Research Perspectives on the Use of Phosphogypsum in the Brazilian Cerrado

G. Marchi[1,*], C.R. Spehar[2], J.C. Sousa-Silva[1], L.R.G. Guilherme[3] and E.S. Martins[1]

[1]Embrapa Cerrados, Rodovia BR-020, Km 18, Caixa Postal 08223, CEP: 73310-970 - Planaltina–DF, Brazil

[2]Universidade de Brasília, Campus Universitário Darcy Ribeiro, Asa Norte, CEP 70910-970, Brasília, DF, Brazil

[3]Universidade Federal de Lavras, CP 3037, CEP 37200-000, Lavras, MG, Brazil

Abstract: The theoretical aspects, benefits, research contributions, technical recommendations, side effects, limitations, environmental concerns as well as the legislation on the application of phosphogypsum to Brazilian savanna (Cerrado) soils are discussed in this review. It is shown why it is important to apply phosphogypsum to Cerrado soils, and its effect on plant resilience to drought periods. The application of this product may become a main practice in Cerrado soils − a region in which crops as well as pastures are grown − as temperatures rise, and dry periods turn extended, due to climate change. Sulfate, as a component of phosphogypsum, does not leach to groundwater such as in temperate climate soils, turning the use of phosphogypsum environmentally friendly. The phosphogypsum produced in Brazil is a clean by-product of phosphate industry, whose rock source plays an important role providing low trace element and radionuclide contents. It is noteworthy that the Brazilian experience based on phosphogypsum application may work in many tropical soils around the globe, and many populations may be benefited from this technical knowledge.

Keywords: Phosphogypsum, Brazilian savanna, Cerrado, plant drought resilience.

I. INTRODUCTION

Once regarded as a wasteland where crop production was unthinkable, the Brazilian savanna (Cerrado) − a region extending to 204,667,716 ha [1] − is now one of the most productive areas around the world (Figure **1**). Until the 1960s these vast flat areas of acidic soils, devoid of nutrients and with low productivity were used for beef cattle ranching with low production efficiency.

Even so, for the last 50 years, thanks to adequate soil management and crop adaptation, this picture has changed dramatically. Lime, a simple and effective soil amendment in tropical regions, helped to overcome soil acidity constrains, providing calcium and magnesium. Later on, the benefits of phosphogypsum, a by-product of the phosphate fertilizer industry, to these soils were demonstrated [2]. Phosphogypsum mobilized calcium deep in the soil favoring plant root growth, and allowing them to withstand dry spells during the rainy season. At present, the Cerrado accounts for 60% of the Brazilian grain production, and is regarded as one of the last global frontiers for agricultural expansion [3].

Factors underpinning crop productivity relate to longstanding investments in agricultural research, which have enabled Brazil to achieve advanced technology for tropical agriculture [4]. At the same time, while Brazilian researchers and farmers struggle to boost productivity, Cerrado deforestation needs to be reduced − a practice which can be achieved via land use intensification, the most effective way to reduce pressure on virgin areas [5]. Yet, the environmental impact of agricultural expansion and land use in the Cerrado has called public attention, both nationally and internationally [4]. The agricultural development in the Cerrado has reduced the savanna area to 54.6% of its original vegetation [6].

Satellite observations have suggested that the effect of conversion of native Cerrado vegetation into cropping areas induced local warming [8]. Therefore, remaining savanna lands must be preserved, especially in a climate change scenario [9]. Phosphogypsum has played a role in this scenario, increasing crop productivity and carbon sequestration in lower layers of soil, besides mitigating drought stress that might be intensified by future changes in climate.

Nowadays, phosphogypsum is a cost-effective agromineral, depending on the distance of the source and the farming areas where it shall be applied. Brazilian annual production amounts to 4.5 million tons in São Paulo and Minas Gerais State. The current phosphogypsum stock is of approximately 150 10^6 Mg [10]. Out of this total, 1.7 10^6 Mg yr^{-1} have been used as soil amendment, 0.7 10^6 Mg yr^{-1} in cement industry, and the remaining 2.1 10^6 Mg yr^{-1}, stored in open-air piles [11]. Phosphogypsum has been discarded as a

*Address correspondence to this author at the Embrapa Cerrados, Rodovia BR-020, Km 18, Caixa Postal 08223, CEP: 73310-970 - Planaltina–DF, Brazil; Tel: +55 61 33889870; Fax: +55 61 33889879;
E-mail: giuliano.marchi@embrapa.br

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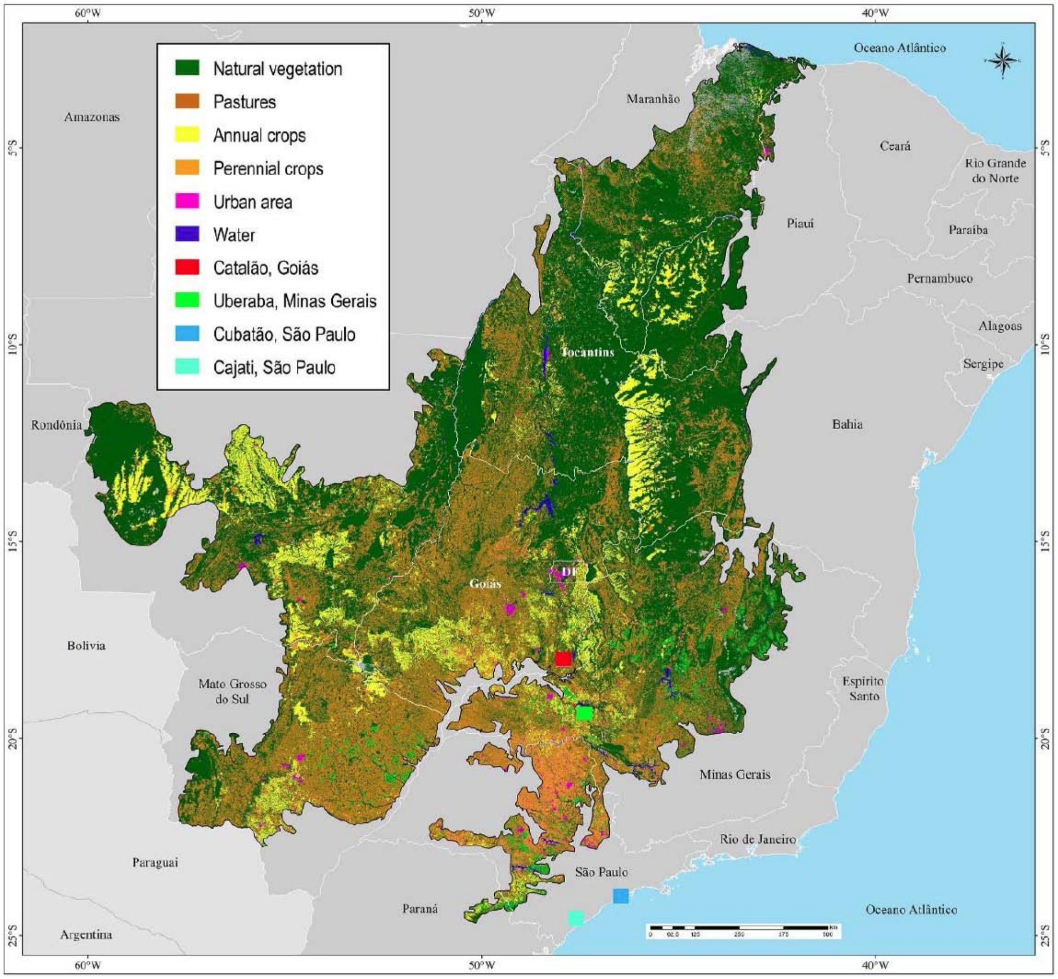

Figure 1: Cerrado area, soil use, and main phosphogypsum production sites in Brazil [7].

waste, buried in phosphate mines or disposed into the sea [12] in many areas worldwide. However, for tropical soils, one of the best options to use this material is certainly its application in soils, improving Ca availability to plants and increasing crop resilience and productivity.

This review addresses the main research contributions on phosphogypsum use in agroecosystems of the Cerrado region in Brazil. The latest recommendations of use and insights for crop resilience against drought periods are provided, as well as the environmental concerns about its use and the Brazilian legislation regarding possible pollutants that may be carried to soils.

II. PHOSPHOGYPSUM: HOW AND WHY IT WORKS IN CERRADO SOILS

Cerrado soils are mostly deep, highly weathered soils, i.e. Oxisols. They cover more than half of the Cerrado area, where crop production is concentrated [13]. Oxisols have low native fertility, resulting from its very low nutrient reserves, high phosphorus adsorption, and low cation exchange capacity (CEC). Most nutrients in Oxisol ecosystems are contained in the standing vegetation and decomposing plant material. Their low fertility, when circumvented by liming, fertilization and phosphogypsum, renders highly productive and stable cropping.

Oxisols from the Cerrado region are mostly absent of weatherable minerals and are rich in crystalline hydroxides and oxides of Fe (goethite, hematite) and Al (gibbsite), and 1:1 layer silicates (kaolinite). The presence of reactive surface hydroxyl groups in these soils confers them “variable charge”, resulting from protonation and deprotonation of OH groups. The pH is the master key for charge changes in these soils. The presence of organic matter, amendments, and addition of phosphate increase negative charges and consequently soil CEC [14]. At deeper layers below the surface, pH in some of these soils is rather low, presenting positive net charge. Due to the presence of positive charges in particle surfaces, these soils work like a “filter” for anions, attracting and preventing them from leaching [15].

Like Oxisols in tropical region, Mollisols are very resilient cropping soils in temperate region [16]. Mollisols are among some of the most important and productive agricultural soils in the world, and they are extensively used. Mollisols, contrasting with Oxisols, have not undergone intensive weathering and their mineralogy is, therefore, often dominated by minerals inherited from parent material. Clay mineralogy of Mollisols is dominated by 2:1 (illite, vermiculite, and smectite), and 2:2 (chlorite) layer-silicates. This type of clay is spread over its whole profile, and unlike 1:1 layer silicates, it presents permanent negative charges. Management of fertilizers in Mollisols is responsible for the impact of nitrogen and phosphate in the ecosystem [17, 18], as the soil is not able to prevent them from leaching. Use of phosphogypsum in these soils could generate pollution by SO_4^{2-} leaching.

Regarding variable-charge soils, adsorption of SO_4^{2-} is related to the increase of positive surface charges as pH decreases [19]. Sulfate is both specifically – adsorption by ligand exchange; ionic exchange of SO_4^{2-} for surface OH^- ions [20] – and non-specifically – attracted to positive charges – adsorbed to variable-charged soils (Figure **2**). This feature is important not only for Cerrado soils, but also for many soils on the African savanna, as there is a large portion of Oxisols being cultivated in that continent. Thus, phosphogypsum experimentation in the Cerrado, and knowledge generated thereafter, should be recognized as a strategic technology that could as well be applied to improve productivity in that continent.

Adsorption of sulfate is pH-dependent and is also favored under low pH conditions (Figure **3**). Sulfate adsorption itself may also affect soil pH slightly. This happens due to release of hydroxyl (ligand exchange reactions) during the adsorption reaction. Yet, at the same time Al^{3+} may be displaced from exchange sites by Ca^{2+} and further Al^{3+} hydrolysis might release H^+ back to solution [20]. The release of OH^- contributes to Al precipitation as $Al(OH)_3$, but not all ligand exchange reaction is related to OH^-, as sulfate can be exchanged by other anions, such as NO_3^-. Anion adsorption in soils decrease according to the following order: phosphate >> sulfate > chloride = nitrate [21], thus excess of sulfate may also displace nitrate, decreasing its adsorption and increasing the problem of nitrate leaching (below the root zone) [22].

Following its addition to tropical regions, some sulfate will be adsorbed onto soil particle surfaces, while part of it will interact with cations forming ionic pairs such as $K_2SO_4^0$, $CaSO_4^0$, $MgSO_4^0$, and, as expected, $AlSO_4^+$, which reduces Al^{3+} toxicity. Exchangeable aluminum is also neutralized via reactions of fluoride (F^-) found in phosphogypsum, with Al^{3+}, which results in less toxic forms of Al (e.g., AlF^{2+}). At low pH and higher SO_4^{2-} activities, alunite, $KAl_3(SO_4)_2(OH)_6$, is one of the most stable species of oxysulfates formed [23], which also decreases chemical activity of Al^{3+}.

III. PHOSPHOGYPSUM USE AND ITS ROLE AGAINST GLOBAL WARMING IN DEEP, WEATHERED, TROPICAL SOILS

The rainy season in the Cerrado extends for six to seven months, from September/October to April/May, and records show a total precipitation ranging between 800 and 2.000 mm yr^{-1} [24]. Dry spells of varied intensity occur during the rainy season, and a very dry period prevails for the rest of the year [25].

Dry spells are expected to be intensified as global surface temperatures rise. This increase is consistent with model predictions and is related to increasing concentrations of CO_2 and other greenhouse gases derived from human activity [9]. Agriculture shall be severely affected by changes in temperature, erratic precipitation, and lower water availability [9]. In tropical

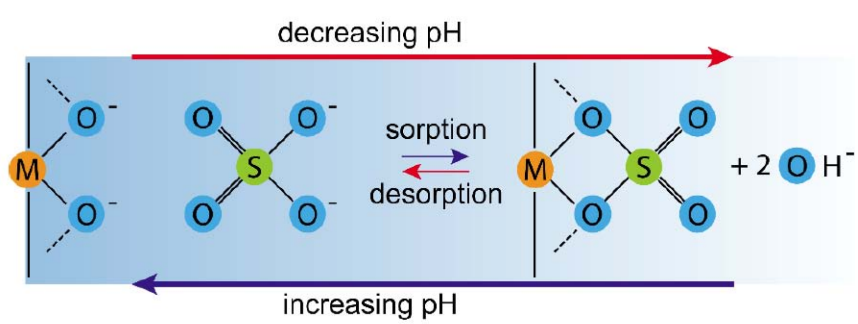

Figure 2: Sulfate adsorption by bidentate ligand exchange on oxide surface according to pH variations (M = Fe or Al).

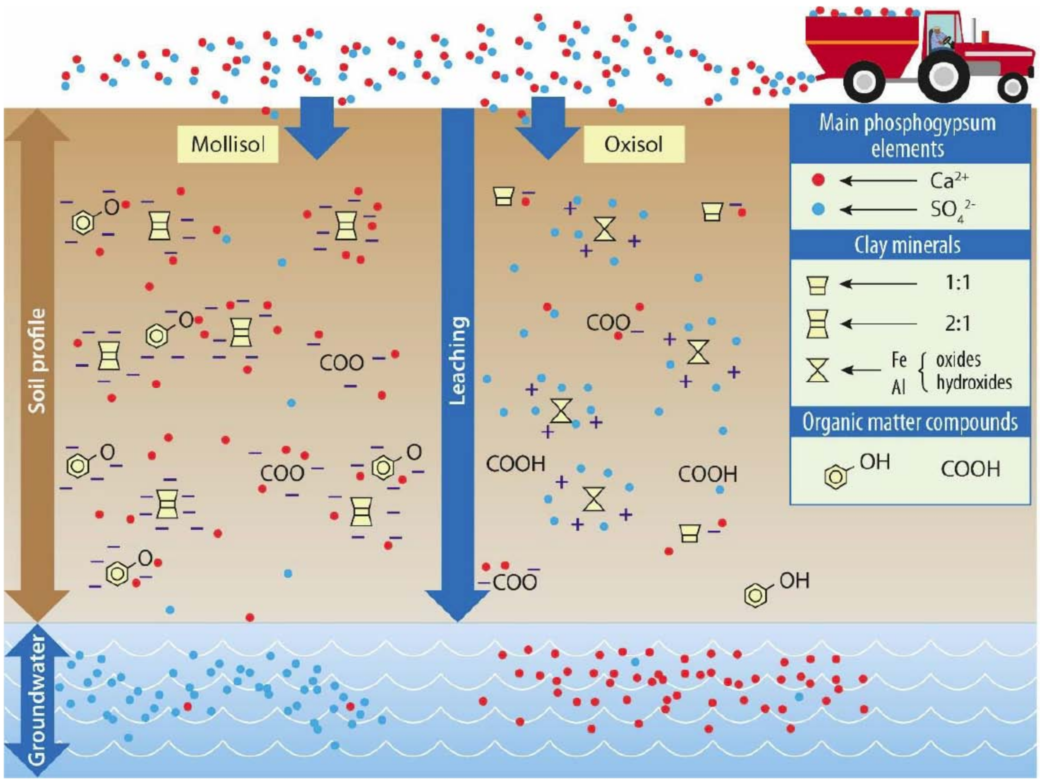

Figure 3: Conceptual model of cation and anion leaching in two kinds of soil.

and subtropical regions, where temperatures are currently close to the maximum tolerable as far as crops are concerned, productivity is expected to drop at growing pace, reaching one third of present levels [9].

With regard to the Cerrado, research results of Global Climate Models [26] indicate a slight decrease of annual rainfall due to longer dry seasons. Comparisons of climatic normal period (1961-1990) and projections for 2010-2039, 2040-2069, and 2070-2099 have predicted precipitation anomalies concerning wetter rainy seasons and more pronounced dry seasons, including a temperature increase by up to 5°C [27].

It is clear that countries in the region must target investments to climate change adaptation. Agricultural policies have been adopted on crop breeding and soil improvement to mitigate the effects of climate change on agriculture [9]. Increases in temperature imply less storage of carbon in the soil, considering that organic matter decomposition rate is higher with increases in the temperature. Researchers are looking for management practices in cropping areas to promote carbon sequestration and storage in soil [28]. One strong mitigating agent to influence policies should be the use of phosphogypsum.

Phosphogypsum effects were evaluated on carbon storage in the soil under sugarcane ratoon for four years [29]. Increases of 16.9% in stalk and 17.1 in straw production were reported when 5 Mg ha^{-1} phosphogypsum were applied. Total carbon in the 0-100 cm layer increased by 5.4 Mg ha^{-1} (total of 126.7 Mg ha^{-1}) when compared to the non-treated area. Most importantly, 4.4 Mg ha^{-1} were stored in the 40-100 cm layer, while carbon mineral sequestration increased 6.8%. The latter is the most permanent and stable carbon storage. Increments of C in the mineral pool of soil represent a very important sink, due to slow mineralization of C when compared to particulate carbon [30]. Increasing C content in depths below 40 cm in soil is desirable, and, over time, contributes to crop resistance to dry spells. Breeding for resource-use efficiency and "climate-resilient" bioenergy crops is a goal in long-term planning for food and energy production in the years to come [31].

Phosphogypsum does not change pH significantly; charge changes in clay particles are not substantial, causing no attraction or repulsion of clay particles. However, dissociation of phosphogypsum increases Ca^{2+} and SO^{2-} in solution. These ions act to neutralize the repulsive forces so that clay particles may flocculate [32]. Therefore, phosphogypsum could contribute beneficially to a structural organization of soil, increasing pore size in depth, creating conditions for fine root development, and promoting better spatial distribution. Homogeneous distribution vertically in soil profile shall increase plant resistance to dry spells, as observed in coffee plants [33].

IV. BRAZILIAN TECHNICAL RECOMMENDATIONS

Appropriate management of phosphogypsum is of paramount importance. Positive results of its use in crop production contrast with lack of response. In soils where phosphogypsum was not necessary, according to recommendations, there was no positive result. Increases in crop productivity depend primarily on the levels of available Ca and Al in the soil.

The Brazilian literature is abundant on phosphogypsum recommendations [34-41]. Approaches have been rather variable and non-specific. Phosphogypsum doses have been mostly focused on soil clay content. Soil sampling in the Cerrado biome must consider depths of 0-20 cm and 20-40 cm for annual crops, as well as 40-60 cm for perennial crops [41]. As a rule of thumb, phosphogypsum must be applied if Al saturation is > 20% (depending on the crop/source) or exchangeable Ca < 0.5 $cmol_c\ kg^{-1}$. In sugarcane, for example, Al saturation should be ≥ 40% [42]. When following these rules, the use of phosphogypsum has led to high probability of success, which is reflected by increasing crop yields and plant resistance to dry spells. In the Cerrado, 86% of native soils present available Ca < 0.4 $cmol_c\ kg^{-1}$, ensuring crops response to phosphogypsum [36]. Use of phosphogypsum under this condition improves root development and plant growth [43].

The ultimate phosphogypsum (PG) recommendation follows the formula [41]:

PG ($kg\ ha^{-1}$) = 50 × Soil clay content at the depth of 30 to 50 or 40 to 60 cm.

The amount of phosphogypsum applied has proved to be effective, although it is quite empirical and adjustments to cover different soil types are needed [44].

Phosphogypsum may also be applied as a source of sulfur in S-deficient pastures. Sulfur content in soil samples from 0-20 and 20-40 cm should be added up and divided by two according to Table **1** [45].

All recommendations consider a minimum of nutrients. The agricultural phosphogypsum must contain at least 16% of Ca and 13% of S, as ruled by the Brazilian Ministry of Agriculture, Normative nº5 [46]. On average, when 1 Mg of phosphogypsum (~15% humidity) is added to one hectare (ha), 200 kg Ca, 160 kg S, and 8 kg P_2O_5 are added to the soil. The amount of Ca added is able to increase exchangeable Ca at the 0-20 cm soil layer by 0.5 $cmol_c\ kg^{-1}$. This information is important to estimate Ca:Mg ratios in soils [47].

Overcoming Cation Leaching

Cation leaching caused by excessive phosphogypsum application in Cerrado soils has been a major concern. When following agronomic recommendations, leaching in Cerrado soils has been small, and it does not interfere in crop yield [37, 45]. Moreover, a time span of five years is recommended before re-applying phosphogypsum, which must be preceded by soil analysis [41].

Table 1: Average sulfur in soil samples from 0-20 and 20-40 cm, extracted by $Ca(H_2PO_4)_2$ 0.01 mol L^{-1} in water (soil:solution = 1:2.5), and recommended phosphogypsum dose.[1]

Phosphogypsum dose	Average S in soil [(0-20 + 20-40 cm)/2]
$kg\ ha^{-1}$	$mg\ dm^{-3}$
Soil with ≥ 20% clay	
10 × clay (%)	≤ 4
5 × clay (%)	5 to 9
-	≥ 10
Soil with ≤ 20% clay	
200	≤ 4
100	5 to 9

[1]Adapted from [45].

Table 2: Concentration Limits of Most Phosphates of Sedimentary or Igneous Origin[1]

Elements and radioactivity	Sedimentary origin	Igneous origin
P_2O_5 (%)	30-37	35-40
CaO (%)	46-52	48-54
F (%)	3-4	1-4
As (mg kg^{-1})	10-20	1-10
Cd (mg kg^{-1})	5-50	0-2
Hg (mg kg^{-1})	<0.2	0.1
Pb, Zn, Cu, Ni, Cr (mg kg^{-1})	200-800	50-150
Rare Earth Elements (mg kg^{-1})	100-900	1400-6300
Radioactivity (Bq kg^{-1}, Ra-226)	700-1400	10-110

[1][50].

When the amount of phosphogypsum applied to soils is higher than the recommended, it is likely that cations may leach down, beyond the reach of roots [39]. In this situation, the soil must be analyzed; losses of exchangeable Mg could be amended by lime with high Mg content (dolomitic), as well as other cations, such as K, that could be supplemented by fertilizers.

V. PHOSPHOGYPSUM: ENVIRONMENTAL CONCERNS

The main environmental problems of phosphogypsum in stack piles are the free moisture, low pH, HF acid; P_2O_5, radioactivity and heavy metals. The main problems associated with phosphogypsum applied to soils are related to radioactivity and heavy metals. These points are discussed here on account of current Brazilian legislation.

Phosphogypsum is classified as a class-II solid residue – i.e., not dangerous and not inert –, according to the Associação Brasileira de Normas Técnicas [48]. A solid residue class II means that after all (economically viable) available treatments and recovery were comprised, it may still be disposed in environmentally adequate deposits. This normative is used by Brazilian legislators to classify materials and ensure proper use, storage, and commercialization. Phosphogypsum production is so large that surpasses its use, and therefore, must be piled in stacks around the production site.

In Brazil, 95% of the phosphorus source comes from carbonatite igneous rocks [49]. Depending on the origin, the by-product may present different concentrations of heavy metals and radionuclides (Table **2**).

Heavy Metal Content

Heavy metal content of phosphogypsum used in crops cannot be higher than the values specified by normative 27 (Brazilian rule IN 27, [51]; Table **3**). Samples must be evaluated following specific methodologies [52]. The application of phosphogypsum in agriculture is safe as far as contamination by metals and radionuclides is concerned [53]. Levels of contaminants in three evaluated sources of the main Brazilian producers – Copebras, Fosfértil and Ultrafértil – were below the limits required by law.

Table 3: Maximum Concentration of Heavy Metals in Phosphogypsum Used as Soil Amendment[1,2]

Heavy metal	Maximum concentration (mg kg^{-1})
Arsenic	10
Cadmium	20
Lead	100
Chromium	200
Mercury	0.2

[1][51]; [2]Phosphogypsum may also be registered as soil acid neutralizer, or as a soil conditioner, where different limits apply.

Phosphogypsum may also be used to increase adsorption of arsenic (As) in soil materials. This is particularly useful to decrease as availability in areas of gold mining or other uses where its mobility in the environment needs to be reduced. Phosphogypsum was used in mixtures with red mud and reported increases in the efficiency of arsenic adsorption due to the presence of Ca^{2+}, which alters the charge balance of the adsorbent, leading to ternary complexes formation [54].

Radionuclide Content

In rock phosphate, uranium (U) and thorium (Th) decay-series are in equilibrium. During the industrial process, the equilibrium is disrupted and the radionuclides migrate to intermediate, final products and by-products according to the solubility and chemical properties of each element [11]. During the sulfuric attack of phosphate concentrates, 86% of the U-238 and 70% of the Th-232 are retained by phosphoric acid. Regarding the phosphogypsum, 86% of the Ra-226 is retained, as it shows a chemical behavior similar to Ca [50].

According to the Comissão Nacional de Energia Nuclear (CNEN), phosphogypsum is classified i) as a residue of low radioactivity level, containing radionuclides from natural series U-238 and Th-232; ii) as a Naturally Occurring Radioactive Material (NORM) [55]. This Commission also presents a rule directly for phosphogypsum used in agriculture limiting in 1000 Bq kg^{-1} the concentration of the Ra-226, or Ra-228 activities [56]. Under the United States Environmental Protection Agency (USEPA) regulation, the agricultural use of phosphogypsum is permitted if a stack pile is less than 10 pCi g^{-1} (≈ 370 Bq kg^{-1}; 1 pCi ≈ 0.037 Bq) of Ra-226 [57].

Radionuclides concentration in phosphogypsum samples collected in Uberaba (Minas Gerais State), and in Cubatão (São Paulo State) was evaluated [58]. The results varied from 144 ± 11 to 294 ± 5 Bq kg^{-1} for Ra-226, from 149 ± 4 to 352 ± 23 Bq kg^{-1} for Pb-210, from 155 to 346 Bq kg^{-1} for Po-210, from 86 ± 8 to 210 ± 6 Bq kg^{-1} for Th-232 and from 116 ± 1 to 228 ± 6 Bq kg^{-1} for Ra-228.

After adding gypsum to the soil, as recommended, the conclusion is that it did not represent any increase in the final activity concentration. The health risk post application indicated the lowest concentration levels for phosphate fertilizer products of 21 pCi g^{-1} (≈ 777 Bq kg^{-1}; TFI, 2000). In the Brazilian Cerrado scenario, which is one of remarkably lower CEC than in temperate regions, and at the rate of application for phosphogypsum, once at every 5 to 15 years, 1000 Bq kg^{-1} was considered adequate [56]. In a 27-year-simulation for the Cerrado region, Ra-226 remained mostly in the first 27 cm of soil and in low concentrations [59].

VI. CONCLUSION

As a final comment, it can be stated that phosphogypsum usage is expected to consolidate in long-term cropping of Oxisols and in similar soil types in the tropics, increasing the prospects of sustainable production. The Brazilian contribution should be perfected, according to observations and monitoring over time, so that to increase the benefits and reduce setbacks, serving as a worldwide technical reference.

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