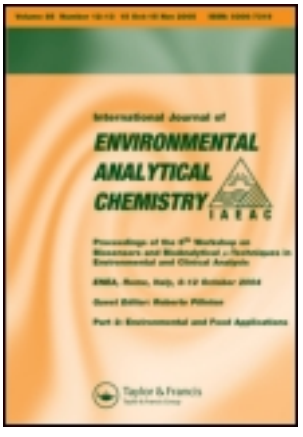

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Natural radionuclides and metals intake into soya, corn and lettuce grown on soil amended with phosphogypsum

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Natural radionuclides and metals intake into soya, corn and lettuce grown on soil amended with phosphogypsum

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Phosphogypsum is a by-product of the phosphate fertilizer industry. It is produced by precipitation during wet process of phosphate rocks, thus posing serious problems with its utilization and safe disposal. In Brazil, three main industries are responsible for the production and storage of about 5.5×10^6 tons per year. Phosphogypsum may contain trace metals and radionuclides of U and Th series. Since, in Brazil, phosphogypsum has been used for many years as soil amendment, it is important to know its availability in the environment. The main objective of this study is to evaluate the radionuclides and metals transfer in the soil-to-plant system. To accomplish this task an experiment was carried out in a green house, where two major crop groups (soya bean and corn) and leafy vegetables (lettuce) were grown in two types of soil (clay and sandy) amended with phosphogypsum. The transfer-factors were evaluated for the metals (As, Cd, Cu, Ni and Pb, Ba, Co, Cr, Fe, Zn and REE) and for the radionuclides U, Th, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po. The addition of PG to the two soils studied, did not significantly alter the TFs values for all the elements studied.

Keywords: natural radionuclides; metals; phosphogypsum; transfer-factor; trace elements

1. Introduction

It is recognized that several non-nuclear industries have a potential threat to cause environmental and occupational radiological impact. The main problem associated with these industries is the generation of effluents, residues and by-products containing not just natural radionuclides, but also other toxic elements, such as heavy metals and anions.

Phosphogypsum (PG) is a TENORM (Technologically Enhanced Naturally Occurring Radioactive Material) by-product of the phosphate fertilizer industry. In Brazil, three main industries (Copebrás, Ultrafertil and Fosfertil) are responsible for the production and storage of about 5.5×10^6 tons per year. It may contain high quantities of P_2O_5, trace metals and radionuclides of U and Th series. Depending upon the level of radioactivity the TENORM industries are subjected to the recommendations given by *ComissãoNacional de*

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Energia Nuclear (CNEN), which include compliance with the radiological protection regulations [1,2]. Several publications are available in the literature related with the radiological characterization of Brazilian phosphogypsum [3–6], however few publications discuss the metals' characterization in phosphogypsum.

In Brazilian factories, the method used for the production of phosphoric acid is based on drastic treatment of the primary igneous rock with sulphuric acid, the so-called wet process, according with the following reaction:

$$Ca_{10}F_2(PO_4)_6+10H_2SO_4+10nH_2O \rightarrow 10CaSO_4nH_2O + 6H_3PO_4+2HF \quad (1)$$

This process forms a precipitate of calcium sulphate, called phosphogypsum, as a by-product, which is stockpiled and is considered waste due to its elevated levels of impurities. Phosphogypsum produced during the process is filtered off and pumped as slurry to nearby ponds, where it stays for a period sufficient to allow complete deposition. This waste is then moved to nearby storage areas, the so-called ''gyp-stacks''. According to previous papers [3–5], it is known that the radium and thorium isotopes, Pb-210 and Po-210 concentrate in the PG, whereas the U isotopes are enriched in the phosphoric acid.

All the countries that produce phosphate fertilizer by acid wet process are facing the same problem of finding solutions for the safe application of phosphogypsum, in order to minimize the impact caused by the disposal of large amounts of this by-product. Phosphogypsumhas been used for many years in agriculture as a soil amendment, however, for its safe application the mobility and intake of natural radionuclides and metals from soil to food crops should be known. Another point that should be taken into account is the long-term accumulation of these elements after several applications, with possible contamination of soil and ground waters. It is, therefore, necessary to evaluate the bioavailability of these elements and their absorption by plants. Although several studies were undertaken with PG of sedimentary origin, considering for instance the radiological impact of PG applied to soils under bahiagrass pasture in Florida [7] or the cumulative effect of three decades of PG amendments in reclaimed marsh soils in Spain [8], no similar study was pursued considering the use of the Brazilian PG of igneous origin.

The main objective of this study is to evaluate radionuclides and metals transfer factor in the soil-to-plant system. The soil-to-plant transfer factor (TF) is defined as the ratio of the concentration of radionuclides/metals in plant ($Bq\,kg^{-1}$ or $\mu g\,g^{-1}$ dry mass) to that in soil ($Bq\,kg^{-1}$ or $\mu g\,g^{-1}$ dry mass), according to:

$$TF = Cp/Cs \quad (2)$$

To accomplish this task an experiment was carried out in green house, in which two major crop groups (soya and corn) and leafy vegetables (lettuce) were grown in two types of soil (clay and sandy) amended with phosphogypsum.

2. Experimental

The experiment was carried out in a green house in the Soil Department of the Universidade Federal de Viçosa–Minas Gerais State. Two major crop groups (soya and corn) and leafy vegetables (lettuce) were grown in two types of soil (clay and sandy) amended with phosphogypsum. The planting of the three cultures was carried out in two pots: one without the addition of phosphogypsum, and the other with the double of the

recommended phosphogypsum dosage, that is, $1.0\,g\,dm^{-3}$ for the clayish soil and $0.4\,g\,dm^{-3}$ for the sandy soil, according to the EMBRAPA recommendation [9].

The PG used comes from Ultrafertil facility, located in Cubatão, São Paulo state. The phosphate rock used in this installation is an igneous rock constituted by apatite, magnetite and olivine, which presents in its composition concentrations of natural radionuclides of the U series (^{238}U, ^{226}Ra, ^{210}Pb and ^{210}Po) up to $1480\,Bq\,kg^{-1}$ and for the Th series (^{232}Th and ^{228}Ra) up to $393\,Bq\,kg^{-1}$ [3,4]. The radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb present in crops and lettuce were determined by radiochemical separation followed by gross alpha and beta counting using a gas flow proportional counter. The same radionuclides in soil and PG samples were determined by gamma spectrometry. ^{210}Po was spontaneously plated on a silver disc and measured by alpha spectrometry. The metals (Ba, Co, Cr, Fe, Th, U, Zn and REE) were determined by instrumental neutron activation analysis (INAA). The elements As, Cd, Cu, Ni and Pb were determined by Atomic Absorption Spectrometry (AAS).

The soil samples were collected from two different locations in the municipal district of SeteLagoas, MG and of JoãoPinheiro, MG, which represent typical soils of the Cerrado region. The soils were never treated with any kind of fertilizer. The first one, classified as red-yellow dystrophic latosol, is composed mainly of caulinita (>30%) fine-grained argilaceoussilty clay (particles diameter around 250 μm); the second one, classified as yellow dystrophic latosol, is composed mainly of quartz (>30%) with particles diameter varying in the range of 105 to 250 μm. The chemical analysis of both soils revealed acid characteristics and low fertility, with low concentration of nutrients such as Ca, Mg, K and P. The argilaceous soil presented slightly better fertility, with higher concentrations of Ca and organic matter. Both soils present higher levels of Al and acid characteristics, which are typical of Cerrado soils, with more than 30% of Al saturation.

Samples of phosphogypsum, soil, phosphogypsum added soil and corn, soya and lettuce grown in soil and in phosphogypsum added soil were analysed for the determination of metals and radionuclides. All the experiments were carried out in triplicate, and the crops were washed to avoid any contamination from soil particles. All the samples, excluding lettuce, were dried at about 60°C to remove moisture and crushed to fine powder (30 to 60 mesh). The lettuce samples were dried in a ventilated oven, at 60°C for 48 hours, ground and sieved.

2.1 *Activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb in soil and phosphogypsum samples using gamma-ray spectrometry*

Activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb were measured in soil and phosphogypsum samples by gamma-ray spectrometry with a hyper-pure germanium detector, EGNC 150-190R, from Eurisys Measures, with a resolution of 1.8 keV for the ^{60}Cophotopeak and 15% efficiency. Samples were packed in 100 cm^3 cans and sealed for about four weeks prior to the measurement in order to ensure that secular equilibrium has been reached between ^{226}Ra and its decay products of short half-life. The ^{226}Ra activities were determined by taking the mean activity of three separate photo peaks of its decay products^{214}Pb at 295 keV and 352 keV, and ^{214}Bi at 609 keV. The ^{228}Ra content of the samples was determined by measuring the intensities of the 911 keV and 968.9 keV gamma-ray peaks from ^{228}Ac. For the determination of ^{210}Pb, the photopeak of 46.5 keV was used. This peak, owing to its low energy, needed auto-absorption correction, which was carried

out according to the procedure proposed by Cutshall [10]. Minimum detectable activity concentrations for gamma spectrometry were obtained by measuring deionized water in the same geometry as the samples, and the results were 10 Bq kg^{-1} for ^{226}Ra, 20 Bq kg^{-1} for ^{210}Pb and 11 Bq kg^{-1} for ^{228}Ra, for a counting time of 150,000 seconds.The accuracy of the measurements was performed by using the reference standard materials Radionuclides in soil (IAEA 326) and Radionuclides in Irish Sea Sediments (IAEA 385). The results obtained are within the confidence interval specified for each reference material, ranged from 4.0 to 11%, attesting the accuracy of the measurement.

2.2 *Activity concentration of ^{226}Ra, ^{228}Ra and ^{210}Pb using alpha and beta gross counting and ^{210}Po using alpha spectrometry in soya, corn and lettuce samples*

For the determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in soya, corn and lettuce samples a 500-mg amount were dissolved in HNO_3 in a microwave digestor. The solution obtained was heated, HCl and H_2O_2 were added and the final solution was submitted to a radiochemical procedure. Radium was co-precipitated as $Ba(Ra)SO_4$ by adding H_2SO_4. The mixed sulphates were dissolved with NTA (nitrilotriacetic acid). Barium (radium) sulphate was re-precipitated by adding acetic acid (pH 4.5–5.0) whereas lead remained in the aqueous phase. The aqueous and solid phases were separated and the $Ba(Ra)SO_4$ was purified by dissolution in an EDTA solution at pH 10. Then the sulphate mixture was again precipitated by acetic acid (pH 4.5–5.0) and filtrated. After the procedure, the ^{226}Ra and ^{228}Ra concentration were determined by gross alpha and beta counting of the $Ba(Ra)SO_4$ precipitate and the ^{210}Pb concentration through its decay product, ^{210}Bi, by measuring the gross beta activity of the $PbCrO_4$ precipitate after separation from interfering elements by complexation with nitrilo tri acetic acid (NTA) at basic pH. Both radionuclides were determined in a low background gas flow proportional detector Berthold LB 770 Low Level Counter.

For ^{210}Po determination, a modified methodology of Matthewswas used [11]. The solution obtained after the chemical attack was evaporated to dryness in the presence of exact aliquots of ^{209}Po used as tracers. The residue was dissolved in 6.25 M HCl, filtered in Millipore 0.1 μm and 20% hydroxylamine hydrochloride, sodium citrate and stable Bi^{+3} was added. After the pH was adjusted to 1.5, polonium contents was spontaneously plated on the silver disc at 90°C for 4 hours, with agitation of the solution. The alpha measurements were performed on a surface barrier detector, EG&G Ortec model 576 A.

2.3 *Concentration of U, Th and metals in soil, phosphogypsum and food crops samples using instrumental neutron activation analysis (INAA)*

Metals characterization (Ba, Co, Cr, Fe, Th, U, Zn and REE) was performed by instrumental neutron activation analysis (INAA). The elements determination was made by irradiation of approximately 150 mg of each sample, during 16 hours at a neutron flux of 10^{12} n cm^{-2} s^{-1}, at Instituto de PesquisasEnergéticas e Nucleares (IPEN) research reactor IEA-R1. The induced radioactivity was measured with a Ge-hyperpure detector, Intertechnique, with 2.1 keV resolution for the 1332 keV ^{60}Co photo peak. The concentration of the analyzed elements was determined by comparing activities obtained in the samples with standard materials Buffalo River Sediment (NIST-2704), Soil-7

(IAEA) and Peach Leaves (NIST-1547). The accuracy ranged from 0.4% to 8.8% and the precision from 1.3% to 8.3%.

2.4 *Metals concentration in soil, phosphogypsum and food crops samples using atomic absorption spectrometry (AAS)*

Metals concentration (As, Cd, Cu, Ni and Pb) were analysed based on EPA 3050B method by atomic absorption spectrometry. Multiple sets of standard solutions for these elements were prepared using $1000\,mg\,g^{-1}$ high purity standard solution of Spec Sol.

These standard solutions were used for calibration curve for the elements to be determined, using Perkin Elmer Analyst 100 model of Atomic Absorption Spectrometer (AAS) in oxidant flame mixture air-acetylene in cathode lamp hollow. The precision and the accuracy of the measurements were performed by using the reference standard material San Joaquin Soil (NIST-2709). The accuracy ranged from 0.2% to 8.4% and the precision from 0.7% to 7.7%.

3. Results and discussion

The results obtained for the radionuclides concentrations (^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra) in soil, PG, soil + PG and crop samples are presented in Table 1. The two kinds of soil presented radionuclides concentrations for the U and Th series in the same range observed for natural soils in UNSCEAR report ($35\,Bq\,kg^{-1}$ for U and Ra, and $30\,Bq\,kg^{-1}$ for Th) [12]; although in clay soil higher concentrations were observed, specially for ^{238}U (average concentration of $137\,Bq\,kg^{-1}$).

The PG used in this study comes from Ultrafertil facility, located in Cubatão, and presents activity concentrations for all the radionuclides similar to the phosphate rock used as raw material, except for ^{238}U [5]. The average concentrations observed were 323 ± 13 for ^{226}Ra, 440 ± 27 for ^{210}Pb, 319 ± 6 for ^{210}Po, 125 ± 8 for ^{232}Th and 210 ± 10 for ^{228}Ra. The addition of PG to the soils did not alter significantly the levels of radioactivity for all the radionuclides; consequently the soil-to-plant transfer factors for U, Th, Ra, Pb and Po did not present significant variations due to the addition of PG (Table 2). The results obtained in this study for the TF of radionuclides were compared with the review made by Vandenhove [13], who compiled data, based on an extensive literature survey, concerning soil-to-plant transfer factors for U, Th, Ra, Pb and Po.

The TF for U was observed only for the corn grown in sandy soil, with a value of 3.1×10^{-2}. This result is in good agreement with the geometric mean observed by Vandenhove [13], of 2.27×10^{-2} for a total of 781 observations of more than 57 references.

Th is a very immobile element. The generic geometric mean for TF-Th evaluated by Vandenhove [13] is 3.5×10^{-3}; in the present study, the TF-Th observed for corn, lettuce and soya were on the average 4.9×10^{-3}, of the same order of magnitude.

Radium is the last member of the alkaline earth elements, a group of metals whose lighter members (Ca and Mg) play a very important role in plant growth and nutrition. The Ra transfer factor depends on soil characteristics, plant type, the plant part concerned, climate conditions, and the physico-chemical form of radium. Radium has also a high affinity for the regular exchange sites of the soil. The TF-Ra obtained in this study for lettuce, corn and soya varied from 1.7×10^{-1} to 6.1×10^{-1} for ^{226}Ra and from 4.1×10^{-2} to 7.4×10^{-1} for ^{228}Ra, independent upon the addition of PG to the two types

Table 1. Activity concentration of ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra in PG, clay and sandy soil, soil + PG and crop samples in Bq kg^{-1}.

	U–238	Ra–226	Pb–210	Po–210	Th–232	Ra–228
PG (5)	<0.9	(3.2 ± 0.1) E+2	(4.4 ± 0.3)E+2	(3.2 ± 0.1)E+2	(1.3 ± 0.1)E+2	(2.1 ± 0.1)E+2
Clay soil (3)	(1.4 ± 0.2)E+2	(5.8 ± 0.2)E+1	(5.2 ± 0.7)E+1	(5.1 ± 0.3)E+1	(1.0 ± 0.2)E+2	(9.6 ± 0.3)E+1
Lettuce (3)	<0.9	9.6 ± 0.9	(2.2 ± 0.2)E + 1	2.7 ± 0.1	(2.1 ± 0.1)E−1	(1.5 ± 0.1)E+1
Corn (3)	<0.9	<2.2	8.3 ± 0.8	1.41 ± 0.04	<0.1	3.9 ± 0.4
Soya bean (3)	<0.9	<2.2	7.6 ± 0.8	3.3 ± 0.1	<0.1	8.5 ± 0.8
Clay soil + PG (3)	(1.3 ± 0.2)E+2	(5.8 ± 0.2)E+1	(5.6 ± 0.7)E+1	(5.5 ± 0.5)E+1	(1.0 ± 0.3)E+2	(10.0 ± 0.5)E+1
Lettuce (3)	<0.9	(1.1 ± 0.1)E+1	(2.3 ± 0.2)E+1	2.2 ± 0.1	(3.5 ± 0.2)E−1	(1.9 ± 0.2)E+1
Corn (3)	<0.9	<2.2	(1.1 ± 0.1)E+1	3.3 ± 0.2	<0.1	4.7 ± 0.5
Soya bean (3)	<0.9	<2.2	8.7 ± 0.8	1.74 ± 0.05	<0.1	(1.4 ± 0.1)E+1
Sandy soil (3)	(3.9 ± 0.6)E+1	(1.5 ± 0.1)E+1	<20	(1.7 ± 0.3)E+1	(3.2 ± 0.2)E+1	(2.9 ± 0.3)E+1
Lettuce (3)	<0.9	7.3 ± 0.7	(2.3 ± 0.3)E+1	2.0 ± 0.1	(2.4 ± 0.1)E−1	(2.2 ± 0.2)E+1
Corn (3)	1.2 ± 0.1	<2.2	(1.1 ± 0.1)E+1	1.7 ± 0.1	(2.1 ± 0.1)E−1	4.7 ± 0.5
Soya bean (3)	<0.9	4.4 ± 0.4	8.3 ± 0.8	2.1 ± 0.1	(2.3 ± 0.2)E−1	(1.4 ± 0.1)E+1
Sandy soil + PG (3)	(4.5 ± 0.7)E+1	(1.5 ± 0.1)E+1	<20	(1.8 ± 0.1)E+1	(3.1 ± 0.1)E+1	(3.0 ± 0.4)E+1
Lettuce (3)	<0.9	9.1 ± 0.9	(2.0 ± 0.2)E+1	2.0 ± 0.1	(2.4 ± 0.1)E−1	(1.9 ± 0.2)E+1
Corn (3)	<0.9	<2.2	6.6 ± 0.6	1.53 ± 0.05	<0.1	4.4 ± 0.4
Soya bean (3)	<0.9	5.2 ± 0.5	6.9 ± 0.7	2.3 ± 0.1	<0.1	(1.6 ± 0.2)E+1

(n) number of samples analysed.
(Mean value ± standard deviation).

Table 2. Radionuclides transfer factor from soil to plant.

	U–238	Ra–226	Pb–210	Po–210	Th–232	Ra–228
Lettuce						
Clay soil	–	1.7E−1	4.2E−1	5.3E−2	2.1E−3	1.6E−1
Clay soil + PG	–	1.8E−1	4.1E−1	3.9E−2	3.5E−3	1.9E−1
Sandy soil	–	4.9E−1	–	1.2 E−1	7.5E−3	7.4E−1
Sandy soil + PG	–	6.1E−1	–	1.1E−1	7.7E−3	6.4E−1
Corn						
Clay soil	–	–	1.6E−1	2.8E−2	–	4.1E−2
Clay soil + PG	–	–	1.9E−1	6.0E−2	–	4.7E−2
Sandy soil	3.1E−2	–	–	1.0E−1	6.6E−3	1.6E−1
Sandy soil + PG	–	–	–	8.5E−2	–	1.5E−1
Soya bean						
Clay soil	–	–	1.5E−1	6.5E−2	–	8.9E−2
Clay soil + PG	–	–	1.6E−1	3.2E−2	–	1.4E−1
Sandy soil	–	2.9E−1	–	1.2E−1	2.2E−3	5.0E−1
Sandy soil + PG	–	3.5E−1	–	1.3E−1	–	5.4E−1

of soil. The TF reported for clay soil were similar for both radionuclides, for the sandy soil, the ^{228}Ra seemed to be 2-fold more available than ^{226}Ra. In the database presented by Vandenhove [13], considering those studies where both ^{226}Ra and ^{228}Ra were measured, an overall 2.5-fold higher TF was found for ^{228}Ra than for ^{226}Ra. The same authors observed that clay and organic soils showed the lowest TF-Ra and sand and loam soil the highest, with difference of only 4-fold, the derived generic TF-Ra geometric mean was 2×10^{-2}, with a range in observed values of 7 orders of magnitude. The results obtained in this study for lettuce, corn and soya TF-^{228}Ra also presented difference of 4-fold, for sandy and clay soils.

The main source of ^{210}Pb and ^{210}Po in the environment is from the decay of ^{222}Rn gas emanated from the soil into the atmosphere. These radionuclides deposit on the ground in association with aerosols via washout and sedimentation. Other sources of theses radionuclides can include burning of fossil fuels and TENORM industries. The uptake of ^{210}Pb in plants can occur through the root system and via direct deposition from atmosphere. In this study, the TF were obtained in a green house and correspond only to the uptake by the root system. The TF-Po obtained in this study for lettuce, corn and soya was on the average 4.5×10^{-2} for clay soil and 1.1×10^{-1} for sandy soil, with difference of only 4 fold, independent upon the addition of PG to the two types of soil. The generic value obtained by Vandenhove [13] for TF-Po was 5.6×10^{-3}, with a range in observed values of 5 orders of magnitude. The TFs for Pb were obtained only for the clay soil, with an average value of 2.4×10^{-1}. The overall geometric mean for the TF-Pb obtained by Vandenhove [13] was 2.0×10^{-2} and the range covered 5 orders of magnitude; the results obtained in this study for corn and soya bean (1.6×10^{-1} on the average) is within this range and for lettuce was 20 fold higher than the geometric mean.

The results obtained for Ba, Co, Cr, Fe, Th, U, Zn and REE, determined by INAA and for As, Cd, Cu, Ni and Pb, obtained by AAS,in soil, PG, soil + PG and crop samples are presented in Table 3.

Some of these metals are micro nutrients, others depending upon their concentrations (As, Cd, Pb, Cr, Ni) can be considered as toxic. The maximum concentration limits for

Table 3. Metals concentration in PG, clay and sandy soil, soil + PG and crop samples (mg kg^{-1}).

	As	Ba	Cd	Co	Cr	Cu	Fe%	Ni	Pb	Zn
PG	1.60 ± 0.05	(2.5 ± 0.3)E+3	(2.3 ± 0.1)E−1	1.53 ± 0.06	(2.2 ± 0.2)E + 1	(1.2 ± 0.2)E+1	(4.2 ± 0.1)E−1	< 19.5	(1.4 ± 0.1)E+1	(1.2 ± 0.1)E+1
Clay soil	(5.3 ± 0.5)E+1	(1.7. ± 0.1) E+2	(8.0 ± 2.0)E−1	2.3 ± 0.2	(9.8 ± 0.3)E+1	(5.8 ± 0.8)E+1	7.7 ± 0.4	(4.4 ± 0.9)E+1	(1.0 ± 0.2) E+2	(1.2 ± 0.5) E+2
Lettuce	(5.0 ± 0.3)E−2	5.5 ± 0.5	(1.25 ± 0.08)E−1	(3.6 ± 0.1)E−1	(4.2 ± 0.4)E+1	3.29 ± 0.06	(2.83 ± 0.02)E−2	(1.27 ± 0.01)E+1	(2.9 ± 0.1)E+1	(3.6 ± 0.2)E+1
Corn	< 0.02	ND	(4.0 ± 0.2)E−3	(5.3 ± 0.2)E−3	1.89 ± 0.19	1.68 ± 0.02	(1.48 ± 0.01)E−3	(2.46 ± 0.08)E−1	(6.34 ± 0.04)E−1	(1.09 ± 0.04)E+1
Soya bean	(1.9 ± 0.1)E−2	9.9 ± 1.1	(1.66 ± 0.02)E−2	(1.73 ± 0.08)E−1	(9.9 ± 0.9)E−1	(1.14 ± 0.01)E+1	(9.39 ± 0.9)E−3	4.66 ± 0.02	(8.8 ± 0.2)E−1	(7.1 ± 0.4)E+1
Clay soil +PG	(7.6 ± 0.1)E+1	(1.3 ± 0.2) E+2	1.2 ± 0.4	2.4 ± 0.3	(9.9 ± 0.2)E+1	(7.3 ± 1.1)E+1	6.9 ± 1.0	(4.6 ± 0.1)E+1	(1.1 ± 0.3) E+2	(1.2 ± 0.1) E+2
Letuce	(1.5 ± 0.7)E−1	6.0 ± 0.6	(7.0 ± 0.1)E−2	(5.8 ± 0.2)E−1	(6.4 ± 0.6)E+1	3.68 ± 0.05	(4.2 ± 0.03)E−2	14.9 ± 0.01	(1.07 ± 0.02)E+1	(3.8 ± 0.2)E+1
Corn	< 0.02	ND	(3.6 ± 0.2)E−3	(1.09 ± 0.04)E−2	1.88 ± 0.19	1.07 ± 0.01	(2.11 ± 0.01)E−3	(2.2 ± 0.2)E−1	(7.6 ± 0.1)E−1	(1.07 ± 0.04)E+1
Soya bean	(8.0 ± 0.1)E−3	ND	(7.8 ± 0.2)E−3	(1.6 ± 0.1)E−1	2.1 ± 0.2	(1.25 ± 0.02)E+1	(7.8 ± 0.07)E−3	4.36 ± 0.04	(1.5 ± 0.1)E−1	(6.7 ± 0.4)E+1
Sandy soil	2.4 ± 0.8	(5.3 ± 0.4)E+1	1.0 ± 0.3	(8.0 ± 1.0)E−1	(2.8 ± 0.2)E+1	(2.1 ± 0.4)E+1	1.6 ± 0.2	7.7 ± 1.3	(2.2 ± 0.5)E+1	(7.0 ± 2.7)E+1
Lettuce	(2.1 ± 0.2)E−2	6.1 ± 0.6	(1.2 ± 0.1)E−2	(1.9 ± 0.1)E−1	1.3 ± 0.1	3.18 ± 0.01	(1.13 ± 0.01)E−2	3.51 ± 0.05	2.77 ± 0.02	(2.6 ± 0.2)E+1
Corn	< 0.02	ND	(3.6 ± 0.2)E−3	(1.67 ± 0.06)E−2	1.31 ± 0.13	1.098 ± 0.002	(2.87 ± 0.02)E−3	(1.78 ± 0.02)E−1	(7.7 ± 0.1)E−1	9.9 ± 0.1
Soya bean	(8.8 ± 0.8)E−3	5.1 ± 0.5	(6.6 ± 0.2)E−3	(1.68 ± 0.05)E−1	(8.0 ± 0.7)E−1	(1.12 ± 0.01)E+1	(7.19 ± 0.06)E−3	3.28 ± 0.01	(1.86 ± 0.06)E−1	(6.6 ± 0.4)E+1
Sandy soil +PG	2.6 ± 0.6	(5.3 ± 0.4)E+1	(8.0 ± 2.0)E−1	(8.2 ± 0.6)E−1	(2.6 ± 0.1)E+1	(2.1 ± 0.3)E+1	1.6 ± 0.1	7.2 ± 2.7	(1.9 ± 0.2)E+1	(6.4 ± 0.3)E+1
Lettuce	(8.7 ± 0.1)E−2	5.5 ± 0.5	(5.0 ± 0.1)E−2	(3.9 ± 0.1)E−1	1.6 ± 0.1	3.88 ± 0.04	(1.23 ± 0.01)E−2	4.50 ± 0.02	(1.8 ± 0.1)E+1	(2.4 ± 0.2)E+1
Corn	< 0.02	ND	(2.8 ± 0.2)E−3	(1.74 ± 0.06)E−2	1.20 ± 0.12	(8.8 ± 0.4)E−1	(1.96 ± 0.01)E−3	(2.46 ± 0.02)E−1	(2.76 ± 0.04)E−1	9.7 ± 0.4
Soya bean	(1.9 ± 0.2)E−2	(1.0 ± 0.1)E+1	(6.6 ± 0.2)E−3	(1.91 ± 0.06)E−1	(9.3 ± 0.9)E−1	(1.126 ± 0.004)E+1	(7.96 ± 0.07)E−3	4.88 ± 0.02	(2.18 ± 0.02)E−1	(6.2 ± 0.3)E+1

Table 4. Maximum concentration limits acceptable in fertilizers and soil conditioner established by Ministério da Agricultura ($mg\,kg^{-1}$).

	Fertilizers	Soil conditioner
As	10	20
Cd	20	8
Pb	100	300
Cr	200	500
Ni	–	175

Table 5. CETESB quality values and intervention levels for agriculture soil and mean values of metals concentration in PG ($mg\,kg^{-1}$).

	Quality values	Intervention levels	PG
Ba	75	300	2486
Cd	<0.5	3	0.23
Co	13	35	1.53
Cr	40	150	21.9
Cu	35	200	12.5
Fe%	–	–	0.42
Ni	13	70	<19
Pb	17	180	14.1
Zn	60	450	12

these metals established by Ministério da Agricultura [14] in fertilizers and soil conditioners are presented in Table 4. The concentrations found in PG for these metals are below the limits adopted by Ministério da Agricultura.

The results obtained in the PG samples can be compared with the limits for metals concentration in soils available in the CETESB report [15]. This agency is a state regulatory body which is responsible for the regulation and control of the environmental quality of soils. All metals concentration present in PG, except for Ba, were below the CETESB intervention values for agriculture area (Table 5). Therefore they do not contribute to an increase in the concentration of these elements in soil, at least if only one application is considered.

All the metals (As, Ba, Co, Cr, Cu, Fe, Ni, Pb, Sc and Zn) studied presented higher concentrations in clay soil, except for Cd, the addition of PG to both soils did not alter significantly the final concentration of these metals. The transfer factors obtained for the metals are generally higher for the sandy soil, giving evidence that the metals are more available in this type of soil; there are two exceptions, Cd in lettuce and Cr, which presented lower values for sandy soil (Table 6). The TF obtained in this study for metals are in good agreement with data available in the literature [16,17], for the same crops but in different types of soil.

The results obtained for La, Ce, Sm, Eu and Sc concentration in soil, PG, soil + PG and crop samples are presented in Table 7. Although the REEs are enriched in PG, when compared with the two types of soil studied, this increase does not affect the final

Table 6. Metals transfer factor from soil to plant.

	As	Ba	Cd	Co	Cr	Cu	Fe	Ni	Pb	Zn
Lettuce										
Clay soil	9.4E−4	3.3E−2	1.5E−1	1.5E−1	4.2E−1	5.6E−2	3.6E−3	2.9E−1	2.8E−1	3.1E−1
Clay soil + PG	2.0E−3	4.7E−2	5.7E−2	2.3E−1	6.4E−1	5.0E−2	6.1E−3	3.2E−1	9.5E−2	3.0E−1
Sandy soil	8.8E−3	1.1E−1	1.2E−2	2.4E−1	4.6E−2	1.4E−1	6.8E−3	4.5E−1	1.2E−1	3.7E−1
Sandy soil + PG	3.3E−2	1.0E−1	6.0E−2	4.7E−1	6.1E−2	1.8E−1	7.4E−3	6.2E−1	9.5E−1	3.7E−1
Corn										
Clay soil	–	–	4.8E−3	2.3E−3	1.9E−2	2.8E−2	1.9E−4	5.6E−3	6.2E−3	9.5E−2
Clay soil + PG	–	–	2.9E−3	4.4E−3	1.8E−2	1.4E−2	3.0E−4	4.8E−3	6.7E−3	8.6E−2
Sandy soil	–	–	3.6E−3	2.1E−2	4.6E−2	5.1E−2	1.7E−3	2.3E−2	3.5E−2	1.4E−1
Sandy soil + PG	–	–	3.3E−3	2.1E−2	4.6E−2	4.1E−2	1.2E−3	3.4E−2	1.4E−2	1.5E−1
Soya Bean										
Clay soil	3.5E−4	5.8E−2	2.0E−2	7.5E−2	1.0E−2	1.9E−1	1.2E−3	1.0E−1	8.6E−3	6.2E−1
Clay soil + PG	1.0E−4	–	6.4E−3	6.7E−2	2.1E−2	1.7E−1	1.1E−3	9.5E−2	1.3E−3	5.4E−1
Sandy soil	3.7E−3	9.6E−2	6.6E−3	2.1E−1	2.8E−2	5.2E−1	4.4E−3	4.2E−1	8.5E−3	9.4E−1
Sandy soil + PG	7.3E−3	1.8E−1	8.0E−3	2.3E−1	3.4E−2	5.3E−1	4.9E−3	6.7E−1	1.1E−2	9.7E−1

Table 7. Rare earth elements concentration in PG, clay and sandy soil, soil+PG and crop samples in mg kg^{-1}. (Mean value ± standard deviation).

	La	Ce	Sm	Eu	Sc
PG	(1.74 ± 0.04)E+3	(2.2 ± 1.2)E+3	(2.02 ± 0.08)E+2	(3.2 ± 0.2)E+1	2.9 ± 0.1
Clay soil	(6.4 ± 0.4)E+1	(1.4 ± 0.2)E+2	9.7 ± 1.2	1.6 ± 0.1	(3.4 ± 0.2)E+1
Lettuce	(2.47 ± 0.03)E−1	(6.0 ± 0.3)E−1	(1.95 ± 0.05)E−2	(7.5 ± 0.7)E−3	(4.1 ± 0.3)E−2
Corn	(7.0 ± 0.1)E−3	ND	ND	(4.2 ± 0.4)E−3	(8.1 ± 0.6)E−4
Soya bean	(8.1 ± 0.2)E−1	(6.8 ± 0.3)E−1	ND	(6.6 ± 0.6)E−3	(1.8 ± 0.1)E−3
Clay soil+PG	(6.4 ± 0.2)E+1	(1.3 ± 0.3)E+2	9.4 ± 0.8	1.6 ± 0.2	(2.8 ± 0.6)E+1
Lettuce	(2.99 ± 0.03)E−1	(6.6 ± 0.3)E−1	(2.54 ± 0.07)E−2	(8.7 ± 0.9)E−3	(7.5 ± 0.5)E−2
Corn	(5.8 ± 0.1)E−3	ND	(3.0 ± 0.1)E−3	(4.2 ± 0.4)E−3	(9.0 ± 0.6)E−4
Soya bean	ND	ND	(1.34 ± 0.04)E−2	(3.4 ± 0.3)E−3	ND
Sandy soil	3.7 ± 0.6	(2.0 ± 0.2)E+1	(5.2 ± 0.4)E−1	(1.11 ± 0.07)E−1	5.5 ± 0.7
Lettuce	(6.1 ± 0.1)E−2	(1.4 ± 0.1)E−1	(5.8 ± 0.1)E−3	(4.2 ± 0.4)E−3	(2.9 ± 0.2)E−2
Corn	(1.62 ± 0.02)E−2	ND	ND	ND	(1.5 ± 0.1)E−3
Soya bean	(8.9 ± 0.2)E−3	ND	ND	(2.0 ± 0.2)E−3	(8.0 ± 0.6)E−4
Sandy soil +PG	3.5 ± 0.1	(2.1 ± 0.1)E+1	0.61 ± 0.05	0.14 ± 0.02	5.5 ± 0.3
Lettuce	(1.06 ± 0.01)E−1	(2.4 ± 0.1)E−1	(5.9 ± 0.1)E−3	(5.9 ± 0.6)E−3	(2.4 ± 0.1)E−2
Corn	(4.6 ± 0.1)E−3	ND	ND	(2.4 ± 0.2)E−3	(1.05 ± 0.07)E−3
Soya bean	(1.21 ± 0.02)E−2	ND	ND	(3.6 ± 0.3)E−3	(1.3 ± 0.1)E−3

Table 8. Rare earth elements transfer factor from soil to plant.

	La	Ce	Sm	Eu	Sc
Lettuce					
Clay soil	4.2E−3	4.6E−3	1.9E−3	4.6E−3	1.2E−3
Clay soil + PG	4.9E−3	4.9E−3	2.1E−3	5.0E−3	2.5E−3
Sandy soil	7.0E−3	7.0E−3	9.6E−3	3.6E−2	5.2E−3
Sandy soil + PG	1.1E−2	1.1E−2	8.2E−3	3.5E−2	4.4E−3
Corn					
Clay soil	1.1E−4	–	–	2.6E−3	2.4E−5
Clay soil + PG	9.1E−5	–	3.2E−4	2.6E−3	3.2E−5
Sandy soil	4.3E−3	–	–	–	2.6E−4
Sandy soil + PG	1.3E−3	–	–	1.7E−2	1.9E−4
Soya bean					
Clay soil	1.2E−2	4.8E−3	–	4.1E−3	5.3E−5
Clay soil + PG	–	–	1.4E−3	2.1E−3	–
Sandy soil	2.4E−3	–	–	1.8E−2	1.5E−4
Sandy soil + PG	3.4E−3	–	–	2.6E−2	2.4E−4

concentration of the mixture soil + PG and also the TFs obtained. Generally, the TFs for the REEs studied are one order of magnitude higher for the sandy soil compared with the clay soil (Table 8).

As with most of the heavy metals in solution, elevated concentrations of REEs, above those which organisms are accustomed to, may cause toxic reactions and negative effects on plants [18]. However, small amounts of REEs have been used in Chinese agriculture to improve crop nutrition. Ushida *et al.* [17] made a review of the uptake of 40 elements, comprising REEs for crops grown in Japan. Their results for La, Ce, Nd, Sm and Eu are in good agreement with the results obtained in this study for lettuce and soya bean.

Linsalata, *et al*. [19] reported TFs for light REEs (La, Ce and Nd) obtained in an area of enhanced natural radioactivity in Brazil: 5.4×10^{-4}, 3.0×10^{-4} and 2.6×10^{-4}, respectively. The soil studied by these authors is composed of fine-grained argillaceous silty clay and is classified as a dystrophic cambisol and red-yellow dystrophic latosol. The TFs obtained in the present study for La (4.2×10^{-3}), Ce (4.6×10^{-3}) and Nd (6.7×10^{-2}) using clay soil are one order of magnitude higher than Linsalata *et al*. [19] results.

4. Conclusion

The addition of PG to the two soils studied, in the dosage of $1.0\,g\,dm^{-3}$ for the clayish soil and $0.4\,g\,dm^{-3}$ for the sandy soil, did not alter significantly the levels of radioactivity, metals and REEs in the final mixture and consequently the TFs obtained for lettuce, soya and corn. Therefore, the impact of one single application of Brazilian PG as soil amendment does not imply in any additional risk owing to the transfer of radionuclides, metals and REEs to crops. It should be emphasized, however, that the conclusion obtained in this case study apply specifically to the Brazilian PG of igneous origin and cannot be extrapolated to other PG of sedimentary origin, which presents different concentration of the elements studied.

The concentration found in PG for some radionuclides (^{226}Ra, ^{210}Pb and ^{210}Po), Ba and REEs were generally higher than the soils content; especially for the sandy soil (20 fold higher for the radionuclides, 50 fold for Ba and two orders of magnitude for the REEs). However, the increase in the concentration of these elements did not affect significantly the soil-to-plant transfer, even considering that the solubility of PG is high. The only exception was the ^{210}Pb, which gave results of TF higher than the stable element. This behavior is explained, considering that the stable lead present in the soil composition is not available to the same extent than the ^{210}Pb present in PG. The availability of these elements in the Brazilian PG was evaluated [6], by applying the sequential extraction procedure of Tessier [20]. It was verified that Ba, and REEs are bound to the residual fraction of the sequential leaching of PG, therefore they are not available to the soil-to-plant system. The sequential extraction showed that most of ^{210}Pb and the radium isotopes are located in the iron oxide fraction and only 13%–18% of these radionuclides are distributed in the most labile fractions.

The TFs values were generally lower for the clay soil than for the sandy soil. Overall, highest TF derivations were obtained for the leafy vegetable while lowest TF estimates were obtained for grains. The TF estimates reported in this study may be valuable for screening assessment, but more sites specific values may be recommended for predicting generic long-term effective impact.

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