

The Geochemistry of Natural Radionuclides in Saline Soils from Brazil Treated with Phosphogypsum Imbituba

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Abstract The soil saltiness in the Brazilian semiarid environment is a common problem caused by incorrect agricultural practices, allied to the local weather and soil condition. The use of phosphogypsum (PG) to recover these soils still is a concern since this material has in its composition natural radionuclides. An experiment was conducted to study the use of phosphogypsum to reduce the salinity and evaluate the bioavailability of radionuclides on the Brazilian semiarid region soils. The radionuclide content of phosphogypsum samples were previously analyzed by gamma spectrometry. Three different doses of phosphogypsum were mixed with samples of surface soil in the greenhouse, and after a reaction time and irrigation, controlled soil samples + phosphogypsum underwent simple extractions based on the sequential extraction method by Tessier et al. Ra isotopes and ^{210}Pb in the extracted fractions were analyzed by counting alpha and beta. The higher concentration of Ra isotopes and ^{210}Pb were associated to residual

fraction, followed by exchangeable fraction due to the low levels of carbonates, organic matter, and manganese and iron oxides. The use of phosphogypsum studied did not contribute to increase the ^{226}Ra activity on the analyzed soils. ^{226}Ra levels in phosphogypsum were lower than those recommended by the USEPA to allow the use of phosphogypsum in agricultural soils, but can contribute to the accumulation of ^{228}Ra and ^{210}Pb . The phosphogypsum Imbituba promoted a satisfactory reduction of electrical conductivity in the soils, which indicates the possibility of recovery of these soils.

Keywords Radioisotopes · NORM · Sequential extraction

1 Introduction

The origin of saline and sodic soils is a phenomenon observed particularly under arid conditions. The high evaporation rates and low rainfall associated with the source material characteristics and the geomorphological and hydrological conditions affects the formation of soils with high levels of soluble salts and exchangeable sodium, which undermine the growth and development of crops (Whitemore 1975).

Although the semiarid soil usually presents high-activity clay, high percentages of base saturation, high pH, and the presence of salts often hinder the development of plants. According to Malavolta (1991), when the pH is slightly alkaline, crop development may be impaired due to low availability of phosphorus and/or micronutrients

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such as iron, manganese, copper, and zinc. On the other hand, according to Sharpley and Menzel (1987) in sodic soils there may be greater availability of phosphorus to the plants, since sodium saturation increases the phosphorus content in the exchange complex. Sodium, substituting calcium, magnesium, and aluminum on the exchange sites, causes the negative potential of the surface increases, leading to desorption of phosphorus.

According to FAO (2010), the use of conditioners such as phosphogypsum (PG), sulfuric acid, sulfur, or application of large amounts of organic matter is the solution to soil salinity and sodicity problems.

In Brazil and in the world, phosphogypsum is stored in large stacks of tailings in areas close to the phosphoric acid industry. As a by-product of this process, in order to reduce the amount of stored waste, stored, has been conducted economic, agronomic and environmental studies, determining the natural radionuclides content aimed at new applications that material.

The presence of natural radionuclides in the phosphogypsum can promote an increase on the concentration of these elements in agricultural soils and thus increase their absorption by the plant. Therefore, knowledge of their behavior is an important tool to understand their effects on the environment.

Radionuclides occur in soil associated with different chemical fractions, depending on environmental factors, such as climate and soil (pH, organic matter, and mineral composition, etc.) and physical and chemical forms of the element. The determination of the binding forms provides useful information about their mobility and bioavailability. However, the soil is a complex environment whose determination of the matrix and the kind of chemical bonding is difficult. One option to determine this is the application extraction methods or fractions coupled with analytical procedures. The most common methods are simple extraction and sequential chemical extractions, developed with the objective of identifying reversible and irreversible chemical bonds in the soil, the possibility of migration of radionuclides of the soil and environment, and the possibility of capture of vegetables and other foods (Blanco et al. 2004). The results show evidence of possible geochemical radionuclide associations with soil components, but the sequential extractions may present some difficulties, such as the element of the re-adsorption on solids before the separation of the aqueous and solid phases, low selectivity of extractors, and incomplete dissolution of landing fractions (Schultz et al. 1998). Simple extractions are the

fraction methods using a single extraction agent, but also these present some problems, such as the extraction of the soluble fraction of the aqueous reactant and the possibility of a puller to affect the extraction of amounts of elements that are not of interest; this so simple extraction procedure cannot be applied to many studies.

However, in spite of decades in which the simple extraction and sequential methods have been developed, studied, and applied, no method has been considered universally accepted to date. Many methods have been tested with focus on the extraction of heavy metals in soil, but the one developed by Tessier et al. (1979) has been widely applied, and adapted to radionuclides. By this method, various reagents are applied sequentially (each extractor is more chemically active than the previous) delimiting different fractions: exchangeable (F1) associated with carbonates (F2) connected to the iron and manganese oxides (F3) on the organic matter (F4) and the residual (F5).

The classical Tessier protocol (Tessier et al. 1979) was developed for sediments, which led to the need to generate a protocol adapted for tropical soils. For studies of the mobility of radionuclides in soils, the adapted Tessier method developed by Wasserman et al. (2005) is the one that has presented the best results.

In this context, the objective of this study was to evaluate the behavior of natural radionuclides (^{210}Pb , ^{226}Ra , and ^{228}Ra) in saline soils treated with phosphogypsum, using a simple extraction procedure. We also evaluated the potential of phosphogypsum to reduce the concentrations of the exchangeable sodium and the electrical conductivity as recovery indicators of degraded soils.

2 Material and Methods

2.1 Phosphogypsum Collected

Samples of phosphogypsum were collected from a stack situated in the city of Imbituba, southern coast of the Brazilian state of Santa Catarina ($28^{\circ} 13' 17''$ S and $48^{\circ} 38' 21''$ W). This material was produced by a phosphoric acid industry that used not only mainly igneous phosphate rocks but also sedimentary phosphate rocks from Brazil and others countries. The samples were homogenized, sieved on a 2-mm sieve and stored in polystyrene containers of 300-cm³ capability. After the hermetic sealing, the samples were stored for 30 days to obtain the radioactive equilibrium of the natural series.

Afterwards, these samples were subjected to direct gamma spectrometry in a hyper pure germanium detector system (Ortec Inc.) in the Nuclear Chemistry Laboratory at Universidade Federal Fluminense (UFF), calibrated through the relation energy channel, with radioactive sources of ^{152}Eu or ^{60}Co (Amersham Inc.). The efficiency and resolution of the detector were, respectively, 45% and 2.3 keV for the 1332 keV ^{60}Co photopeak, for 4096 channels. The background radiation and the efficiency curve were previously calculated.

The concentration of ^{226}Ra was determined through the daughters ^{214}Pb (295.21 keV and 351.93 keV) and ^{214}Bi (609.32 keV). ^{228}Ra was determined by the photopeaks of ^{228}Ac (911.20 and 968.96 keV). The counting time of each sample was 86,000 s. The respective spectrum of each sample was collected with the software Maestro, developed by Ortec Inc. (Bellido et al. 1994) and the spectra analysis were done with the software Aptec-NRC.

2.2 Saline Soils Collected and Chemical Analyses in Soils

Two soils of wide occurrence at the Brazilian semiarid region were selected for this study. They were sampled at the municipality of Belém de São Francisco, on the Brazilian state of Pernambuco, and classified following EMBRAPA 1999 and FAO 2010 classification systems as Fluvisol (FL), located at $38^{\circ} 57' 52.80''$ W and $08^{\circ} 41' 35.54''$ S and collected on the irrigated perimeter of Manga de Baixo, and the other is a Luvisol (LV), located at $39^{\circ} 03' 59.15''$ W and $08^{\circ} 41' 08.39''$ S on a farm. Fluvisol is soil that occurs on wetlands, associated with recent sediments of fluvial origin and, when formed on semiarid environments, often presents with soluble salts or exchangeable sodium in its composition as limitations to its use on agriculture. The Luvisol is a shallow soil, typically occurring on semiarid environments, with a large difference on the sand/clay relation between the A and B horizons. It usually presents stoniness on the surface and high levels of exchangeable calcium and magnesium, and is also subject to salinization. Both sampled soils were cultivated with onion and rice and then were abandoned due to the salinity. Twenty-four samples of 12 kg (12 samples to each soil) were collected from the first 20 cm depth from both soils, and an experiment with these soil samples was conducted in a greenhouse.

The soils were analyzed for fertility and electric conductivity (EC). The following parameters are determined: potential of hydrogen (pH), potential acidity (hydrogen and aluminum exchangeable), organic carbon, the exchangeable (potassium, calcium, magnesium, and sodium) bases, and the exchangeable phosphorus. They were also calculated for cation exchange capacity (CEC) and base saturation (V%), EMBRAPA (1997).

The soils were also analyzed by X-ray fluorescence using X-ray fluorescence equipment by dispersive energy (EDXRF) by Shimadzu brand, EDX 800 HS model. About 10 elements, including Ca, S, Na, Al, Fe, Si, P, Na, K and Mn were evaluated by X-ray diffraction. Particle size was determined using the CILAS model 1064 laser particle analyzer. The classification curve was calculated using the GRADISTAT Statistical Program 4.0.

2.3 Experiment in Greenhouse

The soil amendment experiment consisted on testing three requirements of phosphogypsum (zero, one, and twice the required) based on Eq. (1) (Ribeiro et al. 2003):

$$\text{RP} = (\text{ESP}_i - \text{ESP}_f) \times h \times \text{CEC} \times \text{MW} (\text{CaSO}_4) \times D_s \quad (1)$$

where

- RP is the required amount of phosphogypsum or dose of phosphogypsum used (kg ha^{-1})
- ESP_i is the exchangeable sodium percentage, found in the chemical analysis of the soil (%)
- ESP_f is the final exchangeable sodium percentage in the soil, stipulated on 10% of ESP_i (%)
- h is the depth of application of phosphogypsum that will be applied (0.20 m)
- CEC is the cation exchange capacity ($\text{cmol}_c \text{ dm}^{-3}$)
- MW is the molecular weight of the calcium sulfate ($\text{g} \cdot \text{mol}^{-1}$)
- D_s is the density of the soil (kg dm^{-3})

The ESP_i was calculated following the Eq. (2):

$$\text{ESP}_i = \frac{\text{Na} \times 100}{\text{CEC}} \quad (2)$$

The soil samples were packed in individual buckets with 12 dm^3 of capability and drained with a hole in the bottom, where a 1-dm^3 polyethylene bottle was

engaged. So, each soil sample composed a plot, and each plot received the required amount of phosphogypsum as calculated by the Eq. (1) as a treatment on three repetitions: 0 ton ha⁻¹ (no RP), 16 ton ha⁻¹ (one RP) and 32 ton ha⁻¹ (2 RP) to soil FL and 0 ton ha⁻¹ (no RP), 18 ton ha⁻¹ (one RP) and 36 ton ha⁻¹ (2 RP) to soil LV. The RP was mixed on the 20-cm layer of soils and 1 L of irrigation water every day. After 30 days, samples of 300 g were collected from each bucket, representing each soil and PG amount, homogenized, air dried, ground on a mortar and pestle sieved with a 200- μ m sieve, and then submitted to a quartering.

Subsequently, approximately 5 g were removed and subjected to sequential extraction according to Tessier et al. 1979, with five extraction fractions (Table 1). These extracting steps were done as single extractions, not sequentially, to avoid interferences on the extractions caused by the reagents.

The radium isotopes and ²¹⁰Pb on the extract solution of each fraction were co-precipitated as Ba(Ra,Pb)SO₄ by adding H₂SO₄ and BaCl₂ to one-litter samples. The mixed sulfates were washed and dissolved with nitrilotriacetic acid (NTA). Barium (radium) sulfate was re-precipitated by adding acetic acid until pH 4.5–5.0, whereas lead remained in the aqueous phase. The aqueous and solid phases were separated and the Ba(Ra)SO₄ was purified by dissolution in an ethylenedinitrilo-tetraacetic acid disodium salt, dihydrated (EDTA) in solution at pH 10. Then, the sulfate mixture was again precipitated by acetic acid (pH 4.5–5.0) and filtrated. After 1 month of daughter product growth, ²²⁶Ra was determined by gross alpha counting. ²²⁸Ra was determined by beta counting, whereas the alpha particles of ²²⁶Ra were stopped by a filter paper. Corrections were made if there was any contribution from

the daughter products of ²²⁶Ra (Godoy et al. 1994). The radium isotopes and ²¹⁰Pb counting was performed by alpha and beta counting on a gas flow proportional detector from Canberra, Inc., model S5XLB. These analyses were performed by the Environmental Division laboratories of the CRCN-NE/CNEN at Recife that participate on interlaboratory comparison exercises organized by the IRD/CNEN, Rio de Janeiro.

2.4 Statistical Analysis

In order to evaluate the existence of statistically significant differences between treatments with different doses of phosphogypsum, for each of the radionuclides in the samples analyzed of Fluvisol and Luvisol, the nonparametric Kruskal-Wallis test was conducted. This test assesses whether the set data represent the same population by comparing medians, calculating a significance level called *p* value. For a confidence level of 95%, there is a statistically significant difference, where the *p* value is equal to or less than 0.05 (Kleinbaum et al. 1998).

In order to verify how the chemical fractions contribute to this characterization of the availability of radionuclides and how they relate to the evaluated soils, correlation analyses were performed. Analyses were performed using the STATISTICA 7 software (Copyright © 1984–1987, StatSoft, Inc.).

3 Results

3.1 Chemical and Physical Compositions of Saline Soils

The results of fertility, electrical conductivity (EC), and sieve analysis are shown in Table 2.

These results confirm that the Fluvisol and Luvisol are classified as saline-sodic soils, this characteristic generates a very small osmotic potential, and this phenomenon limits the water uptake by plants.

The pH of both soils is classified as slightly acid, being inappropriate for most crops cultivated in this region. As for the P content, the soils have very different concentrations, ranging from values considered average in Luvisol (9 mg dm⁻³) to high values in Fluvisol (27 mg dm⁻³).

The most abundant particle size class in both soils was silt, ranging between 53.6 and 59.7% in Luvisol and Fluvisol, respectively. The percentage of clay was small, which may be associated with the

Table 1 Description of the radionuclide sequential extraction procedures

Metal forms	Extraction procedure
Free exchange forms (F1)	1 M MgCl ₂ (PH 7, 2 h, 25 °C)
Bound with carbonates forms (F2)	1 M CH ₃ COONa + CH ₃ COOH (PH 5, 12 h, 25 °C)
Bound with Fe/Mn oxides forms (F3)	0.1 M NH ₂ OH.HCl + 0.01 M HNO ₃ (pH 2, 12 h, 25 °C)
Bound with organic forms (F4)	30% H ₂ O ₂ + 0.01 M HNO ₃ (pH 2,3 h, 80 °C)
Residual forms (F5)	Água régia (HCl and HNO ₃) + HF

Adapted from Tessier et al. (1979) by Wasserman et al. (2005)

Table 2 Chemical and physical characteristics of the soils

Soil	pH (H ₂ O) (1:2.5)	Ca ²⁺ cmol _c dm ⁻³	Mg ²⁺ cmol _c dm ⁻³	Na ⁺	K ⁺	Al ³⁺	H ⁺	EC mS cm ⁻¹	P mg dm ⁻³	EPS (%)	V (%)	Areia (%)	Silte (%)	Argila (%)
Fluvisol (FL)	5.20	10.45	3.95	7.00	0.24	nd	3.38	15.87	27	28.00	87	32.1	59.7	8.2
Luvisol (LV)	6.30	16.25	12.75	7.83	0.40	nd	0.24	83.34	9	20.86	99	35.3	53.6	11.1

Soil density: FL = 0.95 g cm⁻³ and LV = 0.96 g cm⁻³ EMBRAPA 1999

nd not detected

presence of salt, which has the ability to dissipate clay and promote breakdown of soil structure. Soils with these characteristics can be classified as silt texture and therefore present a considerable specific surface.

Table 3 shows the results of fluorescence X-ray (XRF). These results show that soils have high levels of SiO₃ and Al₂O₃, and low-Fe₂O₃.

The phosphogypsum, as expected, showed higher values of SO₃ and CaO. The amounts of P₂O₅ were small, showing that phosphogypsum will not act as phosphate fertilizer, but as a source of calcium and sulfur to the soil, acting also in reducing the potential acidity and reducing electrical conductivity. These results corroborate to the P₂O₅ data found by Jacomino (2008) and are of the order of 1.2% in the phosphogypsum collected in Unit Fosfertil / Uberaba - MG.

Table 3 Characterization of the chemical composition of saline soils and phosphogypsum

Mineral	PG	Luvisol	Fluvisol
SiO ₂	0.638 ± 0.014	74.801 ± 0.002	62.860 ± 0.002
SO ₃	50.983 ± 0.019	1.063 ± 0.002	0.365 ± 0.002
Al ₂ O ₃	nd	10.952 ± 0.003	20.570 ± 0.003
P ₂ O ₅	3.419 ± 0.014	nd	3.419 ± 0.002
Cl	nd	1.267 ± 0.001	4.332 ± 0.001
Fe ₂ O ₃	0.802 ± 0.019	2.301 ± 0.002	5.777 ± 0.002
K ₂ O	nd	1.864 ± 0.002	2.595 ± 0.002
MgO	nd	1.296 ± 0.002	1.520 ± 0.003
CaO	40.478 ± 0.016	1.144 ± 0.003	2.460 ± 0.002
Na ₂ O	nd	1.141 ± 0.002	1.215 ± 0.001
SrO	0.907 ± 0.018	0.013 ± 0.001	0.030 ± 0.002

Determined by X-ray fluorescence (%). Raw average (n = 3)

nd not detected

3.2 Concentration of Radionuclides in Phosphogypsum

Table 4 shows the average activity values of natural radionuclides present in phosphogypsum samples of Imbituba and other countries. The average activity of ²²⁶Ra was 95 Bq kg⁻¹ and ²²⁸Ra was 181 Bq kg⁻¹ and were below the limit recommended by the US Environmental Protection Agency (EPA 1998) for the use of phosphogypsum in agriculture whose value is 370 Bq kg⁻¹.

It should be noted that the high concentrations of ²¹⁰Pb found in phosphogypsum from Imbituba, may be associated the low mobility of ²¹⁰Pb which favors the concentration of this element, associated also with the fact of the phosphogypsum stack is old.

Comparing natural radionuclide activity values found in this study with the values of national and international literature, the obtained values were well below those found in the literature, except for the ²¹⁰Pb as noted in Table 4. Probably the difference in the activity of natural radionuclides in different sources of phosphogypsum is due to the different types of phosphate rocks used in the production of phosphoric acid and to the industrial type it was applied to.

3.3 Geochemical Radionuclide Fraction Differences in Soil

Soils were fertilized according to the following recommendations: 0 RP, 1RP, and 2RP. For each condition, the average of three replications was considered for each experiment. Saline soils used in this experiment were the Luvisol and Fluvisol of Recife. Data on the concentration of radionuclides in each single extraction fraction, according to Tessier-Wasserman methodology, can be seen in Fig. 1.

Analyzing the above results, it can be concluded that the studied radionuclides ²¹⁰Pb, ²²⁶Ra, and ²²⁸Ra are

Table 4 Concentration activity of natural radionuclides on PG produced worldwide and this study

Country	Reference	Rock of origin	^{226}Ra , Bq kg $^{-1}$	^{210}Pb , Bq kg $^{-1}$	^{228}Ra , Bq kg $^{-1}$
USA (Flórida)	Rutherford et al. 1994	Flórida central	1140	1370	nd
Austrália	Rutherford et al. 1994	Numerous	500	nd	nd
Espanha	Borrego et al. 2007	Morocco	620	nd	nd
Índia	Burnett and Hull 1996	Vadorado	510	490	nd
Brazil	Mazzilli et al. 2000	Cubatão	225	275	nd
Brazil	Jacomino 2007	Uberaba	252	206	226
This study	Borges et al. 2013	Imbituba	95	388	181

nd not detected

available in different fractions and different concentrations. The values of the dose 0 (ORP) for both soils can be regarded as the concentration in the natural ground, without adding the phosphogypsum.

In Fluvisol, the highest activity was found in the residual fraction (F5) and the lowest in the fraction associated with Fe and Mn oxides (F3) for ^{210}Pb and ^{226}Ra radionuclides. As for the ^{228}Ra , the lowest activity was observed on the bioavailable fraction (F1). However, geochemical fractions F2 and F4 were below the detection limit for the radionuclides ^{226}Ra , ^{228}Ra , and ^{210}Pb ; this fact can be explained by the small amount of carbonate minerals and due to the low content of organic matter associated with lack of induced plant activity, the high salinity in the soil,

and in the phosphogypsum due to its mineralogical composition. And in the case of ^{228}Ra , the F3 fraction was also not quantified.

The total activity and fraction F5 (residual) of natural radionuclides in Fluvisol and Luvisol soils increased with the application of phosphogypsum, corroborating with the literature, which states that the application of certain types of fertilizers or soil conditioners increase radionuclide activity. However, the 1RP and 2RP treatments showed no major differences in activity between these elements themselves, indicating that the increased amount of phosphogypsum applied does not interfere directly in the concentration of these elements (Table 5).

In Luvisol, the highest activity was found in the residual fraction (F5) and the lowest in the exchangeable fraction (F1), for the three evaluated radionuclides and the three treatments applied, as can be evaluated in Fig. 2.

4 Discussion

The ^{226}Ra activity in the F1 fraction in Fluvisol occurred only in 1RP treatment, with an activity of 0.85 Bq kg^{-1} , which corresponds to 4% of the total activity of this element, probably this low bioavailability of ^{226}Ra may be explained by Taskayev et al. (1977), which state that soils with high concentrations of calcium and magnesium affects Ra mobility and plant uptake which are reduced. Generally, the radio concentrations in soil are extremely low and geochemistry is controlled by specific adsorption reactions (inner sphere complexes) or non-specific adsorption (outer sphere complex) with minerals. Radium complexation with anionic species

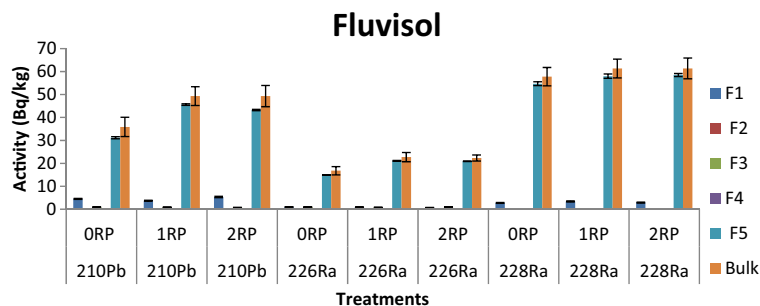


Fig. 1 Activity concentration of radionuclides ^{210}Pb , ^{226}Ra , and ^{228}Ra in geochemical fractions F1, F2, F3, F4, and F5 in the Fluvisol. Indicated in each value is a mean of three replicate measurements. RP required amount of phosphogypsum to reclaim

the soils based on Eq. (1), DL detection limits. ^{210}Pb DL $0.0005 \text{ Bq kg}^{-1}$, ^{226}Ra DL $0.0038 \text{ Bq kg}^{-1}$, and ^{228}Ra DL $0.0018 \text{ Bq kg}^{-1}$

Table 5 Kruskal-Wallis statistical analysis of variance for treatment with phosphogypsum in soils

Fluvisol	^{210}Pb 0RP	^{210}Pb 1RP	^{210}Pb 2RP	^{226}Ra 0RP	^{226}Ra 1RP	^{226}Ra 2RP	^{228}Ra 0RP	^{228}Ra 1RP	^{228}Ra 2RP
Value <i>p</i>	0.702	0.714	0.612	0.617	0.563	0.448	0.563	0.545	0.604
<i>n</i>	9	9	9	9	9	9	9	9	9
Luvisol	^{210}Pb 0RP	^{210}Pb 1RP	^{210}Pb 2RP	^{226}Ra 0RP	^{226}Ra 1RP	^{226}Ra 2RP	^{228}Ra 0RP	^{228}Ra 1RP	^{228}Ra 2RP
Value <i>p</i>	0.248	0.234	0.226	0.710	0.612	0.623	0.589	0.617	0.674
<i>n</i>	9	9	9	9	9	9	9	9	9

For a confidence level of 95%

in the soil, such as OH^- , Cl^- , F^- , SO_4^{2-} , and HCO_3^- acids and organic matter such as amino acids, fatty acids, hydrocarbons and phenols, urea, sugars, and humic and fulvic acids also occur.

F3 to Fluvisol, the ^{226}Ra activity was only found in 0RP and 2RP treatments with concentrations of 0.93 and 0.74 Bq kg^{-1} , respectively. Corresponding to 6 and 3% of the total activity of ^{226}Ra , it can be seen that the application of phosphogypsum contributed to the reduction of these elements in fraction F3, and consequently for the increase in the fraction F5, it is believed that this fact may be associated with formation of radium sulfate. According to Moore et al. 2003, radium sulfate tends to be the most insoluble alkaline of the earth sulfates and is a more radio-insoluble compound that is known. The great importance of this information lies in the fact that phosphogypsum is basically calcium sulfate, where calcium can be replaced by radio, and therefore, in these conditions, the application of phosphogypsum in soil will bring no major problems related to radio release to soil solution.

The highest concentration of ^{226}Ra was in the fraction F5 in all treated samples, yielding 15.82, 21.93 and 21.94 Bq kg^{-1} in 0RP, 1RP, and 2RP treatments, respectively, corresponding to 94, 96, and 97% of the total

activity of ^{226}Ra . Similar results were found by Lima and Penna-Franca (1998), who studied the geochemistry partition ^{226}Ra in four farms in the highlands of Poços de Caldas soils, also using the adaptation of the sequential extraction method of Tessier et al. (1979), and found that the average percentage for ^{226}Ra , which occurred naturally in soils, were 59% for the residual fraction.

For Fluvisol, the three treatments applied to the extraction of the five geochemical fractions at a depth of 0–20 cm, the ^{210}Pb activity extracted in the F1 phase (exchangeable fraction) was 4.5, 3.7, and 5.3 Bq kg^{-1} for treatments 0RP, 1RP, and 2RP, respectively, representing 12, 8, and 10% of ^{210}Pb . The small percentage of ^{210}Pb F1 (exchangeable fraction) have been observed in some studies and are related to low mobility and bioavailability of radionuclide (Köhler et al. 2000; Ewers et al. 2003). Low bioavailability results obtained for ^{210}Pb in this work are in accordance with those obtained by Vasconcellos et al. (1987) in 14 farms surrounding the uranium mine of Poços de Caldas soils. They reported that the ^{210}Pb activity in this fraction was detected in two samples, with nearby activities 6 Bq kg^{-1} dry soil.

In F3, the ^{210}Pb activities occurred only in 0RP and 2RP treatments, with values 0.22 and 0.74 Bq kg^{-1} ,

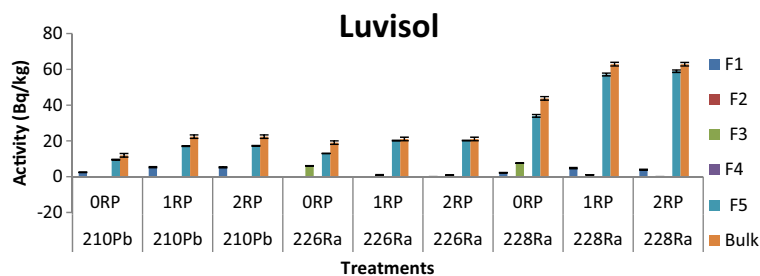


Fig. 2 Activity concentration of radionuclides ^{210}Pb , ^{226}Ra , and ^{228}Ra in geochemical fractions F1, F2, F3, F4, and F5 in the Luvisol. Indicated in each value is a mean of three replicate measurements. RP required amount of phosphogypsum to reclaim

the soils, based on Eq. (1), DL detection limits. ^{210}Pb DL 0.0005 Bq kg^{-1} , ^{226}Ra DL 0.0038 Bq kg^{-1} , and ^{228}Ra DL 0.0018 Bq kg^{-1}

respectively, equivalent to 2% of the total activity of ^{210}Pb . The average texture observed in this soil type may have influenced these concentrations. The high affinity of ^{210}Pb with the iron oxides has been observed in several studies (Köhler et al. 2000; Ewers et al. 2003). However, the small concentration of ^{210}Pb in the fraction associated with Fe and Mn oxides is because low levels of Fluvisol present iron oxides, as can be observed in the fluorescence X-rays.

The residual fraction (F5) predominated, ranging 86–92% in all treatments, ^{210}Pb concentrations of 35.87, 45.3, and 45.31 Bq kg⁻¹ in ORP, 1RP, and 2RP doses, respectively. These results demonstrate that the radionuclide is predominantly associated with the crystal structure of the ground mineral and exhibits very low bioavailability of ecological processes.

The ^{228}Ra activity extracted in the F1 phase (exchangeable fraction), on three treatments, presented the activities 2.72, 3.35, and 2.88 Bq kg⁻¹, corresponding to 6, 6, and 5% of the total activity of ^{228}Ra in ORP, 1RP, and 2RP treatments, respectively. The results of this study demonstrates the low concentration of ^{228}Ra in the exchangeable fraction, even in the treatments that received phosphogypsum; these results are confirmed by the works of Degetto et al. (2000) and Santos (2002) who studied the piles of phosphogypsum in Italy and Cubatão, respectively, and confirm the low solubility of ^{228}Ra in this substrate.

The residual fraction (F5) ^{228}Ra was prevalent in all treatments, with activities 54.7, 58, and 58.5 Bq kg⁻¹, equating to 94, 94, and 95% of the total activity. The fact that this element is associated with more recalcitrant fraction of soil (F5), which is the crystalline structure of primary and secondary minerals and occluded in iron oxide content, which shows that, possibly, radionuclides tested are arising from the material that gave origin to these soils and not the application of phosphogypsum. Although the insolubility of Ra isotopes can also be explained in phosphogypsum, according to Abrão (1994), the presence of high ^{226}Ra and ^{228}Ra isotopes in the residual fraction can be explained by the formation of polyphosphates of rare earth elements and divalent elements. It is noteworthy that the polyphosphates (M^{2+}) + 3 $\text{M}_3(\text{PO}_4)_3$ are kidnappers of divalent cations such as Ca^{2+} , Ba^{2+} , Ra^{2+} , and Pb^{2+} , resulting in their insolubility.

The F3 fraction (fraction associated with Fe and Mn oxides) for ^{226}Ra showed values 6.08, 0.91, and 0.85 Bq kg⁻¹, and the highest activity was observed in

ORP treatment; these levels represent the 32, 5, and 4% of the total activity of ^{226}Ra in Luvisol for ORP treatments 1RP and 2RP, respectively. These results indicate that the application of phosphogypsum, ^{226}Ra contributed to reduction of activity in fraction F3, thus making this element not available for uptake by plants. Probably this ^{226}Ra behavior is associated with radium sulfate and polysulfate formation (Moore et al. 2003), as well as polyphosphates training rare earth elements and divalent elements (Abrão 1994).

In geochemical fractions F1 (exchangeable), F2 (associated with carbonates) and F4 (organically bound) for the Luvisol, ^{226}Ra values could not be quantified because they were below the detection limit.

In Luvisol, the F5 fraction (residual) was prevalent for the ^{226}Ra , occurring 12.96 activity, 20.18 and 20.23 Bq kg⁻¹ for ORP, 1RP, and 2RP treatments, respectively, corresponding to 68, 95, and 96% of ^{226}Ra in this soil. These results corroborate with the data found by Baeza et al. (1996) who studied the bioavailability of radionuclides in nuclear Mediterranean ground near a power plant in the province of Cáceres, in Spain, and reported that the ^{226}Ra activity is prevalent in F5, having a percentage above 60%.

In Luvisol, the three treatments submitted to geochemical fractionation, presented the ^{210}Pb activity in the F1 fraction (exchangeable) 2.48, 6.3, and 5.2 for ORP, 1RP, and 2RP, respectively, equivalent to 21, 24, and 23% of total ^{210}Pb in ground. The percentages of ^{210}Pb in this soil were not very small, especially when compared with the results obtained by Cardoso et al. (2009), which studied the geochemical fractions in soils near the uranium mine in Bahia which found ^{210}Pb values ranging from 2 to 7 Bq kg⁻¹.

For ^{210}Pb , the geochemical fractions F2 (associated with carbonates), F3 (associated with Fe oxides and Mn), and F4 (organically bound) in Luvisol were below the detection limit.

The residual fraction F5 was predominant in this soil to ^{210}Pb , reaching values of 9.47, 17.1, and 17.2 Bq kg⁻¹, equivalent to 79, 76, and 77% of the total of ^{210}Pb in treatments 0NG, 1NG, and 2NG, respectively. These results showed that ^{210}Pb is predominantly associated with the crystalline structure of the soil minerals and also with the applied phosphogypsum, indicating that the radionuclides found are derived from the source material.

The ^{228}Ra activity in F1 extracted (exchangeable fraction) in three different treatments is presented as follows: 2.21, 4.77, and 3.88 Bq kg⁻¹, equating to 5, 8,

and 6% in ORP, 1RP, and 2RP treatments, respectively. The pH is one of the factors that strongly influence the ground Ra mobility: under acidic conditions, it becomes more mobile (Malavolta 1991), probably the increased activity of ^{228}Ra in F1 with the application of phosphogypsum is associated with low pH of the residue.

On the geochemical fractions F2 (associated with carbonates) and F4 (associated with organic matter), it was not possible to quantify the ^{228}Ra .

The ^{228}Ra activities in the fraction associated with Fe and Mn oxides (F3) was low in general, with values 7.56, 1.03, and 0 Bq kg⁻¹, equating to 17, 2, and 0% in the treatments ORP, 1RP, and 2RP, respectively. The small activity of ^{228}Ra may be associated with the presence of lower oxides of Fe and Mn in Luvisol, as can be observed in the X-ray fluorescence. Moreover, the application of phosphogypsum strongly reduced activity in this fraction of the ^{228}Ra , probably by the formation of radio compounds such as sulfates and polysulfates (Moore et al. 2003).

The residual fraction (F5) predominated, reaching values of 34, 57, and 59 Bq kg⁻¹, corresponding to 77, 90, and 93% of the total ^{228}Ra in ORP, 1RP, and 2RP treatments, respectively. Analogously to the scanned medium for ^{226}Ra , the high presence of radio isotopes in the residual fraction may be explained by the formation of polyphosphates of rare earth elements and divalent elements, resulting in the insolubility of these radionuclides (Abrão 1994).

The total concentrations of radionuclides in Fluvisol varied according to the application of phosphogypsum in the following way; for the ^{210}Pb , the ORP treatment changed from 35.87 to 45.3 and 45.31 Bq kg⁻¹ in the 1RP and 2RP treatments, respectively. For the ^{226}Ra the concentration in the ORP treatment was 16.8 to 22.7 and 22.3 Bq kg⁻¹ in the 1RP and 2RP treatments, respectively. And finally, for ^{228}Ra , the ORP treatment presented a concentration of 57.79 Bq kg⁻¹ and increased to 61.35 and 61.38 Bq kg⁻¹ in the 1RP and 2RP tranches, respectively.

For Luvisol, the application of phosphogypsum also increased the concentration of radionuclides. For the ^{210}Pb in the ORP treatment, the concentration increased from 11.95 to 22.4 Bq kg⁻¹ in the 1RP and 2RP treatments. For ^{226}Ra , the ORP treatment increased from 19.04 to 21.08 Bq kg⁻¹ in the 1RP and 2RP treatments. And for ^{228}Ra , there was an increase in the concentration of ORP from 43.77 to 59.09 and 59.88 Bq kg⁻¹ in the 1RP and 2RP treatments, respectively.

Comparing the total values of radionuclides obtained in the different treatments applied in this work with the average values of radioactivity in the soils considered normal, ^{226}Ra 17–60 Bq kg⁻¹ and ^{228}Ra 11–64 Bq kg⁻¹ (UNSCEAR 2000), that all concentrations obtained are within the range presented. For ^{210}Pb , the values were also within the range established by Jacomino 2008 (20–50 Bq kg⁻¹) who studied clay and sandy Brazilian soils.

As can be seen in the Table 5, all the results found a *p* value greater than 0.05, indicating that the data set is of the same population. Consequently, it can be considered that the addition of phosphogypsum, used for all doses, did not alter the concentration of radionuclides in comparison with the reference sample (dose equal to 0 RP).

4.1 Saline-Sodic Soil Recovery

The electrical conductivity values (EC) in soils are presented in Table 6. Comparing the values of the original soil (dose 0), you can see that the EC, 30 days after the addition of PG decreased considerably. The dose 1 showed the best values for both soils, indicating that large quantities of PG can raise EC in these soils. The Luvisol even after the application of phosphogypsum still has EC values that qualify as saline soil (Table 6).

5 Conclusions

The fertility of these soil analyses revealed that they are saline-sodic and have a good level of fertility, a fact proven by the high concentration of available nutrients (Ca, Mg, and K) as well as the high value of the CTC.

The predominant grain-size class in the analyzed soil was silt, a fact of great importance since the textural class controls the exchange complex.

The activity concentration of ^{226}Ra and ^{228}Ra on average in phosphogypsum was 95 and 181 Bq kg⁻¹, respectively; this value is well below the limit recommended by the US Environmental Agency for the use of phosphogypsum in agriculture, whose value is

Table 6 Electric conductivity of the soils on different treatments

Soil	Fluvisol			Luvisol			
	Dose	0RP	1RP	2RP	0RP	1RP	2RP
EC mS cm ⁻¹ (1:5)		15.87	2.74	3.74	83.34	6.81	11.77

370 Bq kg⁻¹. Furthermore, the concentrations of the radio isotopes in phosphogypsum with this study were below the concentrations of Ra in phosphogypsum reported around the world.

The application of phosphogypsum in saline-sodic soils after 30 days promoted the concentration of activity of ²²⁸Ra and ²¹⁰Pb radionuclides in the exchangeable fraction. However, the values obtained from the application of phosphogypsum are still extremely small, reaching maximum concentrations as to ²²⁸Ra 4.78 and ²¹⁰Pb 30.6 Bq kg⁻¹. However, to verify the transfer of these radionuclides to the plant, there is the need for an experiment to be performed.

About the ²²⁶Ra, the application of phosphogypsum had a positive response, reducing the concentration of activity in the fraction associated with iron and Mn oxides (F3) and consequently increasing its activity concentration in the residual fraction (F5).

The three isotopes studied were not detected in the F2 and F4 fractions associated with carbonates and organic matter, respectively.

Evaluating the EC 30 days after the application of the phosphogypsum, it appeared that there was a considerable decrease. Being the best response in the 1RP dose indicates that a very high dose of phosphogypsum can again increase EC due to high Ca and Mg.

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