

UNIVERSIDADE FEDERAL RURAL DE PERNAMBUCO

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**INPUTS OF HEAVY METALS AND RARE EARTH ELEMENTS IN
SOILS VIA PHOSPHATE FERTILIZERS AND CORRECTIVES**

**Recife
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Inputs of heavy metals and rare earth elements in soils via phosphate fertilizers and correctives

Tese apresentada ao Programa de Pós-Graduação em Ciências do Solo, da Universidade Federal Rural de Pernambuco, como parte dos requisitos para obtenção do título de Doutor em Agronomia – Ciências do Solo.

Orientador: Prof. Dr. Clístenes Williams Araújo do Nascimento

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Inputs of heavy metals and rare earth elements in soils via phosphate fertilizers and correctives

ABSTRACT

Phosphate fertilizers and corrective are significant sources of soil contamination by heavy metals and rare earth elements, and long-term cultivated soils can accumulate heavy metals above the maximum permissible limits. In this sense, the objectives of the study were (i) to evaluate the potential contamination of Brazilian soils by heavy metals and rare earth via phosphate fertilizers and corrective; (ii) to evaluate the accumulation of heavy metals in soils intensively cultivated with sugarcane, as well as to identify the possible sources of contamination. Initially, were performed total digests of 53 representative samples of P-containing fertilizers and commercialized in Brazil. Concentrations of As, Cd, Cr, Hg and Pb were investigated in fertilizers, which are elements regulated by national legislation. Also the additions of these metals to Brazilian soils were estimated based on the annual consumption and the average concentrations verified in each product. Subsequently, 60 samples of surface soils from areas cultivated with sugarcane were collected, these areas had a long history of use. In the soils, the environmentally available metals (Cd, Cr, Cu, Ni, Pb and Zn) were evaluated, as well as the physico-chemical characterization. The contents of metals in the soils were compared with the guiding values of quality; correlated with soil properties and; subjected to multivariate statistical analyzes to trace the origin of the metals. Finally, the total and soluble concentrations of Ce, La, Nd, Pr, Sm, Sc, Eu, Y, Dy, Gd, Yb, Er, Tb, Ho and Lu were investigated in 60 supplies samples (phosphate fertilizer, and limestone) used in Brazilian agriculture. In addition, the contributions of these elements to Brazilian soils were estimated through the use of phosphate fertilizers and soil correctives. The results of the study showed that Cd in phosphate rocks are the most worrisome, and that in the medium term the heavy metals present in fertilizers containing P do not represent environmental risk. However, the intensive application of phosphate fertilizers in soils cultivated with sugarcane promoted the accumulation of Cd above the guiding values of quality, and in some cases the soils represented a potential risk to human health. With regard to rare earths, it was observed that the solubility of these elements in phosphate fertilizers is dependent on the raw material used in industry (igneous or sedimentary). The annual additions of these elements to Brazilian soils are $> 4000 \text{ t year}^{-1}$ and that Ce, La, Nd and Y are the most worrisome. Limestone proved to be a significant source of Gd for agricultural soils. Therefore, soils that continuously receive high doses of these inputs are probably enriched with ETRs.

Keywords: Contamination. Trace elements. Agriculture. Risk. Anthropic activity.

Adição de metais pesados e elementos terras raras aos solos via fertilizantes fosfatados e corretivos

RESUMO

Fertilizantes fosfatados e corretivos são fontes significativas de contaminação do solo por metais pesados e elementos terras raras, e, solos cultivados por um longo tempo podem acumular metais pesados acima dos limites máximos permissíveis. Nesse sentido, o estudo teve por objetivos (i) avaliar o potencial de contaminação dos solos brasileiros por metais pesados e terras raras via fertilizantes fosfatados e corretivos; (ii) avaliar o acúmulo de metais pesados em solos intensivamente cultivados com cana-de-açúcar, como também identificar as possíveis fontes de contaminação. Inicialmente, foram realizadas digestões totais de 53 amostras representativas de fertilizantes contendo P e comercializadas no Brasil. As concentrações de As, Cd, Cr, Hg e Pb foram investigadas nos fertilizantes, que são os elementos regulamentados pela legislação nacional. Adicionalmente, as adições destes metais aos solos brasileiros foram estimadas baseadas no consumo anual e nas concentrações médias verificadas em cada produto. Posteriormente, 60 amostras de solos superficiais de áreas cultivadas com cana-de-açúcar foram coletadas, estas áreas tinham um longo histórico de uso. Nos solos, os teores ambientalmente disponíveis dos metais (Cd, Cr, Cu, Ni, Pb e Zn) foram avaliados, assim como as caracterizações físico-químicas. Os teores dos metais nos solos foram comparados com os valores orientadores de qualidade; correlacionados com as propriedades dos solos e; submetidos às análises estatísticas multivariadas para traçar a origem dos metais. Por fim, as concentrações totais e solúveis de Ce, La, Nd, Pr, Sm, Sc, Eu, Y, Dy, Gd, Yb, Er, Tb, Ho e Lu foram investigadas em 60 amostras de insumos (fertilizante fosfatado, gesso e calcário) utilizados na agricultura brasileira. Além disso, os aportes destes elementos aos solos brasileiros foram estimados através do uso de fertilizantes fosfatados e corretivos do solo. Os resultados do estudo demonstraram que Cd em rochas fosfatadas são os mais preocupantes, e, que em médio prazo os metais pesados presentes nos fertilizantes contendo P não representam risco ambiental. Contudo, a aplicação intensiva de fertilizantes fosfatados nos solos cultivados com cana-de-açúcar promoveu o acúmulo de Cd acima dos valores orientadores de qualidade, e em alguns casos os solos representaram potencial risco à saúde humana. Com relação aos terras raras, observou-se que a solubilidade destes elementos nos fertilizantes fosfatados é dependente da matéria prima utilizada na indústria (ígnea ou sedimentar). As adições anuais destes elementos aos solos brasileiros são $> 4000 \text{ t ano}^{-1}$ e que Ce, La, Nd e Y são os mais preocupantes. O calcário se mostrou uma fonte significativa de Gd para os solos agrícolas. Desta forma, os solos que recebem continuamente elevadas doses destes insumos, provavelmente, estão enriquecidos com ETRs.

Palavras-chave: Contaminação. Elementos traço. Agricultura. Risco. Atividade antrópica.

1. GENERAL INTRODUCTION

Heavy metals and rare earth elements are harmful to the functionality of the ecosystem and pose a risk to human health. These elements are found in agricultural supplies, mainly in phosphate fertilizers and soil correctives, in varying concentrations. The use of these supplies can promote the enrichment of these elements in soils above the guiding values of quality. Soils contaminated by metals and rare earth elements are of great public health concern, since these contaminants can enter the food chain.

Brazil is a major agricultural producer that consumes a large amount of phosphate fertilizers and soil correctives annually, which represents a significant source of input of heavy metals and rare earth elements to Brazilian soils. Although there is specific legislation regulating the concentration of some metals in fertilizers and correctives, there are few studies that periodically monitor the presence of these elements in these supplies. In addition, Brazilian legislation is restricted to a limited number of contaminants (As, Cd, Cr, Hg and Pb) and other hazardous elements present in phosphate and corrective fertilizers, such as rare earth elements, may represent a potential risk to the functionality of the agroecosystem. The input of metals and rare earth elements in agriculture via phosphate and corrective fertilizers is dependent on the concentration of these elements in the supplies, frequency and amount applied to the soil. In Brazil, there are no surveys that estimate the quantities of metals and rare earth elements added to the soils by agricultural activities, however, this information becomes important for future studies that aim to model the balance of mass flow of these elements in the agricultural scenario, as well as, in the elaboration of public policies to reduce the additions of metals and rare earth elements to Brazilian agriculture.

The sources of contamination of agricultural soils by metals and rare earth elements are manifold. However, intensively cultivated soils that periodically receive high amounts of phosphate fertilizers may potentially have heavy metal contents above the maximum permissible limits. A typical example of this scenario is the sugar-cane monoculture in the Brazilian northeast, as in the case of sugar-alcohol production in the state of Pernambuco. The cultivation of sugarcane in Pernambuco soils is a historical fact, which began at the time of the colonization of the country. The crop is extensively cultivated in the state and annually adds large amounts of phosphate fertilizers and soil correctives. These soils are likely to be enriched in heavy metals as a result of additions from agricultural activities and other possible industrial and urban sources. Thus, studies are needed to assess the status of contamination of

these soils by heavy metals in order to diagnose possible environmental problems and to guide the planning of actions capable of preventing and/or remedying soil pollution.

1.1 Hypotheses

- The concentrations of heavy metals in P-containing fertilizers marketed in Brazil are higher than the permissible limits and their use represents a potential risk to the agroecosystem.
- Phosphate fertilizers and soil correctives add significant quantities of rare earth elements annually to Brazilian agricultural soils.
- The rare earth elements contained in the phosphate fertilizers present high solubility.
- Soils intensively cultivated with sugarcane are polluted by heavy metals as a result of the use of high doses of phosphate fertilizers over a long period of time.

1.2 General objective

- To evaluate (i) the potential contamination of Brazilian soils by heavy metals (HMs) and rare earth elements (REEs) via P-containing fertilizers and soil correctives and (ii) the accumulation of heavy metals in intensively cultivated soils, as well as to identify possible sources of contamination.

1.3 Specific objectives

- To assess the concentrations of As, Cd, Cr, Hg, and Pb in P-containing fertilizers marketed in Brazil in order to estimate the accumulation of HMs in agricultural soils through phosphorus fertilizer use.
- To estimate the total amount (kg year^{-1}) and the rate ($\text{g ha}^{-1}\text{year}^{-1}$) of HMs applied to soils with aims to calculate the number of mineral fertilizer applications needed to reach the limit of HMs in agricultural soils established by Brazilian legislation.
- To evaluate the contents, the signature and the solubility of REEs (Ce, La, Nd, Pr, Sm, Sc, Eu, Y, Dy, Gd, Yb, Er, Tb, Ho and Lu) in phosphate fertilizers and soil correctives marketed in Brazil.
- To estimate the amounts of REEs entering soils of Brazil through phosphate fertilizers and soil correctives.

- To assess the status of Cd, Cr, Cu, Ni, Pb, and Zn accumulation in soils under long-term sugarcane cultivation in northeast Brazil.
- To trace the possible sources of contamination of agricultural soils through applied multivariate analysis.

2. BIBLIOGRAPHIC REVIEW

2.1 The consumption of fertilizers and soil correctives by Brazilian agriculture

Brazil is a country with continental dimensions and it has a wide diversity of soils in its territory. Most of these soils have limiting factors for agriculture, such as acidity, high levels of exchangeable Al^{3+} , very weathered soils presenting low natural fertility, as well as, low cation exchange capacity and P availability, which are typical characteristics of tropical soils. Based on these factors, it is necessary to adopt management strategies with the objective of maximizing the production of the crops grown in these low fertility soils. Thus, the soil fertilization and correction practices aim to make the soil fertile for the development of agricultural crops, providing the necessary nutrients for the plants and reducing the soil acidity. These practices are adopted worldwide, and are based on the need to produce food to support the rapidly growing population each year (JIAO et al., 2012).

The increasing demand for food production puts a heavy pressure on agricultural activities, which consequently promote an increase in the consumption of fertilizers and soil correctives. Studies show that by the end of the 1960s, world fertilizer consumption was 146 million tons, increasing in 2010 to 176 million tons, representing a significant increase in consumption of these inputs. Brazil is one of the world's largest food producers with 69.2 million hectares of cultivated land (IBGE, 2012; MAPA, 2016). Sugarcane, soybeans and corn are the main agricultural commodities (FAO, 2017) and fertilizer consumption is concentrated in four crops: soybean, corn, sugarcane, and coffee; Central-Western region is the largest consumer (Figure 1). In 2016, the estimated fertilizer consumption was 32.8 million tons, in which 36% were phosphate fertilizers (IPNI, 2017). As a result of such an intensive agriculture, Brazil is the fourth largest fertilizer consumer behind China, India and USA (IFA, 2017).

Phosphated rocks are the raw materials used in the manufacture of soluble phosphate fertilizers. The natural reserves of rock phosphate in Brazil are predominantly igneous (carbonatite), but the country has the potential to exploit phosphate of sedimentary origin (phosphorite). Most of the national fertilizer production is concentrated in the Southeast region, especially in the states of Minas Gerais, São Paulo, and Goiás. The largest active phosphate mine in the country lies in Catalão, Goiás. Catalão mine is a deposit of dolomitic carbonate rock as well as the largest national producer of single superphosphate (SSP) (ABRAM et al., 2011).

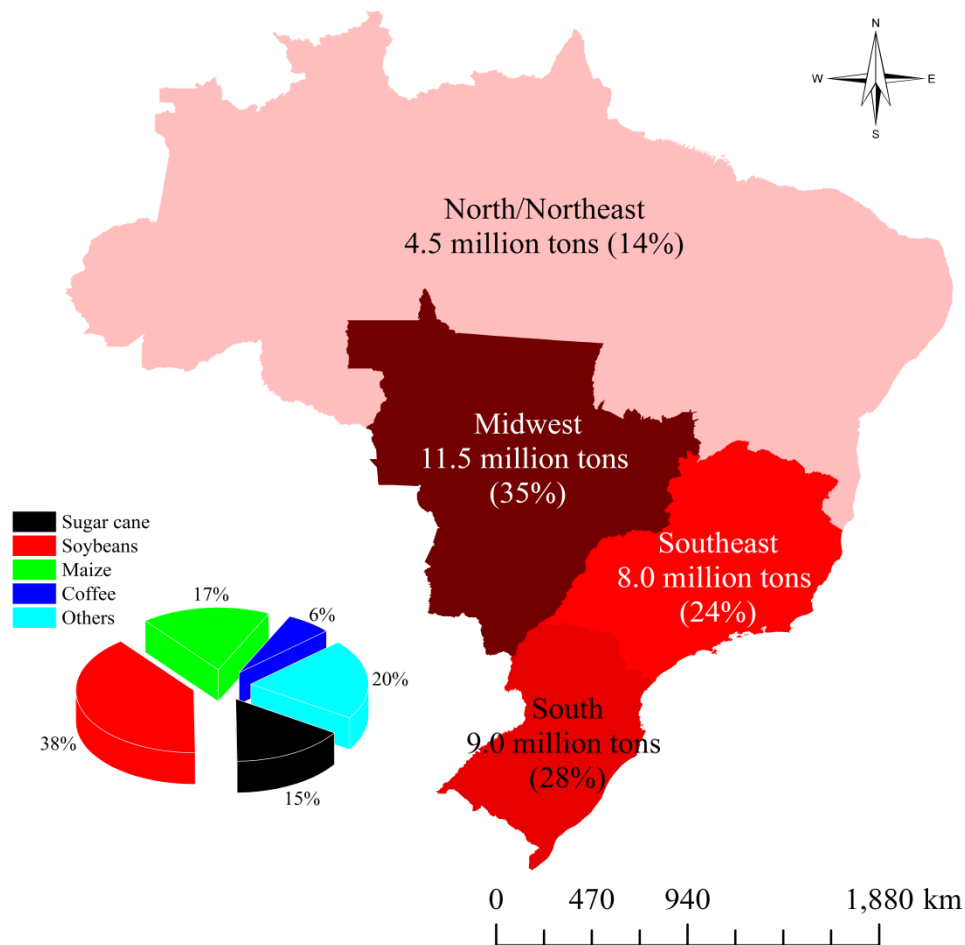


Figure 1. Brazilian fertilizer consumption by crop and region (IPNI, 2017)

The Brazilian production of phosphate fertilizers using sedimentary ore is low, since few mines are currently active in the country (TASSINARI; KAHN; RATTI, 2001) (Figure 2). Brazil imports approximately 50% of its consumption in phosphate fertilizers. The imported amount of phosphate rock and monoammonium phosphate (MAP) in 2014 was 1.7 million tonnes (IFA, 2017), with Morocco being the main supplier of phosphate fertilizers of sedimentary origin (KRATZ; SCHICK; SCHNUG, 2016; CÁNOVAS et al., 2017).

Brazilian agriculture also consumes a large amount of soil corrective (limestone), since soils are typically acidic. The consumption of limestone in the 2015/2016 agricultural harvest was 33.2 million tons, with a higher concentration of use in the South, Southeast and Midwest regions (ABRACAL, 2017).

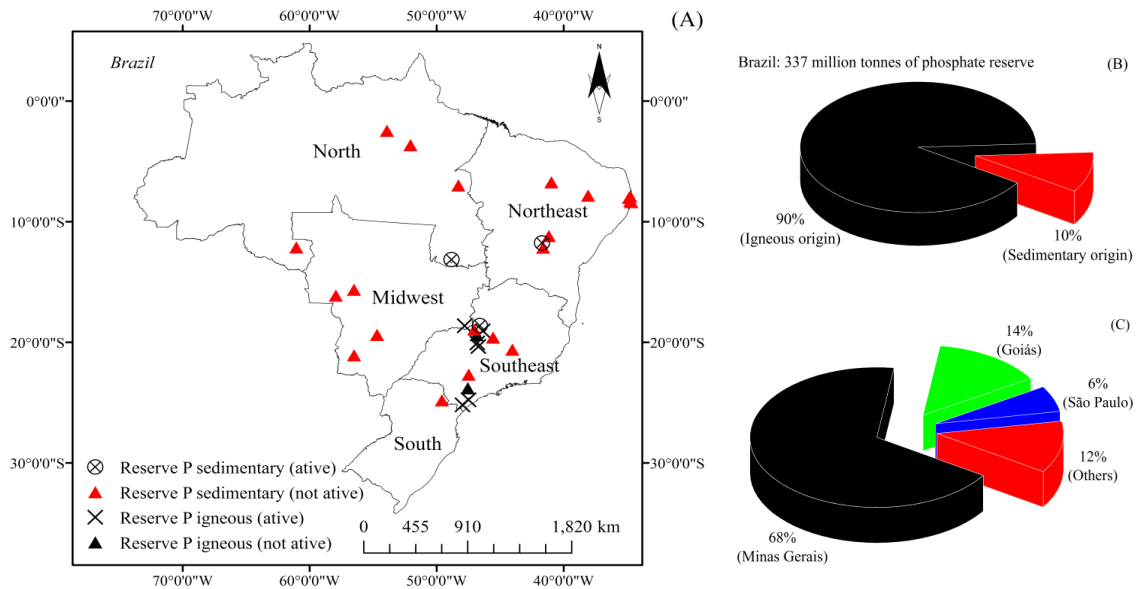


Figure 2. Spatial distribution of phosphate reserves in Brazil (A), percentage of the phosphate reserve between the Brazilian states (B) and percentage/origin of phosphate imported for Brazil (C)

Although the use of fertilizers and correctives is essential in agriculture, it is often not done correctly. The recommendation of the fertilization involves a technical planning that begins with the representative sampling of the soil, followed by the chemical analysis to obtain the recommendation made by a specialized professional. However, many producers do not do this, they usually use pre-defined recommendations without professional assistance. The use of large amounts of fertilizers over a long period tends to increase the concentration of an element or substance of environmental interest above the natural content present in the soil (ROBERTS, 2014). One of the main environmental problems arising from the use of fertilizers, mainly phosphates, is the increased bioavailability of dangerous elements such as heavy metals (Cd, Pb, Cr and V) and rare earth elements in soils (JIAO et al., 2012).

2.2 Heavy metals and rare earth elements in phosphate fertilizers and soil correctives

The continued use of phosphates and limestone can also add heavy metals (HMs) and rare earth elements (REEs) to soil (CAMPOS et al., 2005). The term "heavy metal" is commonly used to refer to a group of metals and metalloids, which are associated with environmental contamination and potential toxicity (eg, As, Cd, Cr, Hg, and Pb). Rare earth elements, in turn, is the denomination given to the group of 17 elements (the Lanthanides serie - La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu plus Sc and Y) present in group IIIb of the periodic table that have similar physicochemical properties (VONCKEN, 2016). Based on their atomic numbers and their masses, REEs are generally

divided into two groups: light REEs (from lanthanum - La to europium - Eu) and heavy REES (from gadolinium - Gd to lutetium - Lu) (DAVRANCHE et al., 2016).

Several studies have evaluated the presence of HMs and REEs in fertilizers and soil correctives (ABDEL et al., 2001, OTERO et al., 2005, NZIGUHEBA; SMOLDERS, 2008, FREITAS et al., 2009, LUO et al., 2009). The concentration of such elements in phosphate fertilizers is dependent on the type of phosphate rock used as raw material in the industry. It is known that phosphate rocks of sedimentary origin (phosphorite) are richer in HMs than phosphate rocks of igneous origin (carbonatite) while REEs are more abundant in fertilizers derived from carbonatites (KRATZ; SCHICK; SCHNUG, 2016; RAMOS et al., 2016).

Kratz, Schick and Schnug (2016), evaluating the HMs content in 68 samples of sedimentary and igneous phosphate rocks obtained from several parts of the world observed that the average concentrations of Cd, U and V in the sedimentary sources were at least 110% higher compared to the igneous sources. The Cd concentrations in phosphate rocks from Florida (USA) are lower than 100 mg kg^{-1} , while phosphates derived from African countries such as Morocco are in the range of $100\text{-}350 \text{ mg kg}^{-1}$ (MCLAUGHLIN et al., 1996). Phosphate rocks from Brazil have low levels of HMs, since 90% of their reserves are of igneous origin; concentrations of Cd, Cr and Pb in such rocks varied from 4-7, 19-80 and 58-127 mg kg^{-1} (CAMPOS et al., 2005; ALCARDE; RODELLA, 2003).

The mean concentrations of Cr, As, Cd, and Pb in phosphate fertilizers marketed in European countries were 89.5; 7.6; 7.4 and 2.9 mg kg^{-1} , respectively (NZIGUHEBA; SMOLDERS, 2008). In China, which is the world's largest fertilizer consumer, HMs concentrations in phosphate fertilizers were 85.7; 38.5; 15.8 and 0.2 mg kg^{-1} for Cr, Pb, As, and Cd, respectively. It was estimated that 1636, 727, 299, and 24 t of Cr, Pb, As and Cd enter the Chinese soils through phosphate fertilization (LUO et al., 2009).

There are few studies in Brazil that evaluated the concentrations of HMs in phosphate fertilizers; in addition, most studies were carried out in a small number of samples and mainly directed at the evaluation of Cd (MENDES et al., 2006; BIZARRO; MEURER; TATSCH, 2008; FREITAS et al., 2009). Mendes et al. (2006) found 45 and 28.0 mg kg^{-1} of Pb and Cd, respectively, for triple superphosphate. Bizarro, Meurer and Tatsch (2008) found that Cd concentrations in phosphate fertilizers were below 17.0 mg kg^{-1} . Freitas et al. (2009) found similar Cd concentration ($14\text{-}15 \text{ mg kg}^{-1}$) in single (SSP) and triple superphosphate (TSP), whereas the Pb concentration was highest in SSP samples.

Unlike HMs, REEs are much more abundant in phosphatic deposits of igneous origin. The REEs concentration in carbonatites may be 150 times higher than phosphorites (RAMOS

et al., 2016). Light REEs are higher than heavy REEs in phosphate rocks and, consequently, in fertilizers. Cerium, La, Pr and Nd are the most enriched elements. Values for Ce, La, Nd, Pr, and Y vary from 1 - 3934; 7-1926; 2-1529; 5,5 – 447, and 41 – 122 mg kg⁻¹, respectively (HU et al., 1998; ABDEL et al., 2001; OTERO et al., 2005; TURRA; FERNANDES; BACCHI, 2011; WAHEED et al., 2011; RAMOS et al., 2016).

REEs in phosphate fertilizers produced from the main Brazilian phosphate mines (Catalão - GO, Araxá - MG and Tapira - MG), all derived from carbonatite, were assessed by Ramos et al. (2016). They found concentrations of 3934 (Ce); 1926 (La); 15 (Nd) and 447 (Pr) mg kg⁻¹ in SSP produced in Catalão; on the other hand, SSP produced in Araxá presented lower levels (1866, 895, 899 and 235 mg kg⁻¹ for Ce, La, Nd and Pr, respectively). On the other hand, TSP and MAP produced from the ores of Tapira had levels varying from 809 - 1801; 399-953; 373-814 and 96-237 mg kg⁻¹ for Ce, La, Nd and Pr, respectively. Ramos et al. (2016) observed that the production of fertilizers more concentrated in P₂O₅ provided less accumulation of ETRs. Turra, Fernandes and Bacchi (2011) evaluating the REEs in a set of phosphate fertilizers, observed the same tendency. Both works attributed the depletion of REEs in these types of fertilizers to the industrial process of P concentration.

Data on the concentration of HMs and REEs in soil correctives are scarce. Limestone and mineral gypsum applied in agriculture are ground rock, without any kind of industrial chemical treatment. Carvalho (2011) found concentrations of HMs in limestone and gypsum of 10.7 (Cr), 10.5 (Pb) and 5.4 (Cd) mg kg⁻¹. Turra, Fernandes and Bacchi (2011) found the following order for REES in limestone: Ce (15) > Nd (7.5) = La (7.5) > Sm (1.3) = Sc (1.3) > Yb (0.7) > Eu (0.2) = Tb (0.2) > Lu (0.1). Although soil correctives have low HMs and REES concentrations compared to phosphate fertilizers, the continued application of high doses of these inputs may be a significant source of these contaminants to soils.

Over a decade ago, Brazil began to regulate As, Cd, Cr, Hg, and Pb levels in fertilizers and Cd and Pb in soil (Normative Instruction No. 27, Ministry of Agriculture, Livestock and Supply – MAPA). The maximum permissible levels of HMs were based on human health risk modeling considering the contribution of HMs to the soil by fertilizers and soil correctives over time. For P-containing fertilizers, HMs concentration are calculated as a function of the percentage of P₂O₅ in the sample. The Regulatory Instruction establishes the following allowable limits for phosphate fertilizers: 0,05; 2.0; 4.0; 20.0 and 40.0 mg kg⁻¹/% P₂O₅ for Hg, As, Cd, Pb and Cr, respectively. For soil correctives, the allowable limits are 20.0 and 1000.0 mg kg⁻¹ for Cd and Pb, respectively (MAPA, 2006). With regard to REEs, there is no legislation regulating their levels of agricultural inputs.

2.3 Contamination of agricultural soils by heavy metals

Soil contamination by HMs is a subject of great environmental and socioeconomic interest. This stems from the problems caused to public health and natural ecosystems. Soils contaminated by HMs represent a high financial cost both to remedy the affected areas and to treat the exposed population (NAVEEDULLAH et al., 2013; SILVA et al., 2017).

Heavy metals are harmful to human health (NRIAGU, 1988; THOMPSON et al., 1988). Studies have related the human exposure (acute or chronic) to heavy metals as a major cause of cardiovascular problems (MYONG et al., 2014), reproductive damages (AL-GUBORY, 2014), kidney problems (JOHRI; JACQUILLET; UNWIN, 2010), disorders of the central nervous system (MASON; HARP; HAN, 2014), and cancer (ZHANG et al., 2014; ITOH et al., 2014).

High concentrations of HMs in the soil are also damaging to the functioning of the ecosystem. Metals can inhibit plant growth (ARAÚJO; NASCIMENTO, 2010), enzymatic activities (STRACHEL; WYSZKOWSKA; BACMAGA, 2017), diversity, and structure of the soil microbial community (JORDANA; PINEDO; BALLESTEROS, 2015).

Heavy metals occur naturally in soil as a result of weathering of parent material (rock) and in trace amounts ($\leq 0.1\%$, except Fe) (KABATA-PENDIAS, 2011). However, HMs also enter the soil through mining (SANTOS et al., 2017), municipal waste treatment (CHARLTON et al., 2016), burning of fossil fuels (WANG et al., 2016), pesticides (LI et al., 2017), and phosphate fertilizers (KRATZ; SCHICK; SCHNUG, 2016).

In agricultural soils, HMs are mainly added by phosphate fertilization (MICÓ et al., 2006; PERIS et al., 2007). Continuous applications of high doses of fertilizers can gradually add HMs to soils beyond permissible limits, such as Cd (JIAO et al., 2012; ROBERTS, 2014). Crops are an important route of human oral exposure to heavy metals. Therefore, the monitoring of HMs soils is of great importance for food safety.

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3. ENVIRONMENTAL RISK OF HEAVY METALS IN P-CONTAINING FERTILIZERS MARKETED IN BRAZIL

Abstract

The input of heavy metals (HMs) into agricultural soils from phosphate fertilizers may compromise the sustainability of agroecosystems and pose a risk to human health. We evaluated 53 sources of P marketed in Brazil in regard to As, Cd, Cr, Hg, and Pb concentrations in order to assess the risks associated with their application to soils. Based on the concentrations of HMs and the consumption of different sources, we estimated the amounts of HMs added annually to agricultural soils. As, Cr, Pb, and Hg concentrations did not exceed those found in fertilizers sold in other regions of the world. Phosphate rocks had Cd concentrations that were twice as high as any other source. The potential risk of Cd affecting soil quality is at least nine times higher than that of the other HMs assessed. Due to high consumption, monoammonium phosphates and single superphosphates are the main sources of HMs to Brazilian soils. In general, HMs in P-containing fertilizers sold in Brazil did not pose a high human health risk in a medium timeframe. Nevertheless, intensive application of fertilizers with high concentrations of HMs requires monitoring of the HM accumulation in soils to ensure the sustainability of agroecosystems.

Key words: Rock phosphate. Agricultural soils. Heavy metals. Cadmium. Arsenic.

Risco ambiental de metais pesados em fertilizantes contendo P comercializados no Brasil

Resumo

A adição de metais pesados (MPs) dentro dos solos agrícolas a partir de fertilizantes fosfatados pode comprometer a sustentabilidade do ecossistema e posar risco a saúde humana. Analisamos 53 fontes de P comercializados no Brasil no que diz respeito às concentrações de As, Cd, Cr, Hg e Pb a fim de avaliar os riscos associados com sua aplicação aos solos. Baseado nas concentrações dos MPs e no consumo das diferentes fontes, estimamos as quantidades de MPs adicionados anualmente aos solos agrícolas. As concentrações de As, Cr, Pb e Hg não excederam aquelas encontradas em fertilizantes comercializados em outras regiões do mundo. Rochas fosfatadas tiveram concentrações de Cd duas vezes superiores a qualquer outra fonte. O risco potencial do Cd afetar a qualidade do solo foi cerca de nove vezes maior do que outro MPs avaliado. Devido ao alto consumo, fosfato monoamônio e superfosfato simples são as principais fontes de MPs aos solos brasileiros. Em geral, MPs nos fertilizantes contendo P comercializados no Brasil não posam alto risco a saúde humana em médio prazo. Porém, aplicação intensiva de fertilizantes com concentrações altas de MPs requer monitoramento do acúmulo de MPs em solos para garantir a sustentabilidade do agroecossistema.

Palavras-chaves: Rocha fosfatada. Solos agrícolas. Metais pesados. Cádmio. Arsênio.

3.1 Introduction

Currently, Brazil has 69.2 million hectares of cultivated land and is one of the leading food producers in the world (IBGE, 2012; MAPA, 2016). As a result of such intensive agriculture, Brazil is the world's fourth largest fertilizer consumer after China, India, and the USA (IFA, 2016). In 2015, the estimated consumption of fertilizers was nearly 30 million tonnes, of which 38% is related to phosphate fertilizers alone (IPNI, 2016).

Although fertilizer use is essential for meeting the crop demand for nutrients exported from soil, fertilizers can contain heavy metals (HMs) that are inadvertently added to the soil (KRATZ; SCHICK; SCHNUG, 2016). The amount of HMs transferred to the soil in a single application of fertilizer is very low or negligible. However, repeated applications of fertilizers with relatively high contents of HMs can lead to significant accumulation (JIAO et al., 2012). Therefore, elements such as As, Cd, Cr, Hg, and Pb can affect soil quality and pose a risk to human and animal health through food chain contamination (HOSSEIWWNPUR; MOTAGHIAN, 2015).

Heavy metals are present in fertilizers as a result of the composition of raw materials used in their manufacture. Phosphate rocks and industrial/animal wastes are among the main sources of HMs in agricultural soils (GONÇALVES JR et al., 2014; SESHADRI; BOLAN; NAIDU, 2015). The concentration of HMs in nitrogen and potassium fertilizers is usually very low, and hence, their application does not imply a significant accumulation of HMs (MCBRIDE; SPIERS, 2001). On the other hand, the prolonged use of P-containing fertilizers is a major source of HMs in soils, particularly Cd (JIAO et al., 2012). For instance, soils cultivated with sugarcane and fertilized for a long period with phosphate fertilizers accumulated Cd levels above the allowable limit according to Brazilian legislation (SILVA et al., 2016). Estimates of the annual input of HMs in soil via phosphate fertilizers range from 22.0 to 299.0; 24.0 to 30.0; 319.0 to 1626.0; 0.1 to 17.0; and 10.0 to 777.0 tonnes for As, Cd, Cr, Hg, and Pb, respectively (LUO et al., 2009).

Due to the risk associated with the presence of HMs in fertilizers, several countries have limited the concentrations of these elements in marketable products (GONÇALVES JR et al., 2014; JIAO et al., 2012; KRATZ; SCHICK; SCHNUG, 2016). In Brazil, Normative Instruction No. 27/2006 of the Ministry of Agriculture, Livestock and Supply (MAPA) established maximum allowable concentrations of HMs in fertilizers (MAPA, 2006). However, few studies have evaluated the concentration and risk of As, Cd, Cr, Hg, and Pb in P-containing fertilizers used in Brazil. Cadmium is the most studied element, especially in

phosphate rocks (FREITAS et al., 2009). There is also a scarcity of data on the supply of HMs via fertilizers in Brazilian soils since a plethora of mineral and organic sources are used.

Human and animal health risks associated with HMs in fertilizers need to be evaluated carefully (HARTLEY et al., 2013). As the concentrations of HMs vary markedly with the raw materials available in each region or country, the production of local and regional data is essential. In this scenario, we aimed to assess the concentrations of As, Cd, Cr, Hg, and Pb in P-containing fertilizers marketed in Brazil in order to estimate the accumulation of HMs in agricultural soils through phosphorus fertilizer use. In addition, we estimated both the total amount (kg year^{-1}) and the rate ($\text{g ha}^{-1}\text{year}^{-1}$) of HMs applied to soils with aims to calculate the number of mineral fertilizer applications needed to reach the limit of HMs in agricultural soils established by Brazilian legislation (MAPA, 2006).

3.2 Material and Methods

3.2.1 Selection, preparation, and analysis of heavy metals in fertilizers

We analyzed 53 P-containing fertilizers sold in Brazil and obtained from the National Agricultural Laboratory (LANAGRO-PE) of MAPA (Table 1). The samples were dried at 60 °C, pulverized in an agate mortar, and passed through a 0.30-mm mesh stainless steel sieve.

Table 1. Description of the phosphate fertilizers evaluated in this study

Product	Number of samples	(%) P_2O_5^a	Consumption (1,000 t) ^b
Rock phosphate (RP)	5	24	184.09
Monoammonium phosphate (MAP)	6	50	3,558.41
Simple superphosphate (SSP)	24	18	5,336.79
Multi-nutrient fertilizers (NPK)	12	13	<i>nd</i>
Organo-mineral + rock phosphate (OM+RP)	6	26	1,519.27

(a) average value of samples certified by manufacturers; (b) Brazilian consumption in 2015 (ANDA, 2015); *nd* not available

1.000 gram of the various fertilizer powder samples was digested by adding 9 mL HNO_3 + 3 mL HCl in a microwave oven at 175°C for 4 minutes and 30 seconds (USEPA, 1998). This method provides similar results to the official method currently in use in Brazil

(MAPA, 2006), and it is preferred due to the lower cost of acids, shorter digestion time, and higher reproducibility (SILVA et al., 2014). All analyses were performed in duplicate.

For quality control, we also analyzed blank samples and a multi-element fertilizer (SRM 695) with certified HMs concentrations (National Institute of Standards and Technology, USA). The recoveries of HMs obtained from the certified sample were 97, 100, 72, 90, and 73% for As, Cd, Cr, Hg, and Pb, respectively. Cd, Cr, and Pb concentrations were determined by optical emission spectrometry (ICP-OES) (Perkin-Elmer/ICP-OES 7000), while As and Hg concentrations were measured by hydride generation atomic absorption spectroscopy (HGAAS) (Perkin-Elmer/AA 800).

3.2.2 Inputs of heavy metals to soils via fertilizers

Equation 1 was used to estimate the total annual inputs (tonne year⁻¹) of HMs in soil via P-containing fertilizers. Other inputs and losses of HMs in agricultural soils such as atmospheric deposition, crop uptake or leaching were not included in this calculation.

$$TA_i = \sum_j (Q_j \times C_{ij}) \times 10^{-6} \quad (Eq. 1)$$

Where TA_i is the total amount of the HM (i) added each year (tonne year⁻¹) from P-containing fertilizers (j), Q_j is the amount of fertilizer (tonne) currently consumed in Brazil, and C_{ij} is the HM concentration in the fertilizer (mg kg⁻¹). The rate of application (g ha⁻¹ year⁻¹) was estimated with equation 2:

$$TA_{ij} = \left[\left(\frac{\bar{D}}{FP_j} \right) \times C_{ij} \right] \times 10^{-3} \quad (Eq. 2)$$

Where TA_{ij} is the amount of HM (i) added annually per unit area through fertilizer (j) (g ha⁻¹), \bar{D} is the average recommended dose for the main crops grown in Brazil (140 kg ha⁻¹ P₂O₅) (CFSEMG, 1999; IPA, 2008), and FP_j is the fraction of P₂O₅ in fertilizers (0.18, 0.24, 0.26 and 0.50 for SSP, RP, OM+RP and MAP, respectively) (dimensionless).

We also estimated the number of applications needed to increase the HM natural background of the soil surface layer (0–0.2 m) up to the permissible limit for agricultural soils established by Brazilian legislation (CONAMA, 2009). The estimate was applied only to fertilizers with high addition of HMs:

$$NA_j = \frac{2.6 \times 10^3 \times AL_i}{TA_{ij}} \quad (Eq. 3)$$

Where NA_j is the number of fertilizer (j) applications required to increase the HM concentration (i) in the topsoil up to the allowable limit (AL) (mg kg^{-1}), and 2.6×10^3 is the unity conversion factor g ha^{-1} to mg kg^{-1} of the parameter TA_{ij} , taking into account the depth of 0.2 m and the soil density of 1300 kg m^{-3} (FERREIRA, 2010) for the calculation of the soil mass in 1 hectare.

3.2.3 Statistical analyses

Descriptive statistics of the dataset were obtained by calculating the mean, median, standard deviation and amplitude. The data with a normal distribution assumption were verified by the Shapiro-Wilk test ($p > 0.05$). Data without a normal distribution were normalized through logarithmic transformation. Hierarchical cluster analysis (AH) was applied to group different types of P-containing fertilizers. AH was carried out using Ward's algorithm with the Euclidean distance as a binding measure and the dissimilarity between the products was assessed as a function of the HM concentration. Statistical analyses were performed using STATISTICA software (version 10.0).

3.3 Results and Discussion

3.3.1 Trace element concentrations in P-fertilizers

The mean concentration of HMs in fertilizers had the following descending order: Cr (67.9) > Pb (19.2) > Cd (9.4) > As (6.6) > Hg (0.1). The highest values found for As, Cd, Hg, and Cr were approximately 7 times higher than their respective median values, and the Pb concentration was 17 times higher than the median Pb value (Table 2). The distributions of As and Pb concentrations in the fertilizers had a similar trend, with over 65% of the data lying in the ranges of 0.5 to 4.2 and 0.3 to 14.7 mg kg^{-1} , respectively. More than 80% of the Cd and Cr concentrations were $<17.2 \text{ mg kg}^{-1}$ and $<148.1 \text{ mg kg}^{-1}$, respectively. On the other hand, Hg showed low variability with a high percentage of samples near the mean concentration.

The As concentration found in P-containing fertilizers marketed in Brazil was the lowest among data from other parts of the world (Table 3). Cr and Pb had high mean concentrations, but the Cr concentration of the fertilizers marketed in the European Union is the largest in the literature, as is the Pb concentration in China. The average concentration of Cd in Brazil, Chile, and Argentina is similar to or higher than those reported for Europe and

China. The concentration of Cd in the USA is the highest among the selected countries. Although there is a scarcity of studies on Hg in fertilizers, Hg concentrations found in phosphate fertilizers used in China amount to 0.8 mg kg^{-1} , which is 6 times higher than in Brazil (LUO et al., 2009).

Table 2. Descriptive statistics of the heavy metals content in fertilizers containing P sold in Brazil

Heavy metals	Minimum	Maximum	Mean	Median	\pm SD	SW- <i>p</i>
	----- (mg kg ⁻¹) -----					
As	0.54	26.72	6.55	3.41	7.23	<0.001
Cd	0.40	40.03	9.39	6.05	10.08	<0.001
Cr	10.72	341.75	67.82	51.67	77.31	<0.001
Hg	0.06	0.54	0.14	0.11	0.09	<0.001
Pb	0.35	102.46	19.18	6.03	27.64	<0.001

SD standard deviation; *SW-p* *p*-value of the Shapiro-Wilk normality test

Three groups of fertilizers regarding HM concentration were distinguished by hierarchical cluster analysis (Figure 1). In the group of high concentrations, the organic-mineral fertilizers were the main representatives, with 83% of the evaluated organic-mineral fertilizers presenting high concentrations of heavy metals. Mixed fertilizers have phosphorus sources with the highest number of cases (58%) in the group with low concentrations of heavy metals. This is due to the fact that sources of N and K present very low concentration of metals (LUO et al., 2009), which causes a dilution effect.

Table 3. Average content (mg kg⁻¹) of As, Cd, Cr, Hg and Pb in phosphate fertilizers marketed in Brazil and in other parts of the world

Site	As	Cd	Cr	Hg	Pb
China ¹	13.5	2.6	<i>na</i>	0.9	30.0
USA (California) ²	10.5	53.0	<i>na</i>	<i>na</i>	<i>na</i>
Europe ³	7.6	7.4	89.5	<i>na</i>	2.9
Argentina ⁴	<i>na</i>	10.1	29.7	<i>na</i>	12.2
Chile ⁵	15.1	12.3	<i>na</i>	<i>na</i>	10.4
Brazil ⁶	6.6	9.4	67.8	0.1	19.2

na not available; *CDF*A California Department of Food and Agriculture; ¹ LUO et al. (2009); ² *CDF*A (1997); ³ Nziguheba and Smolders (2008); ⁴ Carnelo, Miguez and Marbán (1997); ⁵ Molina et al. (2009); ⁶ Present study.

The mean concentrations of As, Hg, and Pb were higher in organic-mineral fertilizers, while monoammonium phosphate (MAP) and phosphate rock (PR) presented the highest concentrations of Cr and Cd, respectively (Figure 2). The mean concentration of Pb in organic-mineral + phosphate rock (OM + PR) was 8 times higher than other sources.

High HM values in the OM + PR can be explained by the use of peat as the main organic matrix for the production of organic-mineral fertilizers in Brazil (JUNEK et al., 2014). Peat is organic sediment formed by the decomposition of plant residues in wet and acidic conditions. Studies have shown that peat soils close to urban and industrial areas can be enriched by HMs through atmospheric deposition (SHUTTLEWORTH et al., 2014); in addition, the metal complexation capacity of organic matter makes peat an important Pb scavenger (FARMER et al., 2005). There have been no studies in Brazil that quantify the levels of HMs in the peat used for organic-mineral fertilizers; however, data from the international literature have shown that high concentrations of heavy metals, especially Pb, can be found in peat (MIGHALL et al., 2002).

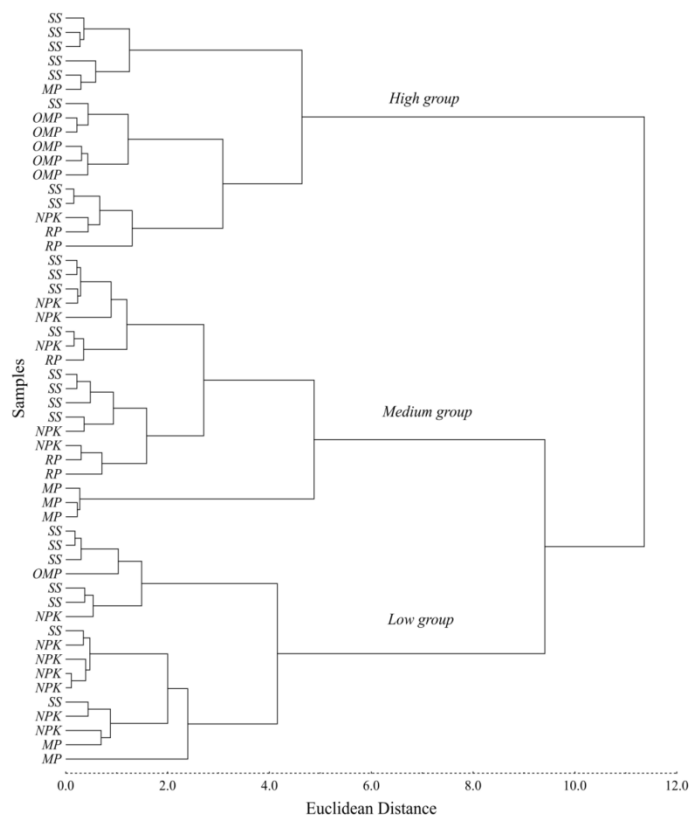


Figure 1. Hierarchical clustering of phosphate fertilizers as the contents metals using as criterion the concentrations of As, Cd, Cr, Hg and Pb in products. *SS* simple superphosphate, *NPK* multi-nutrient fertilizers, *RP* rock phosphate, *OMP* organo-mineral + rock phosphate and *MP* monoammonium phosphate

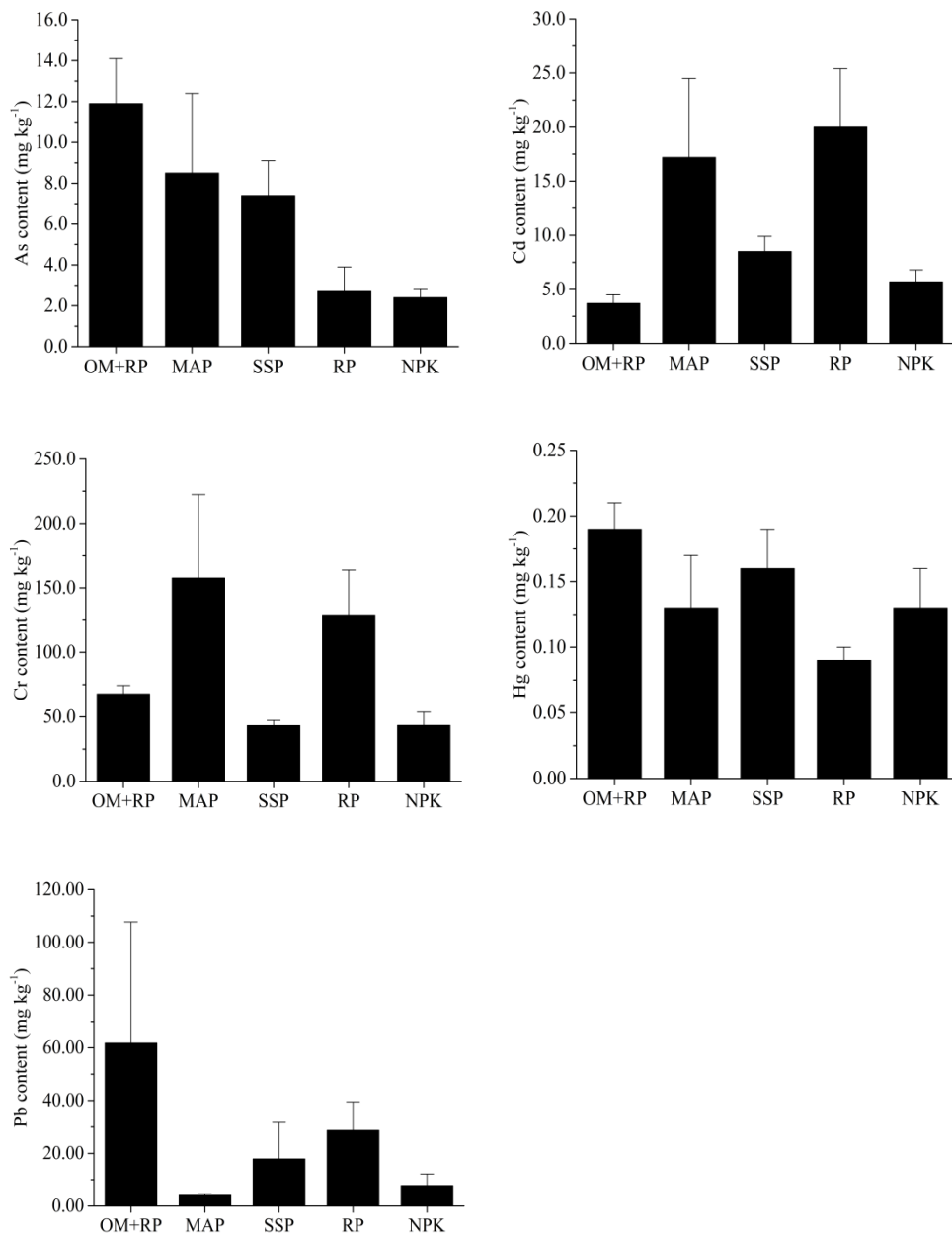


Figure 2. Average contents (standard deviation) of As, Cd, Cr, Hg and Pb in different types of P containing fertilizers marketed in Brazil. *RP* phosphate rock, *SSP* simple superphosphate, *MAP* monoammonium phosphate and *OMP+RP* organo-mineral + rock phosphate

Phosphate rocks presented mean Cd concentrations two times higher than those of other fertilizers except for MAP. A similar concentration of Cd was found in phosphate rocks of sedimentary origin marketed in Germany (KRATZ; SCHICK; SCHNUG, 2016), while the Cd content observed in this study was 4 times higher than in phosphate rocks of igneous origin (CAMPOS et al., 2005). Phosphate rocks are well known for carrying Cd to soils. Cadmium concentrations are generally higher in phosphate rocks of sedimentary origin than those of igneous origin (KRATZ; SCHICK; SCHNUG, 2016). The phosphate deposits in

Brazil are predominantly igneous, but a significant amount of this fertilizer is imported from Morocco, Russia, China, Israel, and the US, which have mainly sedimentary reserves (IFA, 2016); the high Cd concentrations reported here are probably due to these imported levels.

3.3.2 Addition of heavy metals in soil via fertilizers

The average addition rates ($\text{g ha}^{-1} \text{ year}^{-1}$) for the HMs were 4.0 (As), 6.3 (Cd), 47.3 (Cr), 0.08 (Hg), and 16.3 (Pb). The average addition rates for all elements in our study exceed the average additions of European countries, which were 20.7, 1.0, 1.6 and 2.3 $\text{g ha}^{-1} \text{ yr}^{-1}$ for Cr, Pb, Cd and As, respectively (NZIGUHEBA; SMOLDERS, 2008) (Table 4). The higher input of heavy metals via fertilizers in Brazilian soils as compared to Europe is mainly due to the average rate of P applied to the soil. In Brazil, the average recommendation of P_2O_5 is 140 kg ha^{-1} , whereas 43 kg ha^{-1} is the average rate in European countries. The higher demand for P in Brazilian agriculture as compared to other countries is owing to the high concentration of Fe and Al oxides in Brazilian soils that adsorb P through a specific adsorption mechanism (fixation) making it unavailable to plants (FONTES; WEED, 1996). We did not find data on the addition of Hg via fertilizers for European conditions.

Table 4. Mean values (\pm standard deviation) of per unit area additions ($\text{g ha}^{-1} \text{ year}^{-1}$) of heavy metals in agricultural soils via phosphate fertilizers marketed in Brazil

	SSP	MAP	RP	OM+RP
As	5.8 (± 1.3)	2.4 (± 1.1)	1.6 (± 0.7)	6.4 (± 1.2)
Cd	6.6 (± 1.1)	4.8 (± 2.0)	11.7 (± 3.2)	2.0 (± 0.4)
Cr	33.7 (± 3.1)	43.9 (± 17.8)	75.3 (± 20.3)	36.5 (± 3.5)
Hg	0.12 (± 0.02)	0.04 (± 0.01)	0.05 (± 0.01)	0.11 (± 0.01)
Pb	14.0 (± 3.2)	1.1 (± 1.0)	16.8 (± 10.5)	33.3 (± 8.6)

RP phosphate rock, SSP simple superphosphate, MAP monoammonium phosphate and OMP+RP organo-mineral + rock phosphate

We estimated that phosphate rock adds larger amounts of Cd and Cr than other fertilizers containing P, while the use of organic-mineral fertilizers contributes greatly to the input of As and Pb to the soil. Hg additions ranged from 0.04 (MAP) to 0.12 $\text{g ha}^{-1} \text{ yr}^{-1}$ (SSP). The biggest sources of HM are those with the highest levels in their composition except for Cr (Figure 2). Because the MAP samples are more enriched for P_2O_5 than phosphate rock, the amount of MAP needed to achieve the recommended dose is lower than that for phosphate rock.

Based on the Brazilian consumption and concentrations of HMs in fertilizers, we estimated that Cr and Pb represent the largest total additions to soil, 915.8 and 209.9 t year⁻¹, respectively (Table 5). Minor addition was observed for Hg (1.72 t year⁻¹). The sources that incorporate more HMs in soils are SSP and MAP, which are the sources of P most consumed in Brazil (Table 1). Estimates made with fertilizer composition of HMs indicated that SSP and MAP together provide more than 90% of Cd, 86% of Cr, and 79% of As. Organic-mineral fertilizers represented the main input of Pb to soils (45%).

Table 5. Mean values (\pm standard deviation) of total additions (tonne year⁻¹) of heavy metals in agricultural soils via phosphate fertilizers marketed in Brazil

	SSP	MAP	RP	OM+RP	Total
As	39.7 (\pm 8.9)	30.2 (\pm 14.0)	0.5 (\pm 0.2)	18.1 (\pm 8.1)	88.5
Cd	45.6 (\pm 7.5)	61.3 (\pm 25.9)	3.7 (\pm 1.0)	5.6 (\pm 2.9)	116.2
Cr	231.3 (\pm 21.4)	557.7 (\pm 226.7)	23.8 (\pm 6.4)	103.0 (\pm 24.5)	915.8
Hg	0.9 (\pm 0.1)	0.5 (\pm 0.1)	0.02 (\pm 0.00)	0.3 (\pm 0.1)	1.72
Pb	96.0 (\pm 22.2)	14.6 (\pm 12.4)	5.3 (\pm 3.3)	94.0 (\pm 59.3)	209.9

RP phosphate rock, *SSP* simple superphosphate, *MAP* monoammonium phosphate and *OMP+RP* organo-mineral + rock phosphate

In order to assess whether the levels of HMs in fertilizers exceed the maximum permitted concentrations, the values of the metals are based on the percentage points of P₂O₅ established by Brazilian legislation (MAPA, 2006). This practice is also adopted in California (USA) (AAPFCO, 2015) (Figure 3). Unlike other countries that regulate only Cd in phosphate fertilizers (CCR, 2007), Brazilian law regulates the concentrations (mg kg⁻¹ %P₂O₅⁻¹) of As, Cd, Cr, Hg, and Pb.

The ascending order of maximum permissible concentrations is Hg < Cd < As < Pb < Cr. Cd had the highest variability in phosphate fertilizers, with concentrations of 0.33, 0.73 and 1.31 mg kg⁻¹ %P₂O₅⁻¹ for the median, 75th percentile and maximum values, respectively. Arsenic and Pb had the highest numbers of anomalous values. SSP samples showed the highest ratio of As/P₂O₅, while the highest values of Pb/P₂O₅ were observed for OM + PR and SSP samples. When comparing the levels of metals in fertilizers with maximum concentrations allowed by Brazilian law, it was found that the P sources evaluated meet the legislative guidelines and are therefore considered safe.

The increases in the concentrations of HMs in soil (mg kg⁻¹) had the following order: Cr > Pb > Cd > As > Hg. The Cr and Pb concentrations were an order of magnitude higher than those of other heavy metals. The increase of Hg through the richest fertilizer (OM + PR) was negligible, and the estimated number of applications was > 12,000 (Table 6). The

potential risk for soil sustainability resulting from additions of As, Cr, and Pb via phosphate fertilizers are for a medium to long-term time frame. If the estimated additions of Cd are kept high, the concentration in the soil may exceed the allowable limit after 288 applications.

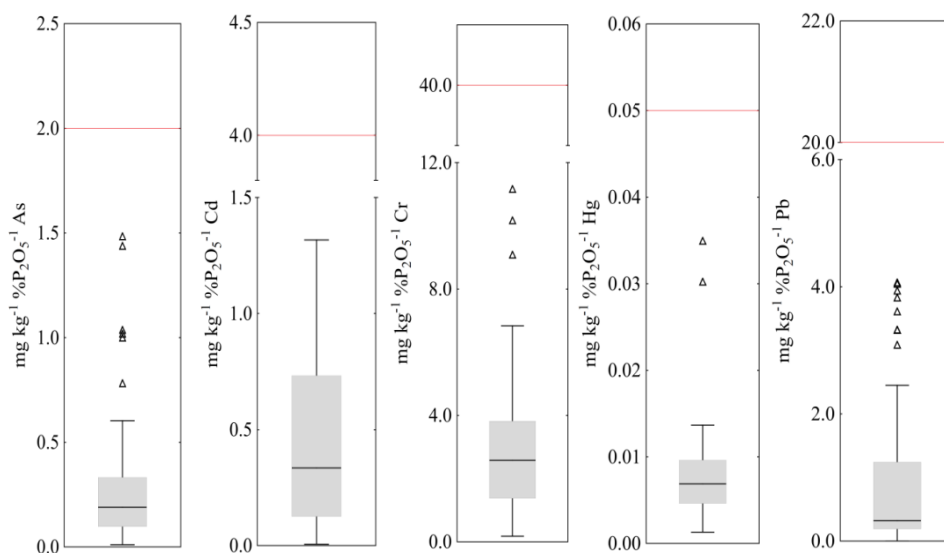


Figure 3. As, Cd, Cr, Hg and Pb concentrations per % of P_2O_5 in fertilizer containing P sold in Brazil. The dashed red line shows the permissible limits of heavy metals in phosphate fertilizers in accordance with Brazilian legislation (MAPA, 2006)

Table 6. Number of applications of fertilizers containing P needed to increase the concentrations of metals in the soil to the permissible limit

	Source	P_2O_5 total (%)	Concentration ^(a) ($mg\ kg^{-1}$)	Increase per application ^(b) ($mg\ kg^{-1}$)	Number de applications
As	OM+RP	26	15.0	0.002	6097
Cd	RP	24	1.3	0.005	288
Cr	RP	24	75.0	0.029	2591
Hg	OM+RP	26	0.5	<0.001	12082
Pb	OM+RP	26	72.0	0.013	5621

(a) Permissible limit in soil (CONAMA, 2009); (b) based on the application of $140\ kg\ ha^{-1}$ of P_2O_5 incorporated 0.2 m depth in soils with bulk density of $1300\ kg\ m^{-3}$, *OM* +*RP* organo-mineral + rock phosphate, *RP* rock phosphate.

3.4 Conclusions

In general, HMs in P-containing fertilizers sold in Brazil did not pose a human health risk in a medium timeframe. Nevertheless, intensive application of fertilizers with high concentrations of HMs requires monitoring of the HM accumulation in soils to ensure the environmental sustainability of agroecosystems. The contents of all evaluated metals were

below the maximum found in other regions of the world. Organic-mineral fertilizers are an important source of As, Hg, and Pb. Monoammonium phosphate and single superphosphates presented higher additions for As, Cd, and Pb in soils of Brazil. Phosphate rocks pose the main potential risk for soil quality owing to the high Cd concentration. Mixed fertilizers had low potential for increasing the concentration of HMs in soils.

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4. ASSESSING HEAVY METALS SOURCES IN SUGARCANE BRAZILIAN SOILS: AN APPROACH USING MULTIVARIATE ANALYSIS

Abstract

Brazil is the world's largest sugarcane producer and soils in the northeastern part of the country have been cultivated with the crop for over 450 years. However, so far, there has been no study on the status of heavy metal accumulation in these long-history cultivated soils. To fill the gap, we collect soil samples from 60 sugarcane fields in order to determine the contents of Cd, Cr, Cu, Ni, Pb, and Zn. We used multivariate analysis to distinguish between natural and anthropogenic sources of these metals in soils. Analytical determinations were performed in ICP-OES after microwave acid solution digestion. Mean concentrations of Cd, Cr, Cu, Ni, Pb, and Zn were 1.9, 18.8, 6.4, 4.9, 11.2, and 16.2 mg kg⁻¹ respectively. The principal component one was associated with lithogenic origin and comprised the metals Cr, Cu, Ni, and Zn. Cluster analysis confirmed that 68% of the evaluated sites have soil heavy metal concentrations close to the natural background. The Cd concentration (principal component two) was clearly associated with anthropogenic sources with P fertilization being the most likely source of Cd to soils. On the other hand, the third component (Pb concentration) indicates a mixed origin for this metal (natural and anthropogenic); hence Pb concentrations are probably related not only to the soil parent material but also to industrial emissions and urbanization in the vicinity of the agricultural areas.

Key words: Agricultural soils. Soil quality. Trace elements. Cadmium. Lead.

Avaliação das fontes de metais pesados em solos brasileiros cultivados com cana-de-açúcar: uma abordagem usando análise multivariada

Resumo

O Brasil é o maior produtor mundial de cana-de-açúcar e os solos da região nordeste do país tem sido cultivado com a cultura por mais de 450 anos. Contudo, até momento, não houve estudo sobre o status do acúmulo de metais pesados nesses solos cultivados por longos períodos. Para preencher a lacuna, nós coletamos amostras de solos de 60 cultivos de cana-de-açúcar a fim de determinar os teores de Cd, Cr, Cu, Ni, Pb e Zn. Nós utilizamos análise multivariada para distinguir entre as fontes naturais e antrópicas destes metais nos solos. Determinações analíticas foram realizadas em ICP-OES após a digestão em forno micro-ondas com solução ácida. As concentrações médias de Cd, Cr, Cu, Ni, Pb e Zn foram 1,9; 18,8; 6,4; 4,9; 11,2 e 16,2 mg kg⁻¹, respectivamente. A componente principal 1 esteve associada com a origem litogênica e compreendeu os metais Cr, Cu, Ni e Zn. A análise de agrupamento confirmou que 68% dos locais avaliados tiveram concentrações de metais pesados nos solos próximo ao background natural. A concentração de Cd (componente principal 2) foi claramente associada com fontes antropogênicas com a fertilização P sendo a mais provável fonte de Cd para os solos. Por outro lado, a terceira componente (concentração de Pb) indicou uma origem mista para este metal (natural e antropogênica); assim as concentrações de Pb são provavelmente relacionadas não apenas ao material parental do solo mas também as emissões industriais e urbanização na vizinhança das áreas agrícolas.

Palavras-chaves: Solos agrícolas. Qualidade do solo. Elementos traços. Cádmiio. Chumbo.

4.1 Introduction

Sugarcane (*Saccharum officinarum*) is a widely grown crop in Brazil. The sugarcane industry – including cultivation, processing and refined products – represents an important segment of the country economy. In 2012, the sugarcane sector contributes US\$43.8 billion to Brazil's gross domestic product (GDP) – equivalent to almost 2% of the entire Brazilian economy and higher than the GDP of a European country like Czech Republic (NEVES; TROMBIM; CONSOLI, 2011). The first sugarcane plantations in the country were established in Pernambuco state, northeast Brazil, in the 16th century (FREYRE, 1986); therefore soils in this state have been grown with sugarcane over 450 years. This implies a long-term application of agrochemicals for promoting crop growth which can contribute to elevate the concentration of heavy metals in soils (MENDES et al., 2006; KELEPERTZIS, 2014).

Over the last decades there has been an increased interest in soil contamination and its effects on humans and environment (NAVEEDULLAH et al., 2013; KELEPERTIS, 2014). Among soil contaminants, heavy metals raise great concern due to their persistence in soils and potential risks to human health and ecosystems (THOMPSON et al., 1988; ELIK, 2003; CUI et al., 2004). The natural concentration of heavy metals in soils is generally low and dependent on the geological parent material; hence, for most metals, anthropogenic sources are known to dominate over lithogenic contributions (NIU et al., 2013). Anthropogenic inputs such as sewage irrigation, pesticides and use of fertilizers are the main responsible for the increase of heavy metals concentrations in agricultural soils (MICÓ et al., 2006; PERIS et al., 2007; WEI; YANG, 2010). In these soils, the presence of heavy metals deserves careful monitoring since they can accumulate in less soluble forms or be transferred into soil solution and consequently deteriorate groundwater and crop quality (SUN et al., 2013; LI et al., 2014; YANG et al., 2014).

Despite the importance of fertilizers in providing nutrients and ensuring high yields, long-term repeated application of fertilizers can gradually add potential metal harmful concentrations in soils (NICHOLSON et al., 2006; LOTTERMOSER, 2009; GRANT; SHEPPARD, 2008; ROBERTS, 2014; CZARNECHI; DÜRING, 2015). Enrichment of soils with Cd is a likely result characterizing soils that have suffered a long history of intensive fertilizer application (MENDES et al., 2006; FREITAS et al., 2009; NIU et al., 2013). Biondi (2010) reported that Cd was above natural background contents in soils cultivated with sugarcane in Pernambuco; the author concluded that this resulted from phosphate fertilizer

application. Cadmium had the highest pollution index in agricultural soils across China and the accumulation was also related to fertilization (NIU et al., 2013). The presence of Cd in phosphate fertilizers is due to its natural occurrence in rocks used for fertilizer manufacturing (KABATA-PENDIAS, 2011). Many countries, including Brazil, regulate the limits of metal concentration in fertilizers in order to protect soils and crops against contamination (MAPA, 2006).

The knowledge of anthropogenic versus natural sources of heavy metals in soils is essential to assess human impact on the environment (PARELHO et al., 2014). Multivariate analysis has been successfully used to assist the interpretation of environmental data and to distinguish between natural and anthropogenic inputs (MICÓ et al., 2006). This differentiation is important to establish soil quality standards regarding heavy metals and to assess contamination risks of crops and groundwater in areas intensively and long-term cultivated (MICÓ et al., 2006; NAVEEDULLAH et al., 2013; NIU et al., 2013; SUN et al., 2013; KELEPERTZIS, 2014).

Nevertheless Brazil is the biggest worldwide sugarcane producer, studies on heavy metal accumulation in soils are still scarce (CONCEIÇÃO; NAVARRO; SILVA, 2013). Actually, for the long-history sugarcane plantations of northeast Brazil they are inexistent. The study was carried out to survey the status of Cd, Cr, Cu, Ni, Pb, and Zn accumulation in soils under long-term sugarcane cultivation in northeast Brazil. Additionally, we correlated metal concentrations with physical and chemical soil properties and employed principal component analysis (PCA), cluster analysis (CA) and discriminant analysis (DA) in order to distinguish between natural (lithogenic) and anthropogenic sources of such metals in soils and create groups according to similarity in the soil contamination levels of heavy metals in the collected areas. To our knowledge this is the first attempt to assess the status of heavy metal accumulation in soils cultivated with sugarcane for centuries in Brazil.

4.2 Material and methods

4.2.1 Study area and soil sampling

The Pernambuco state, situated in northeast Brazil (Figure 1) has been long associated with sugarcane plantations. The earliest plantation in operation was in place in 1518 along the Atlantic coast of the state, but it was not until the 1530's that sugar agriculture was firmly established in this region (FREYRE, 1986). The study area is located in the coast zone of

Pernambuco and it is characterized by a humid tropical climate with an annual average temperature of 25.5 °C, annual average rainfall of 2,200 mm and air relative humidity of 80 % (INMET, 2015). Sugarcane cultivation in this region is characterized by intensive use of pesticides, limestone and fertilizers owing to the natural acidity and low soil fertility. There are no other significant human activities in the region that affect soil pollution by metals.

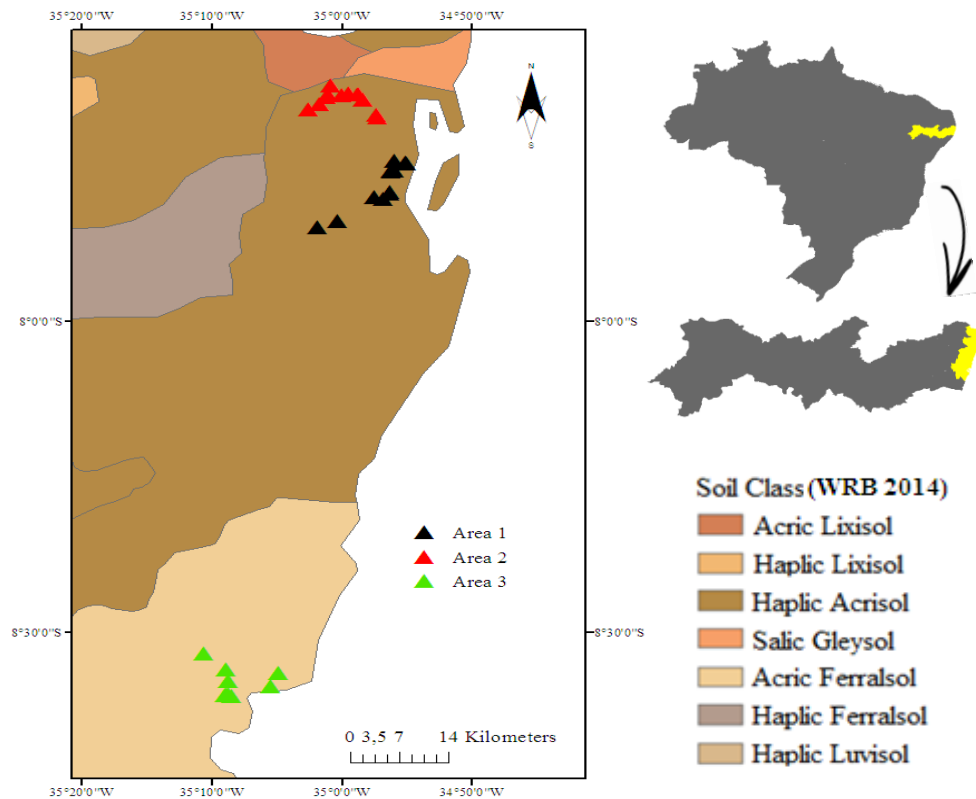


Figure 1. Soil sampling points in areas under sugarcane cultivation and their soil classes along the coastal zone of Pernambuco state, Brazil

For soil sampling, three of the main sugarcane plantations areas were selected. Haplic Acrisol is the soil type prevailing in areas 1 and 2 whereas Acric Ferralsol is the soil type under cultivation in area 3 (Figure 1). Regarding the geology, soils in the study area are originated from clay loam sediments in the north part and crystalline rocks (rhyolites, granites and basalts) in the south (Table 1). We collected four topsoil samples (0.0 - 0.2 m depth) within a 10 m radius from each one of the 60 sampling points; these samples were thoroughly mixed to form a composite sample to analysis.

Table 1. Plane coordinates and geology of the soil sampling sites

Sampling site	Coordinates (X – Y)(UTM, meters)	Parental material
A1.1	286491 – 9140759	
A1.2	286448 – 9140555	
A1.3	285494 – 9139524	
A1.4	285498 – 9139552	
A1.5	284153 – 9139879	
A1.6	284169 – 9139880	
A1.7	279006 – 9135596	
A1.8	279008 – 9135578	
A1.9	276192 – 9134495	
A1.10	276192 – 9134485	
A1.11	286583 – 9144535	Sandy and sandy-clay sediments
A1.12	286583 – 9144518	
A1.13	286986 – 9144582	
A1.14	286998 – 9144566	
A1.15	288819 – 9145841	
A1.16	288825 – 9145835	
A1.17	288572 – 9146101	
A1.18	288582 – 9146109	
A1.19	287044 – 9146301	
A1.20	287052 – 9146311	
A2.1	278059 – 9159665	
A2.2	278038 – 9159664	
A2.3	277654 – 9157943	
A2.4	277649 – 9157945	
A2.5	277372 – 9157605	
A2.6	277365 – 9157605	
A2.7	276384 – 9156361	
A2.8	276365 – 9156357	
A2.9	274796 – 9155432	
A2.10	274790 – 9155454	
A2.11	279613 – 9158056	Sandy and sandy-clay sediments
A2.12	279614 – 9158044	
A2.13	280562 – 9158268	
A2.14	280569 – 9158258	
A2.15	281929 – 9158180	
A2.16	281828 – 9158161	
A2.17	285878 – 9157247	
A2.18	282573 – 9157240	
A2.19	284434 – 9154542	
A2.20	284708 – 9154066	
A3.1	263973 – 9053555	
A3.2	263980 – 9053539	
A3.3	263768 – 9055544	Biotite gneiss, mica schistandmigmatite
A3.4	263770 – 9055544	
A3.5	260572 – 9058412	
A3.6	260582 – 9058413	Biotite gneissandmigmatite
A3.7	264513 – 9050819	
A3.8	264526 – 9050814	
A3.9	264052 – 9051084	
A3.10	264059 – 9051097	Biotite-amphibole granite
A3.11	263651 – 9051051	
A3.12	263672 – 9051073	
A3.13	269313 – 9047639	
A3.14	269289 – 9047624	Alluvialsediments
A3.15	270025 – 9046564	
A3.16	270025 – 9046554	Sandy and sandy-clay sediments
A3.17	269959 – 9052596	
A3.18	269958 – 9052602	Rhyolite
A3.19	271087 – 9054950	
A3.20	271094 – 9054954	Basalt

(A1.n) points samples in area 1, (A2.n) points samples in area 2 and (A3.n) points samples in area 3. (n = 20)

4.2.2 Soil analysis and quality control

One kilogram of topsoil (0 – 20 cm) samples were air-dried and sieved through a 2 mm sieve in order to perform routine soil analysis. Soil pH was measured in a 1:2.5 soil:water suspension. The soil organic matter (SOM) content was determined using the modified Walkley-Black method (SILVA; TORRADO; JUNIOR, 1999), and the cation exchange capacity (CEC) was determined by saturation with sodium acetate followed by Na solubilization with ammonium acetate (MCGEORGE, 1954) and Na determination by flame photometry. Phosphorus total concentration was measured by colorimetry after microwave sample digestion (USEPA, 1998). Particle-size distribution was measured by the Bouyoucos densimeter method modified by Almeida (2008).

For metals determination, 1.0 g soil was digested in Teflon vessels with 9.0 mL of HNO₃ and 3.0 mL of HCl in a microwave oven (USEPA, 1998). All extracts were transferred to 50-mL certified flasks (NBR ISO/IEC) filled with ultrapure water and filtered in a slow filter paper. High purity acids were used in the analysis (Merck PA). Glassware was cleaned and decontaminated in a 5 % nitric acid solution for 24 h and then rinsed with distilled water. The concentrations of Cd, Cr, Cu, Ni, Pb, and Zn were determined by inductively coupled plasma (ICP-OES). Analytical data quality and standard operation procedures, such as curve recalibration, analysis of reagent blanks, limit of quantification calculation (LOQ) and analysis of standard reference material (NIST 2710 - Montana Soil) were carried out. NIST recoveries were 113% (Cd), 92% (Cr), 89% (Cu), 100% (Ni), 101% (Pb), and 85% (Zn). The LOQ calculated were 0.0002, 0.0007, 0.003, 0.0012, 0.0042, and 0.0006 mg L⁻¹ for Cd, Cr, Cu, Ni, Pb e Zn, respectively.

4.2.3 Statistical Analysis

Descriptive statistics (mean, minimum and maximum values, and standard deviation) for raw soil data were established and Shapiro-Wilk distribution test used for data normality assessment. A *p* value higher than 0.05 was used to agree with the hypothesis of the data set belongs to a normal distribution. Multivariate analyses were performed with STATISTICA (v. 10) software. The concentrations of metals were submitted to principal component analysis (PCA) and interpreted according to their natural, anthropogenic or mixed sources. Varimax rotation was applied since orthogonal rotation minimizes the number of variables with high loading on each component and makes data interpretation easier (MICÓ et al.,

2006). Cluster Analysis with adoption Cd, Cr, Cu, Ni, Pb and Zn content as dissimilarity standard was applied to the areas by Ward's method and use of Euclidean distance. The validation of the cluster analysis was accomplished with discriminant analysis. Pearson's correlation was used to relate soil properties and heavy metal concentrations.

4.3 Results and discussion

4.3.1 Descriptive statistics

Soil chemical and physical variables did not present normal distribution according to Shapiro-Wilk distribution test ($p < 0.05$), except for pH (Table 2). The pH values varied from 4.5 to 6.7 and more than one-half of the samples presented a very acidic pH (< 5.5), typical of tropical soils. Soil organic matter (SOM) ranged from 11.1 to 94.4 g kg⁻¹ with an average value of 25.9 g kg⁻¹. Most of the samples analyzed are coarse texture soils with mean values of 674.0 g kg⁻¹ of sand. This is the main reason for the low cation exchange capacity (CEC) of these soils. The values of total P broadly varied from 9.0 to 1118.0 mg kg⁻¹ with most of the soil samples (80%) presenting P concentrations between 100 and 400 mg kg⁻¹. Such results indicate the intensive use of fertilizers that can build P levels in soil higher than sugarcane requirement and add toxic metals to soil system.

Table 2. Descriptive statistic for soil chemical and physical characteristics and heavy metal concentrations

	Mean	Min	Max	SD	S-W test
pH	5.6	4.5	6.7	0.6	0.40
SOM (g kg ⁻¹)	25.9	11.1	94.4	13.3	0.00
CEC (cmol _c dm ⁻³)	11.7	0.2	107.0	27.7	0.00
P _{total} (mg kg ⁻¹)	275.8	9.4	1118.5	239.0	0.00
Sand (g kg ⁻¹)	674.8	174.5	956.7	204.8	0.00
Clay (g kg ⁻¹)	238.8	22.0	678.3	152.2	0.00
Cd (mg kg ⁻¹)	1.9	1.0	4.3	0.8	0.00
Cr (mg kg ⁻¹)	18.8	0.2	111.5	22.8	0.00
Cu (mg kg ⁻¹)	6.4	<LOQ	36.4	8.0	0.00
Ni (mg kg ⁻¹)	4.9	<LOQ	41.2	7.4	0.00
Pb (mg kg ⁻¹)	11.2	1.1	32.3	6.7	0.01
Zn (mg kg ⁻¹)	16.2	2.1	58.5	10.6	0.00

SOM soil organic matter, CEC cation exchange capacity, P_{total} total phosphorus in soil, Min minimum value, Max maximum value, SD standard deviation, S-W test value p in Shapiro-Wilk test, LOQ limite of quantifitation (0.003 and 0.0012 mg kg⁻¹ for Cu and Ni, respectively)

Heavy metal concentrations in soils followed the order $\text{Cr} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Cd}$ (Table 2). All heavy metals presented concentrations above the quality reference values (QRVs) for soils of the state (CPRH 2014) in at least three of the surveyed areas (Figure 2). This clearly suggests that anthropogenic inputs have increased metal concentrations in such soils to levels exceeding the lithogenic contribution through weathering. Significant increments in metal concentration in agricultural soils have been reported in several parts of the world (MENDES et al., 2006; PERIS et al., 2007; SUN et al., 2013; KELEPERTZIS, 2014; PARELHO et al., 2014).

Cadmium concentrations were higher than QRV (0.5 mg kg^{-1}) in all the 60 soil samples, with the mean value for the element being three times higher than the expected background content (Figure 2). Based on the national regulation regarding heavy metal concentrations in agricultural soils (CONAMA, 2009), six sugarcane fields can pose an unacceptable risk to human health since their Cd concentrations are above 3.0 mg kg^{-1} . This implies that such contaminated areas must pass through a site-specific risk assessment to determine the need and urgency of remediation. Soils contaminated with heavy metals in an agricultural scenario can pose a threat to human health mainly through soil ingestion, crop consumption, inhalation of soil particles and dermal uptake via soil (SWARTJES et al., 2012). Copper and Pb concentrations exceeded their QRVs in 37 % of the areas hence anthropogenic influence can be at least partially related to such an increase. Only a few soil samples have Zn, Ni, and Cr concentrations above their region's natural occurrence, although two of these samples are probably contaminated owing to agrochemical inputs.

4.3.2 Correlation matrix

Soil organic matter (SOM) was positively correlated with Cd, Cr and Cu (Table 3) in spite of the low SOM mean value found in soils (Table 2). It is well-known that organic matter strongly binds Cr^{3+} e Cu^{2+} while presents a moderate binding capacity for Cd^{2+} (BLUME; BRÜMER, 1987; KABATA-PENDIAS, 2011).

The clay content exhibited significant correlations with all the metals (Table 3). Clay minerals are probably the main soil colloids regarding heavy metals adsorption in the studied soils owing to the low contents of soil organic matter. Given the low correlation between metals and CEC, it is likely that metals are bound mostly by covalence on kaolinite and iron and aluminum oxides (ARAÚJO et al., 2002). The adsorption mechanisms in these clay

minerals take place by high energy covalent binding (specific adsorption), a common reaction between soil oxides and metallic ions (NAIDU; SUMNER; HARTER, 1998).

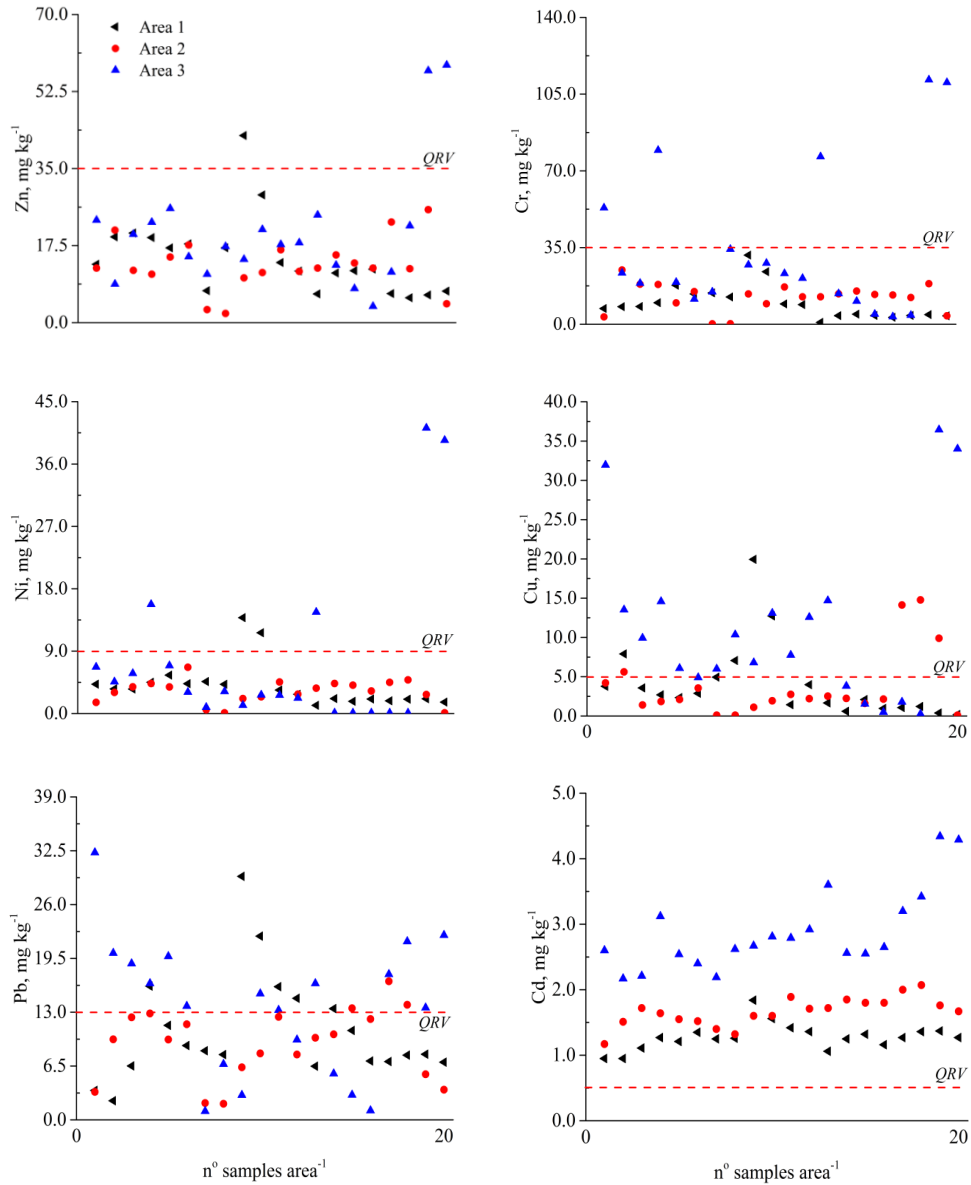


Figure 2. Heavy metal concentrations in sugar cane fields as compared to regional soil quality reference values (QRVs) for metals (CPRH, 2014)

A positive and significant correlation was obtained between total P concentration and metals studied (Table 3) with highest values for Cu as also reported by Kelepertzis (2014). The role P plays in the metal sorption in soils is due to formation of low solubility precipitates resulting from the reaction between free phosphate ions (HPO_4^{2-}) with metallic cations (Cr^{3+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Ni^{2+} e Zn^{2+}) in soil solution (CRANNELL et al., 2000). For instance,

formation of pyromorphite [$\text{Pb}_5(\text{PO}_4)_3(\text{Cl}, \text{Br}, \text{OH} \text{ e } \text{F})$], a low solubility lead phosphate can take place through P amendment to Pb contaminated soils which reduces Pb bioavailability (NIAGRU, 1984; MA, 1996). Additionally, as HPO_4^{2-} is adsorbed on positively charged surfaces of iron oxides, aluminum oxides and phyllosilicates the net superficial charge changes from positive to negative. This increases the cation exchange capacity (CEC) and promotes the formation of oxide-phosphate-metal type complexes (GUILHERME; ANDERSON, 1998; OLIVEIRA et al., 2010).

Table 3. Correlation matrix between heavy metal concentrations and selected soil properties

	SOM	Clay	CEC	P _{total}
Cd	0.35*	0.67**	0.34*	0.35*
Cr	0.35*	0.67**	0.24 ^{ns}	0.41**
Cu	0.29*	0.34*	0.38**	0.67**
Ni	0.16 ^{ns}	0.46**	0.28*	0.37**
Pb	0.09 ^{ns}	0.44**	0.23 ^{ns}	0.32*
Zn	0.14 ^{ns}	0.35*	0.28 ^{ns}	0.43**

SOM soil organic matter, CEC cation exchange capacity, P_{total} total phosphorus in soil, * $p < 0.05$, ** $p < 0.01$, ^{ns} not significant.

4.3.3 Principal Component Analysis (PCA), Cluster Analysis (CA) and Discriminant Analysis (DA)

Given the long-term soils cultivated with sugarcane are clearly enriched in some heavy metals compared to the natural background of the region, PCA was used to distinguish between natural and anthropogenic sources of these elements in soils. The eigenvalues of the first two extracted factors were greater than 1.0 (Table 4); thus heavy metals can be grouped into a three-component model that accounts for 91 % of the total variance. The spatial representation displaying the metals association of the three rotated components is shown in Figure 3. The component matrix showed that Cr, Cu, Ni, and Zn were associated with the first component (PC1); the second component (PC2) included Cd while Pb showed a high loading in the third component (PC3).

The principal component PC1 including Cr, Cu, Ni, and Zn explained 64.2% of the total variance (Table 4). The variability of these elements in soils seems to be related to a common source, in such a case the underlying soil parent material. Indeed, most of the studied

areas showed concentrations of Cr, Cu, Ni, and Zn very similar to those regionally found in natural background condition (BIONDI et al., 2011).

Table 4. Principal component analysis matrix for heavy metal concentrations in soils grown with sugarcane in Pernambuco state, Brazil. Significant loading factors are underlined

Components	Eigenvalues	% Total Variance	% Cumulative Variance
1	3.85	64.26	64.26
2	1.01	16.52	81.08
3	0.59	9.90	90.99
Element	Component1	Component2	Component3
Cd	0.16	0.95	0.16
Cr	0.82	0.42	0.19
Cu	0.89	0.25	0.13
Ni	0.82	-0.26	0.38
Pb	0.30	0.20	0.92
Zn	0.80	0.22	0.35

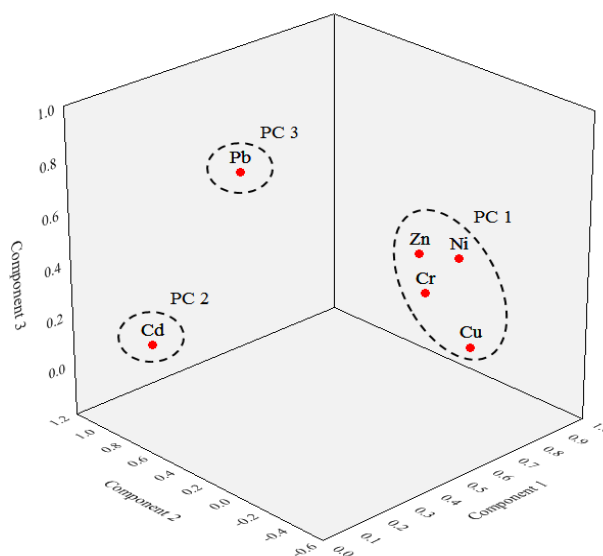


Figure 3. Loading plots of the three components influencing heavy metals variation in soils cultivated with sugarcane

The principal component PC2 includes Cd only. This component is defined as anthropogenic and related to agriculture practices, chiefly fertilization. As mentioned previously, all the soil samples presented Cd concentrations higher than the expected natural content of the element in soils. This confirms the interpretation of Cd anthropogenic origin. Phosphate fertilizers are a well-known source of Cd in agricultural soils (MENDES et al.,

2006; NICHOLSON et al., 2006; FREITAS et al., 2009; CARVALHO; NASCIMENTO; BIONDI, 2012; NAVEEDULLAH et al., 2013; YANG et al., 2014) and the increase of Cd concentration is closely related to the length of time soils have been fertilized (KELEPERTZIS, 2014; PARELHO et al., 2014). Therefore, the long history of sugarcane cultivation along with the use of fertilizers resulted in extensive Cd accumulation in soils from Pernambuco state. However, other sources such as atmospheric deposition, animal manures and sewage sludge applied to soils can also contribute to increased concentrations of Cd in agricultural soils (MICÓ et al., 2006).

PC3 includes Pb and explained only 9.9 % of total variance but it was clearly differentiated from the other components; this is apparently an indication of mixed sources contributing to Pb addition in soils. Lead is generally linked to atmosphere deposition from vehicles emissions and has been widely used in chemical, metallurgical and siderurgical industries (KABATA-PENDIAS, 2011; HU et al., 2013). The highest Pb concentrations were found in soils from the south coast of Pernambuco (Figure 1). This region has a port and industrial complex established in 1978 which comprises several potentially polluting activities, including a petrochemical industry regarded as a major source of Pb contamination to atmosphere (SCHRODER et al., 2000). Thus atmospheric deposition of Pb originated from these industrial sources could explain the above background concentrations of this metal in soils.

The hierarchical cluster analysis (Figure 4) allowed the definition of four geochemical groups which dissimilarity was validated through a discriminant analysis with 98.3 % of total certainty (Table 5). When heavy metals are used as a dissimilarity criterion, there is area intersection for groups 1 and 2 only; these groups present the lowest concentrations of Cr, Cu, Ni, and Pb in soil. The similarity between these two groups (G1 and G2) is indicated by proximity of their centroids in comparison with groups 3 and 4 (Figure 5).

The majority of soil samples assessed (68 %) are in group 1 (Figure 4). These samples presented Cr, Cu, Ni, Pb and Zn concentration in the normal range (\leq QRVs) and are related to soil parent material. A closer scrutiny of group 2 reveals that concentrations of Cd and Cu in the 12 soil samples of this group are above their respective quality reference values while Cr and Pb soil concentrations are higher than the QRV just for some samples. Group 3 includes four soil samples (cases 9, 41, 44, and 53) that presented Cd, Cr, Cu, Ni, and Pb concentrations above background levels. The two soil samples in group 4 (59 and 60) are characterized by the highest concentrations of Cd (4.3 mg kg^{-1}), Cr (110.9 mg kg^{-1}), Cu (35.2 mg kg^{-1}), Ni (40.3 mg kg^{-1}), and Zn (57.9 mg kg^{-1}). For instance, Zn and Cu concentrations in

soils are 2 to 7-fold higher than their QRVs and Cd concentration is 43 % higher than the permissible concentration for Brazilian agricultural soils (CONAMA, 2009).

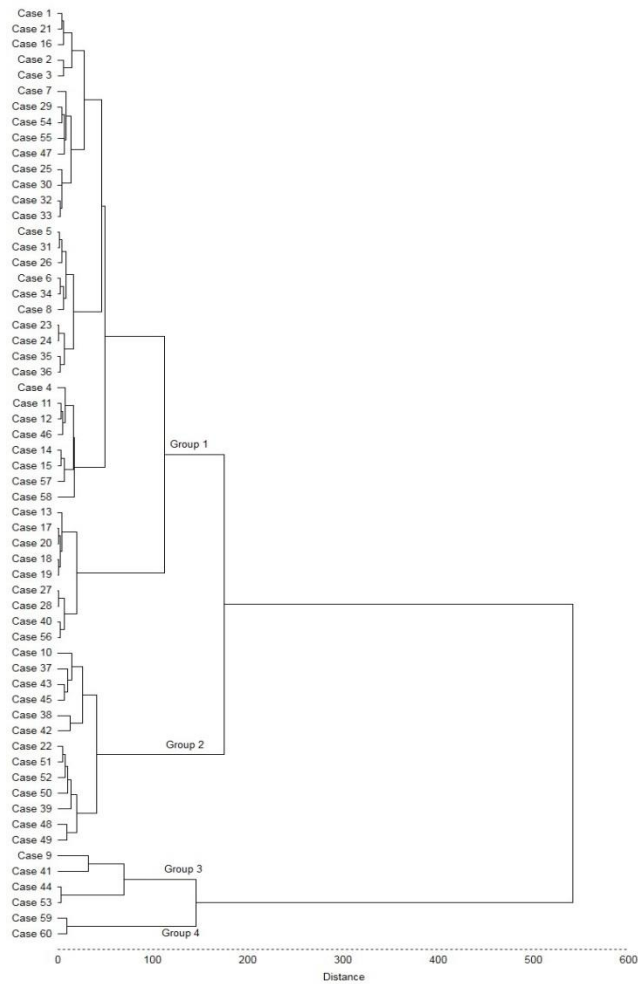


Figure 4. Dendrogram obtain by hierarchical cluster analysis for heavy metals contents in soil samples.

Table 5. Confusion matrix among geochemical groups formed through hierarchical cluster analysis

	G1	G2	G3	G4	Total	Certainty %
G1	41	0	0	0	41	100
G2	1	12	0	0	13	92
G3	0	0	4	0	4	100
G4	0	0	0	2	2	100
Total	42	12	4	2	60	98

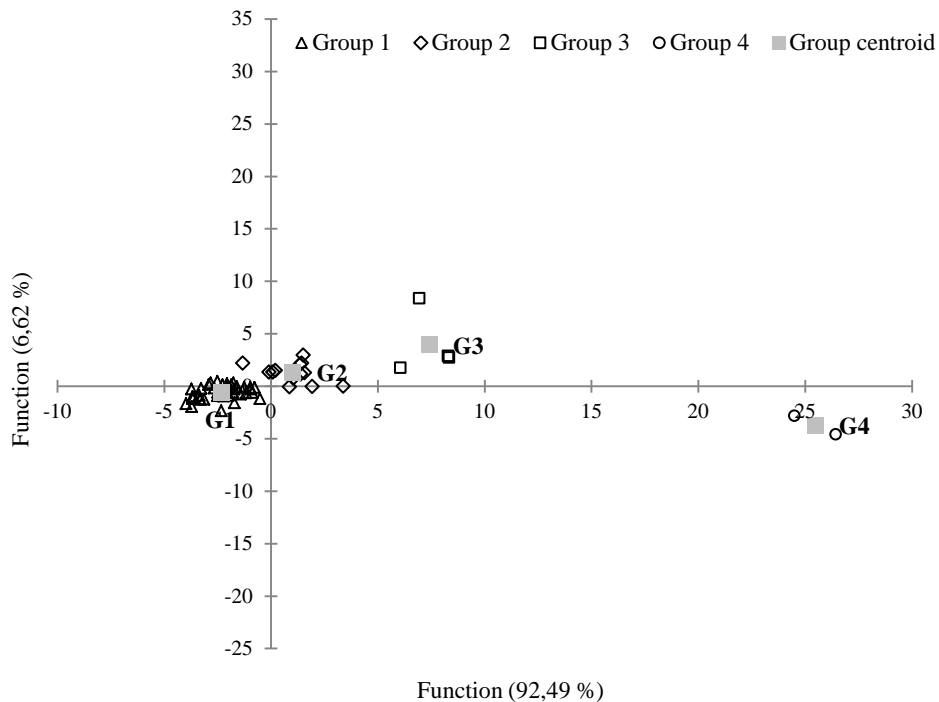


Figure 5. Function discriminant analysis plot for four geochemical groups in soil cultivated with sugar cane

4.4 Conclusions

Agricultural soils have been contaminated by heavy metals in several countries. The results presented here increase our knowledge of the accumulation and sources of heavy metals in soils under long-term sugarcane cultivation in Northeast Brazil. The PCA enabled to distinguish between natural and anthropogenic sources of metals in soils. The principal component one (PC1) was associated with lithogenic origin and comprised the metals Cr, Cu, Ni, and Zn. Indeed, most concentrations of these metals were close to the natural background concentrations for soils of the region. The Cd concentrations (PC2) were clearly associated with anthropogenic sources as a consequence of P fertilization and other amendments to soil. All the soil samples analyzed presented Cd concentrations above the state's soil quality standard; six out of 60 sugarcane fields pose an risk to human health since their Cd concentrations are above 3.0 mg kg^{-1} . Finally, Pb concentration (PC3) indicates a mixed origin for this metal (natural and anthropogenic); hence Pb concentrations are probably related not only to the soil parent material but also to industrial emissions and urbanization in the vicinity of the agricultural areas. The cluster and discriminant analysis allowed the identification of four geochemical groups regarding different levels of soil contamination; most values of Cr, Cu, Ni, Pb and Zn (68%) were in the range of soil background

concentrations while 10% of soil samples were grouped into the more metal enriched soils for Cd, Cr and Ni. Our results are consistent with other reports on accumulation of metals in soils that demonstrate the potential of agriculture to increase the heavy metal concentrations above regulatory standards. The data represent the first survey of metal concentrations in sugarcane soils of Northeast Brazil and highlight the importance of monitoring the concentrations of heavy metals in soils intensively cultivated in order to protect the soil ecological functions and the human health.

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5. RARE EARTH ELEMENTS IN SOIL CORRECTIVES AND P-CONTAINING FERTILIZERS MARKETED IN BRAZIL

Abstract

The mineral exploration of rare earth elements (REEs) and their entry into the soil by pollution or fertilizer application has generated concern about possible environmental impacts and human health. In this sense, we evaluated 60 samples of agricultural inputs (limestone, gypsum and phosphate fertilizers) marketed in Brazil in order to characterize their contents, signature and solubility of REEs. The fertilizers from igneous origin presenting the largest accumulation of REEs. Regardless of origin, the accumulations of the light REEs Ce, La, Nd, Pr, Sm and Eu were larger than the heavy ones (Y, Dy, Gd, Er, Yb, Ho, Tb and Lu). The solubility of fertilizers produced from sedimentary sources was greater than that of igneous sources. The mean annual REEs contribution of SSP and organo-mineral + phosphate rock (both of igneous origin) to soils was $> 4000 \text{ t year}^{-1}$ and the highest additions were for Ce, La, Nd and Y. The limestone contributed 250 t of Gd, more than any other source. Thus, phosphate fertilization and liming were considered to be significant sources of REEs and soils receiving continuously high doses of these inputs are likely to be enriched in REEs.

Key words: Rare earth. Phosphate fertilizers. Agricultural soil. Contamination.

Elementos terras raras em corretivos do solo e fertilizantes contendo P comercializado no Brasil

Resumo

A exploração mineral de elementos terras raras (ETRs) e sua entrada no solo por poluição ou aplicação de fertilizantes, tem gerado preocupação quanto aos possíveis impactos ambientais e na saúde humana. Neste sentido, nós avaliamos 60 amostras de insumos agrícolas (calcário, gesso e fertilizantes fosfatados) comercializados no Brasil a fim de caracterizar seus teores, assinatura e solubilidade de elementos terras raras. Os fertilizantes de origem ígnea apresentaram o acúmulo de ETRs. Independentemente da origem, os acúmulos dos ETRs leves Ce, La, Nd, Pr, Sm e Eu foram maiores do que dos pesados (Y, Dy, Gd, Er, Yb, Ho, Tb e Lu). A solubilidade dos fertilizantes produzidos de fontes sedimentares foram maiores do que das fontes ígneas. O aporte médio anual de ETRs destas fontes para os solos foi $> 4000 \text{ t ano}^{-1}$ e as maiores adições foram observadas para Ce, La, Nd e Y. O calcário aportou 250 t ano^{-1} de Gd, mais do que qualquer outra fonte. Deste modo, a adubação fosfatada e a calagem foram consideradas fontes significativas de ETRs e os solos que recebem continuamente elevadas doses destes insumos, provavelmente, são enriquecidos em ETRs.

Palavras-chaves: Terra rara. Fertilizante fosfatado. Solo agrícola. Contaminação.

5.1 Introduction

Rare earth elements (REEs) are a group of 17 elements, comprising the 15 lanthanides (lanthanum - La, cerium - Ce, praseodymium - Pr, neodymium - Nd, promethium - Pm, samarium - Sm, europium - Eu, gadolinium - Gd, terbium - Tb, dysprosium - Dy, holmium - Ho, erbium - Er, thulium - Tm, ytterbium - Yb, lutetium - Lu), as well as scandium (Sc) and yttrium (Y). REEs have similar chemical and physical properties (VONCKEN, 2016) and are commonly found together in geological deposits of phosphate rocks (RAMOS et al., 2016).

In recent years, the increasing anthropogenic contribution of REEs to the environment through mining activities (LIANG; LI; WANG, 2014; ATIBU et al., 2018), the disposal of industrial effluents (HE et al., 2010) and the extensive application of REEs enriched fertilizers (CAO et al., 2001; PANG; LI; PENG, 2002), has generated concern about possible environmental impacts and human health. Studies have correlated environmental contamination by REEs with diseases in humans, occupational poisoning, water and soil pollution, as well as the reduction in soil macro and microfauna diversity (MARUBASHI; HIRAMO; SUZUKI, 1998; LI et al., 2013; RIM; KOO; PARK, 2013).

Rare earth elements are mainly incorporated in agricultural soils by phosphate fertilization (HU et al., 2006). The contents of REEs in nitrogen and potassium fertilizers, as well as in soil correctives are generally lower than those found in phosphates (TURRA; FERNANDES; BACCHI, 2011). However, the continuous application of high amounts of soil correctives may imply in significant amounts of REEs added to soil (ABDEL et al., 2001). Phosphate rock is the raw material for the manufacture of phosphate fertilizers and is also widely used in natura as a source of phosphorus. Phosphates naturally contain REEs, which may be of concern for environmental contamination (HEIN et al., 2016; POLETTI et al., 2016; RAMOS et al., 2016; XIN et al., 2016; CERVA-ALVES et al., 2017; GARNIT; BOUHLEL; JARVIS, 2017) as significant amounts of REEs remain in the fertilizer after the production (RAMOS et al., 2016).

Phosphate fertilizers are mainly derived from phosphorite (sedimentary rock) and carbonatite (igneous rock). Fertilizers containing P derived from carbonatite are generally enriched in REEs (OTERO et al., 2005). The Brazilian deposits of phosphates are mainly from carbonatite origin. However, Brazil imports large amounts of ore and phosphate fertilizers (IFA, 2016), making it difficult to track the origin of commercial fertilizers. As a solution to this problem, the work of Otero et al. (2005) and Ramos et al. (2016) have shown that REEs can be used as tracers of origin (igneous or sedimentary) of the raw materials used

in the manufacture of phosphate fertilizers. A common method for this purpose is the comparison of the distribution patterns (signatures) of the REEs in the samples and in the possible sources. For this, the normalized REE contents are graphically plotted; in this graph the content of each REE is divided by the content of the same REE in a reference material (normalization) (PIPER; BAU, 2013).

China is the world's largest producer and consumer of REEs; fertilizers enriched in REEs (containing on average 19.8, 5.4, 4.6, 1.9, 0.4, and 0.1% of La_2O_3 , Nd_2O_3 , CeO_2 , Pr_6O_{11} , Sm_2O_3 and Eu_2O_3 , respectively) have been produced for several decades and extensively applied in Chinese agriculture as it is believed that these elements provide greater crop productivity. In Brazil, on the other hand, there is no fertilization recommendation and no legislation to regulate REE reference values in fertilizers and soil correctives. There are few studies in the country that investigated the REEs levels in agricultural inputs (RAMOS et al., 2006; TURRA; FERNANDES; BACCHI, 2011); there is also little information on the uptake of these elements by plants in soils fertilized with different phosphate fertilizers and their long term accumulation in the soil. Thus, the determination of the total and soluble contents of REEs in fertilizers and correctives is important to monitor the risks of contamination and pollution of these elements in soils.

Brazil is currently the 4th largest consumer of fertilizers in the world (IFA, 2016). Phosphate fertilizers and soil corrective are used intensively in Brazilian agriculture; in 2016, the country consumed 11.8 and 33.0 million tons of phosphate fertilizers and limestone, respectively (ABRACAL, 2017; IPNI, 2017). These fertilizers and correctives are an important route of entry of REEs to the soil. In this context, the present work evaluated the contents, the signature and the solubility of REEs in phosphate fertilizers and soil correctives marketed in Brazil. In addition, we estimated the amounts of REEs entering soils of Brazil through these inputs.

5.2 Material and Methods

5.2.1 Selection, preparation and total digestion of fertilizers and soil correctives

We selected 60 samples of fertilizers and soil correctives as follows: limestone (20), gypsum (10), single superphosphate - SSP (12), triple superphosphate - TSP (2), monoammonium phosphate – MAP (6), organo-mineral + phosphate rock (6) and phosphate rock (4). Samples were obtained from the National Agricultural Laboratory (LANAGRO-PE)

of the Ministry of Agriculture, Livestock and Supply (MAPA). The samples were oven dried (65 ° C), powdered in agate mortar and sieved in a 0.3 mm stainless steel mesh.

Samples of 1.000 g of each product were digested at 250 ° C with HF, HClO₄ and HNO₃ (2: 1: 1) in teflon beakers (ESTEVEZ et al., 2001). After digestion, the extracts were filtered (Ø < 2 µm) and the volume measured in 25 mL volumetric flasks with ultrapure water.

5.2.2 REEs signatures as tracers for P sources

The fertilizer samples were grouped according to their REE signatures. The content of each REE in each sample was divided by its content into a reference material, for example:

$$REE_{normalized} = \frac{[REE]_{sample}}{[REE]_{reference\ material}} \quad (1)$$

The reference material used in the present study was Post Archaen Australian Shale (PAAS) (MCLENNAN, 2001). PAAS has been used in other works with the same objective (OTERO et al., 2005; SANDERS et al., 2013). Data were collected in the literature on the mean REE levels in carbonatites (POLETTI et al., 2016; TROFANENKO et al., 2016; CERVA-ALVES et al., 2017) and phosphorites (HEIN et al., 2016; KHATER et al., 2016; XIN et al., 2016; GARNIT; BOUHLEL; JARVIS, 2017), which were also normalized by PAAS. The source of P in the fertilizers was traced by the similarity between the REE signatures in the samples with those of the possible sources (carbonatite or phosphorite).

5.2.3 Solubility of rare earth elements in fertilizers

Samples of 1.000 g of each fertilizer were agitated with 100 mL of 2 % citric acid solution, a standard extractor for analysis of phosphate fertilizers in Brazil (MAPA, 2013) and then filtered. The solubility of the elements was expressed as a percentage relative to the total contents, as follows:

$$\%Sol_{ij} = \left(\frac{CSol_{ij}}{C_{ij}} \right) \times 100 \quad (2)$$

Where % Sol_{ij} is the soluble percentage of REE (i) in the phosphate fertilizer (j), while CSol_{ij} and C_{ij} are the soluble and total concentrations (mg kg⁻¹), respectively.

5.2.4 Measuring REES and P₂O₅ total contents

The contents of the REEs Ce, La, Nd, Pr, Sm, Sc, Eu, Y, Dy, Gd, Yb, Er, Tb, Ho and Lu in the extracts were determined by coupled plasma optical emission spectrometry (ICP - OES/Optima 7000 Perkin Elmer). The total P contents in the fertilizers were determined by photocolometry. Standard procedures for quality control such as recalibration curve, blank sample analysis and reference material SRM 2709 (San Joaquin Soil, NIST - National Institute of Standards and Technology) were used. The recoveries of Ce, La, Nd, Sm, Sc, Dy and Gd ranged from 70 to 98%. All analyzes were performed in duplicate.

5.2.5 Inputs of REEs into soils through fertilizers and soil correctives

Equation 2 was used to estimate the total annual addition (ton ha⁻¹) of REEs in soils through the application of limestone, gypsum and P-containing fertilizers. Other sources of addition and the possible losses of these elements in the soil were not considered in the calculation, since they did not contribute in a significant way to the mass balance of these elements in the soils.

$$TA_i = \sum_j (Q_j \times C_{ij}) \times 10^{-6} \quad (3)$$

Where TA_i is the total amount of REE (i) added annually (ton ha⁻¹) from soil correctives and phosphate fertilizers (j), Q_j is the amount of the input (ton) currently consumed in Brazil and C_{ij} is the REE (i) in the soil correctives and phosphate fertilizers (j).

The addition per unit area (g ha⁻¹ year⁻¹) was estimated according to equation 3:

$$TA_{ij(a)} = \left[\left(\frac{\bar{D}}{FP_j} \right) \times C_{ij} \right] \times 10^{-3} \quad (4)$$

Where $TA_{ij(a)}$ is the amount of REE (i) added annually per unit area through fertilizers containing P (g ha⁻¹), except phosphate rock, \bar{D} is the recommended average dose for the main crops grown in Brazil (140 kg ha⁻¹ P₂O₅) (CFSEMG, 1999; IPA, 2008) and FP_j is the fraction of P₂O₅ in fertilizers containing P (0.18, 0.26, 0.40 and 0.50 for SSP, OM + RF, TSP and MAP, respectively) (dimensionless). For the estimates of REE additions per unit area (g ha⁻¹ year⁻¹) for limestone, gypsum and phosphate rock, equation 4 was used:

$$TA_{ij(b)} = A_{ap} \times C_{ij} \quad (5)$$

Where A_{ap} is the simulated amount of phosphate rock, agricultural gypsum and limestone applied to Brazilian soils (1.0, 3.0 and 4.0 ton ha⁻¹, respectively).

5.2.6 Statistical analyses

Mean, minimum, maximum and standard deviation values were calculated from the data set. Pearson's linear correlation analysis ($p < 0.05$) was performed between the P_2O_5 levels and the sum of the REES in the fertilizers. Hierarchical grouping analysis (HGA) was performed with the purpose of defining the similarity between the REEs distribution patterns in fertilizers, carbonatites and phosphorites. Ward's algorithm and the measure of Euclidean distance were used. The normalized values of REE in fertilizers plus phosphorites and carbonatites were the variables used to define the groups. The entire statistical procedure was performed using STATISTICA software (v.10.0).

5.3 Results and Discussion

5.3.1 Signatures and concentrations of REEs

Gypsum samples presented the lowest REEs concentrations, while the maximum values were verified in OM + RP and SSP samples (Table 1). The variability total of REEs in the samples followed the order $Ce > La \approx Pr > Nd > Sm > Dy > Ho \approx Eu \approx Sc \approx Y > Yb > Gd > Er \approx Lu \approx Tb$.

Table 1. Range rare earth elements concentrations in correctives and P-containing fertilizers marketed in Brazil

REEs	Lime stone	Gypsum	RP	OM+RP	SSP	STP	MAP
	(mg kg ⁻¹)						
Ce	1.3 – 9.7	0.2 – 3.3	3.5 – 85.1	1.1 – 950.8	6.3 – 1098.5	4.7 – 11.0	4.7 – 381.0
La	1.2 – 5.9	0.4 – 2.1	5.1 – 60.1	4.9 – 449.8	8.1 – 604.6	6.2 – 10.4	3.8 – 151.1
Nd	<LQ – 6.7	<LQ – 0.5	28.3 – 45.4	0.3 – 426.0	3.4 – 442.9	2.2 – 3.5	0.2 – 164.9
Pr	1.1 – 2.1	0.3 – 0.8	1.7 – 14.4	0.7 – 119.4	1.2 – 135.3	1.3 – 2.6	0.3 – 46.5
Sm	1.8 – 3.1	0.5 – 1.2	3.5 – 9.0	1.2 – 65.4	0.7 – 61.0	0.9 – 25.3	0.9 – 25.3
Sc	0.1 – 1.3	0.1 – 0.6	0.4 – 5.5	1.2 – 20.4	1.5 – 18.8	2.0 – 2.8	0.7 – 18.4
Eu	<LQ – 0.2	<LQ	1.6 – 2.2	0.3 – 23.7	0.2 – 14.6	0.1 – 0.3	0.4 – 9.7
Y	0.6 – 3.1	0.2 – 1.0	2.4 – 81.5	9.0 – 210.5	3.5 – 123.7	4.2 – 35.6	3.1 – 120.9
Dy	0.1 – 1.8	0.1 – 0.4	3.9 – 10.4	0.6 – 58.8	1.0 – 31.0	1.1 – 1.9	1.5 – 19.7
Gd	3.0 – 16.3	0.2 – 0.9	4.8 – 11.5	0.8 – 53.1	1.2 – 45.2	3.6 – 20.3	4.4 – 26.1
Er	<LQ – 0.4	<LQ	1.2 – 5.0	0.3 – 17.1	0.3 – 7.7	0.1 – 1.5	2.4 – 7.9
Yb	0.1 – 0.3	<LQ – 0.1	0.2 – 5.1	0.5 – 9.7	0.4 – 5.7	0.4 – 2.2	0.3 – 10.3
Ho	0.2 – 0.3	0.1 – 0.2	0.3 – 2.0	0.2 – 8.4	0.1 – 4.7	0.3 – 0.5	0.3 – 3.3
Tb	0.9 – 2.0	0.5 – 0.8	0.7 – 2.0	0.3 – 8.6	0.1 – 6.6	1.3 – 1.6	0.5 – 3.5
Lu	<LQ	<LQ	0.1 – 0.8	0.1 – 1.5	0.1 – 0.9	0.1 – 0.4	0.1 – 2.0

RP rock phosphate, OM+RP organo-mineral + rock phosphate, SSP single superphosphate, STP triple superphosphate, MAP monoammonium phosphate. LQ limit of quantification (0.013, 0.006, 0.007, 0.009 and 0.005 for Er, Eu, Nd, Yb and Lu, respectively).

The OM + RP, SSP and MAP fertilizers had coefficient of variation (CV) $\geq 118\%$ for Ce, La, Nd, Pr, Sm, Y, Dy and Gd. This can be justified by the different sources of P used as raw material in the manufacture of fertilizers. For this reason, the P sources of these fertilizers were plotted (Figure 1).

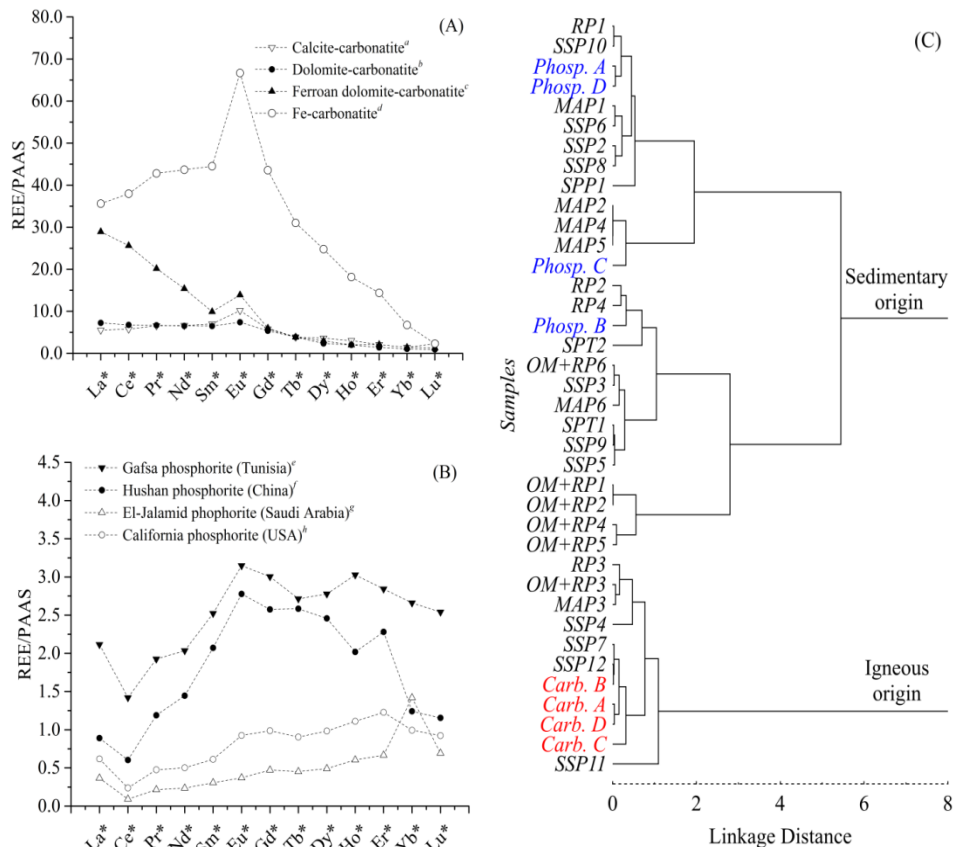


Figure 1. Distribution pattern of rare earth elements in samples phosphate rock of igneous (A) and sedimentary (B) origin. (C) Classification of phosphate fertilizers as origin. RP phosphate rock, OM+RP organo-mineral + phosphate rock, SSP single superphosphate, ST triple superphosphate, MAP monoammonium phosphate, Phosp. A-D phosphorite samples, Carb. A-D carbonatite samples, REE rare earth elements, PAAS Post Archaean Australian Shale (McLennan 2001), *normalized values with PAAS (for example: Cesample/CePAAS). a Cervantes et al. 2017; b Poletti et al. 2016; c Trofanenko et al. 2016; d Ramos et al. 2016; e Garnit et al. 2017; f Xin et al. 2016; g Khater et al. 2016; h Hein et al. 2016.

The normalized REEs values of carbonatites and phosphorites were graphically plotted to visualize their respective distribution patterns (Figure 1A - B). REEs signatures were distinct and well defined for each source of phosphorus. Fertilizers produced from carbonatites are more enriched in REEs than those from phosphorites (OTERO et al., 2005; RAMOS et al., 2016). However, carbonatites of the calcitic and dolomitic type presented lower levels, mainly for La, Ce, Pr and Nd, which can be reflected in the fertilizers produced from these sources.

Based on the results of the hierarchical cluster analysis, 77% ($n = 23$) of the fertilizers were grouped as sedimentary origin (phosphorite derivatives) (Figure 1C). Around 90% of the Brazilian phosphate reserve is igneous and a few sedimentary reserves are active in the country (ABRAM et al., 2011); on the other hand, Brazil imports about 50% of the phosphate fertilizers used in the country. The imported amount of phosphate rock and MAP in 2014 was 1.7 million tonnes (IFA, 2016). The phosphate reserves of the country that exported these fertilizers (Morocco) are predominantly sedimentary (KRATZ; SCHICK; SCHNUG, 2016; CÁNOVAS et al., 2017).

In general, the fertilizers derived from carbonatite had Σ REEs higher than fertilizers derived from phosphorite. The Σ REEs in OM + RP and SSP of igneous origin were 5 to 8 times larger, respectively, as compared to the ones of sedimentary origin (Figure 2A - B). A similar result was obtained by Ramos et al. (2016), which evaluated REEs in phosphate concentrates and fertilizers derived from carbonatites and phosphorites. Other studies have shown that apatite carbonatite minerals are more enriched in REEs than phosphate apatites (FLEISCHER; ALTSCHULER, 1986; LAPIDO-LOUREIRO; FIGUEIREIDO; TOREZAN, 1989; HUGHES; CAMERON; MARIANO, 1991).

The OM + RP and SSP sources presented the highest Σ REEs, while the sources concentrated in P_2O_5 posed the lowest ones. Significant and negative correlation between Σ REE and P_2O_5 levels was observed for fertilizers, either sedimentary or igneous origin (Figure 2 C - D). Turra, Fernandes and Bacchi (2011) evaluating REEs concentrations in agricultural inputs found the lowest Σ REEs (12.0 mg kg^{-1}) for MAP among phosphate sources. Ramos et al. (2016) found that Σ REEs in TSP and MAP samples was 57% and 233% lower than the phosphate concentrate that gave rise to them, respectively. The industrial processes of purification of these sources are the probable causes of reduction in REEs (TURRA; FERNANDES; BACCHI, 2011; RAMOS et al., 2016).

Regardless of origin, fertilizers had a higher accumulation of light REEs (Light Σ REE - Ce, La, Nd, Pr, Sm, Sc and Eu) in relation to the heavy ones (Σ REE - Y, Dy, Gd, Er, Yb, Ho, Tb and Lu), except for MAP and TSP. The mean accumulation of light REEs was 154 and 660% higher than the heavy REEs in phosphorus and carbonatite derived fertilizers, respectively. Light REEs are more abundant in the crust than the heavy REEs (VONCKEN, 2016) and the depletion of the light REEs in MAP and TSP may be related to the greater solubility of these elements in H_3PO_4 and their possible loss in the washing process during fertilizers production.

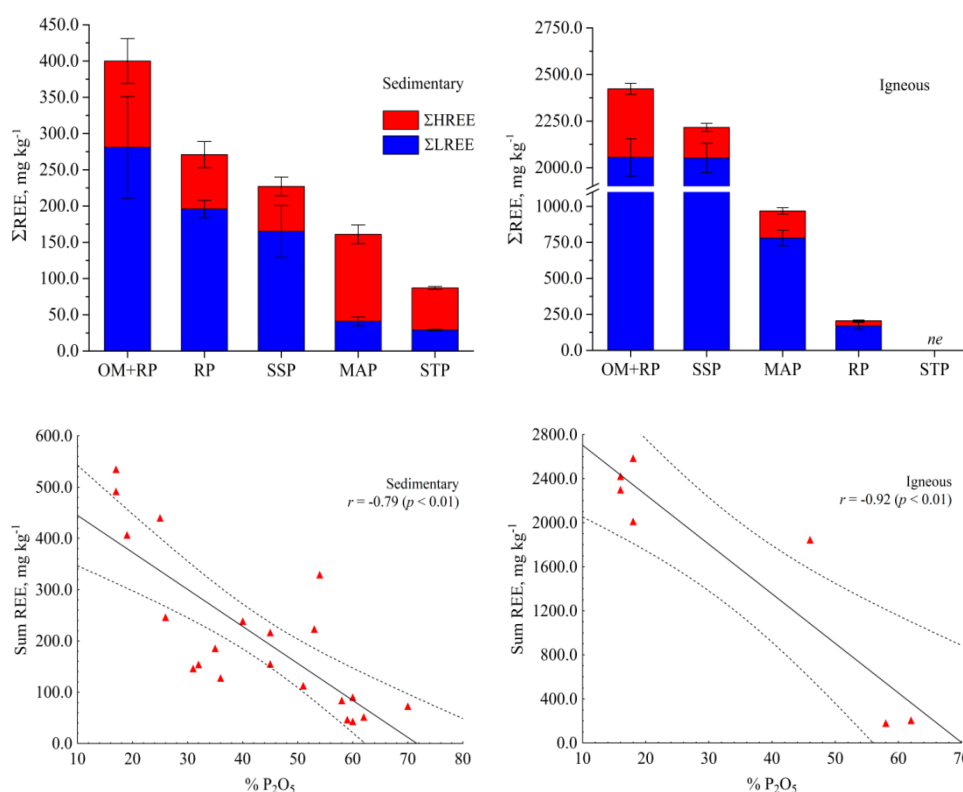


Figure 2. Sum (\pm standard error) of light rare earth elements (Σ LREE), heavy rare earth elements (Σ HREE) and total (Σ REE); linear correlation between P_2O_5 and rare earth elements in containing-P fertilizers marketed in Brazil. r correlation coefficient, *ne* not evaluated, $p < 0.01$ significant effect at probability level of 99%. *OM+RP* organo-mineral + rock phosphate, *SSP* single superphosphate, *MAP* monoammonium phosphate, *STP* triple superphosphate, *RP* rock phosphate

The mean Σ REEs in limestone and gypsum were $27.1 (\pm 6.6)$ and $4.6 (\pm 2.6)$ $mg\ kg^{-1}$, respectively, i.e. they were much lower than fertilizers. The Σ REE-light / Σ REE-heavy ratio was 1.12 (limestone) and 0.31 (gypsum). In carbonated rocks, the Σ REEs can vary from 21.4 - 52.0 $mg\ kg^{-1}$ (KABATA-PENDIAS, 2011).

The average REEs content in the fertilizers derived from carbonatite was higher than the phosphorite derivatives (Figure 3). The mean contents of the light REEs followed the order $Ce > La > Nd > Pr > Sm > Sc > Eu$. For the heavy REEs, the order was $Y > Gd > Dy > Er > Yb > Tb > Ho > Lu$.

The highest concentrations for Ce, La, Nd, Pr and Y were observed in the OM + RP, SSP and MAP sources derived from carbonatite. The TSP was the fertilizer with the lowest levels. Mean Ce concentrations in SSP, OM + RP and MAP originating from carbonatite differed by 1362%, 660% and 348% relatively to phosphorite, respectively. Among fertilizers derived from phosphorite, TSP and MAP were the ones that had the highest levels of Gd. Phosphate rocks derived phosphorite had mean values of heavy REEs higher than those of carbonatite.

	S1	S2	S3	S4	S5	S6	S7	S8	S9
Ce	7.9 ±3.2	35.2 ±10.5	57.8 ±27.1	78.8 ±11.8	85.5 ±73.9	125.2 ±65.6	381.0 ±95.3	512.2 ±267.4	950.8 ±237.5
La	8.3 ±2.1	27.4 ±6.0	34.4 ±16.0	41.8 ±9.2	38.9 ±28.1	60.1 ±28.7	151.1 ±36.3	264.5 ±139.1	449.8 ±134.9
Nd	2.9 ±0.6	16.6 ±4.7	38.0 ±3.7	28.3 ±4.2	37.2 ±32.0	54.0 ±29.2	164.9 ±33.0	213.9 ±111.3	426.0 ±93.7
Pr	2.0 ±0.7	5.5 ±1.5	8.5 ±3.7	8.7 ±2.2	10.3 ±9.0	17.5 ±9.6	46.5 ±8.3	62.8 ±32.8	119.4 ±35.8
Sm	3.1 ±0.5	3.8 ±1.0	6.6 ±1.6	4.4 ±1.0	6.9 ±4.3	9.7 ±4.7	25.3 ±5.0	29.5 ±14.9	65.4 ±16.2
Sc	2.4 ±0.4	3.8 ±0.7	3.0 ±1.5	3.4 ±0.7	6.9 ±4.3	5.6 ±1.7	1.5 ±0.3	7.6 ±3.8	20.4 ±4.9
Eu	0.2 ±0.1	0.8 ±0.2	2.0 ±0.1	1.6 ±0.4	2.9 ±2.3	5.2 ±2.6	9.7 ±2.2	8.3 ±6.3	23.7 ±7.1
Y	19.9 ±15.7	41.3 ±9.7	41.0 ±22.8	17.3 ±4.3	78.9 ±22.1	56.9 ±23.3	120.9 ±36.3	56.9 ±24.9	210.5 ±54.7
Dy	1.5 ±0.4	4.0 ±0.9	9.1 ±0.8	3.9 ±1.2	8.1 ±3.0	16.7 ±5.8	19.7 ±3.6	13.3 ±6.6	58.8 ±17.4
Gd	12.0 ±8.4	4.6 ±1.2	7.7 ±2.0	5.0 ±1.3	10.3 ±4.0	9.3 ±4.6	26.1 ±5.2	19.9 ±10.0	53.1 ±12.7
Er	0.8 ±0.7	2.3 ±0.6	3.8 ±0.6	1.2 ±0.3	5.8 ±1.2	4.7 ±2.2	7.9 ±2.0	3.2 ±1.6	17.1 ±3.4
Yb	1.3 ±0.9	2.4 ±0.6	2.6 ±1.4	1.3 ±0.4	5.6 ±1.9	3.1 ±1.2	5.5 ±1.4	2.6 ±1.1	9.7 ±2.5
Ho	0.4 ±0.1	0.9 ±0.2	1.2 ±0.5	0.6 ±0.1	1.5 ±0.5	2.0 ±0.9	3.3 ±0.8	2.0 ±1.0	8.4 ±2.4
Tb	1.4 ±0.2	1.0 ±0.3	1.8 ±0.2	0.7 ±0.1	1.5 ±0.5	1.8 ±0.7	3.5 ±0.9	2.9 ±1.4	8.6 ±1.8
Lu	0.3 ±0.2	0.4 ±0.1	0.4 ±0.2	0.2 ±0.1	1.0 ±0.4	0.5 ±0.2	0.7 ±0.2	0.4 ±0.2	1.5 ±0.6

Figure 3. Heatmap showing means \pm standard deviation of rare earth elements (REE) contents (mg kg⁻¹) for samples fertilizers P-containing (n = 30) marketed in Brazil. S1 triple superphosphate (sedimentary), S2 single superphosphate (sedimentary), S3 phosphate rock (sedimentary), S4 phosphate rock (igneous), S5 monoammonium phosphate (sedimentary), S6 organo-mineral + phosphate rock (sedimentary), S7 monoammonium phosphate (igneous), S8 single superphosphate (igneous), S9 organo-mineral + phosphate rock (igneous). Within each line, darker colors indicate higher REE contents

The REEs contents of the present study were compared with those reported in the literature (Table 2). The average contents of Ce, La, Nd and Y in the fertilizers produced from the Catalão and Araxá ores in southeastern Brazil were the highest cited in the literature.

The mean REEs concentrations reported here (of igneous origin) were among the lowest. The REEs in the fertilizers produced from the Catalão ore were 2 to 7 times higher than the results obtained in the present study. When comparing with other studies in Brazil, our SSP samples presented similar Ce concentrations, while the La and Nd concentrations in

our study were lower than reported elsewhere. On the other hand, the mean REE concentrations in the MAP samples we measured were higher than other studies. Regarding fertilizers of sedimentary origin, the average REEs found in Brazilian fertilizers were the highest.

Table 2. Comparison of rare earth elements contents in different phosphate fertilizers report in literature

Fertilizer	Locality	Origin	Ce	La	Nd	Pr	Y
			----- (mg kg ⁻¹) -----				
SSP	Catalão/Brazil ¹	igneous	3934.0	1926.0	1529.0	447.0	122.0
SSP	Araxá/Brazil ¹	igneous	1866.0	895.0	899.0	235.0	322.0
MAP	Tapira/Brazil ¹	igneous	809.0	399.0	373.0	96.0	168.0
Mixed (12-12-17)	Spanish ²	igneous	600.0	500.0	181.0	na	na
Mixed (15-15-17)	Spanish ²	igneous	744.0	619.0	214.0	na	na
SSP	Brazil ⁷	igneous	512.2	264.5	213.9	62.8	56.9
MAP	Brazil ⁷	igneous	381.0	151.1	164.9	46.5	120.9
SSP	Egypt ³	sedimentary	59.8	na	na	na	na
SSP	Pakistan ³	sedimentary	40.2	18.4	na	na	na
Mixed (10-10-18)	Spanish ²	sedimentary	8.0	14.1	7.0	na	na
Mixed (7-14-16)	Spanish ²	sedimentary	16.0	32.4	16.0	na	na
SSP	Egypt ⁴	sedimentary	8.5	18.0	na	na	na
SSP	Brazil ⁷	sedimentary	35.2	27.4	16.6	5.5	41.3
MAP	Brazil ⁷	sedimentary	85.5	38.9	37.2	10.3	78.9
MAP	Brazil ⁵	na	1.0	7.3	2.4	na	na
SSP	Brazil ⁵	na	673.0	1499.0	770.0	na	na
Mixed	na ⁶	na	65.1	44.4	32.6	8.5	66.2

SSP single superphosphate, MAP monoammonium phosphate, Mixed (N – P – K) and na not available, ¹Ramos et al. (2016), ²Otero et al. (2005), ³Waheed et al. (2011), ⁴Abdel et al. (2001), ⁵Turra et al. (2011), ⁶Hu et al. (1998), ⁷Present study

Mean (mg kg⁻¹) in the limestone samples followed the order Gd (8.1 ± 3.1) > Ce (5.1 ± 2.2) > La (3.7 ± 1.2) > Sm (2.5 ± 0.4) > Y (2.0 ± 0.6) > Nd (1.6 ± 0.8) ≈ Pr (1.6 ± 0.3) > Tb (1.4 ± 0.3) > Dy (0.8 ± 0.5) > Sc (0.6 ± 0.3) > Ho (0.2 ± 0.1) ≈ Yb (0.2 ± 0.1). Limestone samples analyzed by Turra, Fernandes and Bacchi (2011) presented mean concentrations of 15.0, 7.5, 7.3 and 1.4 mg kg⁻¹ of Ce, Nd, La and Sc, respectively, i.e., higher than recorded in our study. Mean concentrations for gypsum were the lowest among all evaluated sources and presented the following order: Ce (1.6 ± 1.2) > La (1.2 ± 0.7) > Sm (0.9 ± 0.2) > Tb (0.7 ± 0.1) > Y (0.6 ± 0.3) > Pr (0.5 ± 0.2) ≈ Gd (0.5 ± 0.2) > Nd (0.4 ± 0.2) > Sc (0.3 ± 0.2) > Dy (0.2 ± 0.1) > Ho (0.1 ± 0.02) ≈ Yb (0.1 ± 0.02). Erbium, Lu and Eu had no detectable levels neither in limestone nor gypsum samples.

5.3.2 REES solubility in P-containing fertilizers

The data of our study are the first records on the solubility of REE in phosphate fertilizers in Brazil. In general, fertilizers derived from phosphorites presented the greatest solubilities for REEs in relation to fertilizers derived from carbonatite, the mean solubilities were 25% and 242% higher for heavy REEs and light REEs, respectively. The phosphorite-derived MAP was the fertilizer that had the highest percentages of soluble REEs. However, the solubilities of Y, Er and Ho were higher in the carbonatite-derived MAP fertilizer. The lowest solubilities were observed in the RP and STP sources (Figure 4).

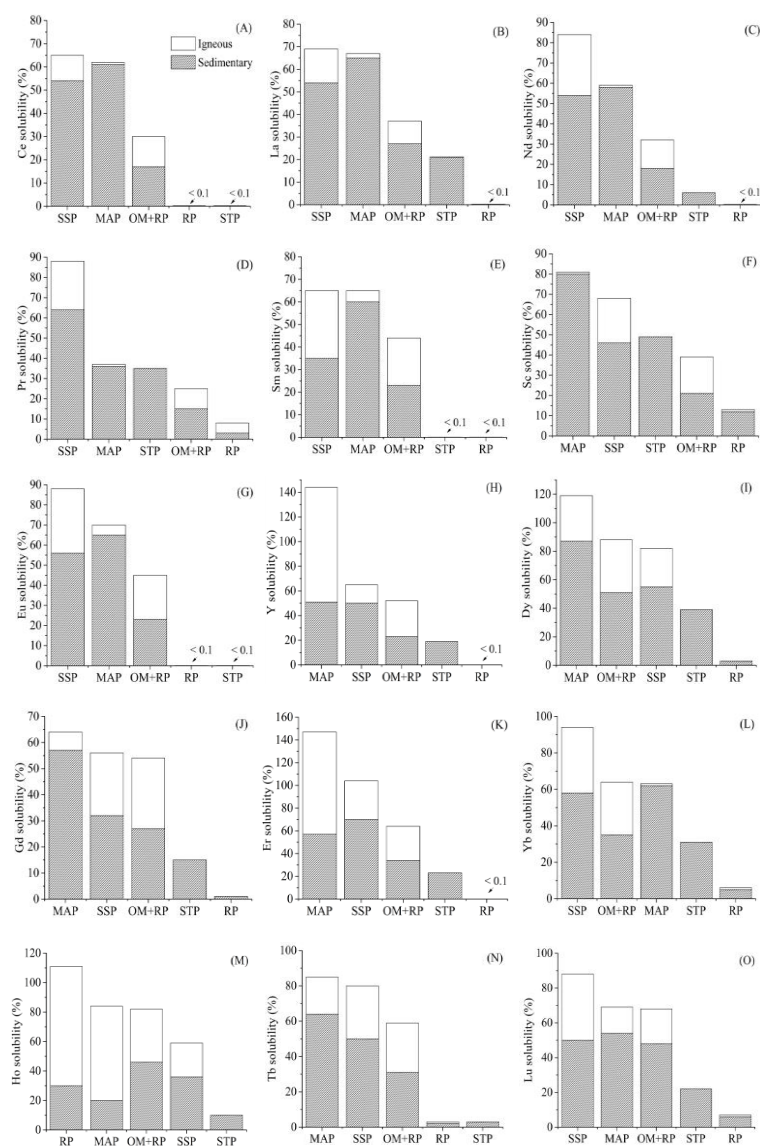


Figure 4. Average solubility rare earth elements in fertilizers containing-P of igneous and sedimentary origin, marketed in Brazil. *SSP* single superphosphate, *STP* triple superphosphate, *RP* rock phosphate, *OM+RP* organo-mineral + rock phosphate, *MAP* monoammonium phosphate

The organo-mineral fertilizers + RP derived from carbonatite, which had the highest levels of REEs, had average solubility for light REEs of 15% and 30% for heavy REEs. SSP fertilizers derived from phosphorite, the most consumed in Brazil, had average solubilities of 52% and 50% for light REEs and heavy REEs, respectively.

Ramos et al. (2016) evaluating the mineralogical assemblage of different phosphate concentrates and fertilizers by X-ray diffraction using synchrotron radiation, obtained the following results: (i) apatite, carbonate-fluorapatite and carbonate-hydroxyapatite were the main mineral phases containing REEs; (ii) samples derived from carbonatite had higher diversity of minerals containing REEs than sedimentary phosphorites; (iii) phosphate fertilizers had greater diversity of minerals containing REEs than the raw materials that originated them. Thus, it is reasonable to assume that (i) the solubility of REEs is directly related to the solubility of phosphates; (ii) that in the process of manufacturing phosphate fertilizers, the step of wet digestion with sulfuric acid on the phosphate concentrate can promote the dissolution of mineral phases and the neogenesis of others.

Thus, the low solubility of REEs in the carbonatite-derived samples may be explained by the following reasons: (i) the carbonatite phosphate has higher Fe values than the sedimentary phosphate (KRATZ; SCHICK; SCHNUG, 2016); (ii) REEs in fertilizers of igneous origin can co-precipitate as Fe/Al phosphate minerals in the industrial stage of wet digestion (ex.: wavellite $[\text{Al}_3(\text{OH}, \text{F})_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}]$; childrenite $[(\text{Fe}, \text{Mn})\text{AlPO}_4(\text{OH})_2 \cdot \text{H}_2\text{O}]$; lazurite $[(\text{Mg}, \text{Fe})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2]$); and (iii) iron and aluminum phosphates have low recoveries (4 - 17%) for the 2% citric acid extraction relatively to the total concentration (ALCARDE; PONCHIO, 1979).

5.3.3 Potential environmental risk and REE additions to Brazilian soils

The REEs concentrations in the phosphate fertilizers were expressed as a function of the percentage of P_2O_5 in the samples (Figure 5A - B) in similarity with what is done by the Brazilian legislation for the investigation of heavy metals of environmental importance (Cd, Pb and Cr) (MAPA, 2006).

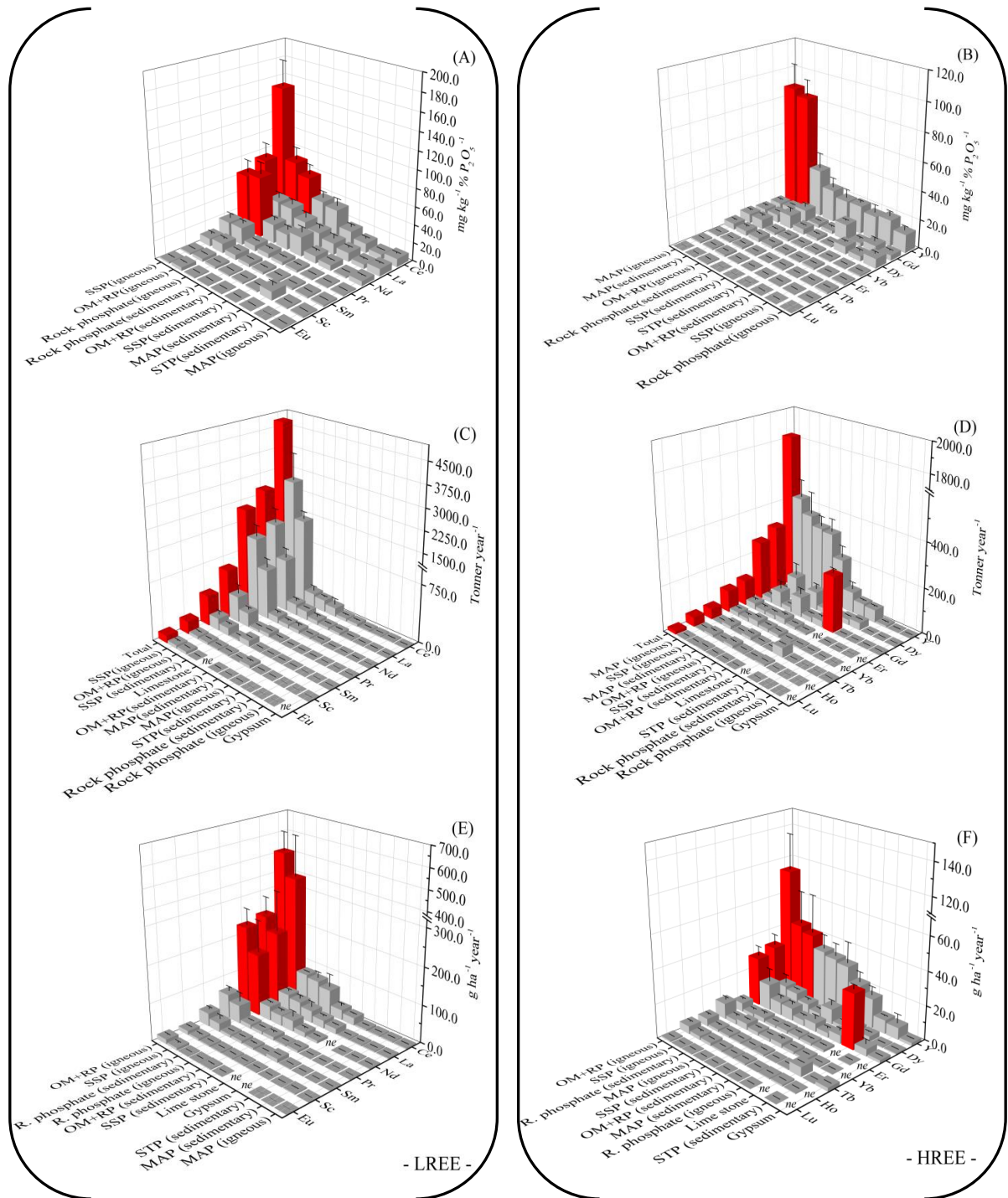


Figure 5. Rare earth elements concentration (\pm standard error) per % P_2O_5 in phosphate fertilizers marketed in Brazil (A-B). Mean values (\pm standard error) of total (C-D) and per unit area additions (E-F) of rare earth elements in agricultural soils via phosphate fertilizers, lime stone and gypsum marketed in Brazil. *LREE* light rare earth elements, *HREE* high rare earth elements, *OM+RP* organo-mineral + rock phosphate, *SSP* single superphosphate, *MAP* monoammonium phosphate, *STP* triple superphosphate, *R. phosphate* rock phosphate. The columns of red color are the most relevant results for the context of soil environmental pollution

There are no regulatory values for REEs in agricultural inputs in Brazil. Therefore, we assumed the maximum permissible value of $40 \text{ mg kg}^{-1}/\% \text{ P}_2\text{O}_5$ (the same for Cr in the legislation) to investigate the potential environmental risk of phosphate fertilizers in contributing REEs to soils. This decision was based on the following aspects: (i) Cr as well as REEs is classified geochemically as a lithophilic elements; (ii) in the environment, Cr and REEs commonly have valence +3 (KABATA-PENDIAS, 2011), and; (iii) since information on the deleterious effects of environmental exposure on REE in agricultural soils is scarce, adopting a less conservative value is an environmentally and economically viable decision.

Mean values higher than $40 \text{ mg kg}^{-1}/\% \text{ P}_2\text{O}_5$ were verified for Ce, La, Nd and Y in fertilizers SSP, OM + RP, RP (all derived from carbonatite) and MAP (from both sources). Among the values of $20\text{-}40 \text{ mg kg}^{-1}/\% \text{ P}_2\text{O}_5$, OM + RP_{phosphorite} (Ce, La and Pr), RP_{phosphorite} (Ce, La, Pr and Y), OM + RP_{carbonatite} (La, Nd and Y) and RP_{carbonatite} (La, Nd and Y). However, 84% of the cases had levels $< 20 \text{ mg kg}^{-1}/\% \text{ P}_2\text{O}_5$. The concentrations of Ce, La, Nd and Y in the SSP, regardless of origin, were higher than those of Cd, Cr and Pb registered in phosphate fertilizers marketed in Brazil (CAMPOS et al., 2005; SILVA; NASCIMENTO; ARAÚJO, 2017).

Mean additions (g ha^{-1}) of La, Nd and Ce by OM + RP and SPP (both carbonatite derivatives) were $\geq 329\%$, 336% and 405% higher, respectively, than the other sources. For light REEs, 65% of the cases had estimated additions $\leq 10 \text{ g ha}^{-1}$ (Figure 5 E).

In general, OM + RP_{carbonatite} had the highest additions (g ha^{-1}) for heavy REEs. The additions of Y and Dy were ≥ 157 and 220% higher, respectively, than the other sources. Yttrium added by the SSP_{carbonatite} and RP_{phosphorite} were higher than 40 g ha^{-1} . The limestone added a significant amount of Gd compared to the other sources (Figure 5F).

According to the estimates, the elements Ce, La, Nd and Y had the highest annual contributions to soils ($> 1800 \text{ t year}^{-1}$) (Figure 5 C-D). The OM + RP and SSP sources (both carbonatite-derived) plus MAP (from both origins) accounted for more than 200 t y^{-1} of yttrium. The limestone annually added 96% of the total estimated Gd. SSP and MAP, both derived from carbonatite, were the most enriched fertilizers in REEs (Figure 3). They contributed annually 6438 and 3678 t year^{-1} REEs, respectively.

5.4 Conclusions

Phosphate fertilizers are more enriched in REEs than soil correctives. The levels of REEs in phosphate fertilizers vary depending on the raw material used in the industry and

industrial processes related to the manufacture of concentrated fertilizers. The geochemical signature of REEs associated with the multivariate analysis are useful tools to trace the origin of the raw material used in the phosphate fertilizer industry.

Light REEs were more abundant than heavy REES in both the phosphate fertilizers and corrective samples. Fertilizers derived from carbonatites (igneous origin) have the largest accumulation of REEs, especially SSP which is the most consumed fertilizer in Brazil. However, the solubility of REEs in fertilizers was higher in those derived from phosphorite (sedimentary origin). The low solubility (< 20%) of REEs in phosphate fertilizers of igneous origin may be associated with the co-precipitation process with Fe/Al phosphates that are newly formed in the industrial stages of wet digestion with sulfuric acid.

The addition of REEs by the continuous application of high doses of P fertilizers and soil correctives to Brazilian soils may represent a potential risk to agricultural and environmental sustainability, since 13,000 tons of REEs are incorporated annually to soils. The SSP derived from carbonatite annually contribute with over 6000 t year⁻¹ of REEs, with the highest additions being recorded for Ce, La, Nd and Y (512, 242, 229, 113 g ha⁻¹, respectively). The limestone contributed 250 metric tons of Gd, more than any other source, since Brazilian agriculture consumes more than 33 million tons of this input annually. Thus, studies on bioavailability, ecotoxicity and the definition of quality reference values for REEs in soils, especially for Ce, La, Nd and Y, are important for environmental safety.

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6. FINAL CONSIDERATIONS

Soils contaminated with heavy metals and rare earth elements pose a potential risk to human health and ecosystem functionality, therefore, monitoring studies of these elements in soils and also identifying possible sources of contamination are necessary for the safety of public and environmental health. In the agricultural scenario, metals and rare earths contained in the soil can be transferred to the food chain and represent risk, and phosphate and corrective fertilizers are two important sources of soil contamination by these elements.

In this context, the study evaluated the concentrations of heavy metals in phosphate fertilizers used in Brazilian agriculture, and although the concentration of the metals in the fertilizers were not above the allowable limits, it was observed that the phosphate fertilization for a long time in cultivated soils was cause of the enrichment with metals, mainly Cd. All evaluated soils have been contaminated by Cd and this metal is mobile in the soil. The transfer of Cd to the biosphere and/or surface and subsurface waters is an important issue to be discussed. Future studies evaluating the content of this element in water resources inserted in the context of sugarcane monoculture are recommended because drinking water as well as fish and other animals may become significant routes of exposure for the rural population.

With regard to soil polluted with Cd, which had concentrations $> 3.0 \text{ mg kg}^{-1}$, more detailed descriptions are necessary to judge the real risk. Studies on the compartmentalization of this metal in the soil, the human bioaccessible fraction and a characterization of the routes of exposure are necessary for the elaboration of action plans.

In relation to the rare earth elements that are another group of contaminants of great environmental interest, but that are less studied. Brazilian phosphate fertilizers and correctives have been shown to be significant sources for soils, mainly for Ce, La, Nd, Gd and Y. There is no regulation for rare earths in soil and not in agricultural inputs. Little is known about the potential deleterious effects of these elements for the functionality of an agroecosystem. Ecotoxicological studies and risk assessment of human health by exposure to rare earths are necessary for the derivation of maximum permissible concentrations. The bioavailability of these elements in the soil after phosphate fertilization is another important issue to be addressed, since it would elucidate the ability of these contaminants to be transferred to other spheres of the environment.