	≥ 70	-	≥ 50

1) According to NI SDA/MAPA Nº 46 of 22/11/2016 (Brasil, 2016b). Analytical methods are described in detail in the Normative Instruction Nº 03 of 2015 - Manual of official analytical methods for mineral, organic, organomineral fertilizers, and soil liming materials (Brasil, 2015).

3.4. Presence of contaminants in the by-product

Besides presenting adequate nutrient contents, in order to be suitable for use as an input in agriculture, the by-product under evaluation needs to contain low heavy metal or contaminant contents. Therefore, Table 7 shows that the contaminant concentrations found in the tested by-product are below the maximum values allowed in this type of material (Brasil, 2016a).

The control of the reactions, especially in the initial phase of the production process, significantly reduces the Pb and Cd levels, while maintaining adequate Zn and Mn contents in the by-product. Although present in the carbonatic rock of origin, Cd and Pb have their contents controlled in the process by pH changes (two CaO additions) and also by the addition of Na_2S in the initial phase, which causes heavy metal precipitation, thus allowing for subsequent metal removal from the solution, before obtaining the final by-product (Abreu and Martins, 2009). The contaminants arsenic (As) and mercury (Hg) are not an integral part of the mineral matrix of origin from which the sulfate solutions are originated and used as feedstock in the manufacture of the by-product. These contaminants are also not inserted by the products and reagents needed in the production process. Because of that, the values found for both metals are below the detection limit of the methodologies and equipment used for the measurements, as presented in Table 7.

Chromium (Cr) is present in low concentration in the by-product, as observed in Table 7. This is possibly due to the participation of Cr as trace element in the carbonatic rock of origin used in the hydrometallurgical production process, to which is associated the sulfated raw material used to obtain the by-product. However, it is noteworthy that the Cr content found of 7.02 mg kg^{-1} is much lower than the legal limit of 200 mg kg^{-1} (Table 7).

In all analyzed samples, the concentrations of the evaluated contaminants found were significantly lower than the maximum levels allowed by the Brazilian legislation. This fact reinforces that the by-product does not have a restriction to be used in agriculture with respect to the presence of the contaminants monitored, therefore fulfilling the legal requirements established by the Brazilian legislation.

Table 7 Contaminant levels present in the tested by-product.

Contaminant		Cd	Pb	Cr		As	Hg
Content	mg kg^{-1}	9.23	< 4.69[2]	7.02	µg kg^{-1}	< 0.20[2]	< 0.02[2]
Legal Limit[1]		20	1,000	500		20	2.50

1) Maximum value admitted according to IN SDA/MAPA Nº 07 of 03/05/2016 (Brazil, 2016a); 2) Detection limit of the method. Values obtained from the average of 20 samples of the by-product.

3.5. By-product incubation in three different soils

The values of pH in water after the final reaction of the lime (48 days) until the end of the incubation with the by-product and with the agricultural gypsum are shown in Fig. 2. First of all, it should be noted that, when agricultural gypsum was applied in both doses, there was a drop or a maintenance in the pH values, which was not observed in the treatments that received the by-product, where the pH values tend to increase during the incubation. This result can be explained by the by-product neutralizing power, as well as by the fact that the agricultural gypsum used in this work (as a control treatment) is a by-product of the phosphate fertilizer industry, thus presenting residual acidity in the form of phosphoric acid as a result of the production process of the phosphate fertilizers via the attack of the phosphate rock with sulfuric acid.

Such effect in raising the soil pH with the application of the by-product occurred even in the treatments that did not receive the previous correction of the pH with the mixture of CaO and MgO in the proportion of 3:1. This fact evidences that the by-product, besides reducing Al toxicity in subsurface due to the presence of calcium sulfate, has also the potential to be used as soil liming material. As aforementioned (see in XRD results), this is attributed to the fact that the by-product presents minerals that act to correct soil acidity after their reaction in the soil, such as carbonates, hydroxides, and silicates.

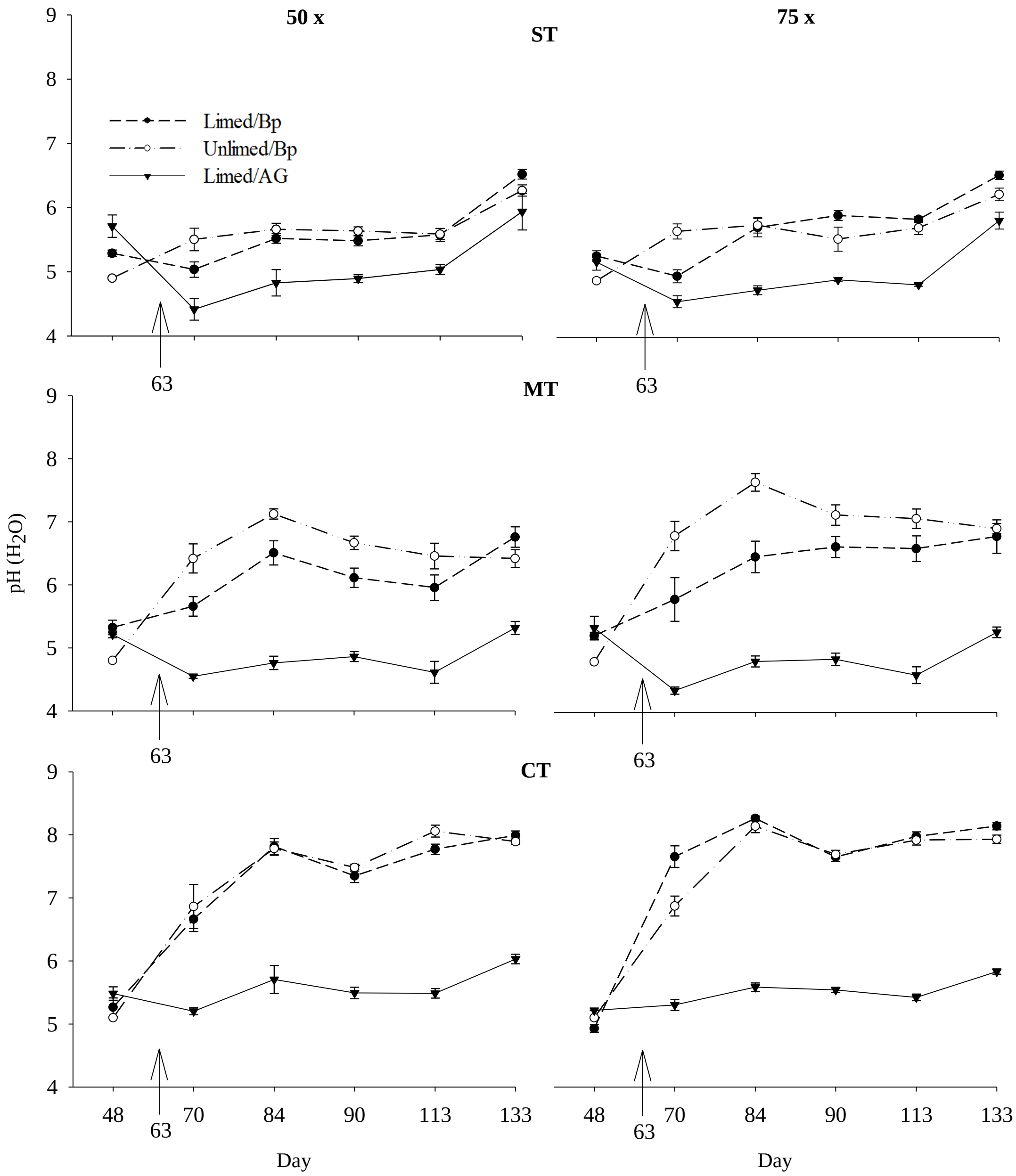

Fig. 2. Hydrogenionic potential (pH) in H_2O of the studied soils as a function of the reaction time after application of the different product doses (Bp: by-product; AG: agricultural gypsum - control) with previous (limed) or non-previous (unlimed) soil acidity correction. The applied doses of the products were calculated multiplying 50 (annual crops) and 75 (perennial crops) by the clay content (%) of the 20-40 cm soil layer. ST: sandy texture soil; MT: medium texture soil; CT: clayey texture soil. The arrows indicate the application of the by-product and agricultural gypsum to the soils, performed 63 days after the beginning of the experiment. Soils were not compared. The bars represent the standard error of each treatment.

Final pH values determined in solution of 0.01 mol L^{-1} $CaCl_2$ at the end of the reaction period (incubation) are presented in Fig. 3. It is noteworthy the significant differences found for both the doses and the products tested, but not for the interaction between them. However, it can be seen that the pH values were lower when agricultural gypsum was used, when compared to the treatments where the by-product was applied, showing also lower values for the smaller dose. Again, it has to be mentioned that the pH values in the treatments with the by-product that did not receive the previous pH correction tended to remain close to the treatments with the previous pH correction, which demonstrates the by-product liming potential feature.

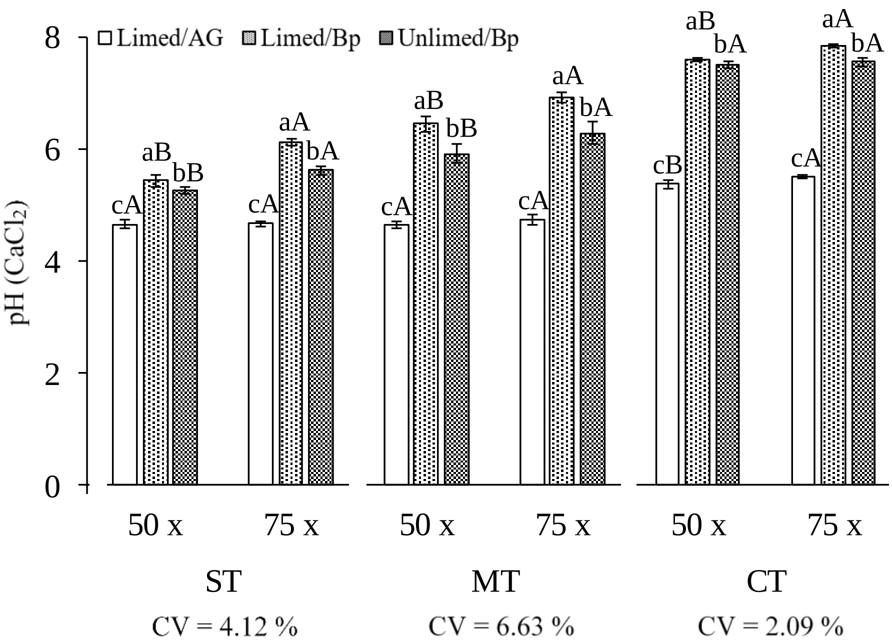

Fig. 3. Hydrogenionic potential (pH) determined in a 0.01 mol L^{-1} solution of $CaCl_2$ as a function of the different product doses (Bp: by-product; AG: agricultural gypsum - control) with previous (limed) or non-previous (unlimed) soil acidity correction. Means followed by the same uppercase or lowercase letter (s) do not differ significantly by Tukey test at $p < 0.05$. The lowercase letters represent the source and the uppercase letters represent the doses applied. The bars represent the standard error of each treatment. The applied doses of the products were calculated multiplying 50 (annual crops) and 75 (perennial crops) by the clay content (%) of the 20-40 cm soil layer. ST: sandy texture soil; MT: medium texture soil; CT: clayey texture soil. Soils were not compared. The bars represent the standard error of each treatment.

Figs. 4 and 5 show the amounts of nutrients leached over time in the three studied soils following the application of gypsum and the by-product. The same trend is observed for Ca and Mg for both products and doses. This is well explained by the similarity of these nutrients with respect to their chemistry and behavior in soils (Maria et al., 1993; Sousa et al., 2005; Neis et al., 2010; Hawkesford et al., 2011). Although the agricultural gypsum does not have Mg, the amounts of Mg leached when agricultural gypsum was added can be explained by the displacement of Mg previously present in the soil by Ca from gypsum, since the last nutrient has preference in the exchange complex, displacing Mg to solution (Pavan et al., 1984; Maria et al., 1993; Favaretto et al., 2006; 2008; Ağar, 2012; Crusciol et al., 2014).

It should be noted that when applied to the soil, the Ca contained in the by-product may displace Mg from the exchange sites, enriching the soil solution with Mg, hence having a great potential and advantage in comparison with agricultural gypsum. In this context, among the secondary macronutrients, Mg has presented the greatest deficiency problems, limiting farmers to reach high crop yields. This may be due to, among other reasons, the use of limestone with reduced Mg content. The lack of Mg affects plant growth, since this nutrient participates in essential functions in plants, such as in chlorophyll formation and, as result, in photosynthesis (Hawkesford et al., 2011).

In this context, the use of the by-product as an input in agriculture would give farmers a viable alternative to supply the soils - and consequently the crops -, with not just Mg, but also with other nutrients that the by-product carries in its composition, which are present in forms that are promptly available for plants, as described in the mineralogical and chemical assessment.

The S amounts found in the leachates as a function of the reaction time of the products with the soils are also shown in Figs. 4 and 5. The higher S amounts were obtained in the sandy soil for all treatments, while for medium and clayey texture soils the values were very low or even lower than the detection limit of the technique. Besides the particle size distribution itself, the fact that S appears in higher quantity in the leachates of the sandy soil can be attributed to the lower content of Fe and Al oxides in this soil. Soils that are rich in oxides present high capacity to retain S (as sulfate) due to the great point of zero charge (7 to 8) (Raij, 1973; Fontes et al., 2001), exhibiting, consequently, positive surface charges at normal pH values of soils, which are known to retain sulfate, which is an anion. Thus, as sandy soils present lower oxide contents, S is less retained in such soils, being more easily leached in sandy than in clayey soils (Raij et al., 1998; Zambrosi et al., 2007b; Crusciol et al., 2014).

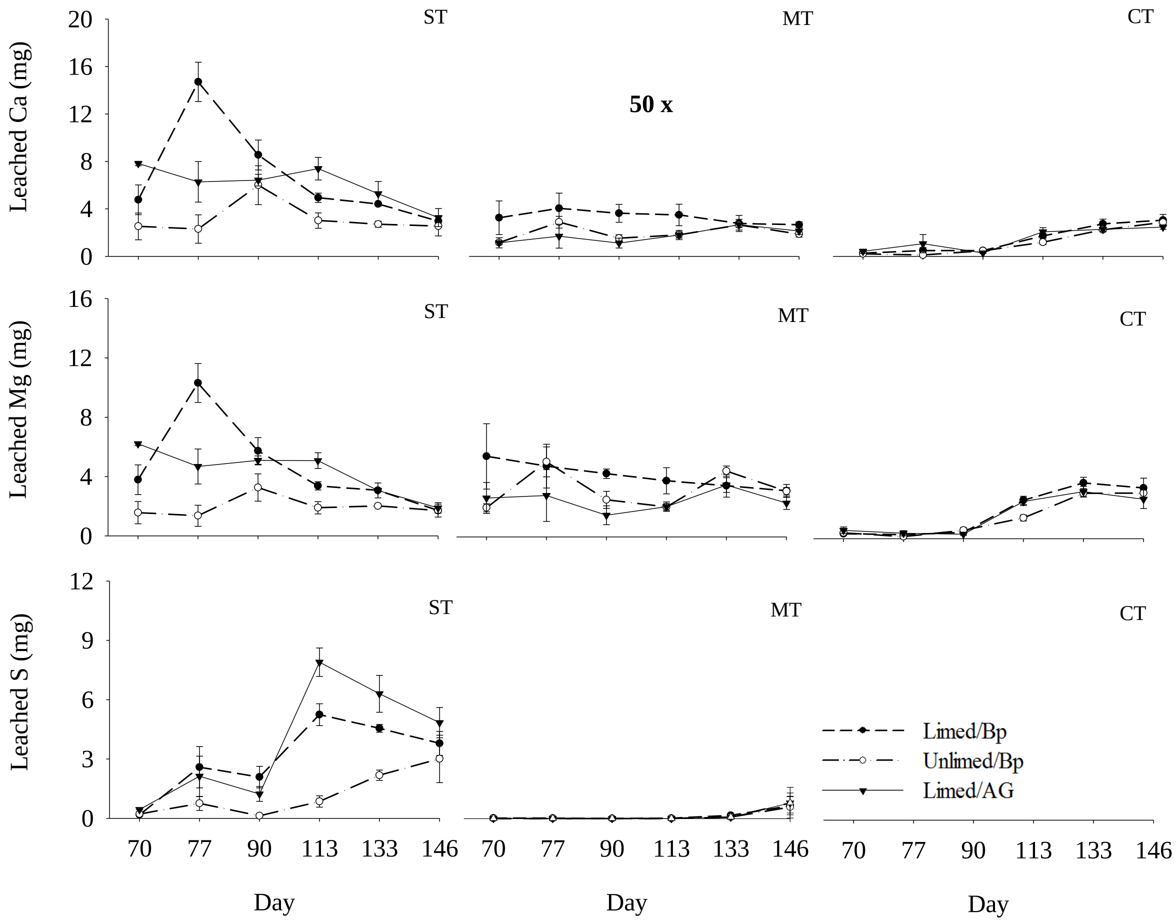

Fig. 4. Amount of Ca, Mg and S (mg) contained in the leachates collected as a function of the different product doses (Bp: by-product; AG: agricultural gypsum - control) with previous (limed) or non-previous (unlimed) soil acidity correction, regarding the different studied soils from the beginning through the end of the reaction period of the materials (146 days after the beginning of the experiment). Amounts not shown were lower than the detection limit of the apparatus. The applied dose of the product was calculated multiplying 50 (annual crops) by the clay content (%) of the 20-40 cm soil layer. ST: sandy texture soil; MT: medium texture soil; CT: clayey texture soil. Soils were not compared. The bars represent the standard error of each treatment.

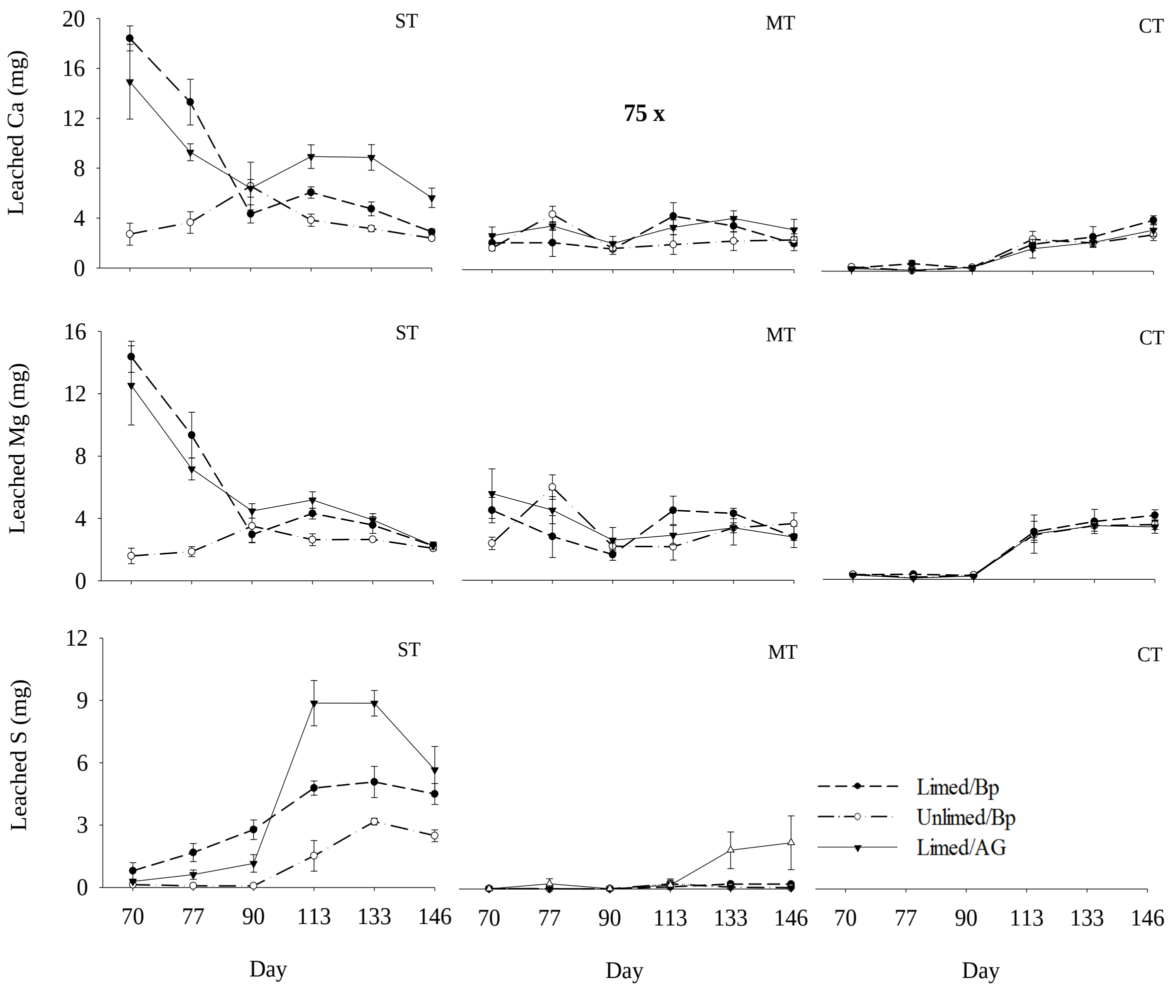

Fig. 5. Amount of Ca, Mg and S (mg) contained in the leachates collected as a function of the different product doses (Bp: by-product; AG: agricultural gypsum - control) with previous (limed) or non-previous (unlimed) soil acidity correction, regarding the different studied soils from the beginning through the end of the reaction period of the materials (146 days after the beginning of the experiment). Amounts not shown were lower than the detection limit of the apparatus. The applied dose of the product was calculated multiplying 75 (perennial crops) by the clay content (%) of the 20-40 cm soil layer. ST: sandy texture soil; MT: medium texture soil; CT: clayey texture soil. Soils were not compared. The bars represent the standard error of each treatment.

Manganese and Zn amounts in the leachates as a function of the reaction time of the products with the soils are presented in Figs. 6 and 7. It is of note the lower Mn quantities found in the leachates collected in the clayey soil, and also the levels of Zn in this soil as well as in the medium texture soil, which occurred below the detection limit of the technique (Figs. 6 and 7).

The behavior of these micronutrients in the three evaluated soils was similar to that observed for the macronutrients Ca and Mg, previously described. This may be explained by the fact that these four nutrients, Ca, Mg, Mn, and Zn are divalent cations. Thus, they tend to behave similarly with respect to its interaction with the soil negative charges. Besides, the micronutrients Mn and Zn are also carried down the soil profile accompanied by sulfate, similarly to what happens with Ca and Mg (Edwards, 1998). Since both the by-product and agricultural gypsum are composed mainly of calcium sulfate ($CaSO_4.2H_2O$), a comparable pattern with respect to nutrients leaching is expected, i.e., it may be noted that the by-product behaves similarly to agricultural gypsum with respect to the mobilization of nutrients in soils.

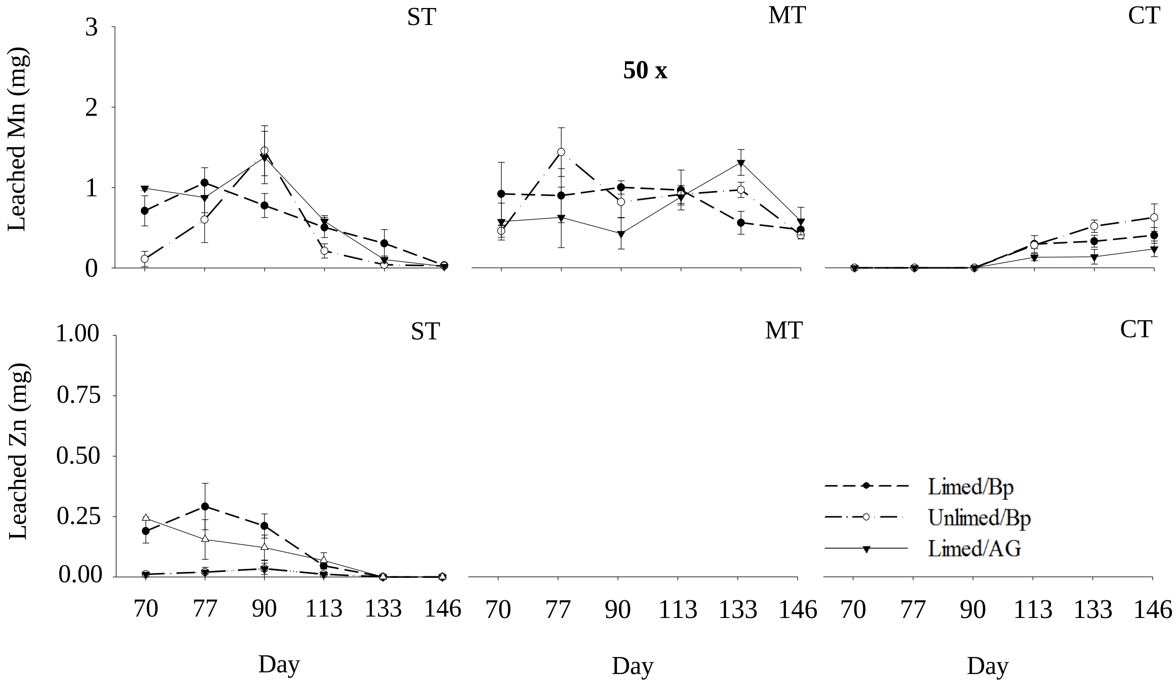

Fig. 6. Amount of Mn and Zn (mg) contained in the leachates collected as a function of the different product doses (Bp: by-product; AG: agricultural gypsum - control) with previous (limed) or non-previous (unlimed) soil acidity correction, regarding the different studied soils from the beginning through the end of the reaction period of the materials (146 days after the beginning of the experiment). Amounts not shown were lower than the detection limit of the apparatus. The applied dose of the product was calculated multiplying 50 (annual crops) by the clay content (%) of the 20-40 cm soil layer. ST: sandy texture soil; MT: medium texture soil; CT: clayey texture soil. Soils were not compared. The bars represent the standard error of each treatment.

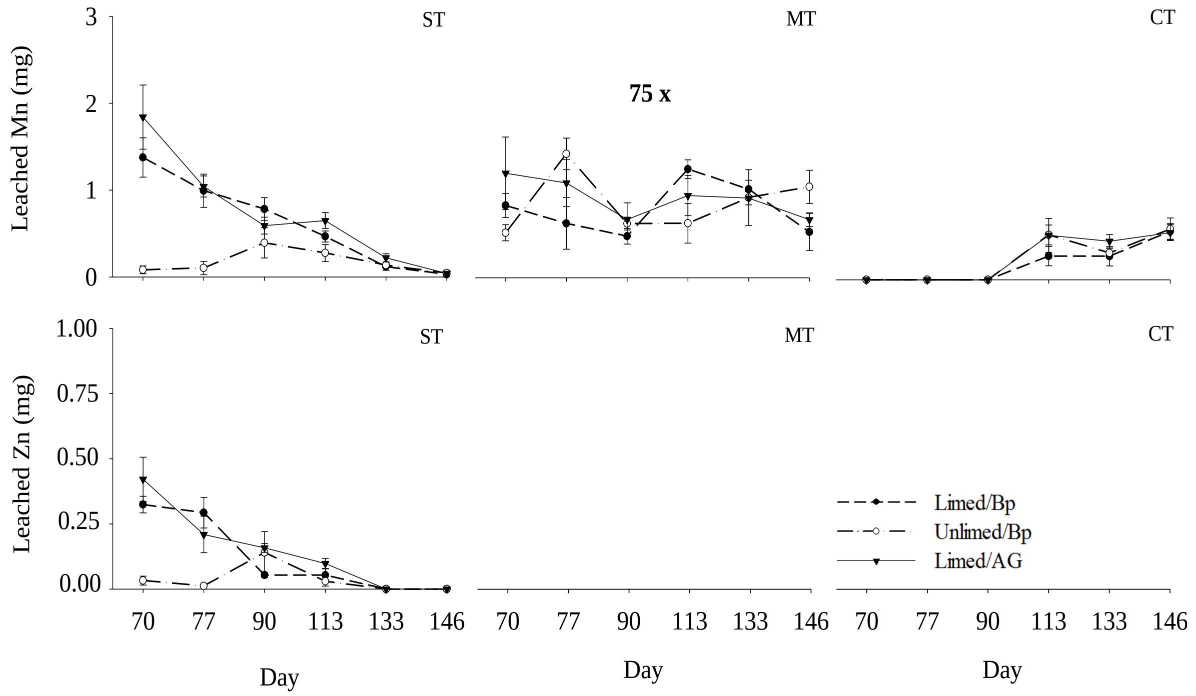

Fig. 7. Amount of Mn and Zn (mg) contained in the leachates collected as a function of the different product doses (Bp: by-product; AG: agricultural gypsum - control) with previous (limed) or non-previous (unlimed) soil acidity correction, regarding the different studied soils from the beginning through the end of the reaction period of the materials (146 days after the beginning of the experiment). Amounts not shown were lower than the detection limit of the apparatus. The applied dose of the product was calculated multiplying 75 (perennial crops) by the clay content (%) of the 20-40 cm soil layer. ST: sandy texture soil; MT: medium texture soil; CT: clayey texture soil. Soils were not compared. The bars represent the standard error of each treatment.

3.6. Greenhouse maize experiment

The accumulation of Ca, Mg, and S in the shoots and roots of maize for all studied soils is presented in Figs. 8 and 9, respectively. In general, it is observed that among soils and doses, the clayey texture and the higher dose (calculated multiplying 75 by the percentage of clay of the 20-40 cm soil layer), respectively, were the treatments that accumulated more Ca, Mg, and S, both in the shoots and in the roots. This can be attributed to the higher amounts applied, which increases the concentration of the nutrients in the soils, making them more plant available.

On the other hand, the fact that the clay soil accumulates more Ca and Mg is linked to the fact that this soil presents a higher CEC (cation exchange capacity), increasing the exchange reactions in the soil, which provides greater possibilities of exchangeable cations (e.g., Ca and Mg) to be present in the soil solution to be taken up by plants. It is well known that the ion exchange capacity of soils represents the capacity of retention and release of nutrients, which favors the maintenance of fertility for an extended period (Novais et al., 2007).

Sulfur accumulated more in the shoots than in the root, which is linked to the role of S in the plant, since this element is part of important amino acids, such as methionine and cysteine, besides important proteins that have a crucial role in the transferring of electrons on the photosynthesis reactions, such as ferredoxin (Hawkesford et al., 2011). The greater accumulation of S by the plants in the clayey soil is probably due to the higher CEC of this soil (Table 1). The higher the CEC, the higher the quantity of negative charges, thus sulfate (i.e., an anion), is more likely to move to the soil solution, being more available for plant uptake.

For Ca accumulation, it can be observed in Figs. 8 and 9 that treatments receiving agricultural gypsum (Limed/AG F) demonstrated higher means when compared to the other treatments. These results were expected taking into account that the agricultural gypsum has higher percentage of Ca in its composition compared to the other tested products (Table 5). Also, the agricultural gypsum (control) has a relative high solubility (0.24 g/100 g H_2O), thus having high available Ca levels in the soil and, consequently, favoring the absorption of the nutrient by the plants, generating greater accumulation.

In addition to the aforementioned factors, the relationship between Ca and Mg contents in soils, which may interfere on plant absorption, is well known (Medeiros et al., 2008). This interference may be due to the competition between Ca and Mg for exchangeable sites (Moreira et al,. 1999; White, 2011ab), directly interfering in the availability of these nutrients to the plants. Thus, in Figs. 8 and 9, it is observed that, unlike what happened for Ca, the control treatments (Limed/AG F) obtained the lowest Mg accumulation due to the absence of Mg in gypsum. Under such circumstances, it is possible that the Mg present in the by-product has interfered in the absorption of Ca by the plants due to the competition of the two nutrients. Despite this, it is known that some crops can obtain high yields even if the Ca:Mg ratio is high, if the Mg contents are within the ideal ranges for the respective crop.

The greater accumulation of Mg in treatments with the tested by-product (Figs. 8 and 9) occurred mainly in those treatments where the previous correction of soil acidity was performed (Limed/Bp F and Limed/Bp). Also with respect to these treatments, it was observed, in some cases that, where zinc chloride was not applied as a source of Zn, high accumulation of Mg was obtained. This can be explained by the lower concentration of Zn in the soil, as Zn can decrease the absorption of Mg by competitive inhibition due to some resemblances, such as in valence, ionic radius, and degree of hydration (Kabata-Pendias, 2011; White, 2011ab).

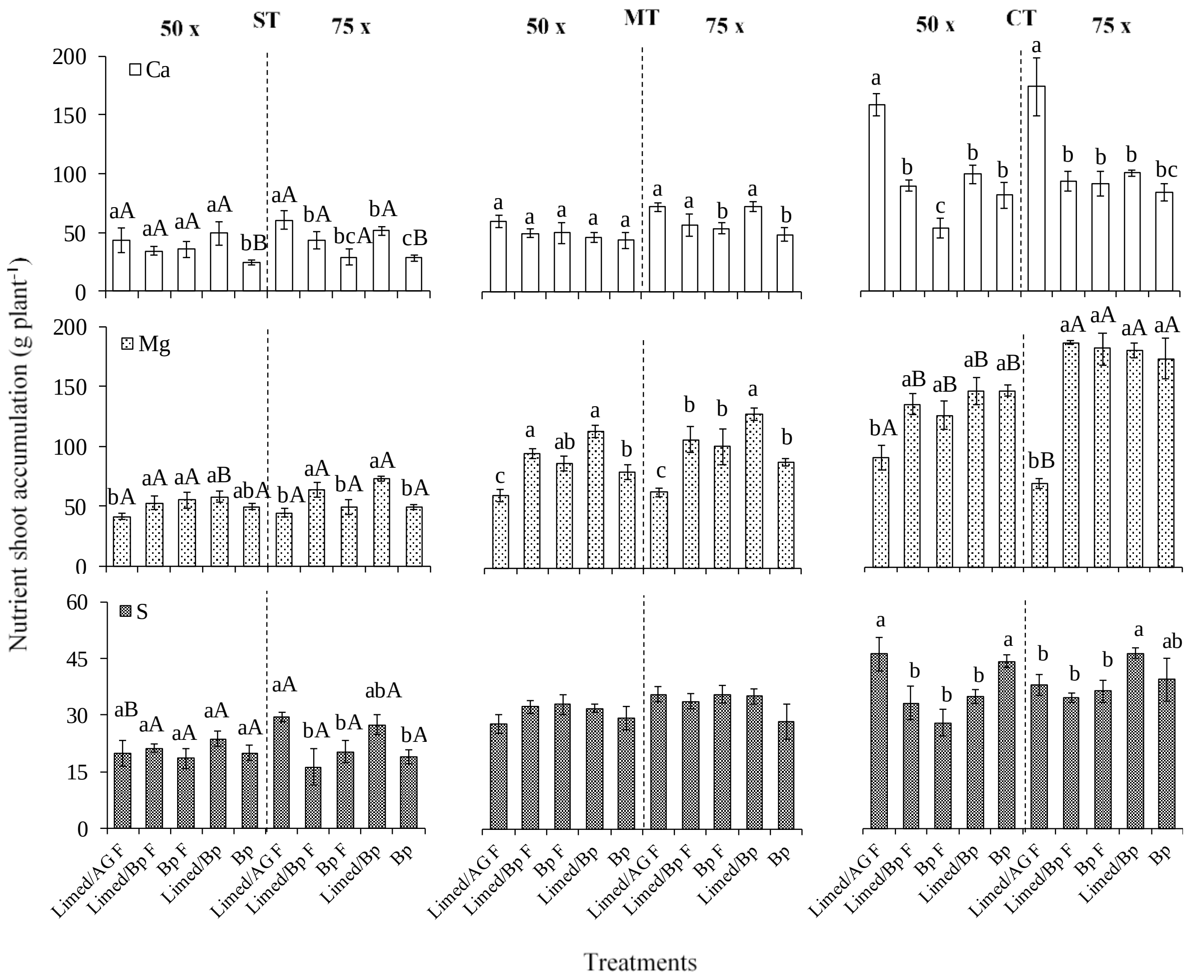

Fig. 8. Accumulation of calcium (Ca), magnesium (Mg), and sulfur (S) (g plant^{-1}) in the shoots of maize for the three evaluated soils (sandy (ST), medium (MT), and clayey (CT) texture soils) under the application of the by-product and agricultural gypsum (control) in the doses of 50 and 75 multiplied by the clay percentage of the 20 to 40 cm soil layer. Means followed by the same uppercase or lowercase letter (s) do not differ significantly by Tukey test at $p < 0.05$. The lowercase letters represent the source and the uppercase letters represent the doses applied and the absence represent no difference. Soils were not compared. The bars represent the standard error of each treatment. Limed: Previous soil correction; AG: Agricultural gypsum; Bp: by-product; F: Fertilization with Mn and Zn. The detailed description of each treatment is better shown in Table 3 in the materials and methods section.

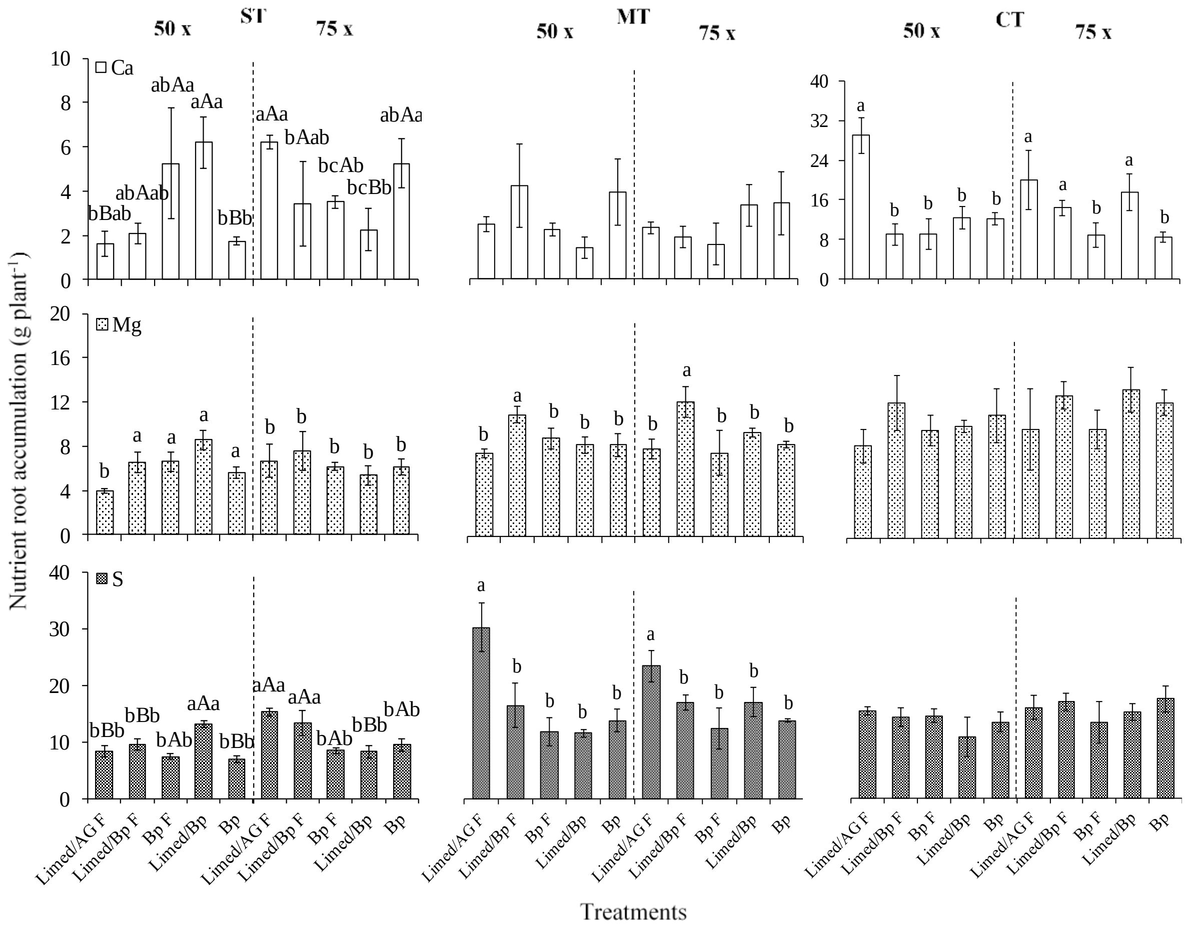

Fig. 9. Accumulation of calcium (Ca), magnesium (Mg), and sulfur (S) (g plant^{-1}) in the roots of maize for the three evaluated soils (sandy (ST), medium (MT), and clayey (CT) texture soils) under the application of the by-product and agricultural gypsum (control) in the doses of 50 and 75 multiplied by the clay percentage of the 20 to 40 cm soil layer. Means followed by the same uppercase or lowercase letter (s) do not differ significantly by Tukey test at $p < 0.05$. The lowercase letters represent the source and the uppercase letters represent the doses applied and the absence represent no difference. Soils were not compared. The bars represent the standard error of each treatment. Limed: Previous soil correction; AG: Agricultural gypsum; Bp: by-product; F: Fertilization with Mn and Zn. The detailed description of each treatment is better shown in Table 3 in the materials and methods section.

The accumulation of Zn and Mn in the shoots and roots of maize are shown in Figs. 10 and 11, respectively. The results show that there were no differences between the doses applied of the products, when comparing the treatments within the same soils. In general, in comparison to the macronutrients, the micronutrient accumulations observed in the roots were smaller.

The highest values of Zn accumulation were found in the sandy and medium soil for shoots and roots respectively, while for Mn, this was observed in the soil of medium texture, for both shoots and roots (Figs. 10 and 11), which are also results linked to the CEC of each soil since Zn and Mn are cations. In addition, in the treatments with the by-product (Limed/Bp F, Bp F, Limed/Bp, and Bp), the results of Zn and Mn accumulations were very similar, even in those treatments where Zn and Mn were not applied in the form of chloride. This fact indicates the potential of the evaluated by-product in providing these micronutrients to the plants.

The Zn and Mn values accumulated by the maize plants, even in the treatments in which these micronutrients were not applied, clearly demonstrate the capability of the by-product to be used as a valuable source for supplying these nutrients to the plants. Also, the values of Zn and Mn found in plants (accumulations) receiving gypsum plus Zn and Mn (as chloride salts) were generally similar to the treatments with the by-product. This demonstrates that the micronutrients contained in the by-product are solubilized similarly to ones added as chlorides.

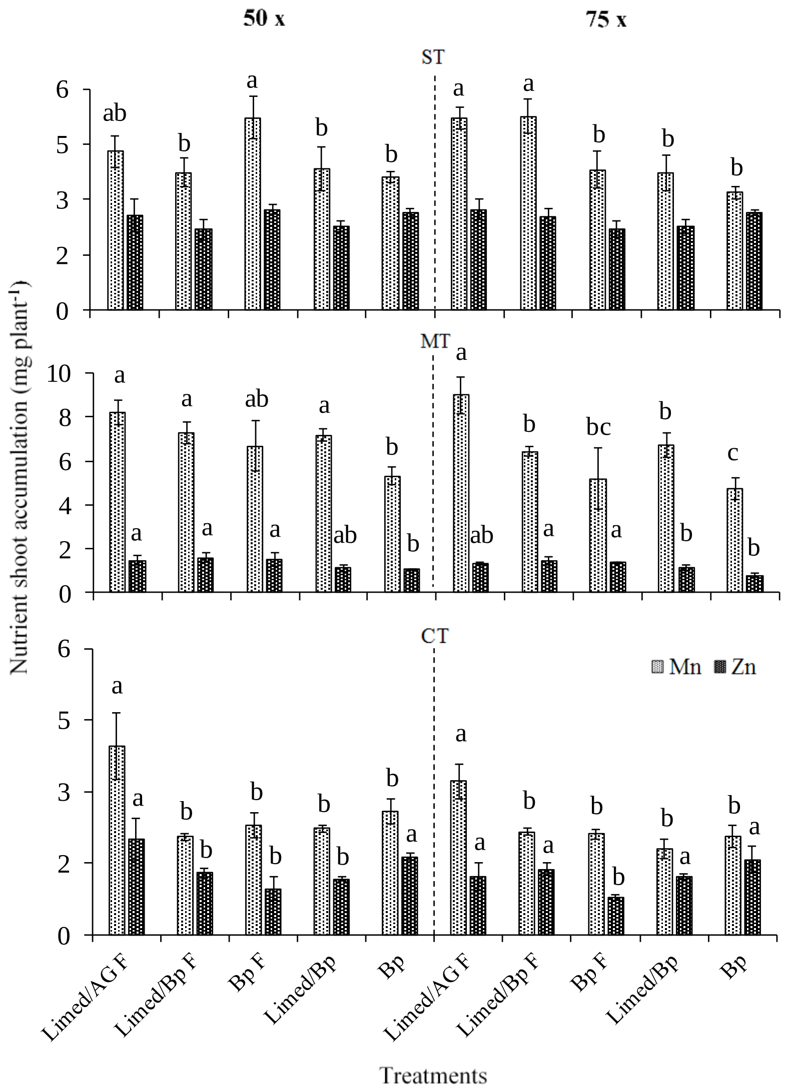

Fig. 10. Accumulation of manganese (Mn) and zinc (Zn) (mg plant^{-1}) in the shoots of maize for the three evaluated soils (sandy (ST), medium (MT), and clayey (CT) texture soils) under the application of the by-product and agricultural gypsum (control) in the doses of 50 and 75 multiplied by the clay percentage of the 20 to 40 cm soil layer. Means followed by the same uppercase or lowercase letter (s) do not differ significantly by Tukey test at $p < 0.05$. The lowercase letters represent the source and the uppercase letters represent the doses applied and the absence represent no difference. Soils were not compared.

The bars represent the standard error of each treatment. Limed: Previous soil correction; AG: Agricultural gypsum; Bp: by-product; F: Fertilization with Mn and Zn. The detailed description of each treatment is better shown in Table 3 in the materials and methods section.

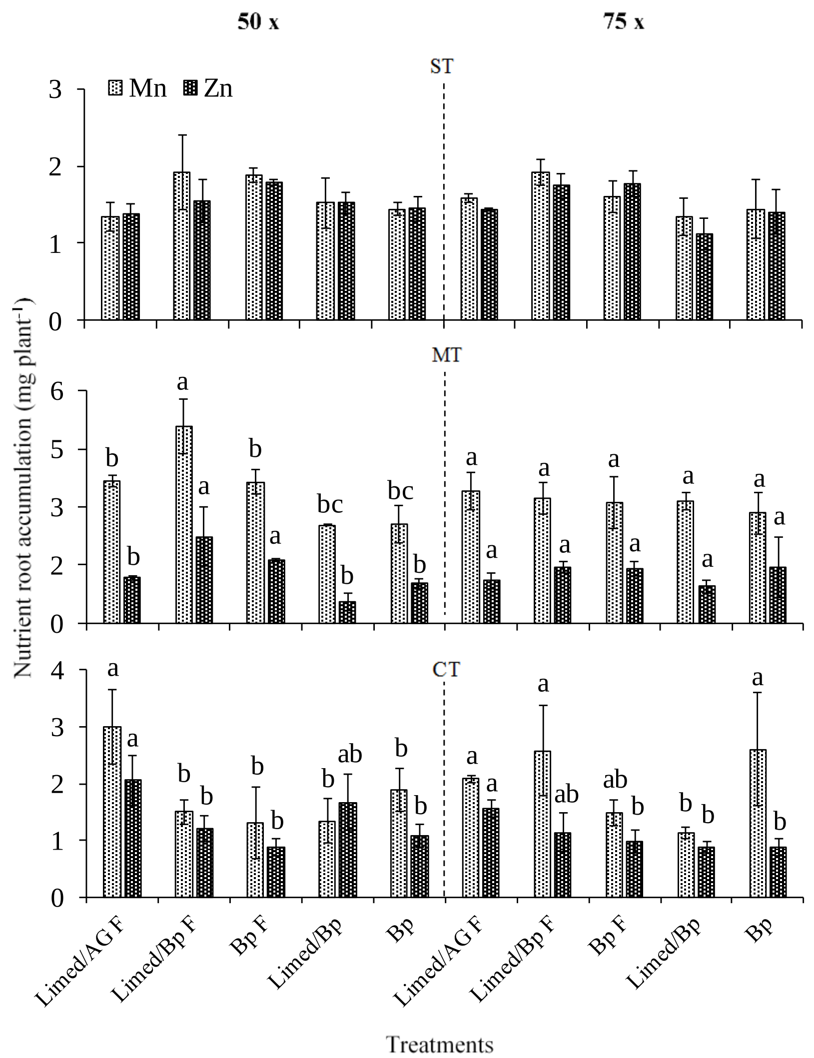

Fig. 11. Accumulation of manganese (Mn) and zinc (Zn) (mg plant^{-1}) in the roots of maize for the three evaluated soils (sandy (ST), medium (MT), and clayey (CT) texture soils) under the application of the by-product and agricultural gypsum (control) in the doses of 50 and 75 multiplied by the clay percentage of the 20 to 40 cm soil layer. Means followed by the same uppercase or lowercase letter (s) do not differ significantly by Tukey test at $p < 0.05$. The lowercase letters represent the source and the uppercase letters represent the doses applied and the absence represent no difference. Soils were not compared. The bars represent the standard error of each treatment. Limed: Previous soil correction; AG: Agricultural gypsum; Bp: by-product; F: Fertilization with Mn and Zn. The detailed description of each treatment is better shown in Table 3 in the materials and methods section.

4. Conclusions

The tested by-product has shown to have essential elements in the form of sulfates, hydroxides, carbonates, and silicates, which gives the by-product its effect on decreasing Al toxicity similarly to agricultural gypsum. Furthermore, it presents a soil liming potential (calcium carbonate equivalent or neutralizing power) close to 40%.

With respect to the requirements of the Brazilian legislation, the by-product does not present toxic trace elements in contents that are not allowed for fertilizers. Although the by-product agronomic efficiency was not assessed in the present study, it contains important plant nutrients, such as Ca, Mg, S, Zn, and Mn, acting similarly to agricultural gypsum with respect to nutrient solubilization and mobilization. Moreover, compared with agricultural gypsum, the tested by-product presents the advantage of having extras nutrients such as Mg, Zn, and Mn, making this by-product a very interesting and innovative agricultural input, especially considering the possibility of uniform distribution of micronutrients in to the soil.

It has to be stated that the by-product meet all requirements to be used as a source of nutrients (fertilizers), but the agronomic efficiency of the tested by-product needs to be assessed in greenhouse and field conditions to prove its possible beneficial use in agriculture. Finally, it should be emphasized that using such the tested by-product in soils as a fertilizer can help the farmers to achieve high crop yields, aggregating economic values for the residue generated in the zinc mining industry and reducing the environmental liability.

Acknowledgments

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ARTICLE 2

Beneficial use of a by-product from a zinc metallurgical industry as fertilizer for cultivation of soybean under field conditions

(Paper to be submitted to the journal Nutrient Cycling in Agroecosystems – Preliminary version)

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ABSTRACT

Reuse of industrial residues is important to reduce their inappropriate disposal and to aggregate value to co-products, transforming them into by-products, with economic value. One possibility of using industrial by-products is in agriculture, when such materials are applied on soils as a source of nutrients and, or, as soils amendments for crop production. In this context, this study aimed to evaluate the effects of a by-product containing Ca, Mg, S, Mn, and Zn obtained from a zinc metallurgical industry as a source of nutrients for the cultivation of two important agricultural crops: maize and soybean. For this, the tested by-product (Bp) was compared with the application of agricultural gypsum (AG) and AG enriched with the same quantities of Zn and Mn present in the Bp (EG) for cultivation of corn during 66 days in greenhouse conditions and of soybean in field conditions until grain production. In both conditions, we have evaluated different doses of the assessed products and their effect on soil properties and plant nutrient status. Results show that the tested by-product can increase Ca and S contents in the soils similarly to what happens when agricultural gypsum is used, while providing other important nutrients, such as Mg, Zn, and Mn. Such effects upon increasing nutrient contents in soils resulted in their accumulation in the studied plants, yet such increases did not improve soybean yields under filed conditions (one cropping season). Therefore, it is noteworthy to state that the by-product application in soils, besides reducing the environmental liability in the industry where this product is generated, may benefit soil and plants. However, further studies evaluating other doses in different soil conditions as well as assessing the residual effect of this tested by-product are recommended.

KEYWORDS: zinc metallurgy, by-product, macro and micronutrients, gypsum, fertilizer.

Introduction

Nutrient cycling in agroecosystems is a very important global issue and one of the main reasons is its direct relation to the sustainability of crop production, even more specifically of the fertilizer use efficiency. It has to be stated that the conventional fertilizers used in agriculture are not enough and available to be used in all crop production forever. Thus, every tonne of nutrient intercepted from a waste flow and processed into a suitable form to be used to fertilize crops represents a tonne less which would have leaked into water, the atmosphere, or ended up in land fill (Buckwell and Nadeu, 2016).

One example of returning the nutrient to the soil is the re-utilization of industrial by-products in agriculture, which aims to take the residues/by-products containing nutrients obtained from industrial processing and reapply it on the soil (acting as fertilizers). Such reuse may not just nourish the plants but also improve soil quality attributes (Bown et al. 1998; Power et al. 2000; Cavaleri et al. 2004; Costa et al. 2012; Lopes et al. 2012; Park et al. 2014; Yang et al. 2015; Valle et al. 2015).

Therefore, industrial by-products from several production sites worldwide have been studied and reused as inputs in agriculture. One of the main examples that could be given is of agricultural gypsum (hereafter used as a general expression for the by-product phosphogypsum derived from phosphate fertilizer industries), which is used to reduce Al toxicity in deeper soil layers, while providing nutrients for the plants, as well as improving other soil physical and chemical attributes (Garrido et al. 2003; Illera et al. 2004; Zambrosi et al. 2007; Garrido et al. 2011; Blum et al. 2013; Watts and Dick, 2014).

In this context, in the zinc hydrometallurgical industry, after ores are processed, a type of residue is obtained as a by-product, containing plant macro and micronutrients, such as sulfur (S), calcium (Ca), magnesium (Mg), manganese (Mn), and zinc (Zn) (Abreu and Martins, 2009). In addition, this by-product also has the capacity of neutralizing soil acidity due to its chemical composition, mainly carbonates, hydroxides and silicates.

Since the by-product is similar to gypsum (i.e. a soil conditioner), it consequently has the same benefits to the soil, promoting a better growing environment for the plants (Messenger et al. 2000; Favaretto et al. 2006, 2008; Fisher 2011; Idris 2012; Lopes et al. 2012). Therefore, the re-utilization of this by-product in agriculture could help benefit and also enrich tropical soils, which are typically highly weathered, i.e., present low pH and low nutrient availabilities (e.g., nitrogen, phosphorus, potassium, Ca, Mg, S, B, Cu, Mn, and Zn), as well as high aluminum (Al) levels (Juo and Franzluebbers 2003; Novais et al. 2007; Lopes et al. 2012; Lopes and Guilherme 2016). It is also important to emphasize that the re-utilization of this by-product, when applied as an input in agriculture helps the recycling of nutrients, returning it to the soil (i.e., sustainability).

Preliminary studies with the by-product have shown promising results and no environmental concerns with its re-utilization (Pereira et al. 2007; Abreu and Martins, 2009). However, few studies have been conducted with this by-product focusing on its beneficial use in agriculture. Thus, considerable research involving the use of this by-product in agriculture is still required for a better understanding of its effects on soils and plants.

Therefore, this study aimed to evaluate the efficiency of a zinc-mining by-product applied as fertilizer soybean cultivation under field conditions, and to assess its effects on plant development and nutrient status, as well as on soil attributes.

Materials and methods

By-product generation process

The generation process of the by-product in evaluation is described in details in another study (Chapter 2, Article 1 of this dissertation). Briefly, the by-product in evaluation is obtained by the means of the silicate circuit, which is integrated with the sulphide ore circuit, a part of the hydrometallurgical zinc production that aims a better Zn recover. The generation of a solid residue containing calcium sulfate ($CaSO_4$) occurs in treatment process of the silicate circuit, due to the reaction between the effluent with sodium sulphide (Na_2S) and calcium oxide (CaO). Between 1700 to 2000 m³ of this residue are produced daily, of which 37% is basically $CaSO_4$ (Feijó, 2007). The addition of Na_2S and CaO is made to guarantee the precipitation of metals and to meet the established levels for the final disposal of the effluent (Blais et al., 2008).

Even though most heavy metals of concern (namely Pb and Cd) are precipitated after the first addition of CaO and Na_2S to the sulfate solution, there is still some level of them left in the solid residue obtained. For this reason, a second addition of CaO is made aiming on lowering the levels of heavy metals to attend the regulation established by the Normative Instruction (NI) Nº 07 (Brasil, 2016a), defined by the Brazilian Ministry of Agriculture, Livestock and Supply (MAPA). The by-product obtained after this second phase contains nutrients in appropriate concentrations to be applied in agriculture and very low contaminant levels, properly meeting the current legal Brazilian legislation requirements.

Soybean field trials

Three field trials were carried out in three different areas. Two areas were set in a farm located at the municipality of Coromandel, in the state of Minas Gerais (MG), Brazil (18° 38' 27,3 S and 46° 54' 98,8 W), with an altitude of 1,117 m and an average annual precipitation of 1,400 mm. The soils that occur in these two areas were classified as very clayey typical Red Latosol (Embrapa, 1999). The other field trial was set up at the experimental farm of the Agricultural Research Company of Minas Gerais (EPAMIG), located in Patos de Minas, MG (18° 31' 02.40" S and 46° 26' 21.44" W), with an elevation of 930 m. This area is located 60 km far from the two first areas aforementioned. The soil of this area is classified as eutrophic Red Latosol (Embrapa, 1999) and the average annual rainfall is 1,422.2 mm. The climate of the two sites (Coromandel and Patos de Minas) is similar, tropical humid presenting temperatures below 18°C during the colder months and above 32°C during warmer months. The climogram of the region is showed in Fig. 1.

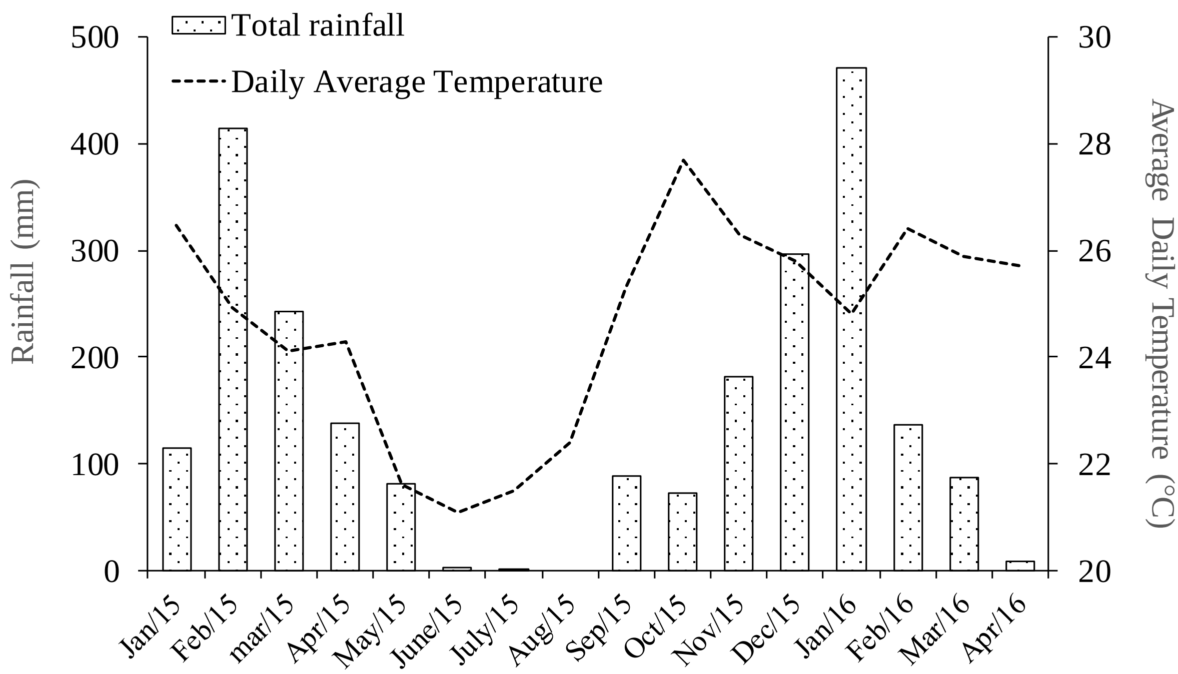

Fig. 1 Climogram of the year 2015 and the beginning of 2016. The period of soybean sowing and harvest are indicated by the arrows.

The two areas selected for soybean cultivation in the farm in Coromandel comprises an uncultivated area (fallow area) and an area that had been previously cultivated, hereafter called "cultivated area". The soybean cultivars M8210IPRO and M6210IPRO were used in the trials for the fallow and cultivated areas, respectively. The sowing of the two areas was carried out on 12/10/2015, using a manual seeder, with seeds previously inoculated with solutions of cobalt and molybdenum and *Bradyrhizobium japonicum* bacteria. In Patos de Minas, the test was carried out in only one area, using the soybean cultivar M8210IPRO, sown on 12/12/2015.

For all the three trials, the spacing used was 0.40 m between rows targeting an average final stand of 170,000 and 330,000 plants ha^{-1} for the M8210IPRO and M6210IPRO, respectively. The values for the final stand of plants were chosen according to the recommendations of the seed suppliers.

The areas received limestone to correct soil acidity one month before sowing, considering the results of the chemical analysis performed in the soils prior to the implantation of the experiments (Table 1). In Coromandel liming was performed aiming to increase the bases saturation to the level between 50 and 60%, using a limestone with the following characteristics: Ca = 21.70%; CaO = 30.35%; Mg = 14.00%; MgO = 23.21%; PRNT = 87.36%. The limestone doses used for the fallow and cultivated areas were 3.875 and 1.563 t ha^{-1}, respectively. On the other hand, the area in Patos de Minas was corrected with 3 t ha^{-1} of dolomitic limestone aiming to increase the base saturation to 60%.

Table 1 Soil chemical and physical analysis of the three areas

Parameter	Unit	Fallow Area		Cultivated Area		Patos de Minas Area	
		Depth (cm)					
		0-20	20-40	0-20	20-40	0-20	20-40
pH_{H2O}	-	5.5	5.6	5.8	5.8	5.8	5.4
pH_{CaCl2}	-	4.5	4.5	5.0	5.0	5.2	5.0
O.M.	dag kg^{-1}	4.4	2.6	4.2	4.1	3.4	3.4
P	mg dm^{-3}	3.4	1.8	2.7	1.5	18.6	21.3
K	mg dm^{-3}	50.7	31.2	105.3	74.1	113.1	78.0
S	mg dm^{-3}	1.2	0.8	11.5	10.2	28.1	34.4
Ca	$cmol_c$ dm^{-3}	0.8	0.4	1.8	1.3	2.1	1.3
Mg	$cmol_c$ dm^{-3}	0.2	0.1	0.8	0.5	1.0	0.6
Al	$cmol_c$ dm^{-3}	0.1	0.0	0.0	0.0	0.0	0.0
H + Al	$cmol_c$ dm^{-3}	7.9	5.9	5.6	5.4	6.1	5.6
$CEC_{pH\ 7.0}$	$cmol_c$ dm^{-3}	9.0	6.5	8.5	7.4	8.8	8.1
V	%	12.5	9.0	33.9	26.9	30.0	30.3

Continuing…

B	mg dm^{-3}	0.2	0.2	0.2	0.2	0.3	0.3
Zn	mg dm^{-3}	1.9	1.3	2.3	2,0	1.6	1.9
Fe	mg dm^{-3}	214.7	93.7	114.4	86.7	20.9	22.7
Mn	mg dm^{-3}	3.2	2.3	7.1	5,0	66.9	56.5
Cu	mg dm^{-3}	1.5	1.1	1.2	1.1	6.7	7.2
Sand	%	11.0	13.0	11.0	13.0	24.0	24.0
Silt	%	26.0	26.0	26.0	26.0	39.0	39.0
Clay	%	63.0	61.0	63.0	61.0	37.0	37.0

Ca, Mg, and Al = KCl, 1 mol L^{-1}; H + Al = Calcium acetate, 1 mol L^{-1}, pH 7.0; P, K, and micronutrients = Mehlich-1; S = $CaHPO_4$; B = Hot water (Embrapa, 2009); MO = Colorimetric method; H^+ (Raij et al., 2001).

The experimental design was carried out in completely randomized blocks, being a factorial 3 x 2, i.e., three products used as nutrient source (gypsum, enriched gypsum, and the tested by-product) and two doses (0.5 and 1.5 t ha^{-1}). Regarding the products, it is noteworthy that the product under evaluation was compared with two other products, a commercial agricultural gypsum and this agricultural gypsum enriched with the same amounts of Zn and Mn present in the by-product (hereafter called “enriched gypsum”) (0.39% and 0.67% of Zn and Mn, respectively). The composition of each product used in this work is presented in Table 2.

All field trials were evaluated in four replicates, totaling 24 plots per trial. The experimental units were composed of six rows of 6.25 m, with spacing of 0.40 m between rows, totaling 15 m² per plot. The useful area of each plot was composed of two central rows, disregarding 0.50 m at each end of the rows.

Table 2 Composition of the products used in this study

Product	Total content (%)									
	S	Ca	Mg	Zn	Soluble Zn[1]	Mn	Soluble Mn[1]	F[2]	NP[3]	P_2O_5
By-product	13.50	16.40	10.30	0.39	0.32	0.67	0.56	0.78	39.90	ND
Agricultural gypsum	16.60	19.13	<0.50	<0.05	<0.05	<0.05	<0.05	ND	1.98	1.40
Enriched gypsum	15.02	18.08	<0.50	0.50	0.20	0.61	0.42	ND	1.24	1.50

1) For Zn and Mn, the soluble contents (% soluble) were extracted with CA (2%) and NAC plus water (1:1), respectively; in compliance with NI N° 46 (Brasil, 2016b); 2) value in ppm; 3) Neutralizing power; ND) Not determined.

It is worth noticing that in the present study the by-product was not evaluated in comparison with the agricultural gypsum as a source of the nutrients Mg, Zn, and Mn since gypsum does not have these nutrients and, as results, it is not used in agriculture for this purpose. However, the agricultural gypsum was used as control because it is the input found in the Brazilian market that most resembles with the by-product in evaluation. Also, the addition of Mg to the enriched gypsum was not performed once the content of this nutrient in the soil before the establishment of the field trials was satisfactory, since a level of Mg in the soil above 0.50 $cmol_c$ dm^{-3} is considered sufficient for soybean cultivation (Ribeiro et al. 1999 and Sousa and Lobato, 2004). In addition, for the fallow area, which had Mg levels lower than 0.50 $cmol_c$ dm^{-3} the supply of this nutrient was performed through liming before sowing.

Seed and cover fertilization were carried out according to the soil analysis (Table 1) and following specific recommendations for soybean cultivation (Ribeiro et al. 1999, Embrapa, 2013), considering also the nutrients added through the application of the products tested in this study.

Leave Samples were collected for analysis during the flowering period, collecting always the diagnostic leaf of each plant (5 leaves per plot). In relation to soil sampling, six subsamples were collected, from 0-20 cm and 20-40 cm depth, in each plot, which were mixed to obtain the composite sample analyzed for each soil attribute.

Soil sampling was performed at harvesting period. Basically, in addition to soybean yield, the variables evaluated in the experiments were the nutrient contents (Ca, Mg, S, Zn, and Mn) in soils and plants (leaves and grains), considering the potential of the tested by-product to provide these nutrients to the soil, besides capacity of the by-product to raise soil pH.

At harvesting the number of plants/plot harvested were 30 and25 for the cultivated and fallow areas in Coromandel site, respectively, and 30 for the area located in Patos de Minas. The plants were manually harvested and the mass of 1,000 grains and yield was then determined (kg ha^{-1}) at 13% moisture. In addition, the grains were sent to the laboratory for evaluation of macro and micronutrients of interest (Ca, Mg, S, Zn and Mn).

Statistical analysis

Data obtained from the experiments were submitted to analysis of variance with the assistance of the software Assistat (Silva and Azevedo 2009). The means of the analyzed variables of each treatment were compared by Tukey test, using a 5% level of significance.

Results and discussion

Soybean field trials

Soil results

Sulphur, Ca, and Mg contents determined in the soils following soybean harvest for all evaluated areas are shown in Fig. 2. In general, contents of the three assessed macronutrients found in the soils after the products application were slightly higher compared with their contents verified before the soybean cultivation, as it is demonstrated by the horizontal lines in Fig. 2. It is important to mention that, in general, the levels of Ca, Mg, and S found in both soil depths after the addition of the evaluated products are considered to be enough for the cultivation of crops such as soybean, with expected medium to high yields (Raij et al. 1996; Sfredo et al.1999, 2003; Comissão de Química e de Fertilidade do Solo, 2004) (Fig. 2).

Contents of Ca did not differ significantly among the treatments, which can be attributed due to the fact that applied products have similar percentage of this nutrient (18, 19, and 16.4% for agricultural gypsum, enriched gypsum, and by-product, respectively). On the other hand, it can be observed that in some cases the by-product use tended to provide a slightly increase in Mg contents in both depths. Such possible increase may be explained since the by-product has Mg in its composition (10.3% of Mg).

Sulphur contents in the soils of the three areas did not differ in relation to the applied products, but it increased upon increasing the applied doses. It has to be emphasize that, besides enriching the soil profile with the cations (e.g., Ca and Mg), the sulfate contained in the by-product can acts to neutralize the exchangeable aluminum, even in deeper soil layers, as can be seen the increase in S content in the deeper evaluated soil layer (Fig. 2). The reaction between sulfate and aluminum results on aluminum sulfate formation, which is not harmful for plants, thus, contributing for better root development, increasing the plant tolerances in drought periods (Ribeiro et al. 1999; Zambrosi et al. 2007; Blum et al. 2013).

Fig. 2 demonstrates the by-product effectiveness to provide the macronutrients Ca, Mg, and S to the soil, which is of special relevance in Brazilian Cerrado soils that are poor in nutrients, being the deeper layers even less fertile (Raij et al. 1996; Ribeiro et al. 1999; Novais et al. 2007; Lopes et al. 2012, Lopes and Guilherme, 2016).

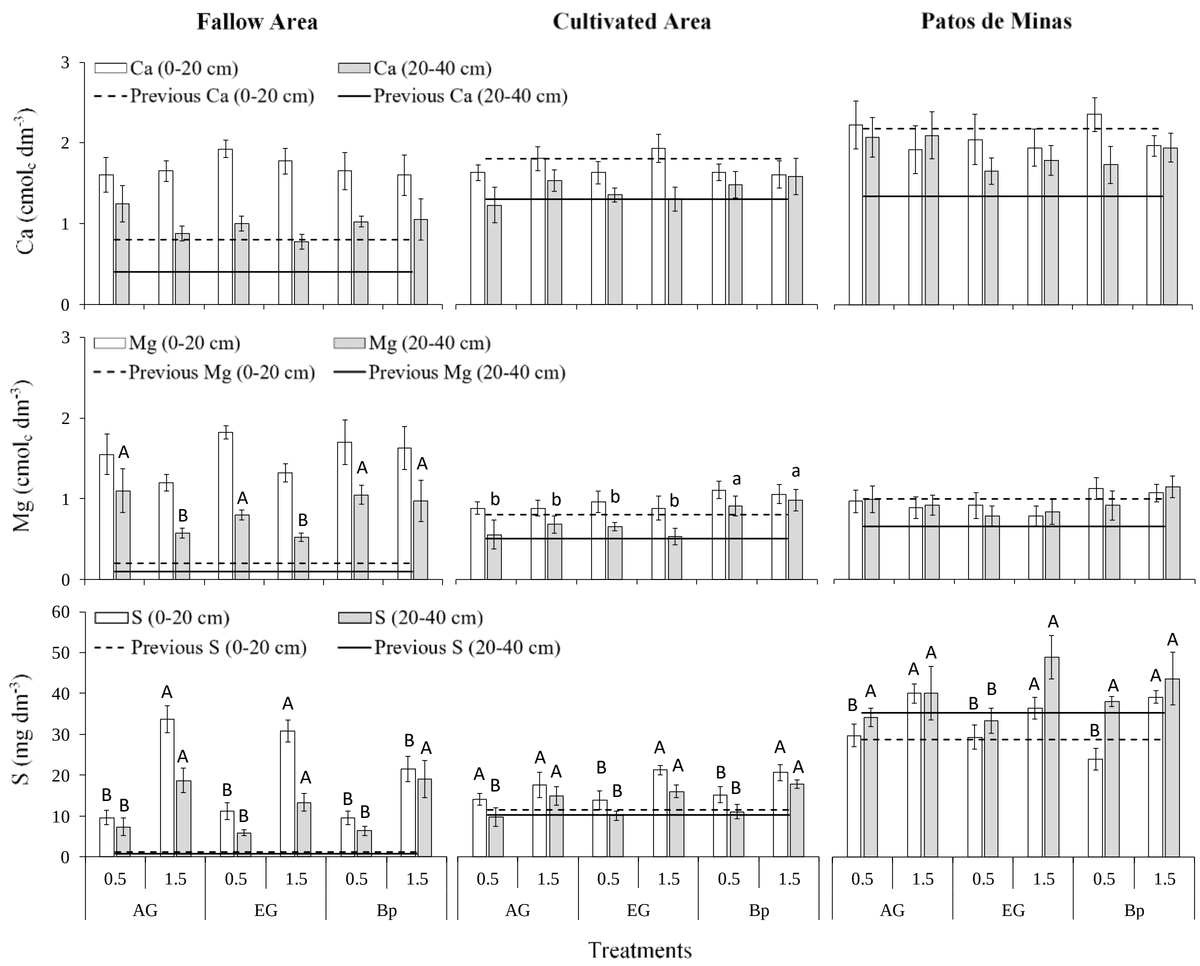

Fig. 2 Calcium (Ca), magnesium (Mg) ($cmol_c\ dm^{-3}$) and sulfur (S) contents ($mg\ dm^{-3}$) in the soils of the three areas, at the depths of 0-20 and 20-40 cm. 0.5 and 1.5 ($t\ ha^{-1}$) on the x-axis are the applied doses of the three evaluated products. AG: Agricultural gypsum; EG: Agricultural gypsum enriched with Zn and Mn; Bp: tested by-product. The horizontal lines represent the respective nutrient content found in the soils prior to the experiment implantation. The lowercase letters represent the differences the source and the uppercase letters represent the differences the doses applied and the absence represent no difference. Means followed by the same letter do not significantly differ by Tukey test at $p < 0.05$. The bars represent the standard error of each treatment.

Zinc and Mn contents in the soils after soybean cultivation for all areas are shown in Fig. 3. It can be noted that the values increased from the fallow to the cultivated area, in Coromandel, being even higher in the area located in Patos de Minas, which presented higher initial values of nutrients. The Zn and Mn values found are considered to be within the limits determined as satisfactory for the cultivation of cereal crops (Raij et al. 1996; Ribeiro et al. 1999; Sfredo et al.1999).

The contents of Zn and Mn were, in some cases, lower than their contents before the products application. This fact may be explained due to the limestone addition to correct soil acidity, since higher pH values decrease the Zn and Mn availabilities (Sims 1986; Teixeira et al. 2003; Fernández and Hoeft 2009; White 2011ab).

In general, the application of the tested by-product in both doses increased Zn and Mn contents in the soil compared to the agricultural gypsum addition, being the by-product effect similar or even more pronounced than that of the enriched gypsum, in which Mn and Zn were included (Fig. 3). This can be linked to the solubility of the Zn and Mn chemical forms (see Table 2) present in the composition of the by-product (82 and 84%, respectively) in comparison with the enriched gypsum (41 and 69%, respectively). This fact indicates the by-product efficiency to improve soil fertility by adding these micronutrients. Thus, the use of this tested by-products may be considered beneficial for tropical soils, where nutrient deficiencies are commonly found (Malavolta, 2006).

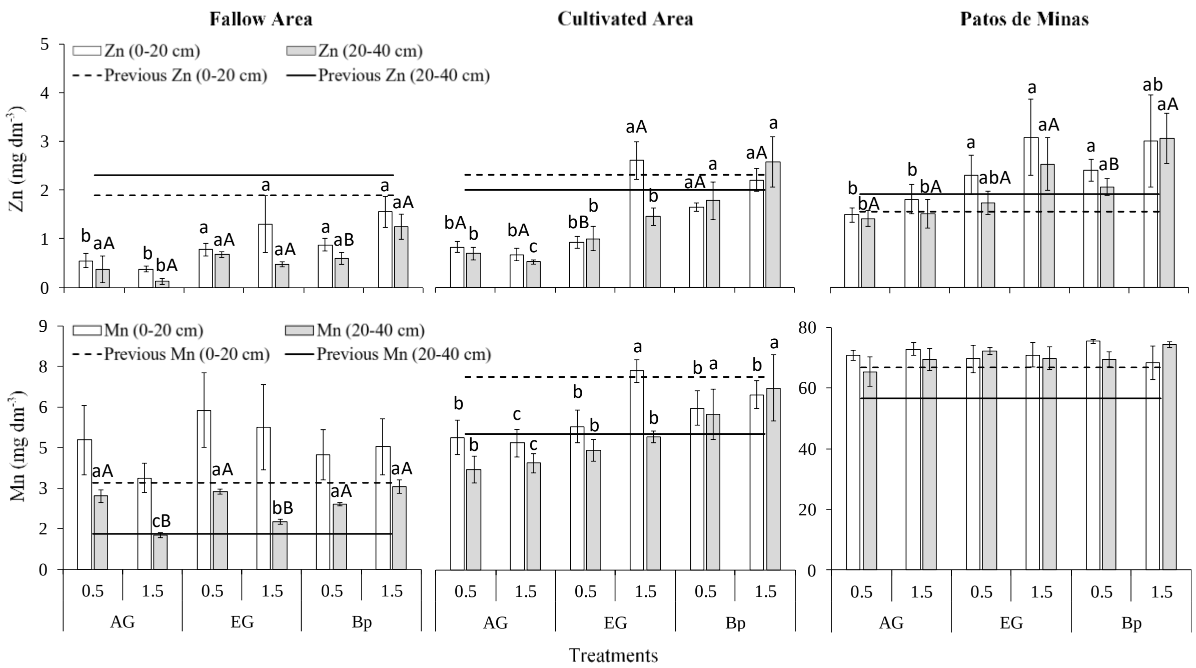

Fig. 3 Manganese (Mn) and zinc (Zn) (mg dm^{-3}) in the soils of the three areas, at the depths of 0-20 and 20-40 cm. 0.5 and 1.5 (t ha^{-1}) on the x-axis are the applied doses of the three evaluated products. AG: Agricultural gypsum; EG: Agricultural gypsum enriched with Zn and Mn; Bp: tested by-product. The horizontal lines represent the respective nutrient content found in the soils prior to the implantation of the experiments. The lowercase letters represent the differences the source and the uppercase letters represent the differences the doses applied and the absence represent no difference. Means followed by the same letter do significantly differ by Tukey test at p <0.05. The results were not compared among the three areas. The bars represent the standard error of each treatment.

Nutrient content in plants and yield

The contents of Ca, Mg, S, Zn, and Mn determined in the diagnostic leaves and in the grains, as well as the soybean yields are shown in Table 3. In the leaves, the contents of the macronutrients followed the decreasing order Ca>Mg>S. Opposite results were observed for nutrient contents in the grains, which may be related, among other factors, to the mobility of these macronutrients in plants (White, 2011a).

Although there were no differences among the treatments with respect to the soybean yield, the macronutrients and micronutrient contents found in the leaves and in the grains were proportional to the yield values (Table 3), corroborating with some studies found in the literature (Maeda 2002; Urano et al. 2006, 2007; Santos et al. 2008; Kurihara et al. 2013).

Regarding the different evaluated products, it was observed that there were no differences in macronutrient Ca, Mg, and S contents in both the leaves and the grains. Also, there were no significant differences among the treatments regarding the Zn and Mn micronutrient content in the leaves and grains. This indicates that the by-product is efficient to increase nutrient levels in soils, maintaining similar levels of these elements in the plant tissues, in comparison with the other products (agricultural and enriched gypsum). Yet it is worth mentioning that the by-product is presented in the powder form, hence it has the advantage of distributing the nutrients more efficiently in terms of uniformity of application, which is a challenge in agriculture. Generally, the sources that contain micronutrients are not efficient on applying it with uniformity on soils

Finally, it should be mentioned that this study presents results from only one agricultural year with soybean cultivation, and therefore, the potential residual effect of this by-product need to be evaluated in additional years.

Table 3 Nutrient contents (Ca, Mg, S, Zn, and Mn) determined in soybean leaves and grains for all studied areas as a function of the products applied in two doses (0.5 and 1.5 t ha^{-1}). AG: Agricultural Gypsum; EG: Enriched Gypsum; Bp: By-product. The respective yields of each treatment are also presented at the bottom of this table.

Part of the	Nutrient	Fallow Area						Cultivated Area						Patos de Minas					
		AG		EG		Bp		AG		EG		Bp		AG		EG		Bp	
		Dose t ha^{-1}																	
		0.5	1.5	0.5	1.5	0.5	1.5	0.5	1.5	0.5	1.5	0.5	1.5	0.5	1.5	0.5	1.5	0.5	1.5
Leaf		g kg^{-1}																	
	Ca	7.4	8.1	7.4	7.9	7.5	6.7	7.5	7.1	7.0	7.3	6.3	6.4	14.8	14.5	15.0	14.1	14.7	15.8
	Mg	4.9	5.0	5.0	4.7	5.2	4.6	4.4	4.0	4.2	3.9	4.3	4.3	5.6	6.1	6.0	6.1	6.3	6.0
	S	2.2	2.3	2.3	2.3	2.3	2.0	2.2	2.3	2.2	2.2	2.2	2.2	5.3	5.1	5.4	5.5	5.1	6.0
		mg kg^{-1}																	
	Zn	30.4	26.1	31.7	31.1	30.6	26.9	28.4	28.0	29.3	33.3	29.7	29.0	44.5	54.9	60.2	59.6	57.2	55.6
	Mn	25.7	26.7	26.9	34.2	27.2	25.4	23.8	24.2	24.5	29.4	25.3	23.3	155.6	174.4	164.6	154.4	167.4	165.0
Grain		g kg^{-1}																	
	Ca	0.8	0.9	0.8	0.8	0.8	0.9	1.8	1.7	1.6	1.7	1.5	1.5	2.2	2.2	2.3	2.2	2.2	2.2
	Mg	2.6	2.5	2.5	2.5	2.5	2.6	2.1	2.0	2.0	2.0	2.1	2.1	2.5	2.5	2.5	2.5	2.6	2.6
	S	3.3	3.4	3.3	3.4	3.4	3.5	2.3	2.5	2.3	2.6	2.3	2.4	2.8	2.8	2.8	2.8	2.8	2.9
		mg kg^{-1}																	
	Zn	42.5	37.8	45.5	47.5	45.3	46.8	27.3	29.0	26.5	32.0	32.0	28.3	23.3	22.5	22.3	0.7	17.7	25.0
	Mn	16.8	16.8	18.0	19.3	17.8	20.5	9.5	9.5	9.5	10.3	8.8	9.3	31.8	32.3	34.8	36.8	39.5	33.3
Yield		kg ha^{-1}																	
		3,960	3,405	4,246	3,969	4,073	3,939	3,862	3,422	3,466	3,489	3,525	4,027	4,681	5,056	5,018	4,900	4,592	4,814
		60 kg bags ha^{-1}																	
		66	57	71	66	68	66	64	57	58	58	59	67	78	84	84	82	77	80

Conclusions

Surface application of the tested by-product provided Ca and S to the plants, similarly to what happens with the application of agricultural gypsum, yet with the advantage of providing also extra nutrients, such as Mg, Zn, and Mn.

Because the evaluated by-product contains the micronutrients Zn and Mn, it can be a useful source of these essential nutrients, with the advantage of applying Zn and Mn in a uniform way, especially considering broadcast applications of the higher dose tested in our studies (e.g., 1.5 t ha^{-1}).

It is recommended that further studies using this by-product should be conducted in order to accumulate information of using it in other agricultural crops, with different doses and soils, as well as to evaluate the residual effect that this by-product may have in the soil for future crops.

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