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Lixiviation of natural radionuclides and heavy metals in tropical soils amended with phosphogypsum

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ABSTRACT

The main phosphate industries in Brazil are responsible for the annual production of 5.5 million tons of a residue (phosphogypsum), which is stored in stacks. The presence of radionuclides and metals puts restrictions on the use of phosphogypsum in agriculture. To assure a safe utilization, it is important to estimate the lixiviation of the radionuclides (^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra) and metals (As, Cd, Cr, Ni, Se, Hg and Pb) present in phosphogypsum. For this purpose, an experiment was carried out, in which columns filled with sandy and clay Brazilian typical soils mixed with phosphogypsum were percolated with water, to achieve a mild extraction of these elements. The results obtained for the concentration of the radionuclides and metals in the leachate were low; giving evidence that, even when these elements are present in the phosphogypsum, they do not contribute to an enhancement of their content in water.

1. Introduction

The Brazilian phosphate fertilizer is obtained by wet reaction of the igneous phosphate rock with concentrated sulphuric acid, giving as final product, phosphoric acid, and phosphogypsum (PG) as a residue. PG presents in its composition radionuclides of the natural U and Th decay series: mainly ^{226}Ra, ^{228}Ra, ^{232}Th, ^{210}Pb and ^{210}Po, while other radionuclides, such as U, originally present in the phosphate rock, migrate to the phosphoric acid. The main phosphate industries in Brazil are responsible for the production of 5.5×10^6 metric tons of PG annually, which is stored in stacks. The level of impurities (metals and radionuclides, among others) present in PG makes its disposal or reutilization an environmental concern. PG can be considered as a NORM (Naturally Occurring Radioactive Material) residue, depending upon its content of natural radionuclides. In Brazil TENORM industries are subjected to the recommendations given by Comissão Nacional de Energia Nuclear-CNEN, which include compliance with the radiological protection regulations (CNEN, 2005). The presence of radionuclides puts restrictions on the use of PG in building materials and in soil amendments. The Brazilian regulatory body ruled that phosphogypsum would only be permitted for use in agriculture or in the cement industry if the concentration of ^{226}Ra and ^{228}Ra does not exceed 1 Bq g^{-1} (CNEN, 2013).

The concentration of metals (As, Cd, Cr, Hg, Ni, Pb and Se) in fertilizers and soil conditioners are controlled by national agriculture regulation agency Ministério da Agricultura, Pecuária e Abastecimento (MAPA, 2006).

The application of PG as soil amendment is mainly due to the characteristics of $CaSO_4$, which improves the root penetration in soil. It provides calcium in the soil depth, reduces the aluminum saturation, contributes to the deepening of the plant root system and favours the absorption of water and nutrients (van Raiji, 1988). The solubility of PG in water is 150 times higher than that of calcareous rock (Vitti, 1987).

Most of the Brazilian arable soils are acid with pH between 4.3 and 6.2, poor in calcium and magnesium, with high aluminum contents and low phosphorus availability to the plants. PG in the soil solution undergoes the dissociation process, in such a way that Ca^{2+} and SO_4^{2-} take part in the ionic exchange reactions. Ion exchange plays an important role in the PG fertilizing properties, since it allows the soil to retain several elements in a form more available to the plants. Due to its high solubility, PG, besides providing Ca^{2+}, also supplies SO_4^{2-} that in presence of Al^{3+} forms $AlSO^{4+}$ complex, which is non-toxic and not available to plants (Sousa et al., 1992).

Few references are available in the literature concerning the speciation of radionuclides and metals in phosphogypsum used in

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agriculture in Brazil (Santos et al., 2006; Mazzilli and Saueia, 2013; Saueia et al., 2013a,b). The study of availability of radionuclides and metals to the soil solution is important, for a better understanding of the mobility of contaminants in water/soil systems, in order to estimate the real environmental impact.

The use of the total quantification of a contaminant element present in the sample for the evaluation of its environmental impact requires the knowledge of how this element is bound to the matrix. In practice, it is useful to evaluate the fraction of the total element concentration, which can be dissolved and available to the environment. A common methodology that gives information about the distribution of the element in soil or sediment is the sequential extraction. In this procedure, the sample is mixed with six different solutions, with extracting strength from mild to drastic, representing the phases: soluble, exchangeable, bound to carbonates, Fe/Mn oxides, organic and residual (Tessier et al., 1979). The first two steps of the sequential extraction correspond to the labile fraction, which better represent the mild lixiviation that occurs by the irrigation of cultivated land.

The main objective of this paper is to study the availability of natural radionuclides, important in terms of radiological protection (^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po), and metals (As, Cd, Cr, Ni, Se, Hg and Pb), present in the Brazilian phosphogypsum used in agriculture. For this purpose, an experiment was conducted in the laboratory, in which columns filled with Brazilian typical sandy and clay soils and phosphogypsum were percolated with water, in order to achieve a mild extraction of these elements. The volume of water to be percolated was based in the average rainfall of the study area. The availability of the radionuclides and metals was evaluated by measuring the total concentration in the soil + phosphogypsum and the concentration in the leachate, in order to establish the ratio between the available fraction and the total one.

2. Experimental

For the determination of radionuclides ^{238}U and ^{232}Th present in soil and phosphogypsum samples, the chosen technique was instrumental neutron activation analysis. For the radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb in the same samples, the technique used was gamma spectrometry. Po-210 was determined by alpha spectrometry. For the determination of the radionuclides in the leachate, the techniques were chosen taking into account their sensibility. The experimental procedure established for the sequential determination of the radionuclides in the leachate was based on the pre concentration and separation by extraction chromatography using Sr-Spec and UTEVA resins and final measurement of alpha emitters such as U and Th isotopes and ^{210}Po by alpha-spectrometry, ^{210}Pb by liquid scintillation counting, and ^{226}Ra and ^{228}Ra by gas flow proportional counting. The validation of the procedure was carried out in terms of trueness and reproducibility with the IAEA-385 Irish Sea Sediment reference material. The results obtained for the precision for the radionuclides ^{238}U, ^{232}Th, ^{210}Po, ^{210}Pb, ^{226}Ra and ^{228}Ra were 6.1%, 9.6%, 2.2%, 0.71%, 3.1% and 3.8%, respectively. The relative error obtained for the radionuclides ^{238}U, ^{232}Th, ^{210}Po, ^{210}Pb, ^{226}Ra and ^{228}Ra were 2.3%, 0.4%, 1.5%, 2.1%, 1.0% and 0.7%, respectively.

The analysis of the elements As, Cd, Cr, Hg, Ni, Pb and Se was performed using the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). For the analysis of Hg, the vapour/hydrides generator coupled to the ICP-OES was used.

2.1. Soil sampling and preparation

Two different types of soil, sand and clay, were collected on April 2012, in the region of Piracicaba (São Paulo State). The GPS coordinates of the sandy soil sampling location is 22° 41′ 34.23″ S and 47° 51′ 15.72″ O. The GPS coordinates of the clay soil sampling location is 22° 43′ 32.13″ S and 47° 34′ 17.70″ O. Samples weighing 150 kg were collected at a depth from 25 to 50 cm. The samples were sieved for the segregation of roots and were analyzed for their chemical and physical characterization. The results are presented in Table 1.

According to the values obtained for the field capacity, 1400 mL of water are necessary in order to saturate the sandy soil for each experiment with 5 kg of soil, and for the clay soil, 2100 mL of water are needed. The chemical analysis of soil (Table 2) was undertaken, in order to determine the soil fertility and correction. According to the results obtained, the soils are considered dystrophic, with base saturation (V%) lower than 50, justifying the necessity of the soil correction with PG.

The samples of Brazilian phosphogypsum used in this experiment were provided by Vale Fertilizantes industry and were collected in Uberaba (Minas Gerais State) installation (PG UBE) and in the unit of Cubatão (São Paulo State) (PG CUB). For the determination of the amount of phosphogypsum necessary for the soil correction, the following equation was used, according with Vitti et al. (2008).

$$\mathrm{NPG} = \frac{(50 - V)\cdot \mathrm{CEC}}{500}\cdot 1.25 \quad (1)$$

where

NPG = amount of phosphogypsum necessary to achieve 50% base saturation in the 25–50 cm layer (ton ha^{-1})
V = soil base saturation in the 25–50 cm layer (%)
CEC = cation exchange capacity in the 25–50 cm layer (mmol$_c$ dm^{-3})

The amount of PG necessary for the sandy soil was 4.14×10^3 kg ha^{-1} that correspond to a dose of 7.388 g for 5 kg of soil; the amount of PG necessary for the clay soil was 1.98×10^3 kg ha^{-1} that correspond to a dose of 3.319 g for 5 kg of soil.

2.2. Columns preparation

The columns were made in PVC with 14 cm diameter and 60 cm long, with the interior coated with epoxy paint. The columns were filled with 5 kg of the two types of soil, two types of PG, mixture of soil + recommended dose (D1) and finally a mixture of soil + 10 times the recommended dose (D10), totalizing 12 columns. Distilled water was added, to achieve the soil field capacity. For the sandy soil, the saturation was achieved by addition of 1400 mL of water, whereas, for the clay soil, 2100 mL of water was necessary. After 48 h, the leaching water was percolated through the columns. The volume of water added took into account 1/12 of the annual average rain fall of the State of São Paulo, around 150 mm, which correspond to 2300 mL of rain water in each column. This volume of water was added in two days: 1000 mL in the first day and the remaining in the following day. The leachate was collected for the determination of the radionuclides concentration.

2.3. Determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in soil and PG samples by gamma spectrometry

The soil and PG samples were dried until constant weight, sieved at 60 mesh and sealed in polyethylene containers for 30 days to allow the radioactive equilibrium between ^{226}Ra and its decay products gamma emitters. The activity measurement of ^{226}Ra, ^{228}Ra and ^{210}Pb in soil and PG samples was undertaken by gamma

Table 1
Characterization of soil samples.

Sample	Depth (cm)	Grain analysis			Density (g cm^{-3})	Field capacity (m^3 m^{-3})
		Sand (g kg^{-3})	Silt (g kg^{-3})	Clay (g kg^{-3})		
Sandy soil	25–50	837	14	150	1.12	0.31
Clay soil	25–50	215	208	577	1.19	0.49

spectrometry, with a Hyper Pure Germanium detector HPGe, GX2518 with 25% relative efficiency, from CAMBERRA, during 250,000 s. The radionuclide ^{226}Ra was determined taking into account the mean value of the photo peaks of the radionuclides: ^{214}Pb (295.21 keV and 351.92 keV) and ^{214}Bi (609.31 keV and 1120.30 keV). The radionuclide ^{228}Ra was determined by measuring the intensity of the photo peaks 911.07 keV and 969.11 keV from ^{228}Ac. The radionuclide ^{210}Pb was measured through its photo peak of 46.50 keV, after correction of the auto absorption of the low energy gamma rays by the sample, according to Cutshall et al. (1983). The gamma spectra were analyzed with the InterWinner 6.0 from Eurisys Measures, taking into account the gamma peak area, the background radiation for the gamma transition considered, the sample weight, the detector efficiency and the counting time.

2.4. Determination of U and Th in soil and PG samples by instrumental neutron activation analysis

The experimental procedure comprises the samples irradiation together with standard reference materials IAEA SL1-Lake Sediment and IAEA SL3-Lake Sediment, under the same conditions. The soil, PG and SRMs samples used, weighing approximately 150 mg, were conditioned in plastic containers and were irradiated in the research reactor IEA-R1 at Instituto de Pesquisas Energéticas e Nucleares, during 8 h at a thermal neutron flux of 10^{12} n cm^{-2} s^{-1}.

The samples measurements were undertaken by gamma spectrometry, using a detector from INTERTECHNIQUE with relative efficiency of 25% and resolution of 2.1 keV for the 1332 keV peak of ^{60}Co. The first counting was done after 5–10 days of decay, for the identification of U. Uranium was determined by measuring the gamma peak of ^{239}Np, with half live of 2.35 d. The second counting was done after 15 days of decay for the identification of Th. Thorium was determined by measuring the gamma peak of ^{233}Pa, with half live of 26.97d. The spectra analysis was performed by using the program InterWiner 6.0 from Eurisys Measures.

2.5. Determination of ^{210}Po in soil and PG samples by alpha spectrometry

A known amount of soil and PG samples were digested on a microwave MARS, after adding 15 mL of 65% HNO_3. The solution obtained was evaporated to dryness at less than 80 °C, and the residue was dissolved with 1 mL of HCl conc and heated almost to dryness, re-suspended with 10 mL of 0.5 M HCl, 5 mL of hydroxylamine hydrochloride 20%, 5 mL of sodium citrate 25%. The pH 2 was adjusted. The final solution was transferred into a deposition cell, on a silver disk, into a water bath at 90 °C for 4 h with mechanical stirring. Polonium was counted on an alpha spectrometer, for 80,000 s.

2.6. Determination of ^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po in the leachate

The methodology implemented for the sequential determination of ^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po in the leachate is based on the publication of International Atomic Energy Agency – AQ/34 (IAEA, 2014). The experimental procedure is described in the following. A volume of 500 mL of the leachate was concentrated to 50 mL. The final solution was mixed with 500 μL of ^{232}U tracer, with activity 0.8989 Bq g^{-1}; 500 μL of ^{229}Th tracer, with activity 0.6264 Bq g^{-1}; 200 μL of ^{209}Po tracer, with activity of 1.7251 Bq g^{-1}; 1000 μL of Ba^{+2} carrier and 1000 μL of Pb^{+2} carrier, both with concentration of 20 mg mL^{-1}. The final solution was evaporated and dissolved three times with 2 mL of concentrated HNO_3, drops of H_2O_2, and finally dissolved with 30 mL of 2M HCl.

The sample solution was loaded onto the Sr resin column preconditioned in advance with 100 mL of 2M HCl. Lead and polonium were retained in the column and U, Th and Ra isotopes were eluted. Po was stripped with 60 mL of 6M HNO_3 and Pb was eluted with 60 mL of 6M HCl. Po was spontaneously deposited on a silver disc and counted on an alpha spectrometer for 80,000 s. The Pb solution was evaporated three times with 5 mL portions of 65% HNO_3 and the final residue was dissolved in 10 mL of 1 M HNO_3. Pb was precipitated as Pb-oxalate, which was dried and weighed to calculate the chemical recovery using the gravimetric method. The precipitate was quantitatively transferred into a liquid scintillation vial together with the filter, and 1 mL of 1M HNO_3 was added into the vial to dissolve the precipitate. The solution was mixed with 15 mL of Hisafe III scintillation solution. The final solution was counted on a 1220 Quantulus™ Ultra Low Level Liquid Scintillation Spectrometer for 24,000 s.

The effluent and the washing solution from Sr resin, containing uranium, thorium and radium, was evaporated and dissolved in 10 mL of 3M HNO_3. The final solution was percolated on the UTEVA resin previously conditioned with 20 mL of 3M HNO_3, washed twice

Table 2
Chemical analysis of soil.

Sample	Depth (cm)	pH ($CaCl_2$)	O.M. (g dm^{-3})	P (mg dm^{-3})	S (mg dm^{-3})	K (mmolc dm^{-3})	Ca (mmolc dm^{-3})	Mg (mmolc dm^{-3})	H + Al (mmolc dm^{-3})	Al (mmolc dm^{-3})
Sandy soil	25–50	3.8	13.0	3	14.6	0.5	7.0	1.4	42	2.6
Clay soil	25–50	4.9	10.0	1	17.9	0.2	20.0	2.0	38	3.0

Sample	Depth (cm)	SB (mmolc dm^{-3})	$CEC_{potential}$ (mmolc dm^{-3})	$CEC_{effective}$ (mmolc dm^{-3})	V (%)	m (%)
Sandy soil	25–50	8.9	50.9	11.5	17	23
Clay soil	25–50	22.2	60.2	25.2	37	12

O.M.: organic matter.
SB: Sum of Bases; CEC: Cation Exchange Capacity; V: Soil base saturation; m: aluminium saturation.

with 5 mL aliquots of 3M HNO_3, and finally with 5 mL of 9M HCl. Under these conditions, U and Th were retained in the resin and radium was eluted. Thorium was eluted firstly by passing 25 mL of a solution of 5M HCl and 0.05M oxalic acid. Finally, uranium was removed from the resin by adding 20 mL of 0.01M HCl. U and Th were electrodeposited onto polished stainless steel discs, which were counted on an alpha spectrometer for 80,000 s.

The final solution containing the radium isotopes in 3M nitric acid was diluted to one litter and the radium was purified in EDTA. The Ba(Ra)SO_4 precipitate was obtained by addition of 3M H_2SO_4 and ammonium sulphate. The activity concentration was measured after 21 days of the radium precipitation. The ^{226}Ra and ^{228}Ra concentrations were determined by measuring the gross alpha and beta activity of the precipitate Ba(Ra)SO_4 on a low background gas flow proportional detector for 200 min.

2.7. Determination of the elements As, Cd, Ni, Pb, Se and Hg

The analyses of the elements As, Cd, Cr, Hg, Ni, Pb and Se were performed using the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) from Varian, model Vista MPX. For the analysis of Hg, the vapour/hydrides generator VGA77 model, coupled to the ICP-OES VARIAN, was used. The validation of the measurements for the element As, Cd, Cr, Ni and Pb was performed using reference material EnviroMat Contaminated Soil SS-1 and for Hg using IRMM Estuarine Sediment ERM-CC580-Total and methyl mercury.

The values obtained for the metals quantification limits are 50 μg L^{-1} for As, 13 μg L^{-1} for Cd, 3 μg L^{-1} for Cr, 5 μg L^{-1} for Ni, 14 μg L^{-1} for Pb, 20 μg L^{-1} for Se and 0.4 μg L^{-1} for Hg.

3. Results and discussion

The results of the activity concentration of ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra, in soil, PG and soil + PG are presented in Table 3. The radionuclides of the U and Th natural series are in equilibrium in the soils analyzed. The concentrations observed in the clay soil are approximately four times higher than the sandy soil; the results are in good agreement with literature values for Brazilian soils (Peres, 2007; Mazzilli et al., 2012). It can be observed that the radionuclides concentrations in the mixture soil + PG are not statistically different from the concentration observed in the soils. This observation was expected, due to the fact that the added PG was in a very small quantity: in the worst case, 74 g of PG (10 times the recommended dose), for 5 kg of sandy soil. However, this addition of PG is not trivial in terms of availability of radionuclides, if the solubility of $CaSO_4$ (0.25 g/100 g H_2O) is taken into account. The activity concentration of ^{238}U, ^{226}Ra and ^{232}Th in the soil studied are of the same order of magnitude of world average values in soils (35 Bq kg^{-1} for ^{238}U, 35 Bq kg^{-1} for ^{226}Ra and 30 Bq kg^{-1} for ^{232}Th) (UNSCEAR, 2010).

The concentration of PG from the two provenances, Cubatão and Uberaba installations, varied from 144 to 294 Bq kg^{-1} for ^{226}Ra, from 149 to 352 Bq kg^{-1} for ^{210}Pb, from 155 to 346 Bq kg^{-1} for ^{210}Po, from 86 to 210 Bq kg^{-1} for ^{232}Th and from 116 to 228 Bq kg^{-1} for ^{228}Ra, respectively. The ^{238}U concentrations observed are below 7 Bq kg^{-1}. As for the other radionuclides analysed, the differences observed depend of the phosphate rock used as raw material in the two installations and are in good agreement with literature values for the same phosphogypsum (Mazzilli et al., 2000; Saueia and Mazzilli, 2006). The two Brazilian PG studied showed compliance with the exemption limits adopted by Comissão Nacional de Energia Nuclear for the safe use of phosphogypsum in agriculture and cement industry (CNEN, 2013).

The results obtained for the mean concentration of the radionuclides ^{238}U, ^{232}Th, ^{210}Pb, ^{226}Ra and ^{228}Ra in the leachate are presented in Table 4. All the samples were analysed in triplicate. The concentration observed for ^{238}U and ^{232}Th in the leachate were below the detection limit, except for ^{238}U in the leachate of phosphogypsum, which presented mean values of 265 mBq L^{-1} and 1487 mBq L^{-1}, for the installation of Cubatão and Uberaba, respectively.

A possible explanation to the presence of ^{238}U in the PG leachate, in spite of this element being present in the PG in low concentrations, below 7 Bq kg^{-1}, could be the residual presence of phosphoric acid in the porous of the PG in the industrial process. The solubility of uranium present in the phosphoric acid is much higher than its solubility in the PG itself (Santos et al., 2006). The absence of ^{232}Th in the PG leachate was expected, since this radionuclide presents low solubility and, therefore, is not usually available in water. In a paper from Santos et al. (2006), the Brazilian phosphogypsum was submitted to the sequential extraction of Tessier et al. (1979). The authors concluded that the Th although present in the phosphogypsum, is bound to the insoluble residual phase.

The available fraction, obtained by the ratio of the radionuclides concentration found in the leachate and the corresponding concentration found in the soil and PG samples, is presented in Table 5. The available fraction presented in most cases values below 1%, giving evidence that although the radionuclides ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra are present in PG in higher concentrations, they are not available to the water. Similar trend was also observed by

Table 3
Mean concentration and standard deviation of ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra in samples of soil, phosphogypsum and soil + phosphogypsum (Bq kg^{-1}).

Sample	U-238	Ra-226	Pb-210	Po-210	Th-232	Ra-228
PG CUB	<7	294 ± 5	352 ± 23	346 ± 7	210 ± 6	228 ± 6
PG UBE	<7	144 ± 11	149 ± 4	155 ± 11	86 ± 8	116 ± 1
Clay soil	40 ± 2	38 ± 1	46 ± 8	38 ± 2	52 ± 1	51 ± 2
Clay soil + PG CUB_D1	51 ± 2	39 ± 1	51 ± 7	33 ± 2	49 ± 1	51 ± 1
Clay soil + PG CUB_D10	51 ± 2	39 ± 2	54 ± 17	42 ± 4	53 ± 1	51 ± 2
Clay soil + PG UBE_D1	55 ± 4	38 ± 1	54 ± 6	39 ± 3	46 ± 5	51 ± 3
Clay soil + PG UBE_D10	43 ± 2	38 ± 2	47 ± 10	41 ± 3	50 ± 3	50 ± 1
Sandy soil	11 ± 1	6 ± 1	13 ± 2	14 ± 1	14 ± 2	12 ± 1
Sandy soil + PG CUB_D1	9 ± 2	7 ± 1	21 ± 6	16 ± 2	18 ± 3	12 ± 3
Sandy soil + PG CUB_D10	12 ± 3	9 ± 1	19 ± 2	19 ± 1	19 ± 3	16 ± 1
Sandy soil + PG UBE_D1	7 ± 1	7 ± 1	19 ± 5	16 ± 1	15 ± 1	13 ± 2
Sandy soil + PG UBE_D10	9 ± 1	9 ± 1	21 ± 4	19 ± 1	15 ± 2	15 ± 1
PERES – Reference values for soil quality (interval)	<47–411[a]	1–61.8	<20–121	–	8–82	3.3–97.6
PERES – Reference values for soil quality (geometric mean)	93 ± 1.8[a]	17.1 ± 2.4	46 ± 1.6	–	30 ± 1.8	27.8 ± 2.2

[a] Values of Unat.

Table 4
Mean concentration and standard deviation of ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra in the leachate samples (mBq L^{-1}).

Sample	U-238	Ra-226	Pb-210	Po-210	Th-232	Ra-228
PG CUB	265 ± 135	81 ± 2	18 ± 7	59 ± 6	<7.5	<4
PG UBE	1487 ± 337	57 ± 18	11 ± 4	200 ± 19	<7.5	<4
Clay soil	<1.5	21 ± 13	15 ± 7	35 ± 13	<7.5	29 ± 12
Clay soil + PG CUB_D1	<1.5	38 ± 15	39 ± 4	40 ± 21	<7.5	52 ± 16
Clay soil + PG CUB_D10	<1.5	40 ± 22	18 ± 3	41 ± 3	<7.5	62 ± 22
Clay soil + PG UBE_D1	<1.5	26 ± 5	17 ± 4	25 ± 3	<7.5	26 ± 14
Clay soil + PG UBE_D10	<1.5	32 ± 7	10 ± 3	37 ± 4	<7.5	38 ± 9
Sandy soil	<1.5	17 ± 11	14 ± 8	20 ± 3	<7.5	20 ± 14
Sandy soil + PG CUB_D1	<1.5	67 ± 21	30 ± 18	35 ± 4	<7.5	132 ± 21
Sandy soil + PG CUB_D10	<1.5	54 ± 10	30 ± 21	47 ± 4	<7.5	68 ± 10
Sandy soil + PG UBE_D1	<1.5	87 ± 6	35 ± 6	47 ± 4	<7.5	161 ± 33
Sandy soil + PG UBE_D10	<1.5	69 ± 12	38 ± 9	37 ± 24	<7.5	142 ± 39

Mazzilli and Saueia (2013), who studied the availability of radionuclides present in PG, in water and EDTA. According to them, the concentration of ^{226}Ra, ^{228}Ra and ^{210}Pb found in the residue, after almost complete dissolution of the PG samples in water (more than 90%), are less than 10% of the total available content of these radionuclides in PG.

The mean activity concentration of the radionuclides in the sandy soil is about 4 times lower than the clay soil (Table 3). If the concentration of the radionuclides in the leachate for all the sandy soil and clay soil, with and without PG, are taken into account, it can be observed that the leachate from sandy soil presents 1.5 more activity compared to the leachate from clay soil (Table 4). The same trend is also observed in the available fraction, the values obtained for all the sandy soil is 5 times higher than the clay soil (Table 5). It can be concluded that the radionuclides are more available in the sandy soil leachate. A possible explanation to this behaviour is the lower pH and lower CEC of the sandy soil compared with the clay soil (Table 2).

Available fractions obtained for the radionuclides ^{226}Ra and ^{228}Ra in the leachate of sandy soil and clay soil are similar. The radium isotopes (^{226}Ra and ^{228}Ra) belong to different natural decay series of ^{238}U and ^{232}Th, respectively, therefore they present different concentrations in soil. However, since they have the same chemical behaviour, the available fractions observed are similar for all the soil samples analysed.

Po-210 presented higher available fractions compared to ^{210}Pb, for all the samples analysed; lead is considered as a low mobile element in soil whereas ^{210}Po presents higher solubility.

The average concentration of the elements As, Cd, Cr, Ni, Pb, Se and Hg are presented in Table 6, together with the Maximum Permissible Values of contaminants in soil conditioner and fertilizers (MAPA, 2006). The values obtained for the detection limit for the elements As, Cd, Cr, Ni, Pb, Se and Hg were 4.5 mg kg^{-1}, 1.1 mg kg^{-1}, 0.9 mg kg^{-1}, 0.5 mg kg^{-1}, 0.7 mg kg^{-1}, 1.0 mg kg^{-1} and 0.01 mg kg^{-1}, respectively.

The clay soil presented concentration of the elements higher than the sandy soil, except for Hg, which presented similar concentrations. The element selenium was not found in all the samples analysed. The results of the elements concentration are in accordance with literature values for soil from São Paulo State (Mazzilli et al., 2012).

In Brazil, the Guideline for controlling metals in fertilizers and soil amendment is established by "Instrução Normativa n° 27 from Ministério da Agricultura, Pecuária e Abastecimento (MAPA, 2006). The results obtained in the present study for the concentration of As, Cd, Cr, Ni, Pb, Se and Hg in PG are below the maximum permissible concentration for these elements.

The elements concentration found in the PG samples are of the same order of magnitude of values available in the literature for the Brazilian PG (Saueia et al., 2013a). Concentrations below the detection limits were observed for the elements As, Cd and Se in PG samples from Cubatão and Uberaba. The elements Cr, Ni, Pb and Hg presented measurable concentrations, but the values are lower than the Maximum Permissible Concentration in fertilizer and soil conditioner established by Ministério da Agricultura, Pecuária e Abastecimento (MAPA, 2006).

The clay soil presented concentration of the element Cr four times higher than the sandy soil, nickel seven times higher and Pb five times higher. It can be also observed that the metals concentrations in the mixture soil + PG are not statistically different from the concentration observed in the soils.

The average concentrations of the elements in the leachate are presented in Table 7. The concentration of As, Cd, Cr and Ni in the leachate solution from the PG columns of Cubatão and Uberaba,

Table 5
Available fraction for the radionuclides (%).

Sample	U-238	Ra-226	Pb-210	Po-210	Th-232	Ra-228
PG CUB	–	0.03	0.01	0.02	–	–
PG UBE	–	0.04	0.01	0.13	–	–
Clay soil	–	0.06	0.03	0.09	–	0.06
Clay soil + PG CUB_D1	–	0.10	0.08	0.12	–	0.10
Clay soil + PG CUB_D10	–	0.10	0.03	0.10	–	0.12
Clay soil + PG UBE_D1	–	0.07	0.03	0.06	–	0.05
Clay soil + PG UBE_D10	–	0.08	0.02	0.09	–	0.08
Sandy soil	–	0.28	0.11	0.14	–	0.17
Sandy soil + PG CUB_D1	–	0.96	0.14	0.22	–	1.10
Sandy soil + PG CUB_D10	–	0.60	0.16	0.25	–	0.43
Sandy soil + PG UBE_D1	–	1.24	0.18	0.29	–	1.24
Sandy soil + PG UBE_D10	–	0.77	0.18	0.19	–	0.95

Table 6
Average concentration and standard deviation of As, Cd, Cr, Ni, Pb, Se and Hg in samples of soil, soil + PG and PG, Maximum Permissible Concentration in fertilizer and soil conditioner from MAPA (mg kg^{-1}).

Sample description	As	Cd	Cr	Ni	Pb	Se	Hg[a]
PG CUB	<4.5	<1.1	3.4 ± 0.4	1.5 ± 0.5	21.9 ± 0.5	<1	29.3 ± 4.0
PG UBE	<4.5	<1.1	1.4 ± 0.1	<0.5	6.5 ± 0.5	<1	51.1 ± 0.4
Sandy soil	<4.5	<1.1	7.7 ± 0.4	1.9 ± 0.2	3.1 ± 0.7	<1	21.5 ± 0.4
Sandy soil + PG CUB_D1	<4.5	<1.1	7.9 ± 0.1	2.1 ± 0.5	3.4 ± 0.2	<1	21.1 ± 2.5
Sandy soil + PG CUB_D10	6.2 ± 1.6	<1.1	7.7 ± 0.3	2.0 ± 0.3	3.7 ± 0.2	<1	18.6 ± 0.6
Sandy soil + PG UBE_D1	<4.5	<1.1	7.5 ± 0.9	2.0 ± 0.3	2.7 ± 0.2	<1	21.4 ± 2.8
Sandy soil + PG UBE_D10	<4.5	<1.1	6.5 ± 0.6	1.5 ± 0.4	2.8 ± 0.4	<1	19.8 ± 1.3
Clay soil	6.3 ± 2.1	2.2 ± 0.1	29.1 ± 2.6	12.3 ± 3.3	15.9 ± 1.1	<1	26.4 ± 0.5
Clay soil + PG CUB_D1	7.4 ± 1.5	2.3 ± 0.1	25.7 ± 1.2	14.5 ± 4.5	16.2 ± 0.6	<1	24.6 ± 2.8
Clay soil + PG CUB_D10	6.9 ± 1.5	2.3 ± 0.1	27.8 ± 1.7	17.2 ± 2.8	16.9 ± 0.7	<1	25.4 ± 1.6
Clay soil + PG UBE_D1	7.3 ± 0.1	2.2 ± 0.2	27.3 ± 6.5	13.8 ± 4.8	14.9 ± 1.5	<1	22.2 ± 0.1
Clay soil + PG UBE_D10	6.8 ± 0.6	2.3 ± 0.1	28.4 ± 1.0	13.9 ± 4.5	15.5 ± 0.7	<1	23.6 ± 1.7
Maximum Permissible Concentration in fertilizer	10	20	200	–	100	–	0.2[b]
Maximum Permissible Concentration in soil conditioner	20	8	500	175	300	80	2.5[b]

[a] Concentration in μg kg^{-1}.
[b] Concentration mg kg^{-1}.

Table 7
Average concentration and standard deviation of As, Cd, Cr, Ni, Pb, Se and Hg in the leachate of soil, soil + PG and PG (μg L^{-1}).

Sample description	As	Cd	Cr	Ni	Pb	Se	Hg
PG CUB	142 ± 14	13.8 ± 0.6	29.3 ± 4.1	424 ± 48	<14	<20	<0.4
PG UBE	243 ± 47	16.5 ± 0.8	55.2 ± 16.0	239 ± 43	<14	<20	<0.4
Sandy soil	<50	<13	4.2 ± 0.4	20.4 ± 0.2	<14	<20	<0.4
Sandy soil + PG CUB_D1	<50	<13	5.9 ± 1.6	11.9 ± 8.8	<14	<20	<0.4
Sandy soil + PG CUB_D10	<50	<13	3.2 ± 0.4	10.5 ± 4.5	<14	<20	<0.4
Sandy soil + PG UBE_D1	<50	<13	<3	8.1 ± 3.9	<14	<20	<0.4
Sandy soil + PG UBE_D10	<50	<13	3.3 ± 0.2	11.0 ± 1.0	<14	<20	<0.4
Clay soil	<50	<13	<3	7.8 ± 3.5	<14	<20	<0.4
Clay soil + PG CUB_D1	<50	<13	<3	12.0 ± 3.5	<14	<20	<0.4
Clay soil + PG CUB_D10	<50	<13	<3	5.6 ± 0.1	<14	<20	<0.4
Clay soil + PG UBE_D1	<50	<13	<3	7.4 ± 0.8	<14	<20	<0.4
Clay soil + PG UBE_D10	<50	<13	<3	17.4 ± 1.3	<14	<20	<0.4

presented results above the limit of quantification, showing that these elements are available in the water. The concentration of Pb, Se and Hg in the leachate solution from the PG columns did not surpass the detection limits. The available fraction was determined only for Cr and Ni; with results up to 5% and 30%, respectively. As for the other elements studied (As, Cd, Pb, Se and Hg), it was not possible to determine the available fraction, since they were not present in the PG or in the leachate.

The concentration of As, Cd, Pb, Se and Hg, in the leachate solution from the mixture soil + PG, presented results below the limit of quantification, showing that these elements are not available in the water. The mean concentration for Cr and Ni in the leachate of the sandy soil was 4.1 μg L^{-1} and 12.4 μg L^{-1}, and for Ni in the clay soil was 10.0 μg L^{-1}; therefore, the available fraction in the sandy soil was 0.1% and 1% for Cr and Ni and in the clay soil was 0.1% for Ni. It can be concluded that Ni is more available in the sandy soil percolation water. A possible explanation to this behaviour is the lower pH and lower CEC of the sandy soil compared with the clay soil.

4. Conclusion

The results obtained for the activity concentrations of ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra in the clay soil are approximately four times higher than the sandy soil. The results obtained for the radionuclides concentration in the PG varied from 144 ± 11 to 294 ± 5 Bq kg^{-1} for ^{226}Ra, from 149 ± 4 to 352 ± 23 Bq kg^{-1} for ^{210}Pb, from 155 to 346 Bq kg^{-1} for ^{210}Po, from 86 ± 8 to 210 ± 6 Bq kg^{-1} for ^{232}Th and from 116 ± 1 to 228 ± 6 Bq kg^{-1} for ^{228}Ra. However, the addition of PG to the soils studied did not represent any increase in the final activity concentration. The final concentrations observed in the soils are of the same order of magnitude of the values reported by UNSCEAR (2010) for the worldwide average values. The available fraction obtained by the ratio of the radionuclides concentration found in the leachate and the corresponding concentrations found in the soil + PG samples were below 1%, giving evidence that although the radionuclides ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra are present in PG in higher concentrations, they are not available to the water.

The elements Cr, Ni, Pb and Hg presented measurable concentrations in the PG samples, but the final concentrations in the mixture soil + PG were not statistically different from the concentration observed in the soils. It was also observed that the available fractions for these elements were below 1%.

Finally, it can be concluded that the addition of PG to the soils, even in quantities that exceeded 10 times the amount of phosphogypsum necessary to achieve 50% of the soil base saturation, does not contribute to an enhancement of the radionuclides and metals contents in water.

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