Radiological impact of the application of phosphogypsum in agriculture

B.P. Mazzilli[1], C.H.R. Saueia[1]

Instituto de Pesquisas Energéticas e Nucleares

Laboratório de Radiometria Ambiental

Av. Prof. Lineu Prestes 2242 CEP 05508-000 São Paulo Brasil

chsaueia@ipen.br, mazzilli@ipen.br

Abstract. Phosphogypsum is a TENORM waste and one possible of this application is in agriculture. This paper aims to evaluate the dose due to ingestion of natural radionuclides present in phosphogypsum that could be incorporated in the food chain. For this evaluation, a conservative scenario was defined, considering a theoretical long term exposure due to annual applications of phosphogypsum in agriculture. This scenario covers estimation of the increment of radionuclides activity concentration in soil due to phosphogypsum applications; the uptake from soil by edible portions of vegetable and crops and activity concentration of radionuclides in milk and meat as part of the food chain; based on a model, transfer factors and conversion factors provided by IAEA and ICRP. The higher doses were found for the ingestion of vegetables and grain crop, up to 4.2 10^{-1} mSv per year. It is concluded that the radiological impact of this practice is negligible.

1 Introduction

In Brazil, several TENORM industries are in operation, which require an adequate environmental and occupational radiological control. Depending upon the level of radioactivity, these TENORM industries are subjected to the recommendations given by the national regulatory body, Comissão Nacional de Energia Nuclear – CNEN, which include compliance with the radiological protection regulations [1, 2].

Among these installations are the phosphate fertilizers industries, which generate a waste, calcium sulphate dihydrate, known as phosphogypsum. This residue is produced by precipitation during wet sulphuric acid processing of phosphate rocks, thus posing serious problems with its utilization and safe disposal. In Brazil, three main phosphate industries are responsible for the production of approximately $5.5x10^6$ tons per year of phosphogypsum. The material 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 residue is then moved to nearby storage areas. The phosphogypsum stacks can pose serious environmental impact, not only from a chemical, but also from a radiological point of view. All the countries that

produce phosphate fertilizer by acid wet processing of phosphate rock are facing the same problem of finding solutions for the safe application of this residue, in order to minimize the impact caused by the disposal of large amounts of phosphogypsum.
In Brazil, one possibility is to use phosphogypsum in agriculture, as soils amend. Phosphogypsum is useful for highly weathered soils, with relatively low exchange capacities and/or low levels of extractable nutrients; for soils with high sodicity; for acid soils with high levels of Al and for calcareous soils. Its application, however, should take into account the increment of radionuclides activity concentration in soil; the uptake of radionuclides from soil by edible portions of vegetable and crops and activity concentration of radionuclides in milk and meat as part of the food chain.
This paper aims to characterize the contents of natural radionuclides present in the Brazilian phosphogypsum and to evaluate the dose due to ingestion of natural radionuclides that could be incorporated in the food chain by the application of phosphogypsum as soil amend. The activity concentration of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra was measured by gamma and alpha spectrometry. For the evaluation of the dose, a conservative scenario was defined, considering a theoretical long term exposure due to successive annual applications of phosphogypsum in agriculture for 50 years. This scenario covers estimation of the increment of radionuclides activity concentration in soil due to phosphogypsum applications; the uptake of radionuclides from soil by edible portions of vegetable and crops and activity concentration of radionuclides in milk and meat as part of the food chain; based on a model, transfer factors and conversion factors provided by IAEA [3,4] and ICRP [5]. The results obtained were compared with literature data and with the doses obtained by using Brazilian phosphate fertilizers (TSP, SSP, MAP and DAP).

2 Material and Methods

Radioactivity measurements were carried out in 12 samples of phosphogypsum obtained from the three main Brazilian installations: two located in Cubatão – São Paulo State, named Copebras and Ultrafertil; one located in Uberaba – Minas Gerais State, named Fosfertil. After collection, the samples were dried at about 60^{o}C to remove moisture and crushed to fine powder (30 to 60 mesh).
Activity concentrations of ^{228}Ra and ^{210}Pb were measured in samples by gamma spectrometry with a hyper-pure germanium detector, GEM–15200, from EG&G Ortec. Samples were packed in 100 cm^3 cans and sealed for about four weeks prior to the measurement in order to ensure that equilibrium has been reached between ^{226}Ra and its decay products of short half-life. The detector was calibrated using natural soil spiked with radionuclides certified by Amersham. The ^{228}Ra content of the samples was determined by measuring the intensities of the 911.07 keV and 968.90 keV gamma-ray peaks from ^{228}Ac. For the determination of ^{210}Pb, the photopeak of 46.5 keV was used. This peak, due to its low energy, needed auto-absorption correction, which was carried out according to the procedure proposed by Cutshall [6]. Minimum detectable activity concentrations for gamma spectrometry were obtained by measuring deionized water in the same geometry as the samples, and the results were 3.0 Bq kg^{-1} for ^{228}Ra and 19.0 Bq kg^{-1} for ^{210}Pb, for a counting time of 150,000 seconds.

Activity concentration of the alpha emitters ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Po and ^{232}Th was measured by alpha spectrometry. The radiochemical procedure was based on the total dissolution of the samples (300 mg), by addition of concentrated acids under heating at 80°C, in the presence of exact aliquots of ^{232}U, ^{229}Th, ^{209}Po and ^{133}Ba used as tracers, followed by purification with anionic exchange resins. In the first column the solution is eluted in a Dowex 1x8 resin in 9M HCl: U and Po are retained whereas Th isotopes and Ra flow through the resin. U is eluted with 0.1M HCl and the final solution electrodeposited in a disc for alpha counting. For the ^{210}Po determination, a modified methodology of Matthews [7] was used. The Po was eluted with 1M HNO_3 and the solution was evaporated to dryness. The residue was dissolved in 6.25M HCl, filtered in Millipore 0.1μ and 20% hydroxylamine hydrochloride, sodium citrate and stable Bi^{+3} were added. After the pH was adjusted to 1.5, polonium was spontaneously plated on the silver disc at 90°C for 4 hours, with agitation of the solution. The eluate containing Th and Ra is passed through two columns: the first one (Dowex 1x8 resin in 8M HNO_3) for the retention of Th and the second one (Dowex 1x8 resin in 0.75M HBr) for the purification of Ra. Th is eluted with 9M HCl and is electrodeposited for alpha counting. A seeding suspension of $BaSO_4$ is added to the solution containing Ra; the $BaRaSO_4$ micro precipitated formed is retained in a Polypropylene membrane filter and counted on the alpha spectrometer. All the measurements were performed on a surface barrier detector, EG&G Ortec.

The precision and accuracy of the method were determined by analyzing reference materials: soil IAEA-326, sediment IAEA-300 and sediment IAEA-368. The precision achieved was 6.7% for U isotopes, 7.9 % for Th isotopes, 4.7 % for ^{226}Ra and 4.3 % for the ^{210}Po; the accuracy obtained was 5.4 %, 7.6 %, 4.4 % and 1.0%, respectively. Typical lower limits of detection for the alpha measurement of the radionuclides were 1.9 Bq kg^{-1} for ^{238}U, 1.7 Bq kg^{-1} for ^{234}U, 1.3 Bq kg^{-1} for ^{230}Th, 1.3 Bq kg^{-1} for ^{226}Ra, 5.9 mBq kg^{-1} for ^{210}Po, and 2.0 Bq kg^{-1} for ^{232}Th, respectively.

In order to estimate the radiological impact of the use of phosphogypsum in agriculture, a scenario was defined considering a long term exposure due to successive phosphogypsum applications along the years. In this theoretical scenario, the phosphogypsum is spread on land thus leading to a surface contamination which depends on the radionuclide concentration in the phosphogypsum and on the thickness of the layer on the land; the uptake of radionuclides from soil by edible portions of vegetable and crops and activity concentration of radionuclides in milk and meat as part of the food chain. All the estimations were carried out according to models, transfer factors and conversion factors provided by IAEA [3, 4] and ICRP [5].

To estimate the increment of activity concentration in the soil it was assumed that the phosphogypsum is added to the soil before the harvesting, at a rate of 0.2 kg of phosphogypsum per m² according to the recommendations of the manufacturers (2000 kg ha^{-1}) and is incorporated to the rooting zone depth forming a uniform mixture. The deposition rate for each radionuclide in the soil is represented by the product of the activity concentration of the radionuclide in the phosphogypsum by the surface application rate. The removal factor for each radionuclide present in the soil is obtained by the application of a factor exponentially proportional to the deposition rate. Two mechanisms contribute to the reduction of activity in the root zone: the radioactive decay and the radionuclides infiltration to deeper layers of soil. The uptake of radionuclides from soil by edible portions of vegetation and the transfer to

milk and meat trough the food chain, were estimated according to the models recommended by IAEA [3]. It was assumed that the foliar absorption is negligible and that the uptake from soil to plant is mainly by the root. Finally, the effective doses due to ingestion were evaluated, considering the application of phosphogypsum for 50 years. All the parameters used were taken from IAEA [4]. A full description of the methodology adopted and equations used for these calculations are described in more details in Saueia [8].

3 Results and Discussion

The activity concentration obtained for the radionuclides ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra in samples of phosphogypsum from the main Brazilian phosphate industries are presented in Table 1. The results show that all the radionuclides of the U and Th series are enriched in the phosphogypsum, except for the U isotopes, which concentrate in the phosphoric acid formed during the chemical attack of the phosphate rock [9]. The radionuclides of the U series (^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po) reached values up to 1011 Bq kg^{-1} in phosphogypsum samples from Copebras installation, where as the other two industries presented values up to 357 Bq kg^{-1}. As for the Th series (^{232}Th and ^{228}Ra), phosphogypsum from all provenances presented values up to 231 Bq kg^{-1}.

Table 1. Activity concentration in Bq kg^{-1} for radionuclides in phosphogypsum samples

	U- 238	U- 234	Th- 230	Ra- 226	Pb-210	Po-210	Th-232	Ra-228
Copebras industry (Cubatão)								
(M ± sd)*	50 ± 3	57 ± 5	742 ± 19	697 ± 24	1011 ± 27	669 ± 31	239 ± 7	233 ± 7
Range	42-53	54-63	655-978	550-940	834-1163	541-752	212-257	210–273
Fosfertil industry (Uberaba)								
(M ± sd)*	33 ± 5	59 ± 8	39 ± 3	149 ± 12	231 ± 16	172 ± 21	74 ± 4	148 ± 6
Range	23-50	40-89	32-68	122-215	136-228	158-189	60-102	124-179
Ultrafertil industry (Cubatão)								
(M ± sd)*	46 ± 6	50 ± 6	296 ± 10	300 ± 15	357 ± 19	349 ± 30	195 ± 7	231±10
Range	40-58	48-52	252-223	280-329	316-378	322-388	172-218	191-247

* Mean value ± standard deviation

The results obtained for the radionuclides concentration in soils are presented in Table 2.

Table 2. Activity concentration for radionuclides in soils (Bq kg^{-1}) after 50 years of phosphogypsum (PG) application

Radionuclides	PG Copebras	PG Fosfertil	PG Ultrafertil	UNSCEAR 2000
U-238	1.85	1.42	1.88	35
U-234	2.27	2.49	1.92	
Th-230	30.0	1.92	11.3	
Ra-226	28.3	7.07	13.1	35
Pb-210	20.7	3.55	6.77	
Po-210	24.8	5.95	12.2	
Th-232	8.69	3.31	7.84	30
Ra-228	1.53	0.96	1.38	

These results should be regarded as an increment of the concentration of the radionuclides in the original soil, after 50 years of phosphogypsum application. As expected, the concentrations are negligible for the U isotopes, since this element is not present in the phosphogypsum itself. The progeny of the U decay series, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po, are present in significant concentrations only in the soil in which phosphogypsum from Copebras industry was applied. For the application of phosphogypsum from the other industries (Ultrafertil and Fosfertil), the increment in the soil concentration can be considered as negligible, even after 50 years of application.

In an earlier paper, the same authors [10] studied the content of radioactivity in several commercial fertilizers produced by the Brazilian industries: MAP, DAP, TSP and SSP. By taking into account the radionuclides' content in these fertilizers, the amount added in one single application, they observed an increment of radioactivity in soil up to 0.87, for the application of SSP in grain crop and 7.6 Bq kg^{-1}, for the application of SSP in green crop. In the present study, the increment of radioactivity considering one single application of phosphogypsum was 2.92 Bq kg^{-1}, since both values are of the same order of magnitude it is expected the same radiological impact of using both fertilizers and phosphogypsum.

Abril [11] measured the ^{226}Ra and ^{238}U concentrations after two application of phosphogypsum in soil, resulting in an input of the initial concentration of 2.5 Bq kg^{-1} and 0.76 Bq kg^{-1}, respectively. These results, obtained experimentally, are in agreement with those evaluated in this work. In the same paper, Abril [11] studied the cumulative effect of three decades of phosphogypsum amendments in reclaimed

marsh soils in SW Spain. According to these authors, a significant increment of ^{226}Ra in the soil was observed, from 22.4 Bq kg^{-1} to 35.3 Bq kg^{-1}.This result agrees well with our estimation of 28.3 Bq kg^{-1} for the ^{226}Ra content in soil after 50 years of phosphogypsum application.

The results obtained for the radionuclides concentration in soil can be compared also with the data from the United Nations Scientific Committee on the Effects of Atomic Radiation – UNSCEAR [12] for natural soil (Table 2). Only in the application of phosphogypsum from Copebras industry, the soil concentration reached values of the same order of magnitude as the UNSCEAR data for ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po. It can be concluded that the dilution factors are very high and any possible radiological impact of the ingestion of food produced using phosphogypsum as soil amend, is only predictable in the scenario which uses phosphogypsum from Copebras.

Therefore, the doses due to ingestion were evaluated, considering only the use of phosphogypsum from Copebras. The results are presented in Table 3.

Table 3. Effective doses (E) due to ingestion after 50 years of application of phosphogypsum in soil (mSv y^{-1})

Phosphogypsum from Copebras industry (Cubatão)				
Radionuclides	E grain	E green	E meat	E milk
U-238	$7.8x10^{-4}$	$4.7x10^{-4}$	$6.1x10^{-6}$	$1.2x10^{-5}$
U-234	$9.6x10^{-4}$	$5.8x10^{-4}$	$7.5x10^{-6}$	$1.5x10^{-5}$
Th-230	$3.1x10^{-2}$	$1.8x10^{-2}$	$1.6x10^{-5}$	$3.2x10^{-5}$
Ra-226	$1.5x10^{-1}$	$9.2x10^{-2}$	$1.0x10^{-3}$	$1.9x10^{-3}$
Pb-210	$6.9x10^{-2}$	$4.2x10^{-2}$	$2.5x10^{-4}$	$5.1x10^{-4}$
Po-210	$1.3x10^{-1}$	$8.6x10^{-2}$	$3.7x10^{-3}$	$7.3x10^{-3}$
Th-232	$9.7x10^{-3}$	$5.8x10^{-3}$	$5.1x10^{-6}$	$9.9x10^{-6}$
Ra-228	$1.9x10^{-2}$	$1.2x10^{-2}$	$1.3x10^{-4}$	$2.5x10^{-4}$
$\sum$	$4.1x10^{-1}$	$2.6x10^{-1}$	$5.2x10^{-3}$	$1.0x10^{-2}$

The radionuclides, that more contributed for the doses, due to ingestion of grain crops and green crops, were ^{226}Ra (37%), ^{210}Po (32%), ^{210}Pb (16%) and ^{230}Th (7%). As for the ingestion of milk and meat, ^{210}Po (72%) and ^{226}Ra (20%) were mainly responsible for 92% of the doses. The higher doses were found for the ingestion of vegetables and grain crop, up to 4.2 10^{-1} mSv per year. The doses due to the ingestion of meat and milk reached values several orders of magnitude lower than the doses due to

vegetables and grain crop ingestion. It can be concluded that the radiological impact of this practice is negligible.

Papastefanou [13] measured the ^{226}Ra content in rice cultivated in fields tilled with phosphogypsum. Although, a significantly higher radium content was found in cultivated fields tilled with phosphogypsum (average 205 Bq kg^{-1}), compared with regular soil (average 48 Bq kg^{-1}), the uptake from the soil to rice was very low (Ra concentration of 1.53 Bq kg^{-1}) and the corresponding final dose reached value of 0.86 μSv y^{-1}. It is interesting to note that, although higher concentrations were found in the soil, the uptake to rice and corresponding dose due to ingestion was 3 orders of magnitude lower than the results obtained in this study.

Nasim-Akhtar [14] measured the content of ^{226}Ra and ^{232}Th in agriculture farms that used phosphate fertilizers during 35 years, obtaining concentrations of 57.18 Bq kg^{-1} and 34.45 Bq kg^{-1} for ^{232}Th and ^{226}Ra, respectively. The concentration values are within the range specified by UNSCEAR[12] in 2000 report. The wheat grain produced in this site reached values of 1.50 for ^{232}Th and 1.25 Bq kg^{-1} for ^{226}Ra, and the corresponding dose was 206.1 μSv y^{-1}. Their result is in agreement with the dose obtained in this work, 163 μSv y^{-1}, considering only the ^{232}Th concentration (0.87 Bq kg^{-1}) and the ^{226}Ra concentration (11.3 Bq kg^{-1}) in grain crops.

In Figure 1, the results obtained in the present study for the doses are compared with data obtained from the use of Brazilian phosphate fertilizers, SSP and TSP [15].

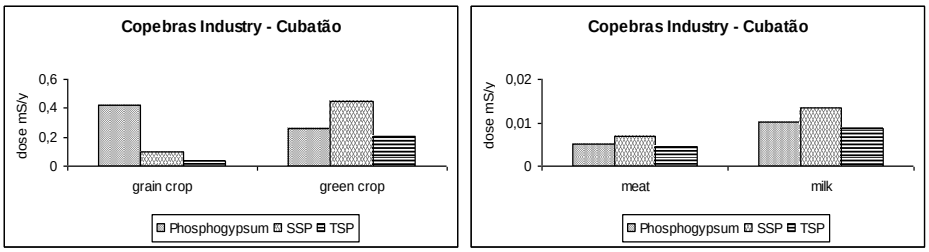

Fig. 1. Effective 50 years dose per annual application of phosphogypsum and fertilizers (Saueia and Mazzilli[10])

It is interesting to note that the doses due to the use of phosphogypsum in the agriculture are of the same order of magnitude as those derived from the use of the fertilizers SSP and TSP. This fact can be explained, considering that the radionuclides contents in phosphogypsum and the fertilizers SSP and TSP are similar.

Doses reported by the European Commission [16], on the radiological impact resulting from the use of the fertilizer products, using a similar scenario, ranged from 0.1 to 1 mSv y^{-1}. It can be concluded that the doses derived from the use of phosphogypsum in agriculture are in the range observed for the use of fertilizers in Europe and in Brazil, and therefore, pose no health risks to the final consumers.

4 Conclusion

The activity concentration obtained for the radionuclides of the U series (^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po) and for the Th series (^{232}Th and ^{228}Ra), in samples of phosphogypsum from the main Brazilian phosphate industries, reached values ranging from 33 Bq kg^{-1} to 1011 Bq kg^{-1} and from 74 Bq kg^{-1} to 239 Bq kg^{-1}, respectively. The phosphogypsum from Copebras presented the higher contents of radioactivity. The increment of the concentration of the radionuclides in the original soil, after 50 years of phosphogypsum application, was negligible for the Fosfertil and Ultrafertil industries. For the use of phosphogypsum from Copebras, the soil concentration was more significant for the radionuclides ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po, with average value of 26 Bq kg^{-1} of the same order of magnitude as the UNSCEAR data for natural soil. The higher doses were found for the ingestion of vegetables and grain crop, up to 4.2 10^{-1} mSv per year, with the application of phosphogypsum from Copebras. The doses due to the use of phosphogypsum in the agriculture are of the same order of magnitude as those derived from the use of the fertilizers SSP and TSP. It can be concluded that the radiological impact of this practice is negligible.

Acknowledgment

The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico CNPq, grant 300835/95-7 and 141792/2001-9.

References

1. CNEN-NN 3.01 “Critérios de exclusão, isenção e dispensa de requisitos de proteção radiológica.” published in Diário Oficial da União (DOU), Janeiro 2005.
2. CNEN-NN 4.01 “Requisitos de Segurança e Proteção Radiológica para Instalações Mínero-industriais” published in Diário Oficial da União (DOU), Janeiro 2005.
3. IAEA, INTERNATIONAL ATOMIC ENERGY AGENCY. *Evaluating the reliability of predictions made using environmental transfer models*. Vienna, 1989 (Safety Series No.100)
4. IAEA, INTERNATIONAL ATOMIC ENERGY AGENCY. *Generic Models for Use in Assessing the Impact of Discharges of Radioactive Substances to the Environment*. Vienna, 2001 (Safety Series No.19)
5. ICRP, INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION. *Age-dependent doses to members of the public from intake of radionuclides: part 2 ingestion dose coefficients*, publication 67, 2001 Pergamom Press.
6. Cutshall,N.H, Larsen,I.L, Olsen,C.R. Direct analysis of ^{210}Pb in sediment samples: self-absorption corrections. *Nucl. Instrum. Methods* v. 206, p.309-312, 1983.
7. Mattheus, K.M, Kim, C, P. Martin. Determination of ^{210}Po in environmental materials: A review of analytical methodology. *J. Appl. Radiation Isotopes*. v. 65, p. 267-279, 2007.
8. C.H.R.Saueia, Distribuição elementar e de radionuclídeos na produção e uso de fertilizantes fosfatados no Brasil. Tese (Doutorado) – Instituto de Pesquisas Energéticas e Nucleares, São Paulo, 2006.
9. Mazzilli B. P.; Palmiro V.; Saueia C.H.R; Nisti M. B Radiochemical characterization of Brazilian phosphogypsum. *J. Environ. Radioact*., v.49, n.1, p.113-122, 2000.
10. Saueia,C.H.R.; Mazzilli, B.P. Distribution of Natural Radionuclides in the Production and Use of Phosphate Fertilizers in Brazil. *J. Environ. Radioact*. v.89, p.229-239, 2006.

11. Abril J, Garcia-Tenório R, Enamorado S. M, Hurtado M. D, Andreu L, Delgado A.. The cumulative affect of three decades of phosphogypsum amendments in reclaimed marsh soils from SW Spain: ^{226}Ra, ^{238}U and Cd contents in soils and tomato fruit. *Sice Tot. Environ.* v 403, p.80-88, 2008.
12. UNSCEAR, UNITED NATIONS SCIENTIFIC COMMITTEE ON THE EFFECTS OF ATOMIC RADIATION *Sources and Effects of Ionizing Radiation*, New York, 2000 (Report to the General Assembly v.1, 2)
13. Papastefanou, C, Stoulos S, Ioannidou A., Manolopoulou, M *J.* The application of phosphogypsum in agriculture and the radiological impact. *J Environ. Radioact*, v. 89, p.188-198, 2006.
14. Nasim-Akhtar, M. Tufail, Natural Radioactivity intake into wheat grown on fertilized farms in two districts of Pakistan. *Radiat.Protec. Dosim*., v.123 n. 1, p.103–112, 2007.
15. Saueia, C.H.R, B.P. Mazzilli, D.I.T. Fávaro, Natural radioactivity in phosphate rock, phosphogypsum and phosphate fertilizers in Brazil *J. Radioan. Nucl. Chem.* v. 264 n. 2, p. 445-448, 2005.
16. European Commission. *Natural Radionuclide Concentrations in Materials Processed in the Chemical Industry and the Related Radiological Impact.*, 2000 (Report EUR 19264).