

Radiological Impact Associated to the Use of a NORM Material as a Soil Conditioner in Brazilian Agriculture – ID 10009

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ABSTRACT

This study involved phosphogypsum (PG), a TENORM by-product from phosphate fertilizer industry (wet process). Since it contains U and Th series radionuclides, P₂O₅, and trace metals, it is necessary to comprehend radionuclide transfer mechanisms and evaluate if PG in soil contributes to human exposure to natural radioactivity. Within greenhouse experiments, PG, soils, soil treated with PG (for lettuce, corn and soy cultivation), as well as leached water samples, were analyzed for key radionuclides (U-238, Th-232, Ra-226, Ra-228, Pb-210, Po-210). Average Ra-226 activity in PG ($252 \pm 26 \text{ Bq kg}^{-1}$) was below USEPA limit. Ra-228, Pb-210, and Po-210 values were within Ra-226 magnitude order. Transfer factors varied from $9.4\text{E-}04$ to $3.4\text{E-}01$. Total effective dose for the public was determined to be $1.3\text{E-}02 \text{ mSv year}^{-1}$; below ICRP dose restriction limit. In general, radionuclide mobility in soil was low and demonstrated the viability of PG as soil amendment in the Cerrado agriculture.

INTRODUCTION

The main raw material in Brazilian phosphoric fertilizer industries is the apatite present in rocks, of which approximately 80 % are of igneous origin [1]. 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 (H₃PO₄), simple super-phosphate (SSP), and triple super-phosphate (TSP). Dehydrated calcium sulphate (phosphogypsum) and hydrofluoric acid are by-products of phosphate rock processing.

The phosphogypsum (PG) generation rate is approximately 4.8 tons per ton of phosphoric acid produced. Annual world production is estimated to be 150 million tons, approximately 12 million tons of which are generated in Brazil [2]. At present, this material is stored in piles located near the factories. However, this practice may represent a potential risk of contamination, mainly to organisms and hydrological systems located close to the pile.

Global demand has spurred interest in finding processes that generate great amounts of both phosphoric acid and chemical fertilizers. However, there are several important environmental concerns that remain unaddressed regarding PG disposal. These problems exist because phosphogypsum, although being mainly composed of dehydrated calcium sulfate, also contains fluoride, heavy metals, and radionuclides (from the U-238 and Th-232 natural radioactive series). These impurities can percolate through the pile and contaminate

groundwater, eventually causing damage to human health [2]. Another problem is Rn-222 exhalation, which can affect populations close to the piles, especially workers.

The possibility of using PG in agriculture has been the focus of research in several countries and in Brazil, especially in the agriculture of the Cerrado [3], where soils have characteristics which are compatible with the use of this material. In this system, fast mineralization of organic matter associated with intense leaching produces soils with naturally low fertility. These are acidic soils (pH between 4.3 and 6.2) with high levels of exchangeable aluminum and low levels of phosphorus available for plants; they are also poor in calcium and magnesium, elements involved in root development [4].

Acidity is the largest limitation of soils in extensive tropical and temperate areas. Toxic concentrations of soluble aluminum 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 calcium, and/or magnesium are commonly employed to neutralize soil acidity [5]. 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 residues generated by industries have been studied as possible substitutes for limestone. Among them, the industrial waste phosphogypsum (PG), or “agricultural gypsum” (AG), has been considered mainly to be applied in conjunction with limestone in order to improve the effects of the subsuperficial acidity on the root growth. In Brazil, the application of PG as a soil conditioner is a practice that has been done for several years [6]. Nevertheless, due to the presence of toxic elements (as an example, heavy metals, metalloids and radionuclides) in PG and taking into account the environmental aspects related to the reuse of residues in agriculture [7,8], a study has been carried out to evaluate whether its application to improve soil fertility can cause an impact to human health and to the environment.

Migration and accumulation of contaminants in cultivated soils is complex, involving processes such as leaching, capillary rise, runoff, sorption, root uptake, and resuspension into the atmosphere. Assessment models normally make use of plant/substrate concentration ratio (TFs) to estimate transport of radionuclides and other elements to the food [9,10]. TF describes the amount of element expected to enter a plant from its substrate under equilibrium conditions [11]. Some parameters can influence TF values such as: soil characteristics, weather conditions, plant type, concerned plant parts, radionuclide physico-chemical form, and effect of competitive species [12].

Due to the presence of radionuclides in PG and taking into account the environmental aspects related to reuse of residues in agriculture [7,8], this study was carried out to evaluate whether its application to improve soil fertility in the Cerrado region of Brazil, can result in a radiological impact to human health and the environment.

MATERIALS AND METHODS

Phosphogypsum from storage piles and soil were radiochemically characterized. Their mixture was employed in several compositions to cultivate lettuce (chosen due to the market demand), corn and soil (representative from Cerrado region). In addition to the cultures, leached water was also radiochemically characterized. Transfer Factors in the soil-plant system were determined along with evaluation of human dose from food ingestion.

Collection and Sample Preparation

Samples of PG were collected in a fertilizer facility that produces phosphoric acid by means of a wet method. The phosphate rock used at the industrial site has igneous origin and comes from the Alkaline-Carbonate site in Tapira, MG, Brazil [1]. Thirty samples were collected from the surface of the piles at different locations, according to the Environmental Protection Agency guidelines [13]. PG samples were then dried in the laboratory at 60°C for 48 hours 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.

Soil samples were collected from two different locations in the Sete Lagoas municipal district (clayey yellow rhodic ferralsol (hapludox) - LVSL) and in the Três Marias municipal district (sandy rhodic ferralsol (hapludox) - LVTM), that represent typical soils from the Cerrado region. Soil samples were air dried and sieved through 2 mm mesh.

Chemical characterization of soil samples was done by means of the following analyses: 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); Cationic Exchange Capacity at pH 7.0 (CEC); Index of Bases Saturation (V); Index of Aluminum Saturation (m), and Organic Matter Content (OM).

Leaching and Dissolution/Solubilization Tests

A composed sample of PG was submitted to leaching and solubilization tests for waste classification. Brazilian regulations consider two waste categories have been established: (1) Class I - dangerous solid waste, with hazardous characteristics such as inflammability, corrosiveness, reactivity, toxicity, and/or pathogeneticity; (2) Class II – Harmless solid waste - IIA (non-inert) and IIB (inert), wastes that do not present any of the characteristics that were described previously.

Leaching and dissolution/solubilization tests were done according to ABNT NBR Norms [14, 15]. All substances listed in the F and G Annexes of ABNT NBR 10004/2004 [16] were analyzed and toxicity classification tests were done by leaching and dissolution of inorganic and organic substances (pesticides and other chemicals).

Greenhouse Experiments

Experiments to evaluate the use of phosphogypsum in soil were accomplished in a non-climatized greenhouse with a metallic structure, as showed in Fig. 1. Soil samples were subjected to lime treatment [5] and were kept humid during 15 days, such as to follow their humidity capacity in the field. They were then mixed with recommended doses of

phosphogypsum, half and twice the recommended amount, in order to verify the effect of this practice on radionuclide bioavailability in both types of soils studied (sandy and clayey).

Phosphogypsum dose (recommended mass) equivalent to 1NG (gypsum need) was of 0.5 g dm^{-3} for clayey soil and 0.2 g dm^{-3} for sandy soil, according to criteria established by EMBRAPA [6]. Additional fertilization with phosphorus was done using a dose of 300 mg dm^{-3} [17]. For comparison, each experiment was accomplished in triplicate vessels for each type of soil (1NG, 0.5NG, and 2NG phosphogypsum doses), using a blank vessel (without phosphogypsum) as control.

After completion of germination cycle, culture samples were collected, dried at 60°C until constant weight, grinded in a Wiley type grinder, weighted and stored in polyethylene containers for further analyses to be carried out in the edible parts of the plants.



Fig. 1. General view of the greenhouse experiments.

Analytical Methodologies

All analytical methodologies described in this paper were applied according to procedures described by Siqueira [18]

UV-Vis Spectrophotometry with Arsenazo III was the technique employed to determine uranium and thorium activity concentration in samples of phosphogypsum and leached water. For uranium (VI), extraction was done with tri-n-butyl-phosphate (TBP), in the presence of $\text{Al}(\text{NO}_3)_3$ saline complexation agent, EDTA, and tartaric acid. Uranium reextraction in the organic phase was carried out with Arsenazo III solution, forming a redviolet stable complex with absorbance at $650\text{ }\mu\text{m}$ [19].

The procedure for thorium determination was based on separation from impurities by extraction with trioctylphosphine oxide (TOPO), re-extraction with oxalic acid, and colorimetric reaction with Arsenazo III. A stable complex with absorbance read at 665 μm was formed.

Determination of Th-232 specific activity was carried out by k0-AAN method for Neutronic Activation [20,21]. In this case, 200 mg of each sample were weighed in polyethylene tubes, sealed and irradiated in a TRIGA MARK I IPR-R1 reactor located at CDTN/CNEN, using 100 kW with a thermal neutron flow equivalent to 6.35×10^{11} neutrons $\text{cm}^{-2} \text{s}^{-1}$, for 8 hours. After irradiation and an appropriate time for decline, the procedure followed medium and long half-life radionuclide determination. Gamma Spectrometry was done using an HPGe detector with 15 % efficiency.

The U-238 activity concentration was determined through retarded neutron fission activation method, 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 seconds, 30 seconds were allowed for decline time, and counting took 60 seconds. The irradiation process and counting utilized an automated pneumatic system. A $^{10}\text{BF}_3$ detector was used to count retarded neutrons. Uranium concentration was calculated through linear regression, adjusted according to established patterns.

Alpha Spectrometry was employed for the determination of U and Th isotope concentration in plants. Lettuce, corn, and soy samples were chemically digested by a multi-acid attack. The final residue was dissolved with 8M HNO_3 under heating. Thorium isotope separation was done through an anionic DOWEX 1x2 resin with concentrated HCl. Uranium isotope separation was done by an UTEVA resin with 0.01M HCl. Both aliquots were dried and electrodeposited during 1 hour in previously polished silver planchets, under 1 A and 1.2 A currents, for thorium and uranium, respectively. Th-232, Th-229, U-238, and U-232 quantification was accomplished in an Alpha Analyst System, Canberra model, with surface barrier semiconductor detectors of 450 mm^2 active areas.

The determination of Po-210 was also done by Alpha Spectrometry, according to the procedure described by Vajda *et al.* [22]. Before dissolution with concentrated mineral acids, a known amount of ^{209}Po was added to the samples in order to obtain Po-210 chemical recovery. The final residue was dissolved in 1.5M HCl and 0.5 g of ascorbic acid was added. Polonium isotopes spontaneously deposit in silver planchets from an acidic medium adjusted to 80-90°C range, during a period of 4 hours under constant agitation. For leached water samples, radionuclide co-precipitation with iron hydroxide was done to eliminate main interfering elements. After decanting, the final precipitate was treated as described above.

Gamma Spectrometry was employed for Ra-226, Ra-228, and Pb-210 measurement in soil and phosphogypsum. Samples were grinded to a Number 80 granulometry. They were then sealed in acrylic containers and analyzed by Gamma Spectrometry after thirty days; enough time to ensure radioactive equilibrium between Ra-226 and its daughters Pb-214 and Bi-214. One HPGe Canberra detector with 45% relative efficiency was employed, along with Genie 2000 version 3.1 software for spectral analysis. Photopeaks of 609 keV and

1,020 keV from Bi-214, and 351 keV from Pb-214, were used to measure Ra-226. A photopeak of 911 keV equivalent to ^{228}Ac ($t_{1/2} = 6.12$ hours) was used to determine Ra-228. A characteristic photopeak of 46.5 keV was used to measure Pb-210, which also underwent self-absorption corrections [23].

Radiochemistry was employed for Ra-226, Ra-228, and Pb-210 determination in plant and leached water samples. Barium and lead carriers were added. Solid samples suffered a multi-acid chemical digestion, while liquid samples were filtered. The method was based on radium and lead separation from other present elements and separation from themselves by selective precipitation, with Ra being co-precipitated as $\text{Ba}(\text{Ra})\text{SO}_4$ and Pb as PbCrO_4 . Ra and Pb determinations were accomplished through Total Alpha and Beta Counting, respectively, in an Ultra-Low Background Proportional Gas Flow Counting System, S5XLB Tennelec, Canberra Model.

RESULTS AND DISCUSSION

Phosphogypsum Classification and Characterization

Phosphogypsum residue was classified as Class IIA – Non-Hazardous, Non-Corrosive and Non-Inert. Its chemical composition revealed predominant presence of calcium and sulfur (40.12% CaO and 58.12% SO_4). Percentage ranges for these parameters in phosphate mineral fertilizers are between 10-28% and 15-20%, respectively, showing that phosphogypsum may be employed as a calcium and sulfur source in agricultural activities. Granulometry analysis showed that phosphogypsum is mainly composed of Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

Soil Characterization

Soil fertility and granulometry analysis showed that Red-Yellow Latosol was mainly composed of clay, being classified as clayey, while Yellow Latosol was composed of fine sand and classified as sandy. Both soils were acidic, with low fertility.

Radionuclide Activity in Phosphogypsum and Soil Samples

The results of radionuclide activity in phosphogypsum (PG) and soil samples are showed in Table I. In general, the PG generated by phosphoric acid industries in Brazil has natural radionuclides activity concentrations well below those observed in other countries [4, 10].

The U-238 concentration in PG was well below the concentration found in the clayey soil. It is important to mention that: (1) PG samples usually have low ^{238}U concentration compared to other natural radionuclides. In phosphoric rock, members of the natural series of U-238 and Th-232 are in radioactive equilibrium. During acid attack to phosphoric rocks, phosphoric acid is enriched with U-238, while Th-232, isotopes of radium, and Pb-210 tend to concentrate in phosphogypsum; (2) Brazilian phosphoric rock has an igneous origin, with smaller U-238 concentrations than Th-232 concentrations; and (3) the clayey soil used in this study was developed from weathering of granite rocks over 2,700 million years old which typically present contents of U-238 from 5 to 10 ppm.

Table I. Results for natural radionuclides activity concentrations of PG and soil samples.

Activity Concentration (Bq.kg ⁻¹)	Samples		
	PG	Sandy Soil	Clayey Soil
U-238	80 ± 20	<50	150 ± 25
Th-232	111 ± 13	36 ± 1	117 ± 3
Ra-226	252 ± 26	< 20	69 ± 5
Ra-228	226 ± 29	34 ± 2	114 ± 5
Pb-210	206 ± 29	20 ± 5	50 ± 8
Po-210	230 ± 26	<13	43 ± 6

An average activity concentration value of 206 ± 29 Bq kg⁻¹ was found for Pb-210, within the same order of magnitude reported by Silva [4]. The value found in this study for lead was similar to the value found for Po-210 (230 ± 26 Bq kg⁻¹), implying that there was radioactive equilibrium between these two radionuclides. Findings from this study ensured that Ra-226, Ra-228, Pb-210, and Po-210 are predominantly incorporated to phosphogypsum.

This study found higher activity concentrations for all studied radionuclides in Red- Yellow Latosol (clayey). U-238 average activity in this soil (150 ± 25 Bq kg⁻¹) was above the value found in phosphogypsum (78 ± 10 Bq kg⁻¹). This is due to the fact that this soil comes from a region characterized by sedimentary rocks, formed from weathering of granitic rocks and enriched with uranium [24].

According to UNSCEAR [25], U-238, Ra-228, and Ra-226 specific activities in soils vary from 16-110 Bq kg⁻¹, 11-64 Bq kg⁻¹, and 17-60 Bq kg⁻¹, respectively. Evidently this value depends on site geological characteristics. As normally observed in Brazilian soils, Ra-228 activity (114 ± 5 Bq kg⁻¹ and 34 ± 2 Bq kg⁻¹ for clayey and sandy soils, respectively) was above the activity found for Ra-226 (69 ± 5 Bq kg⁻¹ and < 20 Bq kg⁻¹ for clayey and sandy soils, respectively).

Pb-210 average activity was found to be 50 ± 8 Bq kg⁻¹ for clayey soil and 20 ± 5 Bq kg⁻¹ for sandy soil in this study. Po-210 activity concentration was equivalent to 43 ± 6 Bq kg⁻¹ and <13 Bq kg⁻¹, for clayey soil and sandy soil, respectively. Analysis of a reference material (IAEA/Soil 7) provided by the International Atomic Energy Agency, was accomplished in order to provide some type of quality control. Results obtained were within the specified value range for the reference material, ensuring good method accuracy.

Papastefanou *et al.* [10] studied soils fertilized with phosphogypsum in Greece and some cultivated products. The authors presented values for Ra-226, Ra-228, and Pb-210 in soils in the ranges of 50 - 479 Bq kg⁻¹, 28 - 55 Bq kg⁻¹, and 105 - 585 Bq kg⁻¹, respectively. Such values are much smaller than the values found in this study for soils fertilized with phosphogypsum in Brazil; except for Ra-228, which presented values similar to the average found for sandy soil (30 Bq kg⁻¹). Ra-226 activity concentration varied from 49 - 58 Bq kg⁻¹ for clayey soil, while the activity concentration found in sandy soil was < 20 Bq kg⁻¹.

Average Pb-210 activity was 47 Bq kg^{-1} and $< 30 \text{ Bq kg}^{-1}$ for clayey and sandy soil, respectively. Po-210 activity concentration varied between $38 - 42 \text{ Bq kg}^{-1}$ and $< 11 \text{ Bq kg}^{-1}$ in clayey and sandy soil, respectively.

For clayey soil, U-238 activity concentrations varied from $125-142 \text{ Bq kg}^{-1}$ and $109-116 \text{ Bq kg}^{-1}$ for Th-232. Activity concentrations for U-238 and Th-232 in sandy soil were lower than 50 Bq kg^{-1} and 31 Bq kg^{-1} , respectively. Umisedo [26] evaluated and compared U-238 and Th-232 activity concentrations in fertilized soils from São Paulo Metropolitan Region and concluded that Th-232 activity concentrations were similar to U-238. Average activity values for fertilized soils were 66 Bq kg^{-1} and 71 Bq kg^{-1} for Th-232 and U-238, respectively. These values are much higher than the values found in this study for sandy soil and smaller than values found for clayey soil.

Radionuclide Activity Concentration in Plants

Ribeiro [3] measured radionuclide activity concentrations in lettuce (dry weight) cultivated in Brazilian soil fertilized with several fertilizers, and found values from 0.32 to 2.77 Bq kg^{-1} for Ra-226; 0.13 to 7.5 Bq kg^{-1} for Ra-228; and 0.94 to 8.48 Bq kg^{-1} for Pb-210. This study found maximum activity concentration values for lettuce equivalent to 2.0 Bq kg^{-1} for Ra-226; 8.0 Bq kg^{-1} for Ra-228; and $< 8.0 \text{ Bq kg}^{-1}$ for Pb-210. The same author also analyzed bean samples, which along with soy, belongs to the leguminous family, and found Pb-210 activity values of up to 8.1 Bq kg^{-1} . The value found for soy in this study was of 9.0 Bq kg^{-1} . These results indicated that employment of phosphogypsum residue may concentrate fewer amounts of radionuclides in the plants when compared to other fertilizers.

Activity of Radionuclides in Leached Water Samples

Activity concentrations found in leached water samples were very low, most of them below the Minimum Detectable Activity ($< 0.110 \text{ Bq kg}^{-1}$ for U-238, $< 0.006 \text{ Bq Kg}^{-1}$ for Th-232 and Po-210, and $< 0.02 \text{ Bq kg}^{-1}$ for Ra-226, Ra-228, and Pb-210).

There is practically no difference observed between values for that sample with maximum phosphogypsum dosage and the reference sample (without PG), which indicates that contamination of both soils by PG (sandy and clayey), for all doses considered, did not result in radionuclide leaching into soil profiles.

Estimation of Soil-Plant Transference Factors

As mentioned earlier, Transfer Factor (FT) is defined as the ratio between radionuclide concentrations in plant and soil, in the root zone, expressed as Bq kg^{-1} (dry weight). This study calculated radionuclide FTs for those conditions in which specific activity were found to be above the Minimum Detectable Activity. Thus only Th-232 and Ra-228 Transfer Factors were obtained for sandy soil.

According to Portilho [27], the fact that FTs are larger in sandy soils can be explained due to less organic matter content, low cationic exchange capacity, leading to low radionuclide

retention and availability to the plant. It is worth mentioning that larger FT values obtained are those corresponding to radium isotopes, in lettuce and soy cultures.

Calcium demand by these plants is higher and radium has similar chemical and metabolic behavior as compared to calcium. In addition, soy is a plant that fixes atmospheric Nitrogen, and as such, its nitrate absorption is limited. This causes an “unbalance” in adsorbed cation /anion ratio, which is compensated by proton extrusion acidifying the rizosphere. As a consequence, there is an increase in solubility for several elements in the region next to the root system, facilitating absorption of nuclides by the plant.

Results obtained in this study indicated that in a general way, radionuclide mobility was low in both soils studied. It must be emphasized that the process involving radionuclide mobility in soil is very complex and it depends on many factors involving physical, chemical, and biological soil characteristics.

Tables II and III present Transfer Factor results for lettuce, corn, and soy cultivated in clayed and sandy soil, respectively.

Table II. Soil-Plant Transference Factor (clayey soil).

PG Dose	U-238	²³² Th-232	Ra-226	Ra-228	Pb-210	Po-210
0 NG	1.6E-03	2.6E-03	1.0E-01	2.0E-02	8.6E-02	7.7E-02
0.5 NG	1.6E-03	7.6E-03	1.7E-01	5.1E-02	9.8E-02	5.3E-02
1.0 NG	2.2E-03	3.1E-03	2.2E-01	8.4E-02	9.3E-02	2.9E-02
2.0 NG	1.0E-03	5.1E-03	1.5E-01	4.3E-02	8.5E-02	4.8E-02

Table III. Soil-Plant Transference Factor (sandy soil).

PG Dose	U-238	Th-232
0 NG	2.4E-02	2.0E-01
0.5 NG	2.0E-02	3.9E-01
1.0 NG	2.9E-02	6.4E-01
2.0 NG	3.3E-02	5.8E-01

Dose Estimation

This study estimated the effective equivalent annual dose considering only average specific activities for radionuclides that were superior to the Minimum Detectable Activity.

Measured committed effective dose ($1.3E-02 \text{ mSv year}^{-1}$) was below the dose restriction limit established for the general public by the International Commission on Radiological Protection [28], equivalent to $0.3 \text{ mSv year}^{-1}$ (see Table IV). Evidently this result is due to the small fraction represented by the plants studied in a typical daily diet [29]. It can be inferred that phosphogypsum application, in clayey and sandy soil, did not result in increased human exposure to natural radioactivity, in the current experimental conditions.

Table IV. Results of the Committed Effective Dose Estimation for each type of crop.

Nuclide	Type of crop		
	Lettuce	Soy	Corn
	Committed Effective Dose (mSv year ⁻¹)		
U-238	5.9E-05	8.6E-06	-
Th-232	1.3E-04	2.7E-05	2.0E-04
Ra-226	4.6E-04	1.1E-03	-
Ra-228	4.8E-03	3.2E-03	-
Pb-210	-	1.2E-03	-
Po-210	1.7E-03	-	-
Total dose ((mSv year ⁻¹)	1.3E-02		

CONCLUSION

This residue was classified as Class IIA according to ABNT NBR 10004:2004 Technical Norm. Chemical analyses revealed predominance of calcium and sulfur (40.12% CaO and 58.12% SO₄), compatible with values found in phosphate fertilizers.

Both soils had elevated acidity and low organic matter content; typical from Cerrado region. Ra-226 average activity in PG (252 ± 26 Bq kg⁻¹) was below EPA recommended limit (370 Bq kg⁻¹) for its use in agriculture activities.

Ra-226, Pb-210, and Po-210 activity concentration values were within the same order of magnitude as Ra-226, U-238 and Th-232 activities were smaller, indicating that there is an equilibrium break during digestion of phosphate rocks, with radionuclide redistribution: 80% of U-238 and 70% of Th-232 end up in phosphoric acid, while 80% of Ra-226, Ra-228, Pb-210, and Po-210 end up in phosphogypsum.

Transfer factors obtained for plants studied varied from 9.4E-04 to 3.4E-01, considering all radionuclides. Generally, results from this study indicated that radionuclide mobility in soils was low.

Total compromised effective dose was determined to be 1.3E-02 mSv year⁻¹ for the general public, which is below the ICRP recommended dose limit restriction (0.3 mSv year⁻¹). Thus phosphogypsum was found to be adequate for use in Cerrado agricultural activities.

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REFERENCES

- [1] CANUT, M. Estudo da viabilidade da substituição do gesso pelo rejeito Fosfogesso em material de construção. Belo Horizonte, Master Thesis (2006).
- [2] MAZZILLI, B., PALMIRO, V., SAUEIA, C., NISTI, M.B. Radiochemical characterization of Brazilian phosphogypsum. *Journal of Environmental Radioactivity*, 49, 113 – 122 (2000).
- [3] RIBEIRO, F. C. A. Manejo agrícola e teores de radionuclídeos naturais em vegetais cultivados no Rio de Janeiro. Rio de Janeiro, Master Thesis (2004).
- [4] SILVA, L.H.C. Aspectos econômico-ambientais do uso do fosfogesso na agricultura. Rio de Janeiro, Master Thesis (1997).
- [5] CFSEMG. Recomendações para o uso de corretivos e fertilizantes em Minas Gerais, Comissão de Fertilidade do Solo do Estado de Minas Gerais, Lavras (1999).
- [6] EMBRAPA. Uso de gesso agrícola nos solos do Cerrado, Empresa Brasileira de Pesquisa Agropecuária, Planaltina (Circular Técnica 32) (2005).
- [7] CETESB. Aplicação de lodos de sistemas de tratamento biológico em áreas agrícolas - critérios para projeto e operação - Manual Técnico P- 4.230, Companhia de Tecnologia de Saneamento Ambiental, São Paulo (1999).
- [8] ANDRADE, J.C. & ABREU, M.F. Análise química de resíduos sólidos para monitoramento e estudos agroambientais. Editora do Instituto Agronômico de Campinas, Campinas (2006).
- [9] MORTVERDT, J.J. Plant and soil relationships of uranium and thorium decay series radionuclides - A review. *Journal of Environmental Quality*, 23, 643–650 (1994).
- [10] PAPASTEFANOU, C., STOULOS, S., IOANNIDOU, A., MANOLOPOULOU, M. The application of phosphogypsum in agriculture and the radiological impact. *Journal of Environmental Radioactivity*, 89, 188 – 198 (2006).
- [11] HEPPARD, M.I. & SHEPPARD, S.C. The plant concentration concept as applied to natural uranium. *Health Physics*, 48, 494–500 (1985).
- [12] BETTENCOURT, A.O., TEIXEIRA, M.M.G.R., ELIAS, M.D.T., FAISCA, M.C. Soil to plant transfer of Ra-226. *Journal of Environmental Radioactivity*, 6, 49–60 (1988).
- [13] USEPA. Background Information Document: Statistical Procedures for Certifying Phosphogypsum for Entry Into Commerce, As Required by Section 61.207 of 40 CFR Part 61, U.S. Environmental Protection Agency, Washington, DC 402-R-98-008 (1988).
- [14] ASSOCIAÇÃO BRASILEIRA DE NORMAS. ABNT NBR 10005:2004. Procedimento para obtenção de extrato lixiviador de resíduos sólidos (2004).

- [15] ASSOCIAÇÃO BRASILEIRA DE NORMAS. ABNT NBR 10006:2004. Procedimento para obtenção de extrato solubilizado de resíduos sólidos (2004).
- [16] ASSOCIAÇÃO BRASILEIRA DE NORMAS. ABNT NBR 10004:2004. Resíduos sólidos – Classificação (2004).
- [17] ALVAREZ, V. V. H. Equilíbrio de formas disponíveis de fósforo e enxofre em dois Latossolos de Minas Gerais. Viçosa, Master Thesis (1974).
- [18] SIQUEIRA, M.C. Caracterização radioquímica do Fosfogesso para sua utilização na agricultura na região do Cerrado. São Carlos, Master Thesis (2009).
- [19] SAVVIN, S.B. Analytical use of Arsenazo III. Determination of thorium, zirconium, uranium and rare earth elements. *Talanta* 8: 673-685 (1961).
- [20] DE CORTE, F. The k₀ - standardisation method: a move to the optimisation of neutron activation analysis. Rijksuniversiteit Gent, Faculteit Van de Wetenschappen, Thesis (Doctor) (1986).
- [21] MENEZES, M.A.B.C. & JACIMOVIC, R. Optimized k₀-instrumental neutron activation method using the TRIGA MARK I IPR-R1 reactor at CDTN/CNEN. *Nuclear Instruments & Methods in Physics Research*, 564: 707 – 715 (2006).
- [22] VAJDA, N., LAROSA, J., ZEISLER, R., DANESI, P., & KIS-BENEDEK, G. A novel technique for the simultaneous determination of Pb-210 and Po-210 using a crown ether. *Journal of Environmental Radioactivity*, 37(3): 355 – 372 (1997).
- [23] CUTSHALL, N.H., LARSE, I.L., OLSEC, C.R. 1983. Direct analysis of Pb-210 in sediment samples: self-absorption corrections”. *Nuclear Instruments and Methods*, 206: 309 – 315 (1983).
- [24] CETEM. Impactos Radiológicos na Indústria do Fosfato. Série Estudos e Documentos - CETEM/MCT56, Centro de Tecnologia Mineral, Rio de Janeiro (2004).
- [25] UNSCEAR. Sources and effects of ionizing radiation. In: United Nations Scientific Committee on the Effects of Atomic Radiation. United Nations, New York (2000).
- [26] UMISEDÓ, N.K. Dose de radiação ionizante decorrente do uso de fertilizantes agrícolas. São Paulo, Ph.D Thesis, (2007).
- [27] PORTILHO, A.P. A influência da adição de composto orgânico na mobilidade e biodisponibilidade do Cs-137 e do Co-60 em solos tropicais. Rio de Janeiro, Master Thesis (2005).
- [28] ICRP. Annual limits on intake of radionuclides by workers based on the 1990 Recommendations, International Commission on Radiological Protection, Oxfordshire, vol. 21 (4), Publication 61 (1991).

[29] IBGE. Instituto Brasileiro de Geografia e Estatística; Ministério do Planejamento, Orçamento e Gestão. Estimativas populacionais 1980 – 2010: Brasil, regiões geográficas e unidades da federação, Rio de Janeiro (Brasil): IBGE (2004).