EU-NORM2

2014

Lixiviation of natural radionuclides in tropical soil amended with phosphogypsum

M.B. Nisti, C.R. Saueia, L.H. Malheiro, G. H. Groppo, B.P. Mazzilli

Laboratório de Radiometria Ambiental
Instituto de Pesquisas Energéticas e Nucleares - IPEN
São Paulo, Brazil

Introduction

Phosphogypsum (PG) is a NORM residue of the phosphate fertilizers industry. In Brazil, it is produced at a rate of 5.5×10^6 metric tons per year and is currently being stockpiled, posing major environment concerns.

PG presents in its composition radionuclides of the natural U and Th decay series: mainly Ra-226, Ra-228, Th-232, Pb-210 and Po-210, while other radionuclides, such as U, originally present in the phosphate rock, migrate to the phosphoric acid.

In Brazil TENORM industries are subjected to the recommendations given by Comissão Nacional de Energia Nuclear, which include compliance with the radiological protection regulations (CNEN-NN-4.01, 2005).

PG use in agriculture as soil conditioner

PG has been used in Brazil as soil amendment 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.

It favors the absorption of water and nutrients.

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.

The study of availability of radionuclides 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 .

Objectives

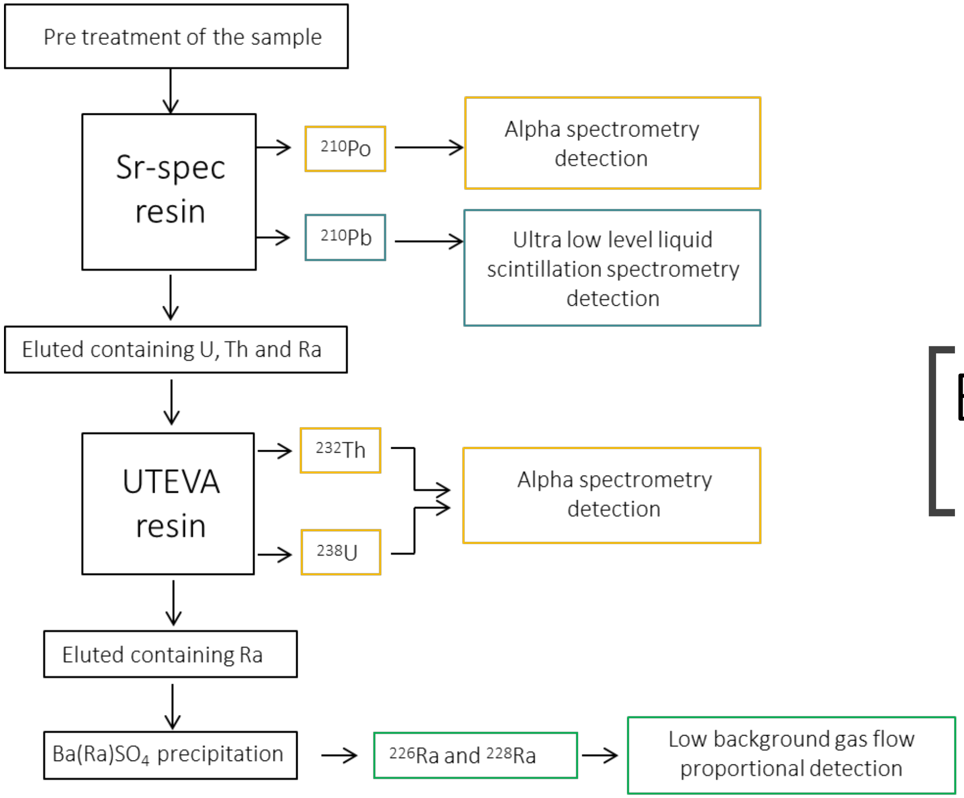
The main objective of this paper is to study the availability of natural radionuclides, important in terms of radiological protection (U-238, Ra-226, Ra-228, Th-232, Pb-210 and Po-210), present in the Brazilian phosphogypsum used in agriculture.

For this purpose, an experiment was conducted in the laboratory, in which columns filled with Brazilian typical sandy soil, clay soil 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 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.

Experimental procedure



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.

Materials and Methods
Soil characterization

Table 2 – Chemical analysis of soil.

Sample	Depth	pH	O.M.	P	S	K	Ca	Mg	H+Al	Al
	(cm)	($CaCl_2$)	g dm^{-3}	mg dm^{-3}		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

O.M.: organic matter

Table 2 – Chemical analysis of soil cont.

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

SB: Sum of Bases; CEC: Cation Exchange Capacity; V: Soil base saturation; m: aluminium saturation

The chemical analysis of soil was undertaken, in order to determine the soil fertility and the necessary chemical 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.

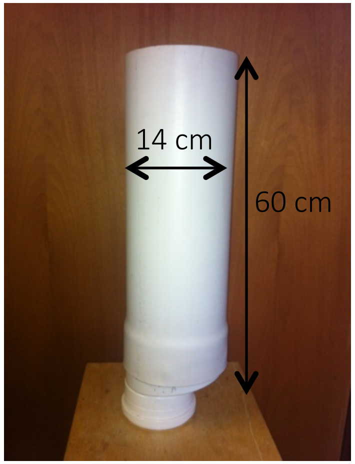
Materials and Methods
Soil preparation

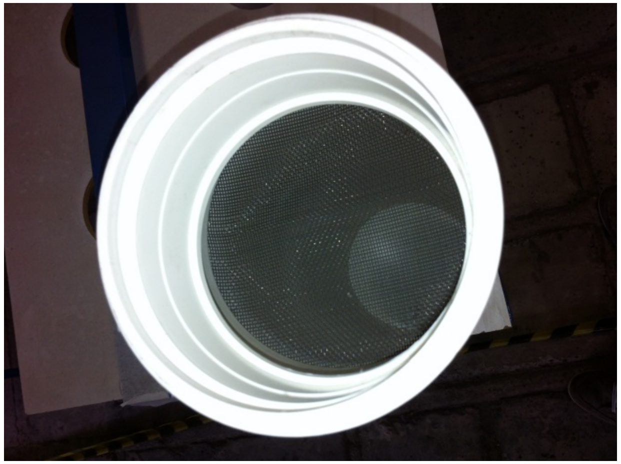
The samples of Brazilian phosphogypsum used in this experiment were provided by Vale Fertilizantes and were collected in Uberaba (Minas Gerais State) installation and in the unit of Cubatão (São Paulo State).

The amount of PG necessary for the sandy soil was 4.14 10^3 kg ha^{-1} that correspond to a dose of 7.39 g per repetition; the amount of PG necessary for the clay soil was 1.98 10^3 kg ha^{-1} that correspond to a dose of 3.32 g per repetition.

The soil samples were corrected with the addition of different amounts of PG: the recommended dose and 10 times the recommended dose.

Materials and Methods
Columns preparation





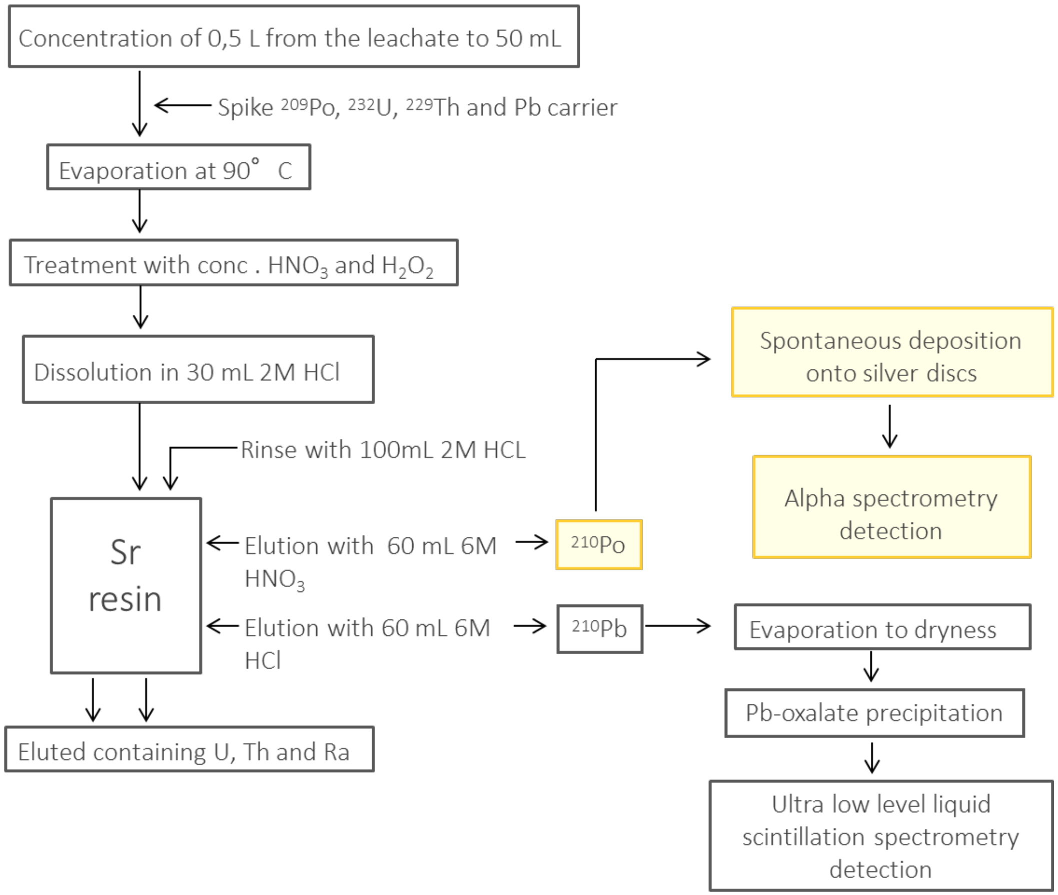
The columns were filled with 5 kg of the two types of soil, two types of PG, mixture of soil + recommended dose and finally a mixture of soil + 10 times the recommended dose, totalizing 12 columns.

Water was added, to achieve the soil field capacity.

According to the values obtained for the field capacity, 1,400 mL of water are necessary in order to saturate the sandy soil for each experiment with 5 kg of soil, for the clay soil, 2,100 mL of water are needed.

Materials and Methods

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

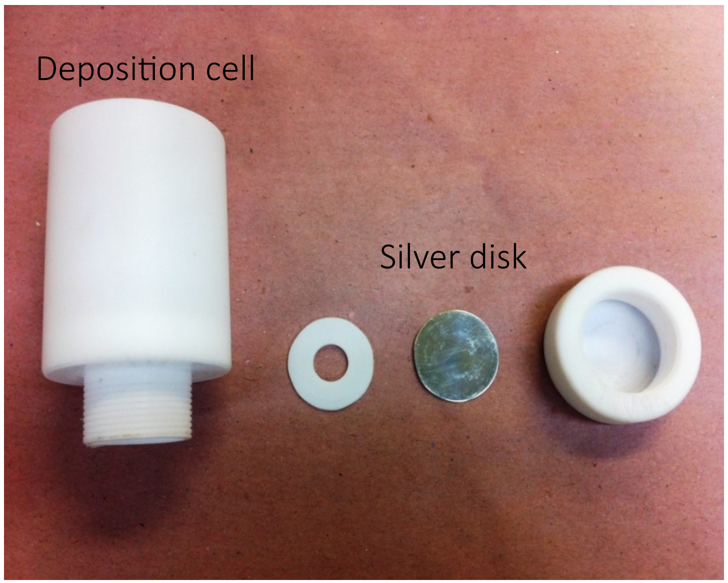


Materials and Methods

Determination of ^{210}Po in the leachate

Materials and Methods

Determination of ^{210}Po by alpha spectrometry



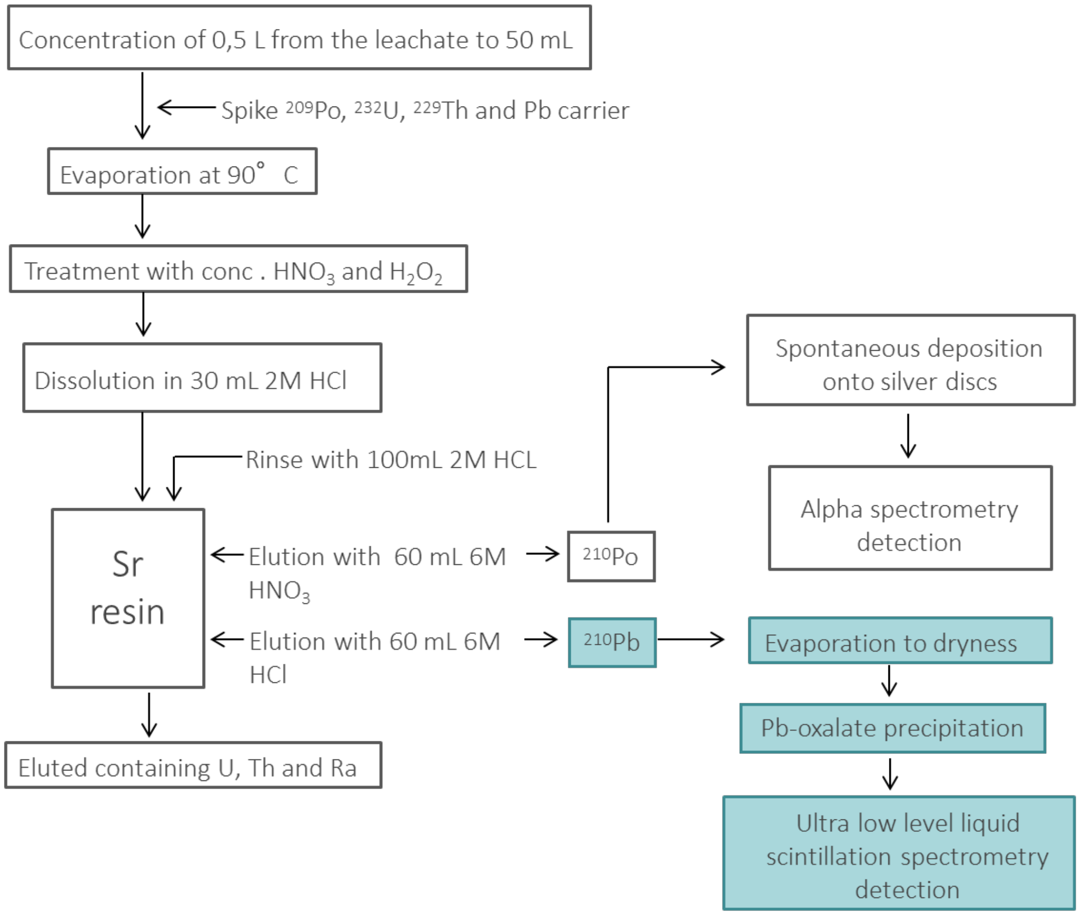
The activity concentration of Po-210 was determined by spontaneous deposition on a silver disk.

Materials and Methods
Determination of ^{210}Po by alpha spectrometry

Measurement of Po-210 by alpha spectrometry during 80,000 seconds.

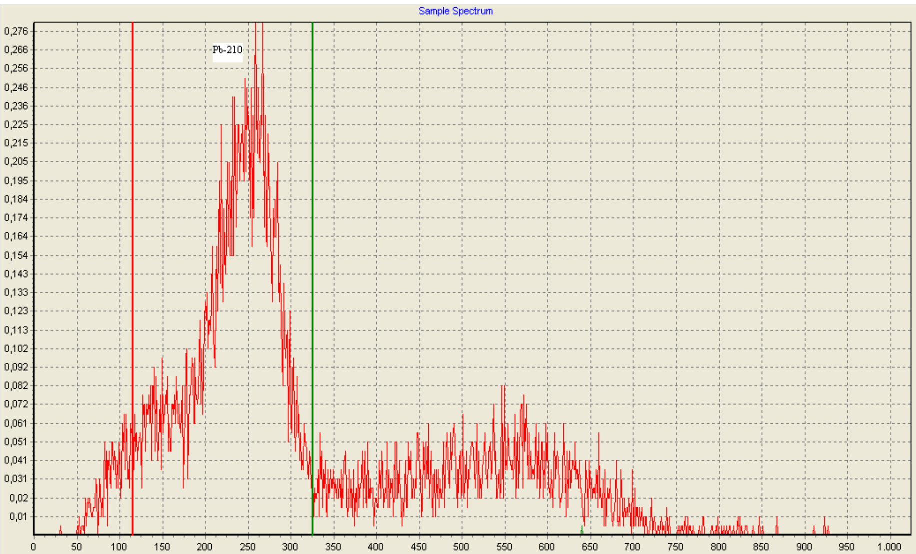
Materials and Methods

Determination of ^{210}Pb in the leachate



Materials and Methods

Determination of ^{210}Pb by LSC

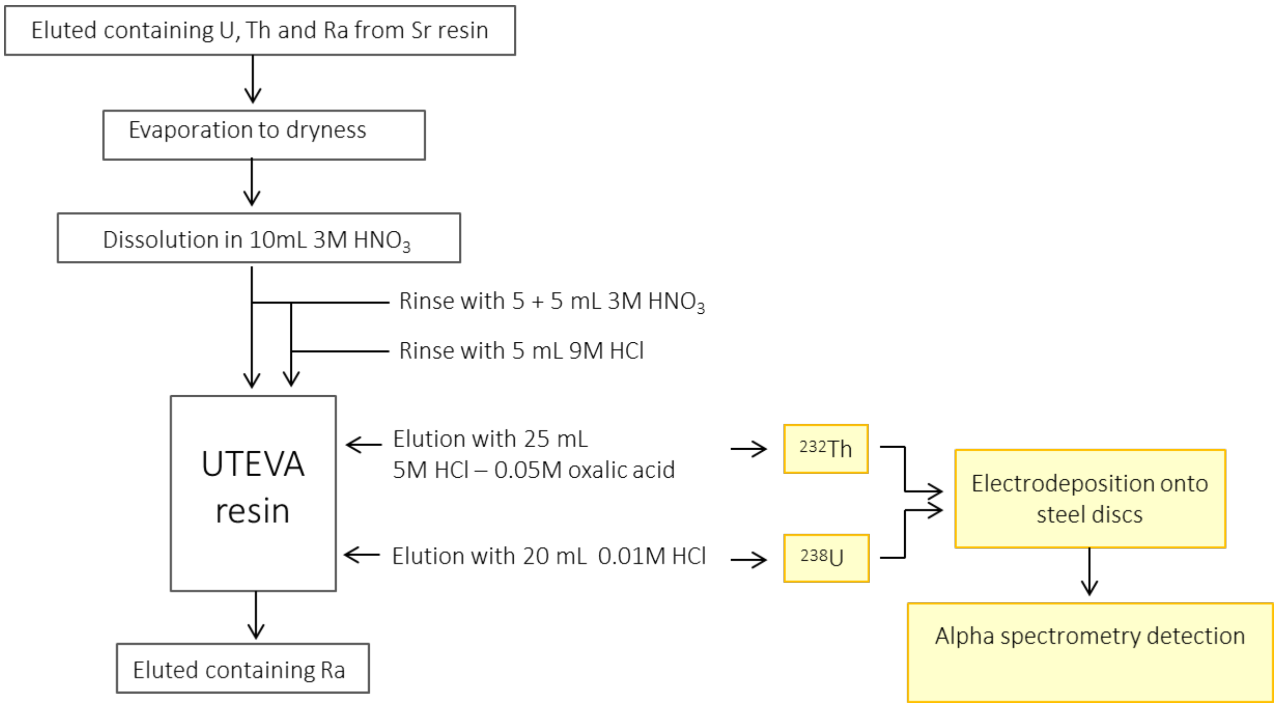


Beta spectrum obtained by LSC

Quantulus™ Ultra Low Level Liquid Scintillation Spectrometer

Materials and Methods

Determination of ^{238}U and ^{232}Th in leachate



Materials and Methods

Determination of ^{238}U and ^{232}Th in the leachate - purification

Examples of the UTEVA resin columns used for U and Th purification.

Materials and Methods

Determination of ^{238}U and ^{232}Th in the leachate - electrodeposition

Example of the electrodeposition cell used in the experiment.

Materials and Methods

Determination of ^{238}U and ^{232}Th in the leachate - electrodeposition

Electrodeposition during one hour.

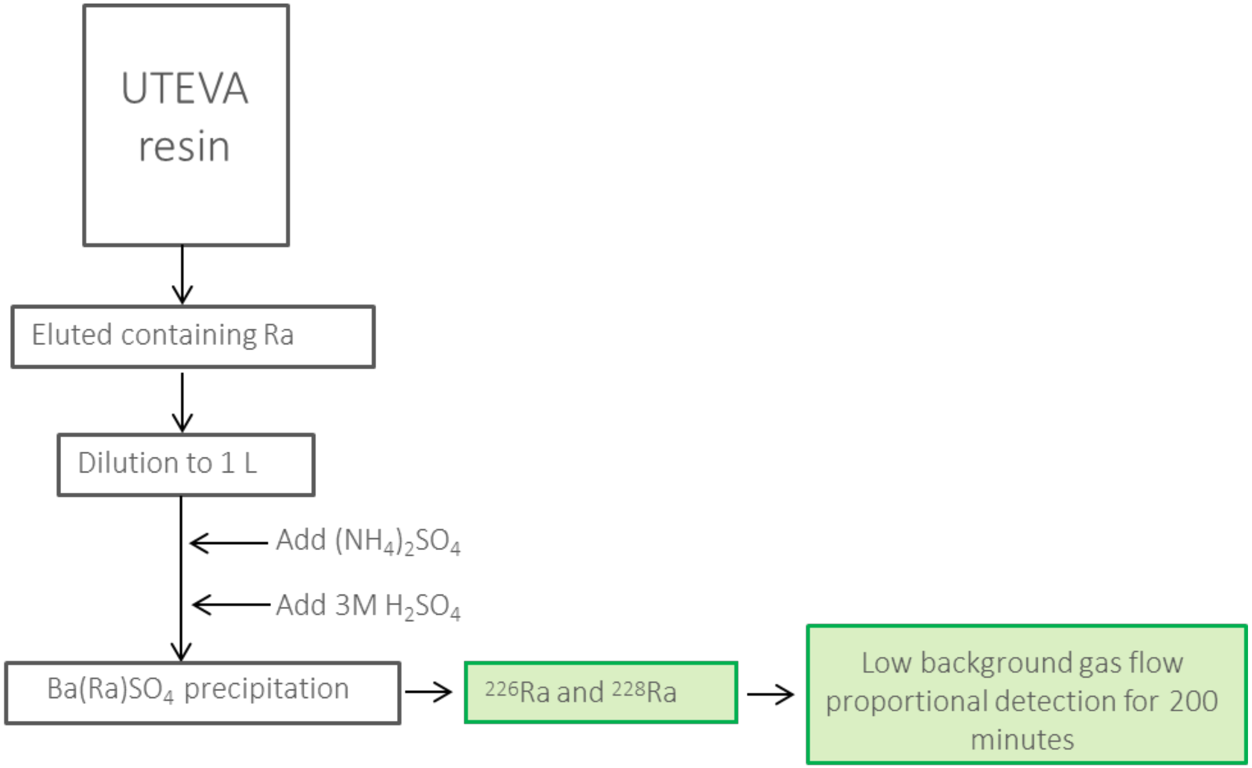
Materials and Methods

Determination of ^{238}U and ^{232}Th in the leachate - alpha counting

Measurement of U and Th by alpha spectrometry during 80,000 seconds.

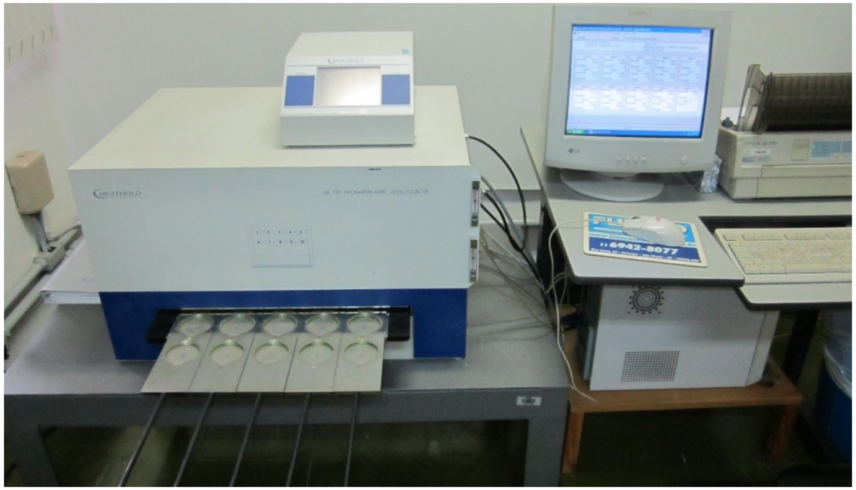
Materials and Methods

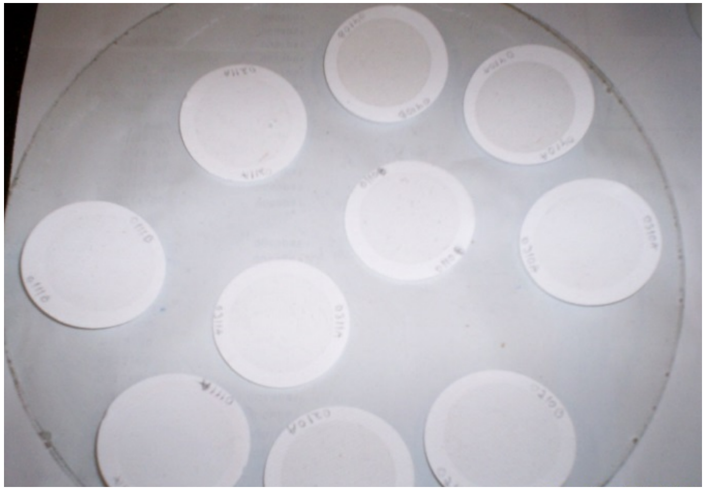
Determination of ^{226}Ra and ^{228}Ra in the leachate



Materials and Methods

Determination of ^{226}Ra and ^{228}Ra in the leachate





Low background gas flow proportional detector

Results and Discussion

Concentration 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
Mean all Clay soil	48±6.2	38.4±0.5	50.4±3.8	38.6±3.5	50±2.7	50.8±0.4
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
Mean all Sandy soil	9.6±1.9	7.6±1.3	18.6±3.3	16.8±2.2	16.2±2.2	13.6±1.8

The concentrations observed in the clay soil are four times higher than the sandy soil.
It can be observed that the radionuclides concentrations in the mixture soil + PG are similar to the concentration observed in the soils.

Results and Discussion

Concentration 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
Mean all Clay soil	48±6.2	38.4±0.5	50.4±3.8	38.6±3.5	50±2.7	50.8±0.4
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
Mean all Sandy soil	9.6±1.9	7.6±1.3	18.6±3.3	16.8±2.2	16.2±2.2	13.6±1.8

The ^{238}U concentrations observed in PG are below the detection limit of the equipment used, showing that this radionuclide concentrates in the phosphoric acid.

As for the other radionuclides analysed, the differences observed depend of the phosphate rock used as raw material in the two installations.

ipen

Results and Discussion

Concentration 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
Mean all Clay soil	48±6.2	38.4±0.5	50.4±3.8	38.6±3.5	50±2.7	50.8±0.4
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
Mean all Sandy soil	9.6±1.9	7.6±1.3	18.6±3.3	16.8±2.2	16.2±2.2	13.6±1.8
UNSCEAR (2000)-Soil	35	35	-	-	30	-

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, 2000).

Results and Discussion

Concentration 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	79±10	10±3	37±4	< 7.5	114±14
Mean all Clay soil	-	40.8	19.8	35.6	-	56.6
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
Mean all Sandy soil	-	58.8	29.4	37.2	-	104.6

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.

ipen

Results and Discussion

Available fraction of ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra (%)

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	-	0.21	0.02	0.09	-	0.23
Mean all Clay soil	-	0.11	0.04	0.09	-	0.11
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
Mean all Sandy soil	-	0.77	0.15	0.22	-	0.78

The available fraction presented usually 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.

Results and Discussion

Available fraction of ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra (%)

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	-	0.21	0.02	0.09	-	0.23
Mean all Clay soil	-	0.11	0.04	0.09	-	0.11
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
Mean all Sandy soil	-	0.77	0.15	0.22	-	0.78

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.

Results and Discussion

Available fraction of ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra (%)

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	-	0.21	0.02	0.09	-	0.23
Mean all Clay soil	-	0.11	0.04	0.09	-	0.11
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
Mean all Sandy soil	-	0.77	0.15	0.22	-	0.78

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.

General Conclusions

The mean activity concentration of the radionuclides in the sandy soil is about 4 times lower than the clay soil.

If the mean 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 around 1.5 more activity compared to the leachate from clay soil.

The same trend is also observed in the available fraction, the mean values obtained for all the sandy soil is 5 times higher than the clay soil.

It can be concluded that the radionuclides are 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.

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 content in water.

Acknowledgments

This project was supported by

Fundação de Amparo à Pesquisa do Estado de São Paulo – FAPESP, research contract 2010/10587-0

Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq for grants.

PhD. Barbara Mazzilli

mazzilli@ipen.br