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SEÇÃO IX - POLUIÇÃO DO SOLO E QUALIDADE AMBIENTAL

RADIONUCLIDES AND HEAVY METAL CONTENTS IN PHOSPHOGYPSUM SAMPLES IN COMPARISON TO CERRADO SOILS⁽¹⁾

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ABSTRACT

Phosphogypsum (PG) or agricultural gypsum, a solid waste from the phosphate fertilizer industry, is used as soil amendment, especially on soils in the Cerrado region, in Brazil. This material may however contain natural radionuclides and metals which can be transferred to soils, plants and water sources. This paper presents and discusses the results of physical and chemical analyses that characterized samples of PG and compares them to the results found in two typical soils of the Cerrado, a clayey and sandy one. These analyses included: solid waste classification, evaluation of organic matter content and of P, K, Ca, Mg, and Al concentrations and of the mineralogical composition. Natural radionuclides and metal concentrations in PG and soil samples were also measured. Phosphogypsum was classified as Class II A - Not Dangerous, Not Inert, Not Corrosive and Not Reactive. The organic matter content in the soil samples was low and potential acidity high. In the mean, the specific ²²⁶Ra activity in the phosphogypsum samples (252 Bq kg⁻¹) was below the maximum level recommended by USEPA, which is 370 Bq kg⁻¹ for agricultural use. In addition, this study verified that natural

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radionuclides and metals concentrations in PG were lower than in the clayey Oxisol of Sete Lagoas, Minas Gerais, Brazil. These results indicated that the application of phosphogypsum as soil amendment in agriculture would not cause a significant impact on the environment.

Index terms: phosphogypsum, soil fertility, radionuclides, metals, contamination.

RESUMO: CONTEÚDO DE RADIONUCLÍDEOS E METAIS PESADOS EM AMOSTRAS DE FOSFOGESSO, COMPARATIVAMENTE AO DE SOLOS DE CERRADO

O fosfogesso ou “gesso agrícola” – um resíduo sólido da indústria de produção de fertilizantes fosfatados – é usado como condicionador de solos, em especial do solo da região do Cerrado, Brasil. Entretanto, esse material contém radionuclídeos naturais e metais que podem ser transferidos para o solo, as plantas e o lençol freático. Neste trabalho são apresentados e discutidos os resultados de análises químicas e físicas para caracterização do fosfogesso e compara seus resultados com aqueles encontrados em solos típicos do Cerrado, sendo um argiloso e outro arenoso. As análises incluíram: a classificação do resíduo sólido, a avaliação do conteúdo de matéria orgânica e da concentração de P, K, Ca, Mg e Al das amostras de solo, bem como a composição mineralógica e das concentrações de radionuclídeos naturais, metais e metalóides presentes nas amostras selecionadas. O fosfogesso foi classificado como Classe II A - Não Perigoso, Não Inerte, Não Corrosivo e Não Reativo. Os solos analisados apresentaram baixo conteúdo de matéria orgânica e baixa fertilidade natural. A atividade específica média do ^{226}Ra (252 Bq kg^{-1}) das amostras de fosfogesso ficou abaixo do limite recomendado pela Agência Ambiental Americana (USEPA) para uso na agricultura, cujo valor é de 370 Bq kg^{-1} . Além disso, o estudo mostrou que as concentrações de radionuclídeos naturais e de metais apresentaram-se inferiores aos valores obtidos para o Latossolo Vermelho-Amarelo de textura argilosa coletado em Sete Lagoas – MG. Esses resultados indicam que a aplicação do fosfogesso na agricultura como condicionador do solo não resulta em impacto significativo ao meio ambiente.

Termos de indexação: fosfogesso, fertilidade do solo, radionuclídeos, metais, contaminação.

INTRODUCTION

The main raw material in Brazilian phosphoric fertilizer industries is the apatite, of which approximately 80 % are of igneous origin (Canut, 2006). The most commonly used process in the production of phosphoric fertilizers is the attack of the phosphate rock with concentrated sulfuric acid and water. In this case, the main products from chemical reactions are phosphoric acid (H_3PO_4), and simple superphosphate (SSP). Dehydrated calcium sulphate (phosphogypsum) and hydrofluoric acid (HF) are by-products of phosphate rock processing.

The phosphogypsum (PG) generation rate is approximately 4.8 t t^{-1} of phosphoric acid produced. The annual world production is estimated to be 150 million tons, approximately 12 million tons of which are produced in Brazil (Mazzilli et al., 2000). At present, this material is stored in piles near the factories. However, this practice represents a potential risk of contamination, mainly to organisms and hydrological systems in the surroundings of the storage sites.

The global demand has spurred interest in processes that generate great amounts of both H_3PO_4 and chemical fertilizers. However, there are several fundamental environmental questions regarding PG disposal that remain unaddressed. Phosphogypsum, although being mainly composed of dehydrated calcium sulfate, also contains fluoride, heavy metals, and radionuclides (of the ^{238}U and ^{232}Th natural radioactive series). These impurities can percolate through the pile and contaminate groundwater, eventually causing damage to human health (Mazzilli et al., 2000). Another problem is ^{222}Rn exhalation, which can affect people in the surroundings of the storage sites (Santos et al., 2006), especially workers.

The possibility of using PG in agriculture (FIRP, 1996; El-Mrabet et al., 2003; Papastefanou et al., 2006) has been the focus of research in several countries and in Brazil, especially with regard to the agriculture in the Cerrado (Ribeiro et al., 2000; Ernani et al., 2001). The soil properties in this region are compatible with the use of this PG. These are acidic soils (pH between 4.3 and 6.2) with high levels of exchangeable Al and low levels of plant-available P;

they are also poor in Ca and Mg, elements involved in root growth (Silva & Azevedo, 2002).

According to Kochian et al., 2004, acidity is the greatest limitation of soils in extensive tropical and temperate areas.

Toxic concentrations of soluble Al in soils that negatively influence crops can be avoided with the addition of acidity correctives, which buffer the soil pH over 5.0. Rocks that contain alkaline constituents such as oxides, hydroxides, carbonates and silicates of Ca, and, or, Mg are commonly employed to neutralize soil acidity (Bellingieri & Bertin, 2003). Calcareous materials are included in this category and are known as limestone that contains calcium and, or, magnesium carbonates. However, it is more difficult and expensive for farmers to obtain limestone, mainly due to its use in more profitable industrial sectors, such as cement production, metallurgic sites, building sites, etc.

Various industrial residues have been studied as possible substitutes for limestone. Among them, the industrial waste phosphogypsum (PG), or “agricultural gypsum” (AG), has been considered mainly for a combined application with limestone, to reduce the effect of subsuperficial acidity on root growth. In Brazil, PG has been applied as soil conditioner for several years (Embrapa, 2000; Ernani et al., 2001). Nevertheless, due to the presence of toxic elements (e.g., heavy metals, metalloids and radionuclides) in the substance, and taking into account the environmental aspects related to the reuse of residues in agriculture (CETESB, 1999; Andrade & Abreu, 2006), a study has been carried out to evaluate whether PG application can affect human health and the environment.

This paper aims to present and discuss the results of a set of experiments involving the physical, chemical, and radiological characterization of two soil types (clayey and sandy) of the Cerrado. These results are compared with those related to the characterization of phosphogypsum samples collected from a fertilizer plant in the industrial area of Uberaba, MG, Brazil, which have been used by the local growers as soil conditioner.

MATERIALS AND METHODS

Sample collection and pre-treatment

PG samples were collected in a fertilizer plant that produces H_3PO_4 by means of a wet method. The H_3PO_4 rock used at the industrial site is of igneous origin and comes from the Alkaline-Carbonate site in Tapira, MG, Brazil (Canut, 2006). Thirty samples were collected from the surface of the piles at different locations, according to the Environmental Protection Agency guidelines (USEPA, 1988). PG samples were

then dried in the laboratory at 60 °C for 48 h and sieved through 30 and 60 mesh (590 and 250 μm). Afterwards, small fractions of the samples were mixed, and divided to form a composed sample.

The soil samples were collected from two different locations in the municipal district of Sete Lagoas (clayey Yellow Rhodic Ferralsol (Hapludox) - LVSL) and of João Pinheiro (sandy Rhodic Ferralsol (Hapludox) - LVTM), that represent typical soils of the Cerrado region. The samples were air-dried and sieved through 2 mm mesh. In the chemical analysis the following properties were measured: pH in water (1:2.5); P and K extractable by Mehlich-1; exchangeable Ca, Mg, and Al by extraction with 1 mol L^{-1} KCl; Sum of Exchangeable Bases (SB); Cation Exchange Capacity at pH 7.0 (CEC); Base Saturation Index (V); Aluminum Saturation Index (m), and Organic Matter Content (OM).

Leaching and dissolution/solubilization tests

A composed PG sample was submitted to leaching and solubilization tests for waste classification. Brazilian regulations consider two waste categories: (1) Class I - dangerous solid waste, with hazardous properties such as inflammability, corrosiveness, reactivity, toxicity, and, or, pathogeneticity; (2) Class II - Harmless solid waste - IIA (non-inert) and IIB (inert), wastes with none of the above hazardous properties.

Leaching and dissolution/solubilization were tested according to ABNT NBR 10005/2004 and 10006/2004 Norms. All substances listed in the F and G Annexes of ABNT NBR 10004/2004 were analyzed and classified according to the toxicity by leaching and dissolution of inorganic and organic substances (pesticides and other chemicals).

Mineralogical analysis

For the mineralogical analysis, soil and PG samples were first disassembled by hand on a table using a cylindrical roll and then sieved through 16 meshes. A fraction of each sample was removed for mineralogical analysis by X-ray diffraction (powder method). These analyses were carried out using a Rigaku X-ray Diffractometer with a Cu tube. The crystalline phases were identified by comparing sample diffractograms with those of the International Center for Diffraction Database (JCPDS, 2000). These analyses took into account intensities of main reflections and comparison of diffractograms to determine the relative concentrations of different minerals in the samples.

Determination of radionuclide activity concentrations

The ^{226}Ra , ^{228}Ra , and ^{210}Pb activity concentrations in PG and soil samples were determined by Gamma

Spectrometry using an HPGe detector (relative efficiency 45 %). The samples were sealed in plastic containers for 30 days, the period required to ensure the radioactive balance between ^{226}Ra and its daughters, ^{214}Pb and ^{214}Bi . Energy photopeaks at 609, 1,020 and 351 keV were used to determine ^{226}Ra , corresponding to ^{214}Bi and ^{214}Pb , respectively. A 911 keV energy photopeak for ^{228}Ac ($T_{1/2} = 6.12$ h) was used to determine ^{228}Ra ; a 46.5 keV energy photopeak was used for ^{210}Pb determination.

The ^{210}Po activity concentration was measured using an Alpha Spectrometry system, by determination of the powder deposited in a silver plate, using a reducing HCl and ascorbic acid medium. The matrix was purified with a specific SR-Spec chromatographic resin from Eichrom.

The ^{232}Th activity concentration in both PG and soil samples were determined by the Neutron Activation Analysis technique (AAN), k_0 method (Menezes et al., 2003), which is a sensitive multi-element analytical technique used for both qualitative and quantitative analyses of major, minor, trace and rare elements. In this case, 200 mg of each sample were weighed in polyethylene tubes, sealed and irradiated in a TRIGA MARK I IPR-R1 reactor (at the Centro de Desenvolvimento da Tecnologia Nuclear - CDTN/CNEN), at 100 kW and a thermal neutron flow equivalent to 6.35×10^{11} neutrons $\text{cm}^{-2} \text{s}^{-1}$, for 8 h. After irradiation and an appropriate decline time, the medium and long radionuclide half-life were determined. Gamma Spectrometry was applied using an HPGe detector with 15 % efficiency. KAYZERO/SOLCO software was used to calculate the concentration of the elements.

The ^{238}U activity concentration was determined by retarded neutron fission activation, and samples were irradiated with a flow of thermal neutrons. This method uses fast irradiation followed by a reading of retarded neutrons. Samples were irradiated for 50 s, with decline time of 30 s, and counting took 60 s. An automated pneumatic system was used for irradiation and counting and a $^{10}\text{BF}_3$ detector to count retarded neutrons. Uranium concentration was calculated based on linear regression, adjusted according to established patterns.

Determination of metal and metalloid concentrations

The metal and metalloids (Ni, Cr, Cd, Pb, Hg, As, and Se) concentrations in soil and PG samples were analyzed as described below.

For the determination of Ni, Cr, Cd, and Pb concentrations, 1.0 g (dry weight) of each sample was digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2), according to the USEPA Method 3050B (USEPA, 1996). Inductively coupled plasma - atomic emission spectrometry (ICP-AES) was used to determine Ni and Cr, and atomic

absorption spectrophotometry coupled with a graphite furnace (GF-AAS) to determine Cd and Pb. Calibration solutions were prepared with 1,000 mg L^{-1} Merck certified solutions. A lake sediment reference material IAEA-SL-1, supplied by the International Atomic Energy Agency, was analyzed to check the accuracy of the method. Values measured were within the confidence interval (95 %) of the recommended values.

Total Hg was determined by cold steam generation coupled with Atomic Absorption Spectrophotometry (CV-AAS). Samples were processed according to the adapted procedure of USEPA (1995), which involved the addition of 1.0 mL of water purified in a Milli-Q® system and 2.5 mL of a 3:7 mixture of concentrated nitric and sulfuric acids (0.0000005 % maximum Hg level) per approximately 200 mg of sample.

These samples were later heated to 75 °C for 4 h. After that, 4.0 mL of a 5 % (m/v) aqueous potassium permanganate solution was added along with 2.0 mL of 5 % (m/v) aqueous potassium persulfate solution. The excess of permanganate was eliminated by adding 1 mL of 20 % (m/v) hydroxylamine and the final volume was adjusted to 50.0 mL. An aliquot was centrifuged for 10 min (2,000 rpm) and the floating material was analyzed by CV-AAS.

Calibration curves were prepared from a certified 1,000 $\mu\text{g mL}^{-1}$ Hg Merck standard solution (1.0 to 5.0 ng mL^{-1}), measuring patterns under the same conditions as the samples. Method accuracy was verified by analyzing a CRM 320 reference material, a river sediment provided by the BCR Community Bureau of Reference.

As and Se concentrations were analyzed by the Neutron Activation Analysis (AAN), k_0 method. In this case, two 200 mg aliquots of each sample were weighed in polyethylene tubes and sealed; one tube was used to determine As and the other Se concentrations. Afterwards, the samples were sent to the CDTN/CNEN, for irradiation in the TRIGA MARK I IPR-R1 reactor, at 100 kW, with a thermal neutron flow of 6.35×10^{11} neutrons $\text{cm}^{-2} \text{s}^{-1}$, for 8 h, as described above. The reference material IAEA/Soil-7 was analyzed together with the PG and soil samples to test the accuracy of the method.

RESULTS AND DISCUSSION

Results from solid waste classification tests showed that PG was considered neither corrosive nor reagent, according to ABNT norms. It was classified as non-inert waste, based on NBR 10004/2004 (Class II A, non-dangerous/non-inert) due to the presence of As, F, Al, Fe, Mn, and sulfates above threshold limits in the dissolution/solubilization test (Oliveira, 2008).

Chemical characterization revealed that both soils were acidic and fertility levels low (Table 1). This is related to the low nutrient levels of (Ca, Mg, K, and P), as well as low CEC values. The low base saturation indexes (V) indicated low proportions of exchangeable Ca^{2+} , Mg^{2+} , and K^{+} occupying negative charges sites of the colloids. Conversely, exchangeable Al^{3+} was dominant, as indicated by a relatively high Al^{3+} saturation index ($m > 30\%$). The fertility of the clayey soil was slightly higher, with higher Ca and organic matter (OM) levels. In general, both soils had high Al^{3+} levels and potential acidity. These are typical characteristic of acidic Cerrado soils, where exchangeable Al^{3+} is considered toxic to most cultivated plants.

Mineralogical analysis revealed that anydrite and bassanite were the dominant mineral phase in PG (Table 2). PG has a yellowish white coloration and the granulometry distribution analyses showed that it consists mainly of particles with a diameter between 53 and 74 μm (Oliveira, 2008).

The mineralogy of the sandy soil was dominated by quartz (above 30 %). Granulometry distribution analyses revealed that this soil contained particles with a diameter varying from 105 to 250 μm . The main constituent of the clayey soil was kaolinite (more

than 30 %), basically composed of fine particles of approximately 250 μm diameter.

These results corroborated the soil chemical characterization analyses, which indicated low CEC (Table 1). The mineralogical composition was typical of Ferralsols (Hapludox) of the Cerrado region.

Wasserman et al. (2002) demonstrated that the presence of minerals such as kaolinite and gibbsite influences the transfer of pollutants in the soil-plant system. This fact can be related to the low capacity of these minerals to retain cations. On the other hand, Fe and Al oxides, such as goethite and gibbsite, may have high adsorption capacities due to the formation of "inner sphere" surface type complexes with some metals and metalloids in the soil, such as As. These surface complexes are quite stable and can hinder the transfer of soil pollutants to plants as well as alter their bioavailability.

The ^{238}U concentration in PG was well below the concentration found in the clayey soil. It is important to mention that: (1) PG samples usually have a low ^{238}U concentration compared to other natural radionuclides. In phosphoric rock, members of the natural series of ^{238}U and ^{232}Th are in radioactive equilibrium. During acid attack to phosphoric rocks, H_3PO_4 is enriched with ^{238}U , while ^{232}Th , radium

Table 1. Chemical characterization of the soil samples

Soil type	pH	P	K ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	H + Al	SB	CEC	V	m	OM
		mg dm ⁻³	cmol _c dm ⁻³							— % —		g kg ⁻¹
Clay	5.18	1.5	0,02	0.90	0.06	0.48	8.3	0.97	1.45	10.5	33.1	4.43
Sand	5.32	0.4	0,041	0.11	0.02	0.1	3.2	0.17	0.27	5.0	37	1.17

Table 2. Results of the mineralogical composition analyses

Samples	Predominant	Most important	Less important	Trace elements
	> 40 %	< 30 %	< 10 %	< 3 %
PG	Gypsum} (CaSO ₄ ·2H ₂ O)	Anydrite (CaSO ₄) Bassanite (CaSO ₄ ·0.5 H ₂ O)	-	Muscovite [KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂]
Sandy soil	Quartz (SiO ₂)	Gibbsite (α-Al ₂ O ₃ ·3H ₂ O)	Kaolinite [Al ₂ Si ₂ O ₅ (OH) ₄] Goethite (FeO.OH)	Albite (NaAlSi ₃ O ₈) Anatasio (TiO ₂) Hematite (Fe ₂ O ₃) Magnetite (Fe ₃ O ₄) Microcline (KAlSi ₃ O ₈) Muscovite [KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂]
Clayey soil	Kaolinite [Al ₂ Si ₂ O ₅ (OH) ₄]	Gibbsite (α-Al ₂ O ₃ ·3H ₂ O) Goethite (FeO.OH) Quartz (SiO ₂)	Hematite (Fe ₂ O ₃)	Magnetite(Fe ₃ O ₄) Muscovite [KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂] Rutile (TiO ₂)

isotopes, and ^{210}Pb tend to concentrate in PG (Mazzilli, 2000); (2) Brazilian phosphoric rock is of igneous origin, with lower ^{238}U concentrations than ^{232}Th concentrations; and (3) the clayey soil used in this study was developed from the weathering of over 2,700 million-year-old granite rocks, typically containing 5–10 mg kg^{-1} ^{238}U .

In general, the PG generated by H_3PO_4 industries in Brazil has natural radionuclide activity concentrations well below the values observed in other countries (Silva et al., 2001; Papastefanou et al., 2006). The highest ^{232}Th activity concentration in relation to ^{238}U activity concentration can be explained by the igneous origin of the rock used in the H_3PO_4 production process.

Metal (Cd, Pb, Cr, Ni, and Hg) and metalloid (As and Se) concentrations in PG and soil samples are listed in table 4. The values were compared with the contaminant limits for soil conditioners established by the Brazilian Agriculture Department (Brazil, 2006), as well as the maximum heavy metal limits in sewage sludge for use in agriculture (CONAMA, 2006). All values were below the recommended limits.

Table 3. Natural radionuclide activity concentrations

Activity concentration	Sample		
	PG	Sandy soil	Clayey soil
	Bq kg^{-1}		
^{238}U	80 ± 20	< 50	150 ± 25
^{232}Th	111 ± 13	36 ± 1	117 ± 3
^{226}Ra	252 ± 26	< 20	69 ± 5
^{228}Ra	226 ± 29	34 ± 2	114 ± 5
^{210}Pb	206 ± 29	20 ± 5	50 ± 8
^{210}Po	230 ± 26	< 13	43 ± 6

In all cases, concentrations of toxic elements found in the clayey soil were higher than in the sandy soil. This is probably due to the higher CEC and organic matter contents in the clay soil. The concentrations of toxic elements in PG were generally lower than in the soils studied, especially in the clayey soil. Concentrations of toxic elements in PG samples were below the limits established by MAPA Normative Instruction SDA number 27 (Brazil, 2006).

As previously mentioned, the analytical results were verified by analyzing certified reference materials as quality control. Experimental results were similar to the reference values, indicating the accuracy of the methods.

CONCLUSIONS

1. This study showed that PG is classified as non-Hazardous, non-Inert waste (Class IIA), with As, F, Al, Fe, Mn, and sulfate concentrations in the solubilization test above the maximum limit established by ABNT Norm 10004/2004. Both soil types (sandy and clayey Ferralsols) are acidic with low fertility and the Al concentration level was considered toxic to plants.

2. Mineralogical and granulometric analyses indicated that anhydrite and bassanite are the dominant phases in PG in particles varying from 53 to 74 μm diameter. The sandy soil consists of quartz (> 30 %). The main constituent of the clayey soil is kaolinite (> 30 %).

3. The ^{226}Ra (251 Bq kg^{-1}) and ^{228}Ra (226 Bq kg^{-1}) activity concentrations in PG samples were well below the EPA limits recommended for agricultural purposes (USEPA, 1988). The ^{210}Pb and ^{210}Po activity concentration values were similar to the values found for ^{226}Ra and ^{228}Ra . The ^{238}U concentration in PG samples was below the concentration found in the

Table 4. Metal and metalloid concentration analyses

Element	Recommended limits		Concentration		
	CETESB	MAPA	PG	Sandy soil	Clayed soil
	mg kg^{-1}				
Cd	85	3.0	< 0.1	< 0.1	< 0.1
Pb	840	150.0	< 20	< 20	69.7 ± 0.2
Cr	-	200.0	< 17	38.2 ± 0.1	177 ± 47
Ni	420	70.0	15.7 ± 1.5	12.4 ± 0.8	77 ± 4
Hg	57	1.0	< 0.025	< 0.025	0.063 ± 0.013
As	75	20.0	< 0.6	3.4 ± 0.1	61 ± 2
Se	100	80.0	< 1.5	< 1.5	< 1.5

clayey soil. ^{232}Th activity concentration was higher than ^{238}U , due to igneous origin of the rock which is used in the production of H_3PO_4 . The activity concentration for natural radionuclides was higher in the clayey than in the sandy soil. The same was observed regarding the concentration of other toxic elements. These results were related to physicochemical characteristics of the soil samples.

In addition, all heavy metal and metalloid concentrations were lower than the limits established by the Brazilian Agriculture Department (Brazil, 2006) and by the National Environmental Council (CONAMA, 2006). These results, together with those related to the concentration of natural radionuclides, indicate that, in principle, the use of PG for agriculture in the Cerrado does not represent a significant impact on the environment.

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