Radiological impact of phosphogypsum surface application in a no-till system in Southern Brazil

Nivea Maria Piccolomini Dias[1], Eduardo Fávero Caires[2], Luiz Fernando Pires[1], Márcio Arruda Bacchi[3] and Elisabete Aparecida de Nadai Fernandes[3]

[1]Universidade Estadual de Ponta Grossa (UEPG), Laboratório de Física Aplicada a Solos e Ciências Ambientais, CEP 84030-900 Ponta Grossa, PR, Brazil. E-mail: diasnmp@gmail.com, lfpires@uepg.br [2]UEPG, Departamento de Ciência do Solo e Engenharia Agrícola. E-mail: efcaires@uepg.br [3]Universidade de São Paulo, Centro de Energia Nuclear na Agricultura, Laboratório de Radioisótopos, Caixa Postal 96, CEP 13400-970 Piracicaba, SP, Brazil. E-mail: mabacchi@cena.usp.br, lis@cena.usp.br

Abstract – The objective of this work was to determine the impact of phosphogypsum application on ^{226}Ra and ^{228}Ra activities in the soil and on their accumulation in soybean grains. A field experiment was carried out in Paraná state, Brazil, on a loamy Typic Hapludox, under no-till system, with increasing phosphogypsum rates: 4, 8, and 12 Mg ha^{-1}. Gamma-ray spectrometry was carried out using HPGe detectors with 45 and 10% relative efficiencies, for soybean grains and soil, respectively. No increment of ^{226}Ra and ^{228}Ra activities was observed due to the increase in phosphogypsum rates in the soil, and a small reduction was noticed in the grains. Average values found for ^{226}Ra and ^{228}Ra activities were 37 and 57 Bq kg^{-1} in the soil and 1.44 and 3.19 Bq kg^{-1} in soybean grains. The application of phosphogypsum for no-till soybean production is a safe practice regarding the risks of radiation damage to human health.

Index terms: *Glycine max*, gamma spectrometry, radioactivity, ^{226}Ra, ^{228}Ra.

Impacto radiológico da aplicação superficial de gesso agrícola em sistema de plantio direto no Sul do Brasil

Resumo – O objetivo deste trabalho foi determinar o impacto da aplicação superficial de gesso agrícola sobre as atividades de ^{226}Ra e ^{228}Ra no solo e sobre seu acúmulo nos grãos de soja. Foi realizado um experimento de campo no Estado do Paraná, Brasil, em um Latossolo Vermelho de textura média, sob sistema de plantio direto, com doses crescentes de gesso agrícola: 4, 8 e 12 Mg ha^{-1}. A espectrometria de raios gama foi realizada com uso de detectores de HPGe, com eficiência relativa de 45 e 10%, para os grãos de soja e para o solo, respectivamente. Nenhum incremento nas atividades de ^{226}Ra e ^{228}Ra foi verificado no solo em razão do aumento das doses de gesso agrícola, e uma pequena redução foi observada nos grãos. Os valores médios de atividade encontrados para o ^{226}Ra e ^{228}Ra foram 37 e 57 Bq kg^{-1} no solo e 1,44 and 3,19 Bq kg^{-1} nos grãos de soja. A aplicação de gesso agrícola na soja produzida em plantio direto é uma prática segura quanto aos riscos de exposição e danos da radiação para a saúde humana.

Termos para indexação: *Glycine max*, espectrometria gama, radioatividade, ^{226}Ra, ^{228}Ra.

Introduction

Phosphogypsum (PG) is a by-product of the phosphate fertilizer industry that contains mainly calcium sulfate ($CaSO_4.2H_2O$) and small concentrations of phosphorous and fluorine. The huge demand for phosphate fertilizer with high P content in agriculture has led to a global production of about 170 million megagrams of PG per year (Abril et al., 2008). Surface-applied PG followed by its leaching to acidic subsoils results in improvement of root growth and higher absorption of water and nutrients by plant roots as a result of the increase in calcium content, the formation of less toxic aluminum species ($AlSO_4^+$) and precipitation of Al^{3+} (Shainberg et al., 1989; Carvalho & Raij, 1997; Caires et al., 2003). Thus, PG has been largely used in agriculture in order to improve subsoil fertility.

No-till systems with diversified crop rotations have stood out as one of the most effective strategies to improve the sustainability of farming in tropical and subtropical regions, contributing to minimize soil and nutrient losses by erosion. No-till has shown a rapid increase in area in Brazil, currently taking up some 26 million hectares, and soybean is the most commonly cultivated crop. To control soil acidity in established no-till systems, lime is spread on the surface without incorporation. Because surface lime application in

general does not reduce soil acidity far beyond the point of placement (Ernani et al., 2004; Caires et al., 2005), the use of PG has been an effective practice to improve the chemical conditions in the subsoil under no-till farming (Caires et al., 1998, 2003).

Phosphogypsum has radionuclides from uranium (^{238}U) and thorium (^{232}Th) series in its composition, due to their occurrence in the phosphate rocks (Silva, 2001). Amongst such radionuclides, ^{226}Ra, from ^{238}U series, and ^{228}Ra, from ^{232}Th series, are the most important sources of radioactivity in PG (Rutherford et al., 1994). ^{226}Ra is characterized by long half-lifetime (T = 1,602 years), the emission of α particles and by low-energy gamma-rays. ^{228}Ra has the half-lifetime of 5.75 years and the emission of β particles. Both Ra elements have a biological behavior similar to Ca deposited in mammal bones (Choppin & Rydberg, 1980)

The presence of radionuclides has generated discussions on the impact of PG on human health (Ettenhuber & Lehmann, 1986), and its use in agriculture is restricted by certain countries. In the USA, the maximum limit of ^{226}Ra in PG was set as 370 Bq kg^{-1} (United States Environmental Protection Agency, 1998). In Brazil, Mazzilli et al. (2000) registered activities ranging from 10 to 1,200 Bq kg^{-1} for radionuclides from ^{238}U and ^{232}Th series in the phosphate rocks used in the fertilizer industry. Also, ^{226}Ra and ^{228}Ra contents were measured in the Brazilian PG produced from different phosphate fertilizer industries; Saueia et al. (2005) obtained activities for ^{226}Ra and ^{228}Ra that varied from 24 to 700 Bq kg^{-1} and 29 to 273 Bq kg^{-1}, respectively, and Santos et al. (2006) from 214 to 247 Bq kg^{-1} for ^{226}Ra and 350 to 811 Bq kg^{-1}, for ^{228}Ra. Parreira et al. (2001) showed that ^{228}Ac, ^{208}Ti, ^{212}Bi (from ^{232}Th series), ^{214}Pb and ^{214}Bi (from ^{238}U series) and ^{40}K were transferred from the PG to the soil.

Despite the various studies found in the literature on the use of PG in agriculture (Hull & Burnett, 1996; Burnett & Elzerman, 2001; Beddow et al., 2006; Papastefanou et al., 2006; Abril et al., 2008, 2009), there are only few studies on the presence of radionuclides in PG produced in Brazil (Silva, 2001; Silva et al., 2001; Saueia et al., 2005; Santos et al., 2006; Jacomino et al., 2009). Moreover, there is very little information available on the addition of radionuclides through PG application in Brazilian agriculture (Parreira et al., 2001; Dias et al., 2010), mainly in the regions where the no-till farming predominates, as the South of Brazil.

Considering that the use of PG might result in increased amounts of radionuclides in the soil-plant system, and a consequent threat to human health, studies that can provide data aiming at the regulation of PG use in agriculture are essential.

The objective of this work was to determine the impact of phosphogypsum (PG) application on ^{226}Ra and ^{228}Ra activities in the soil and on their accumulation in soybean grains.

Materials and Methods

The experiment was performed in Ponta Grossa, Paraná state, Brazil (25º05'58"S and 59º09'30"W), on a loamy Typic Hapludox. Topsoil (0–0.2 m) had the following characteristics: Ca^{2+}, 16 mmol$_c$ dm^{-3}; P (Mehlich-1), 9.0 mg dm^{-3}, total organic matter, 33 g dm^{-3}; and 295, 240, and 465 g kg^{-1} of clay, silt and sand, respectively. The clay fraction had 265.8 g kg^{-1} of kaolinite (90.1%), 26.8 g kg^{-1} of goethite (9.1%), and 2.4 g kg^{-1} of hematite (0.8%). The experimental site had been used for grain cropping under no-till system for 15 years before the establishment of the experiment.

A randomized complete block design was used, with three replicates. Treatments were applied to plots of 50.4 m^2 (8.0×6.3 m), with four different rates of PG: 0, 4, 8, and 12 Mg ha^{-1} on the soil surface. PG, coming from Cajati county (São Paulo state), had 235 g kg^{-1} Ca, 153 g kg^{-1} S, 3 g kg^{-1} P, and 156 g kg^{-1} water. ^{226}Ra and ^{228}Ra activity concentrations in PG were 47.5 and 43.3 Bq kg^{-1}, respectively.

Soybean (*Glycine max* L. Merril) was cultivated during the spring–summer season, and cereal crops during the autumn–winter season. Fertilizer rates varied with crops and years, according to soil test recommendations for the Paraná state. Nitrogen, P, and K were applied as urea, triple superphosphate, and potassium chloride, respectively. Plant residues were left on the soil surface following grain harvest. More details about the cropping history and fertilization are reported by Caires et al. (2005).

Soil samples were taken after soybean (cv. CD 214 RR) harvest in 2007. In order to obtain a composite sample, 12 soil cores at 0–0.2 m depth, and five soil cores at 0.2–0.4, 0.4–0.6, and 0.6–0.8 m depth were collected from each plot using a hand probe. Samples

were oven-dried at 60ºC for 24 hours, manually ground and sieved (1 mm mesh). Then, they were placed in 150 mL cylindrical containers and sealed. Soybean was harvested from a 12 m^2 plot. Grains were washed with running freshwater dried at 60ºC and sealed in 2 L Marinelli containers. After sealed all samples were stored for a 3-week minimum period, in order to ensure the radioactive equilibrium amongst ^{226}Ra and its short-lived daughters (^{214}Pb and ^{214}Bi).

Determinations of radionuclides were carried out at the Radioisotopes Laboratory of the Centro de Energia Nuclear na Agricultura (Cena/USP), in Piracicaba, São Paulo state, Brazil. Two hyperpure-Ge detectors were used: Ortec model GEM10195 (for soil) and GEM45190 (for grains), with 10 and 45% relative efficiencies and 1.85 and 1.95 keV resolutions for the photopeak 1,332 keV of ^{60}Co, both coupled to a Ortec 919E multichannel analyzer. Soil samples remained in the spectrometer for 12 hours, while soybean samples were measured for 24 hours, since they showed lower activity. Background radiation was evaluated in both detectors during 48 hours, using the same experimental setup and replacing samples by deionized water. For acquisition and spectral analysis, the programs Gamma Vision by Ortec and Quantu, developed in the Cena's Radioisotopes Laboratory, were employed.

The activity of ^{226}Ra in the soil and grains was determined by averaging results from the 295 and 352 keV photopeaks of ^{214}Pb, and 609 keV photopeak of ^{214}Bi. ^{228}Ra was determined from the gamma ray lines: 239 keV of ^{212}Pb; 338, 911, and 969 keV of ^{228}Ac for soil; and 338, 911 and 969 keV of ^{228}Ac for grains. ^{212}Pb was not used for grains due to the lack of radioactive equilibrium between ^{228}Ra and ^{228}Th. Count rates were transformed to activities by using the detection efficiency, calculated by an in-house software based on a semiempirical calibration approach adapted from the literature (Bacchi et al., 2000). The quality of results were checked by analysis of certified reference materials produced by the International Atomic Energy Agency, i.e. Soil 6, IAEA-326, IAEA-327 and IAEA-368. In grains, the minimum detectable activity for ^{226}Ra was 0.36 Bq kg^{-1} and for ^{228}Ra it was 0.55 Bq kg^{-1}, while the minimum detectable activities in the soil were 6 Bq kg^{-1} and 13 Bq kg^{-1} for ^{226}Ra and ^{228}Ra. The count rates obtained for soil samples were at least 20 times higher than the measured background for both ^{226}Ra and ^{228}Ra, while for grain samples the values found were, in average, 4 and 8-fold higher than the background, respectively for ^{226}Ra and ^{228}Ra.

The soil-plant transfer factor (TF) was calculated as: $TF = A_{plant}/A_{soil}$, in which A (Bq kg^{-1}) represents the activity concentrations in grains and in the soil (Papastefanou et al., 2006).

The potential radiological impact from soybean ingestion was assessed through the effective dose (D_e, Sv y^{-1}): $D_e = e(g) \times A \times T$, in which e(g) (Sv Bq^{-1}) represents the effective dose coefficient and T (kg per year) is the soybean annual consumption rate (Papastefanou et al., 2006; Scheibel, 2006).

Data from soybean grain were evaluated by analysis of variance using a randomized complete block design in SAS software (SAS Institute, 1985). Data from soil were evaluated as a split plot design by analysis of variance using PG rates as main plots, and depths as subplots. The PG effects were compared by regression analyses, and the soil depths effects were compared by the Tukey test at 5% probability.

Results and Discussion

Activity concentrations of ^{226}Ra and ^{228}Ra in the soil were not significantly influenced by the interaction between PG rates and soil depth. Surface-applied PG did not significantly modified the concentrations of ^{226}Ra and ^{228}Ra in any of the four depths studied (Figure 1). Concentrations of ^{226}Ra varied from 33.8 to 38.4 Bq kg^{-1} (0–0.2 m), 32.4 to 37.9 Bq kg^{-1} (0.2–0.4 m), 36.6 to 38.4 Bq kg^{-1} (0.4–0.6 m), and 37.3 to 40.1 Bq kg^{-1} (0.6–0.8 m); while ^{228}Ra varied from 51.1 to 55.7 Bq kg^{-1} (0–0.2 m), 53.7 to 56.0 Bq kg^{-1} (0.2–0.4 m), 56.0 to 60.4 Bq kg^{-1} (0.4–0.6 m), and 59.4 to 63.5 Bq kg^{-1} (0.6–0.8 m). It should be noticed that ^{228}Ra concentrations found in the soil were almost twice as much as ^{226}Ra concentrations, which might be due to the soil parent material and to the use of fertilizers or other agricultural inputs. Phosphate rocks, for instance, might be from sedimentary or igneous origin, the former showing higher concentrations of ^{238}U, while the latter shows higher concentrations of ^{232}Th. In Brazil, 80% of the phosphate rock used in the industry for phosphoric acid production comes from igneous origin (Canut, 2006). Therefore, there are higher ^{232}Th concentrations than ^{238}U and, consequently, higher ^{228}Ra concentrations than ^{226}Ra. However, natural phosphates in the USA

are from sedimentary origin (Albuquerque, 1996) and show higher ^{238}U, thus higher ^{226}Ra content.

Concentrations of ^{226}Ra (average value 37 Bq kg^{-1}) and ^{228}Ra (average value 57 Bq kg^{-1}) found in the soil, after PG addition (Figure 1), are within the range cited in the literature for Brazilian soils. Malanca et al. (1993) assessed the activity concentration of ^{226}Ra, in 51 soils of Rio Grande do Norte state, and observed values between 10 and 138 Bq kg^{-1}. Jacomino et al. (2009) determined ^{226}Ra and ^{228}Ra in soils of Minas Gerais state, obtaining respectively 69 and 114 Bq kg^{-1} for a clay soil, and lower than 20 and 34 Bq kg^{-1} for a loam soil. Regarding the PG composition of the main industries producing phosphate fertilizers in Brazil, concentrations varied from 22 to 1,251 Bq kg^{-1} for ^{226}Ra and from 29 to 280 Bq kg^{-1} for ^{228}Ra (Mazzilli et al., 2000; Silva et al., 2001; Saueia et al., 2005; Santos et al., 2006).

In soils of other countries, effects of PG addition on the activity of ^{226}Ra were relatively similar to those observed in the present study. In agricultural areas in Greece, Papastefanou et al. (2006) found activity concentrations of ^{226}Ra varying from 37 to 54 Bq kg^{-1} without PG addition, and 50 to 479.0 Bq kg^{-1} with PG addition to the soil. In Spain, concentrations of ^{226}Ra in the soil (0–0.3 m) were 35.3 and 39.3 Bq kg^{-1}, respectively without and with PG application at 25 Mg ha^{-1}, which

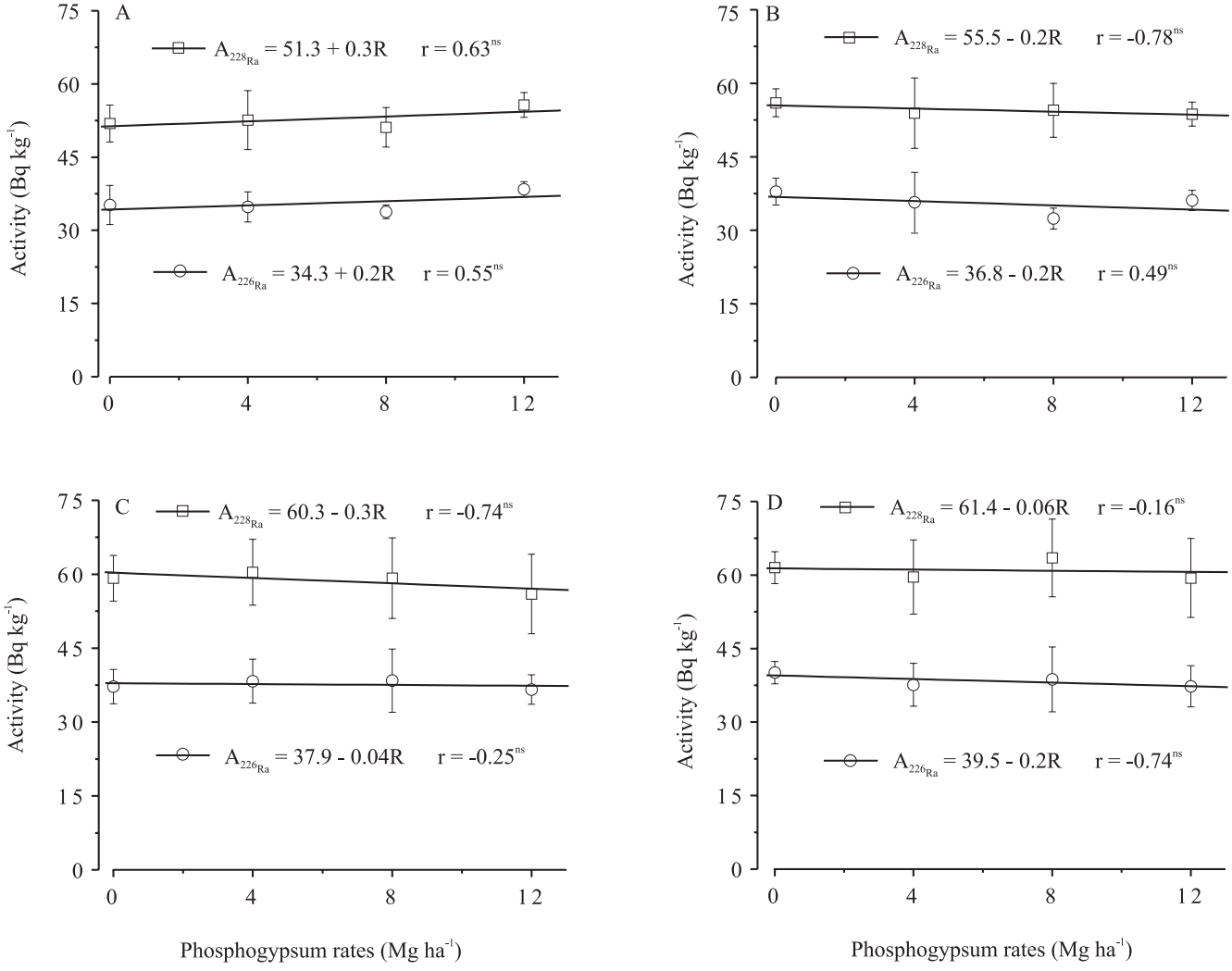

Figure 1. ^{226}Ra and ^{228}Ra activities at different soil depths, according to the applied phosphogypsum rates (R): A, 0–0.2 m; B, 0.2–0.4 m; C, 0.4–0.6; D, 0.6–0.8 m. ^{ns}Nonsignificant at 5% probability. Error bars represent standard deviation (n = 3).

means no significant difference in the activity with the use of PG (Abril et al., 2008).

Regardless the rates of PG applied, an increase in the concentrations of ^{226}Ra and ^{228}Ra was noticed along soil depth. Considering the average rates of PG, ^{226}Ra and ^{228}Ra were significantly lower at 0–0.2 m (35.6 and 52.8 Bq kg^{-1}) and 0.2–0.4 m (35.5 e 54.5 Bq kg^{-1}) than at 0.4–0.6 m (37.6 and 58.7 Bq kg^{-1}) and 0.6–0.8 m (38.5 and 61 Bq kg^{-1}). Bacchi (1996) also observed an increase of ^{226}Ra and ^{228}Ra in deeper layers of Brazilian Oxisols. However, the opposite behavior was observed for temperate soils, in other countries (Bolca et al., 2007; Abril et al., 2008). In Turkey, Bolca et al. (2007) found concentrations of radionuclides positively correlated to the soil organic matter content (r = 0.93), with higher concentrations in the soil superficial layers. In Spain, Abril et al. (2008) observed a decrease in ^{226}Ra concentration, with increasing soil depth up to 0.9 m, for both control samples and for those that received PG at 25 Mg ha^{-1}.

In order to explain the radionuclide variations along soil depth, Belivermis et al. (2010) found strong positive correlations between natural radionuclide levels and clay or silt content, whereas strong negative correlations for sand were observed. In the present study, increases were observed in the clay amount along soil depths, from 340 (0–0.2 m) to 400 g kg^{-1} (0.6–0.8 m), decreases in sand content, from 506 (0–0.2 m) to 443 g kg^{-1} (0.6–0.8 m). One possible explanation for these results is the existence of correlation between the ^{226}Ra and ^{228}Ra amounts and clay and sand contents along soil depth (Figure 2).

Strong positive correlations between the ^{226}Ra and ^{228}Ra amount and clay content along soil depth were also found in the present study. However, a strong negative correlation between these two radionuclides and sand content was observed. Some authors have described that the natural radioactivity shows increases when particle size decreases and surface area increases. Regarding the grain size, radionuclides are adsorbed onto clay surfaces or fixed within the lattice structure (VandenBygaart & Protz, 1995; VandenBygaart et al., 1999; Navas et al., 2002; Belivermis et al., 2010).

A reduction in the transfer factors (TF) for ^{226}Ra and ^{228}Ra was noticed for increasing rates of PG (Figure 3). In fact, concentrations of ^{226}Ra and ^{228}Ra have not changed in the soil, while concentrations in grains decreased with the increasing PG rates applied. Results of ^{226}Ra and ^{228}Ra in soybean grains were, respectively, 14.3 and 8.5% lower for the treatment with PG at 12 Mg ha^{-1} than for the control treatment without PG. The TFs obtained in the present study were of the same order of magnitude as those found for rice grains produced in Greece, in areas with PG (TF = 0.011) and without PG (TF = 0.016) (Papastefanou et al., 2006). The decrease in the concentrations of ^{226}Ra and ^{228}Ra in soybean grains, and consequent reduction of TFs,

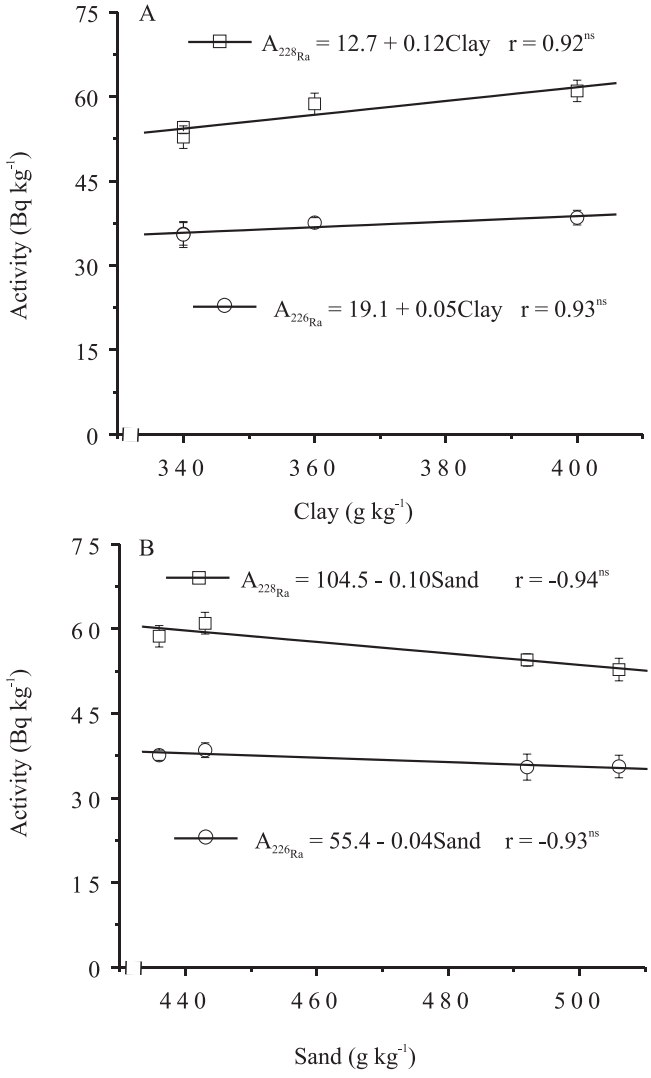

Figure 2. Correlation between clay amount and ^{226}Ra and ^{228}Ra activities along soil depths (0–0.8 m) (A), and between sand amount and ^{226}Ra and ^{228}Ra activities along soil depths (0–0.8 m) (B). Each experimental value represents the activity means for the four phosphogypsum rates applied to the soil (0–12 Mg ha^{-1}). ^{ns}Nonsignificant at 5% probability. Error bars represent standard deviation (n = 4).

caused by PG application, might be due to increases in Ca^{+2} content and to the low solubility of $RaSO_4$ in the soil (Papastefanou et al., 2006; Bolca et al., 2007). Increases in Ca^{+2} concentration in the soil may result in lower Ra transfer from soil to plants due to the chemical similarity between Ca and Ra, both competing for absorption sites in plants (Bolca et al., 2007).

For soybean produced in other Brazilian regions, Venturini & Sordi (1999) found activity concentrations lower than 0.43 Bq kg^{-1} for ^{226}Ra, and lower than 0.57 Bq kg^{-1} for ^{228}Ra, which represents much lower values than those obtained in the present study (Figure 3). Regarding soybean flour, Scheibel (2006) calculated an average value of 3.5 Bq kg^{-1} for ^{228}Ra, similar to those presented here.

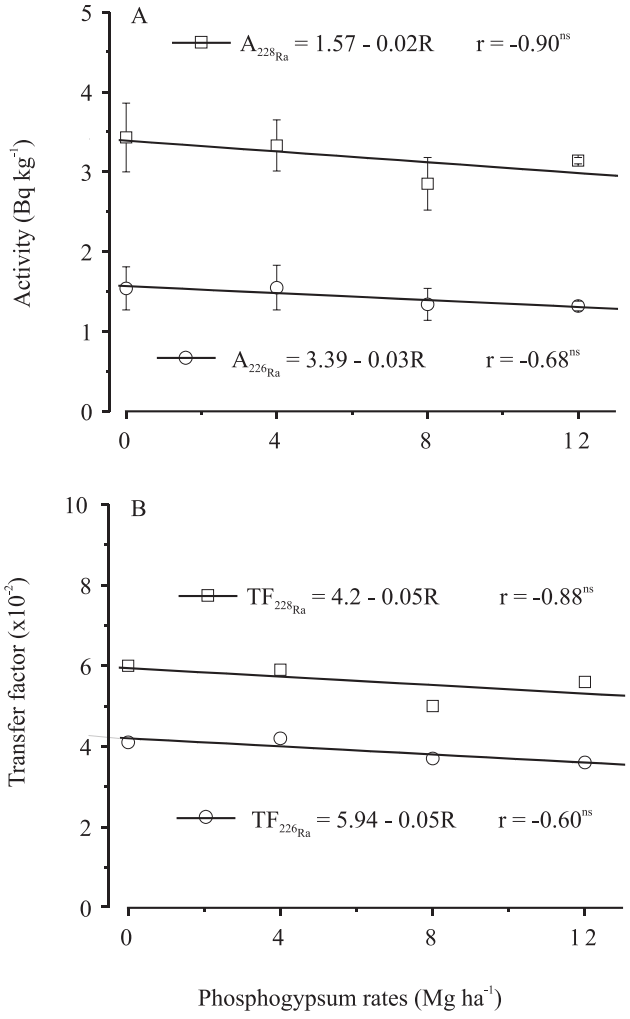

Figure 3. ^{226}Ra and ^{228}Ra activities in soybean grains (A), and soil-plant transfer factor (B) considering the different rates of phosphogypsum. ^{ns}Nonsignificant at 5% probability. Error bars represent standard deviation (n = 3).

Considering an average annual consumption of 1 kg of soybean per person, the values obtained for ingested activity were compared to the reference values published by United Nations Scientific Committee on the Effects of Atomic Radiation (2000) for water and food (Table 1). The ingestion rate of ^{226}Ra varied according to PG rates, from 1.44±0.12 to 3.9±0.3 mBq per day. Regarding ^{228}Ra, it varied from 3.19±0.26 to 8.7±0.7 mBq per day (Figure 4 A, B). The ingestion of ^{226}Ra would be approximately 19% (babies), 10% (children), and 7% (adults) of typical reference values for water and food ingestion. The ingestion of ^{228}Ra would be approximately 58, 28, and 19% of the reference values.

Considering the effective dose coefficient for ^{226}Ra and ^{228}Ra from Table 1, the annual effective dose (D_e) was estimated for humam babies, children and adults (Figure 4 C, D). For ^{226}Ra the values were 1.38±0.12 µSv per year (babies), 1.15±0.10 µSv per year (children), and 0.40±0.03 µSv per year (adults), while for ^{228}Ra the values were significantly higher, i.e. 18.2±1.5 µSv per year (babies), 12.4±1.0 µSv per year (children), and 2.2±0.2 µSv per year (adults). Values of D_e found in the present study were 5.4 (babies), 10.4 (children), and 15.8 (adults) times lower than the ^{226}Ra reference values, and 1.7 (babies), 3.2 (children), and 5.0 (adults) times lower for ^{228}Ra (Table 1). In soybean flour produced in Paraná state, Scheibel (2006) found D_e values of 1.64 µSv per year (babies), 1.12 µSv per year (children), and 0.20 µSv per year (adults) for ^{228}Ra, considering a 0.082 kg annual consumption of soybean flour.

Table 1. Reference values (United Nations Scientific Committee on the Effects of Atomic Radiation, 2000) for ingested activity (A, mBq per day), effective dose coefficient [e(g), µSv Bq^{-1}] and annual effective dose (D_e, µSv per year) of ^{226}Ra and ^{228}Ra for babies (1–2 years old), children (7–12 years old) and adults (over 17 years old).

Values	^{226}Ra			^{228}Ra		
	A	e(g)	D_e	A	e(g)	D_e
Baby	21	0.96	7.5	15	5.70	31.0
Child	41	0.80	12.0	27	3.90	40.0
Adult	60	0.28	6.3	41	0.69	11.0

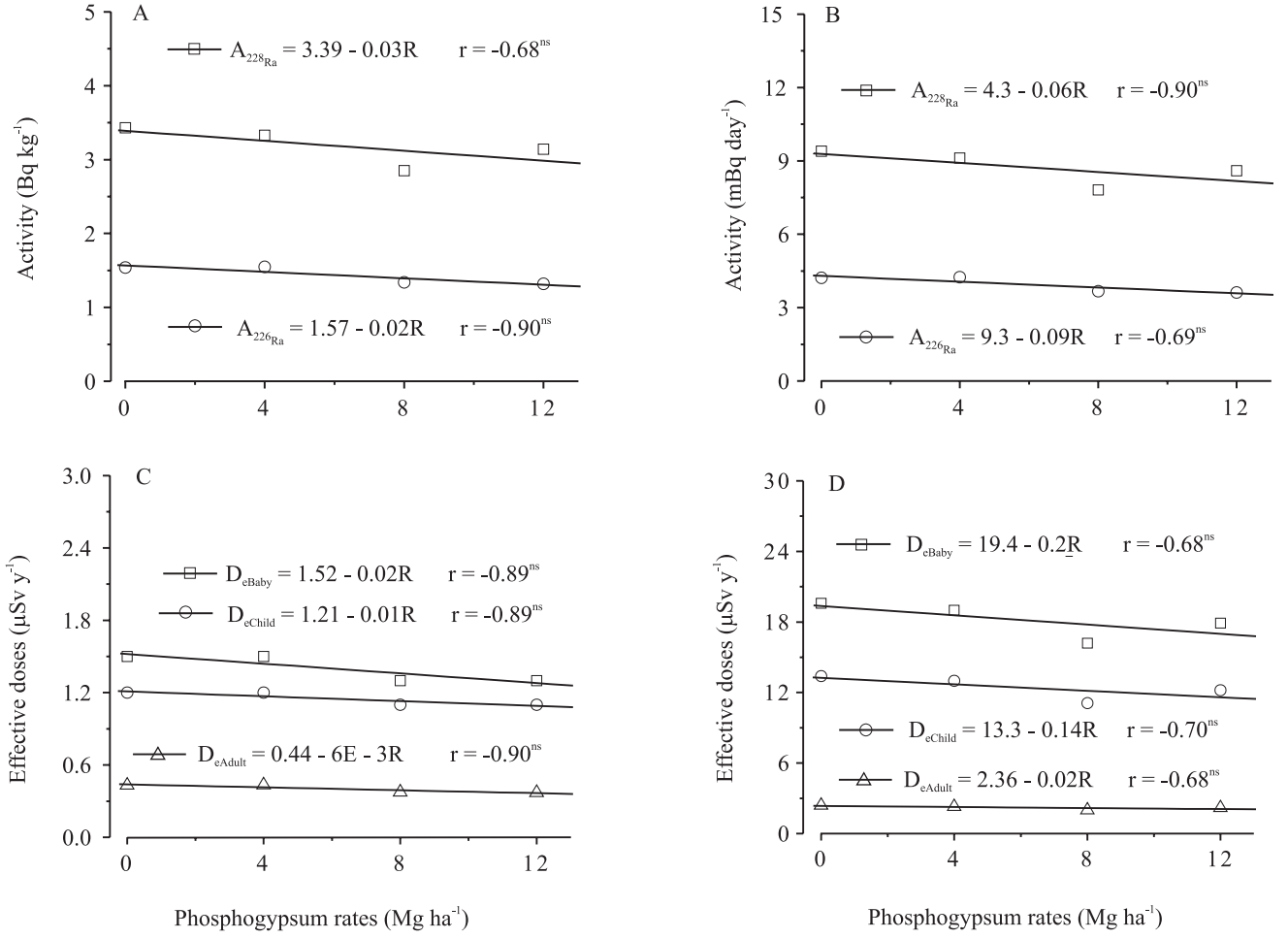

Figure 4. Ingested activity of ^{226}Ra and ^{228}Ra according to phosphogypsum rates applied to the soil: A, ingested activity per year; B, ingested activity per day; C, ingestion effective dose of ^{226}Ra for babies, children and adults; D, ingestion effective dose of ^{228}Ra for babies, children and adults. ^{ns}Nonsignificant at 5% probability.

Conclusions

1. Surface application of phosphogypsum up to 12 Mg ha^{-1} in an Oxisol under no-till system does not increase the concentrations of ^{226}Ra and ^{228}Ra in soil.

2. The concentrations of both radionuclides are higher in the subsoil layers compared to the topsoil.

3. Increasing phosphogypsum rates result in lower soil-plant transfer factor for ^{226}Ra and ^{228}Ra.

4. Surface application of phosphogypsum for soybean production under no-till system is a safe practice regarding possible radiological damage to human health, considering the conditions of this study.

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