

Session 6: Use of NORM Products & Residues

Radioactivity in Phosphogypsum and the Recovery of Sodic Soils from Brazilian Semi Arid Environment

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1. Introduction



Dried subhumid, semiarid and arid climate regions

One third (1/3) of the global land area.

Brazil: 665,543 km² and 15,748,769 inhabitants.
Northeast region

Salinization of soil: first step to desertification

Consequence of environmental factors (soil origin, drainage and slope...) and agricultural practices (irrigation...)

Evaporation >> precipitation

Presence of high levels of exchangeable sodium or magnesium

Affect the electric conductivity (E.C.)







PHOSPHOGYPSUM: alternative to sodium affect soil

Calcium sulphate and impurities : Fluoride, REE and NR





PG is stockpiled

Economic purposes:
Cement industry
Agriculture



Uses on agricultural soils:

- reduce Al concentration;
- increase infiltration rate;
- supply Ca and sulphur to crops;
- reduce the concentration of exchangeable Na

Minimize the problem created by stockpiling.

USEPA: limit of 370 Bq.kg^{-1} ^{226}Ra to agricultural purposes

Radionuclide behaviour in soils:

important tool to understand their potentially effects on the environment

Different forms of binding depending on:

- environmental factors, as climate and soil (pH, mineral and organic fractions composition, etc),
- the physico-chemical form of the element and on characteristics of the soils.

Sequential extractions: identify reversible and irreversible mechanisms in soils

Extractions methods:

More used with heavy metals (Pb, Cr, Zn etc)

Tessier et al, BCR, modified protocols

Objectives

Evaluate the behaviour of natural radionuclides

^{210}Pb , ^{226}Ra and ^{228}Ra

Soils amended with PG

Modification on the extraction procedure adapted from Tessier et al.

Also...

The potential of PG to reduce exchangeable Na concentrations and electric conductivity as indicators of soil reclamation.

2. Material and methods

Samples of phosphogypsum

Sample treatment

Stored at polystyrene containers

Gamma spectrometry (HPGe)



Fluvisol (FL)



Luvisol (LV)





Soil experiment

20 cm

Soil analysis: Na, fertility and CEC, EC

$$RP = (ESP_i - ESP_f) \times h \times CEC \times 86 \times D_s$$

$$ESP_i = \frac{Na \times 100}{CEC}$$

Soil FL : 0 ton.ha⁻¹ (no RP)
16 ton.ha⁻¹ (one RP)
32 ton.ha⁻¹ (2 RP)

Soil LV: 0 ton.ha⁻¹ (no RP)
18 ton.ha⁻¹ (one RP)
36 ton.ha⁻¹ (2 RP)

FG mixed with soils

1 liter of irrigation water

Reaction time: 30 days

300 g soil from each bucket

Homogenized, air dried, quartering

Sieved with a 200 μm sieve

X-Rays Fluorescence and particle size

5 grams of soil

Tessier et al

Extraction fractions: exchangeable (F1),
bound to carbonates (F2),
bound to iron and manganese oxides (F3)
bound to organic matter (F4)
residual (F5).

Total : HNO_3 , HF and HCl.

Single extractions: avoid interferences on the extractions
caused by the reagents

Modification: reagent-to-sample ratio reduce from 15:1 to
10:1.

Ra isotopes and ^{210}Pb on the extract solution of each fraction

Co-precipitated as $\text{Ba}(\text{Ra},\text{Pb})\text{SO}_4$

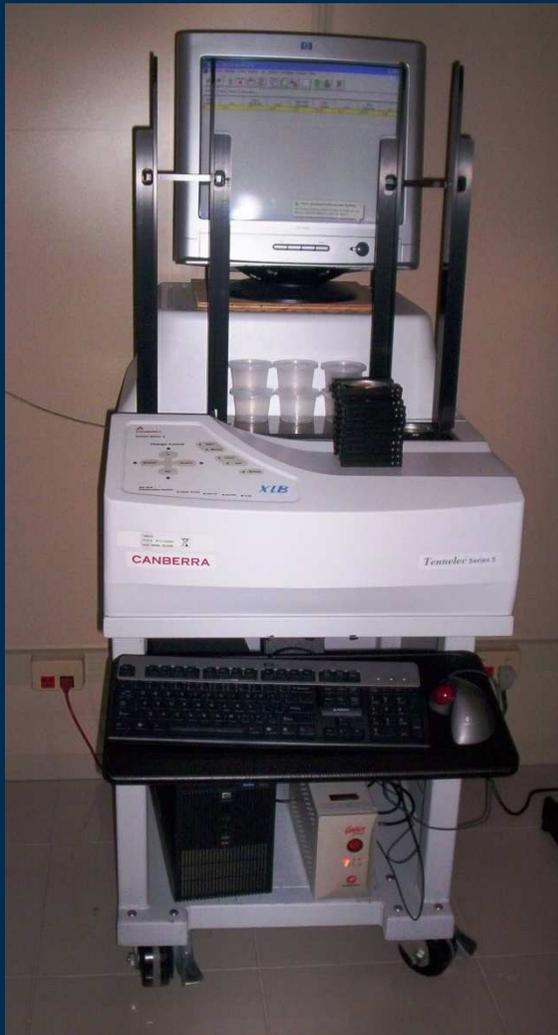
One month

^{226}Ra : gross alpha counting.

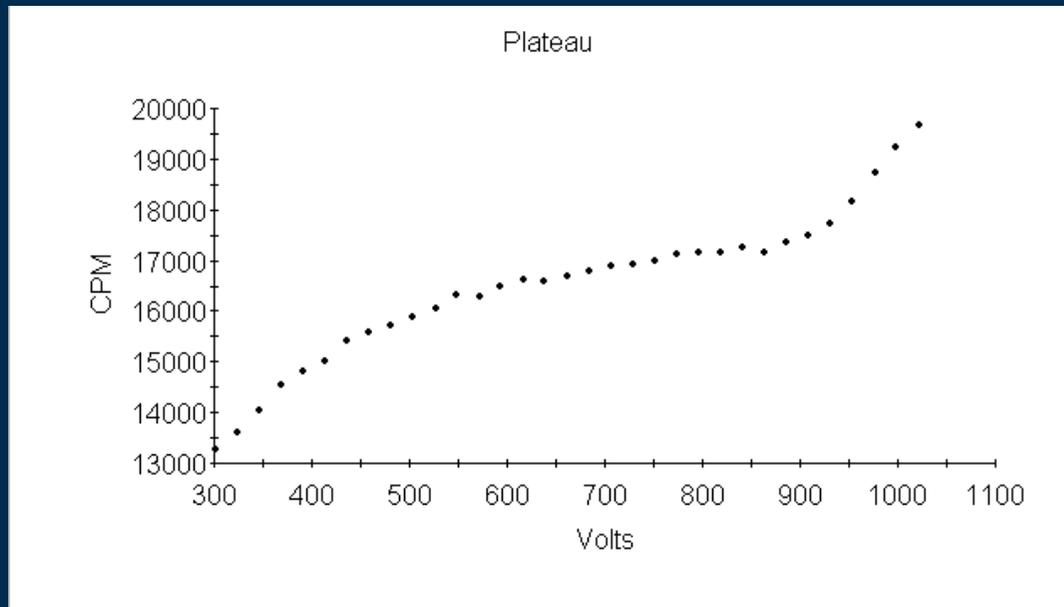
^{228}Ra : beta counting

^{210}Pb : beta counting

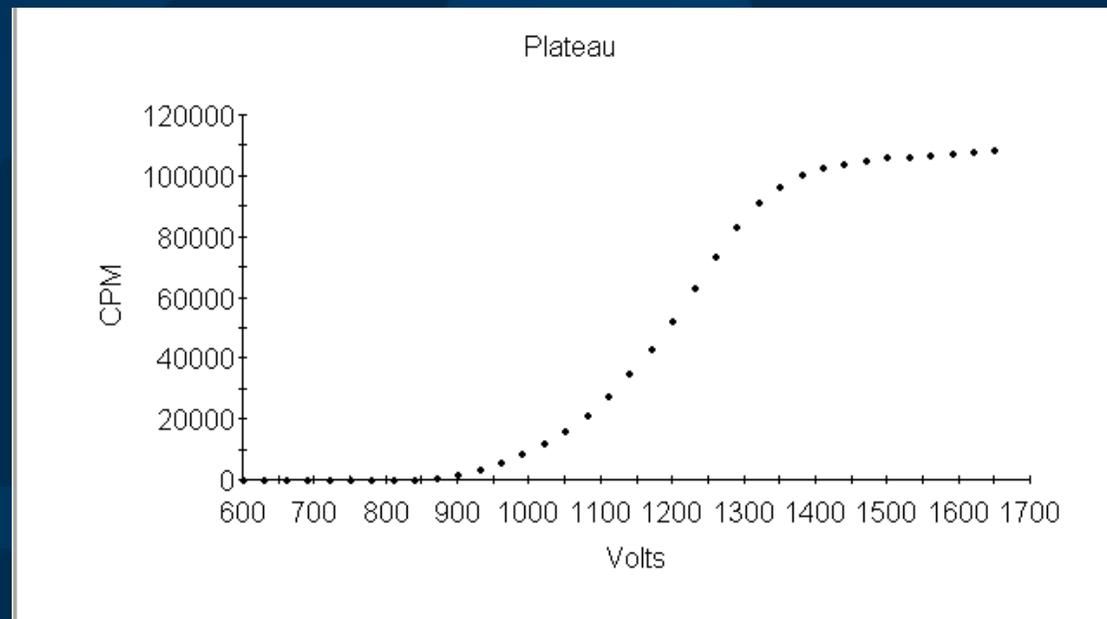
Gas flow proportional detector



Alpha counting plateau



Beta counting plateau



3. Results and discussion

Fertility analysis:

EC, pH and ESP values → Saline-sodic soils

Consequences:

Reduction of available water

Dispersion of clay

Decrease on the infiltration rate.

P content on both is considered low to Brazilian soils

pH: not inadequate to the majority of crops cultivated on the region (rice and onion)

Exchangeable cations are on high values

X-Rays Fluorescence (XRF) :

- Soils have low contents of iron and manganese oxides and high contents of SiO_2 and Al_2O_3 .
- Soil LV : high level of SO_3 (50,98%) and CaO (40,478%).
- PG: high contents of phosphate as P_2O_5 and also oxides as Fe_2O_3 , CaO , Al_2O_3 , and SiO_2 .
- Particle size analyzes: high content of silt and small contents of clay,
- Salt dissipate clay and promote a breakdown on soil structures.

Table 3: Concentration activity of ^{26}Ra , ^{228}Ra and ^{210}Pb on PG produced worldwide and from Brazilian phosphate industry and obtained in this study.

Origin	Bq.kg ⁻¹			Ref.
	^{210}Pb	^{226}Ra	^{228}Ra	
USA Florida	435 - 1369	433 - 1110	N.R.	[22]
Canada	890	N.R.	N.R.	[14]
Australia	451	N.R.	N.R.	[14]
Spain	N.R.	336 - 1220	N.R.	[8]
Brazil	47 - 894	22-695	N.R.	[5]
Brazil	136 - 1163	122 - 940	124 - 273	[19]
This study	484 - 2216	60 - 130	60 - 240	

^{226}Ra : 60-130 Bq.kg^{-1}

Below the 370 Bq.kg^{-1} limit by the U.S. EPA to distribution and commerce of phosphogypsum to agricultural uses.

Slightly below those found in the literature by other Brazilian authors

^{210}Pb : from 484 to 2216 Bq.kg^{-1}

Higher than others studies.

Results of fractionation of the soils

Dose 0: absence of Phosphogypsum

Concentration on the natural soil

The majority of concentration is found on residual fraction (F5)

Smaller on exchangeable fraction (F1), to all doses

^{210}Pb :

Comparing with the total content

Soils FL and LV → slight increase on PG doses 0, 1 and 2

After 30 days, ^{210}Pb can be available to vegetal uptake or association with soil solution or mineral/organic fraction

Lead: very slow mobility in soils.

Low Content of carbonate minerals → lead bound to carbonate (F2) was expected to be low or not detected;

Affinity of ^{210}Pb with carbonates is extremely low.

Not quantified

SAME with the organic matter

^{210}Pb bounded on Fe/Mn oxides (F3): observed in low pH soils and high content of oxides.

X-Rays Fluorescence: both soils has low levels of iron and manganese oxides

FluvisoL: more oxides than LV

Small concentration of ^{210}Pb found on soil FL, while the values to soil LV were below the detection limit.

Residual fraction ^{210}Pb : 50 to 78% of the total to soil FL
48 to 61% for soil LV.

Dose 0 both soils presented compatible ^{210}Pb (60-64%).

Radium isotopes on soils amended with PG

High Ca and Mg concentrations reduce the mobility and uptake of Ra;

Acidic conditions, more mobility on soils

Adsorption on Fe and Mn oxides

Brazilian soils: Th >> U.
 $^{228}\text{Ra} \gg ^{226}\text{Ra}$

Ra isotopes: different behaviors between the extractions.

Ra was not detectable on F2 and F4 fractions: small content of Fe and Mn oxides

Residual fraction: similar values on the two soils

PG seem not increase the ^{226}Ra level on soils.

^{228}Ra :

soil LV Exchangeable F1: 4% (dose 0)
6%(dose 1)
12% (dose 2)

Soil FL fraction F1: close values (4%, 5% 6%)

TF ^{228}Ra can be higher in soils amended with PG

^{226}Ra : Fe/Mn oxide seems to be more important than to ^{228}Ra .

Fraction of ^{226}Ra in the residual fraction is more elevated than the ^{228}Ra .

Brazilian authors performed extractions on PG samples;
Ra and Pb bounded to oxide fractions
Part on exchangeable fraction

Table 5: electric conductivity (E. C.) on the studied soils.

Soil	Dose	E.C. mS.cm ⁻¹ (1:5)
FL	0	15.87
	1	2.74
	2	3.74
LV	0	83.34
	1	6.81
	2	11.77

After 30 days of the addition of PG decreased considerably.

Dose 1: best values for both soils

Over dosage of PG elevate the E. C. on those soils.

Conclusion

^{226}Ra and ^{228}Ra on PG samples: lower than PG worldwide

Accordance with others radiometric characterization of Brazilian.

The ^{210}Pb concentration is higher than values point by others authors.

PG on saline-sodic soils reclamation: 30 days increase of ^{210}Pb and ^{228}Ra in the exchangeable fraction of soil
Increase of the transfer of these radionuclides to plants.

^{226}Ra : PG seems to not increase the activity of this isotope on the studied soils.

Radioisotopes were not detectable on the Carbonates (F2) and Organic matter (F4) fractions.

Low contents of carbonates and organic matter on the soils of the experiment.

Found on F5 (residual) and F1 (exchangeable)

Small content on Fe and Mn oxides, small amount of this mineral phase.

E. C.: decreased considerably

Over dosage of PG may elevate the E.C. due Ca and Mg.

Shoukran!

Thank you!

Merci!

Gracias

Obrigado!

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