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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