440

NATURAL RADIOACTIVITY IN PHOSPHATE ROCK, PHOSPHOGYPSUM AND PHOSPHATE FERTILIZERS IN BRAZIL

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ABSTRACT

Phosphate deposits are generally characterised by enhanced radionuclide concentrations compared to natural levels. The mining and processing of this phosphate ore redistribute radionuclides throughout the environment and introduce them into phosphoric acid and phosphogypsum. Phosphoric acid is the starting material for triple superphosphate (TSP), single superphosphate (SSP), monoammonium phosphate (MAP), diammonium phosphate (DAP), NPK fertilizers *and* di-calcium phosphate (DCP). Contents of natural radionuclides from thorium and uranium series, Ra-226, Pb-210 and Ra-228, were measured in Brazilian igneous phosphate rock, phosphoric acid, phosphogypsum and phosphate fertilizer samples, using high-resolution gamma spectrometry. Neutron activation analysis was used for the determination of U and Th in the same samples. The fertilizers samples which are derived directly from phosphoric acid, MAP and DAP, presented activity concentrations around the detection limits of the counting system for Ra-226 (<5.0 Bq kg^{-1}), for Ra-228 (<3.0 Bq kg^{-1}) and for Pb-210 (<19 Bq kg^{-1}). As for U and Th, the concentrations found in MAP and DAP are more significant, up to 374 and 250 Bq kg^{-1} respectively. SSP, TSP and NPK, which are obtained by mixing phosphoric acid with different amounts of phosphate rock and NH_3, presented higher concentrations

9952

of radionuclides, up to 871 Bq kg^{-1} for Ra-226, 283 Bq kg^{-1} for Ra-228, 1255 Bq kg^{-1} for Pb-210, 413 Bq kg^{-1} for U and 538 Bq kg^{-1} for Th.

INTRODUCTION

Phosphate rock is used worldwide for manufacturing phosphoric acid and various brands of chemical fertilizers. It is known that the phosphate rock contains radionuclides of the U and Th natural decay series. The mining and processing of this phosphate rock redistributes radionuclides throughout the environment and introduce them into final products and by-products. It has been reported by MAZZILLI et al. (2000)[1] that the phosphate rock used as raw material in the Brazilian phosphate industry presents concentration of radionuclides of the U and Th series ranging from 10 to 1200 Bq kg^{-1}. It is important to measure natural radioactivity, not only in the phosphate rock, but also in different types of fertilizers and by-products, because the high radioactive contents may lead to a significant exposure of miners, manufacturers and end users. Furthermore, such measurements provide basic data for the estimation of the amount of radioactivity spread on agricultural land along with fertilizers. Since no regulation in terms of radiation protection principles has been applied to industries containing technologically enhanced naturally occurring radioactive materials (TENORM) so far, members of the public or occupationally exposed may incur undue exposures. The Brazilian phosphate fertilizer is obtained by wet reaction of igneous phosphate rock with concentrated sulphuric acid, giving as final product phosphoric acid, and calcium sulphate dihydrate (i.e. phosphogypsum) as by-product. This by-product is disposed in stacks and no application has been proposed for this waste so far, mainly due to elevated levels of impurities.

Phosphoric acid is the starting material for triple superphosphate (TSP), single superphosphate (SSP), ammonium phosphate fertilizers (DAP and MAP), NPK fertilizers and di-calcium phosphate (DCP), a mineral complements for animal feeding. MAP and DAP are obtained by reacting directly phosphoric acid with different amounts of NH_3. TSP, SSP and NPK are obtained by reacting phosphoric acid with phosphate rock and NH_3. During the reaction of phosphate rock with sulphuric acid, the radioactive equilibrium between U, Th and their decay products is disrupted and the radionuclides migrate according to their solubility. Uranium isotopes form highly soluble compounds with phosphate ions, while Ra isotopes, Pb-210 and Po-210 concentrate in phosphogypsum[1-3]. Mazzilli et al. (2000)[1] found percentages (phosphogypsum to ore rocks) of 90% for Ra-226, 100% for Pb-210 and 78% for Po-210. Several papers have been also published concerning the radiological and elemental characteristics of the stockpiled Brazilian phosphogypsum[4-6] and its environmental radiological impact[7]. Santos[5] reported that the Brazilian phosphogypsum is enriched in the rare earth elements, Ce, Eu, La, Nd, Sm, Tb, Yb, and Ba and Th. The results obtained so far show that the stacks are quite homogeneous and its composition is mainly dependent upon the phosphate rock used as raw material[5].

Although several publications have been concerned about the radioactivity of phosphate fertilizers throughout the world[8-11], few papers were found about the characterisation of the Brazilian phosphate fertilizers. ARRUDA-NETO et al. (1997)[12] reported quite high concentrations of uranium in both animals and humans, which could be attributed to the substantial uranium content in di-calcium phosphate used as animal feeding supplement (up to 200 ppm).

In this work, contents of natural radionuclides from thorium and uranium series, Ra-226, Pb-210 and Ra-228, were measured in Brazilian igneous phosphate rock, phosphoric acid, phosphogypsum and phosphate fertilizers samples, using high-resolution gamma spectrometry. Neutron activation analysis was used for the determination of U and Th in the same samples.

MATERIAL AND METHODS

Activity concentrations of Ra-226, Ra-228, Pb-210 and K-40 were measured in samples of phosphate rock, phosphoric acid, phosphogypsum and fertilizers by gamma spectrometry with a hyper-pure germanium detector, GEM–15200, from EG&G Ortec. The detector was calibrated using natural soil "9809 SO", certified by Instituto de Radioproteção e Dosimetria (IRD-CNEN). The radionuclides used in the efficiency calibration were K-40, Pb-210, Pb-214, Bi-214, Pb-212, Tl-208 and Ac-228, the uncertainties in the efficiency ranged from 4.5 to 11%. 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 Ra-226 and its decay products of short half-life. The Ra-226 activities were determined by taking the mean activity of three separate photopeaks of its daughter nuclides: Pb-214 at 295 keV and 352 keV, and Bi-214 at 609 keV. 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. The concentration of Pb-210 and K-40 were carried out by measuring the activity of their energy peak, 46.5 keV and 1460.8 keV, respectively. Self-absorption correction was applied to Pb-210 since the attenuation for low energy gamma rays is highly dependent upon sample composition.

The approach used was modified from that suggested by CUTSHALL et al. (1983)[13]. All the spectra obtained were analyzed by WinnerGamma Program[14]. Minimum detectable activity concentrations for gamma spectrometry were obtained by measuring deionized water in the same geometry as the samples for 150,000 seconds. The results were 5.0 Bq kg^{-1} for Ra-226, 19 Bq kg^{-1} for Pb-210, 3.0 Bq $kg^{-1}$for Ra-228 and 45 Bq kg^{-1} for K-40. All samples except of phosphoric acid were analysed by neutron activation analysis (NAA), for U and Th. The elements were determinated by irradiation of approximately 150mg of each sample, during 16 hours at a neutron flux of 10^{12} $n.cm^{-2}s^{-1}$, at Instituto de Pesquisas Energéticas 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 photopeak. The concentration of the analysed elements was determined by comparing activities obtained in the samples with standard materials Buffalo River Sediment (NIST-2704) and Soil-7 (IAEA). The precision and accuracy of the method were verified by measuring these reference materials, the results obtained are presented in figure 1. The concentration of U-238 and Th-232 were obtained by taking into account the results of NAA and the specific activities of these radionuclides.

RESULTS AND DISCUSSION

Results obtained for radionuclides activity concentration in the phosphate rock, phosphoric acid, phosphogypsum and fertilizers are presented in Table 1. Radionuclide concentration in the phosphate rock varied from <19 to 1414 Bq kg^{-1} for U decay series and from 56 to 310 Bq kg^{-1} for Th decay series. The results are better understood if the origin of the phosphate rock (PR) used in industries A, B, C and D is taken into account.

Industry A presented the higher concentration of radionuclides from the U and Th series, its PR comes from Catalão (GO); and industry D, which uses PR from Cajati (SP), presented lower activities for all radionuclides studied. Industries B and C presented the same pattern of activity concentration for radionuclides of the U and Th series, PR of industry B comes from Tapira (MG) and that of industry C comes from Catalão. In all cases, the radionuclides Ra-226, Pb-210, Th-232 and Ra-228 migrate predominantly to phosphogypsum. The fertilizers samples which are derived directly from phosphoric acid, MAP and DAP, presented in their composition activity concentrations around the detection limits of the counting system for Ra-226, Ra-228 and Pb-210. As for U and Th, the concentrations found in MAP and DAP are more significant, up to 374 and 250 Bq kg^{-1} respectively. Such results indicate that in the processing of the phosphate rock, a significant amount of U and Th is migrating to phosphoric acid. SSP, TSP and NPK, which are obtained by mixing phosphoric acid with different amounts of phosphate rock and NH_3, presented higher concentrations of radionuclides, up to 871 Bq kg^{-1} for Ra-226, 283 Bq kg^{-1} for Ra-228, 1255 Bq kg^{-1} for Pb-210, 413 Bq kg^{-1} for U and 538 Bq kg^{-1} for Th. No activity was found in di-calcium phosphate, which is used for feeding animals.

From the radiation protection point of view the high radium content of fertilizers is significant in two ways. First, the accumulation of large quantities of phosphate fertilizers in warehouses increases the radon concentration in the surrounding air. The radium equivalent, Ra(eq) is a common index required to compare the specific activities of samples containing Ra-228, Th-232 and K-40, that takes into account the radiation hazards associated with them. The Ra(eq) is defined as[15]:

$$Ra(eq) = C(Ra\text{-}226) + 1.43\ C(Th\text{-}232) + 0.077\ C(K\text{-}40)$$

Where C(Ra-226), C(Th-232) and C(K-40) are the activities of Ra-226, Th-232 and K-40 in Bq kg^{-1}. This formula is based on the estimation that 1 Bq kg^{-1} of Ra-226, 0.7 Bq kg^{-1} of Th-232 and 13 Bq kg^{-1} of K-40 produce the same gamma dose rate. The Ra(eq) is related to the external gamma dose rate and the internal dose due to radon and its daughters. The Ra(eq) values of the phosphate rock, phosphogypsum and fertilizer samples are given in Table 1. The highest Ra(eq) activity among the analysed samples was found in phosphate rock, phosphogypsum, SSP and TSP from industries A, Band C.

The contribution of radioactivity to agricultural lands due to the application of phosphate fertilizers is the second concern for radiation protection point of view. However, this contribution is not easily quantified, since the quantity of radioactivity spread along with fertilizers in the agricultural fields depends upon the quantity of fertilizers used, the type of crop and area of its cultivation. As diet is the main source of intake and human exposure, K-40 should be neglected, since its content in the body is under homeostatic control and its radiation dose is not affected by variations in the environmental levels. The data presented here will be used for a future study of the application of Brazilian phosphate fertilizers.

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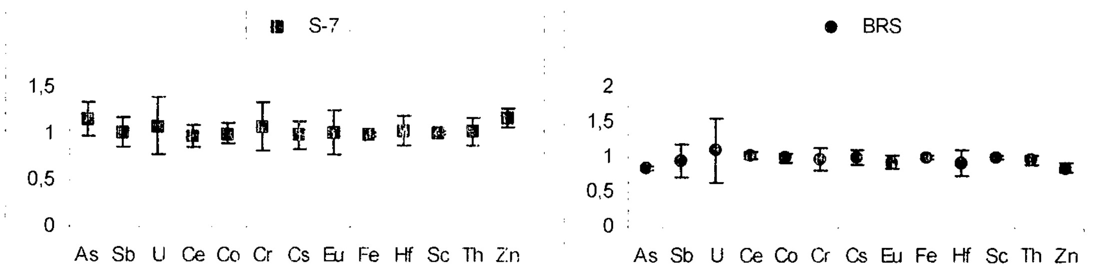

Figure 1 - Ratio between certified and obtained values for Soil 7 and Buffalo River Sediment.

Table 1. Activity concentration of radionuclides (Bq/kg) in phosphate rock (PR), phosphoric acid (PA), phosphogypsum (PG) and fertilizers from Brazilian fertilizer plants A, B, C and D and radium equivalent activities (Bq/kg).

Sample	U-238	Ra-226	Pb-210	Th-232	Ra-228	K-40	Ra (eq)
Industry A							
PR	638±153	723± 28	1414±186	258±18	249±14	<45	1095
PA	ND	<5.0	<19	ND	<3.0	<45	
PG	18±3	700± 38	1135±114	138±9	273± 17	<45	901
SSP	413±32	871±44	1255±114	100±7	196±10	375±26	1043
NPK	350±27	420±22	534±51	80±5	153±8	170±13	547
Industry B							
PR	298±78	257± 14	373±103	284±20	310±17	<45	666
PA	ND	<5.0	<19	ND	<3.0	308±21	
MAP	264±21	7±1	<19	250±17	<3.0	<45	368
TSP	221±21	122±6	198±25	538±36	204±12	147±17	903
NPK	272±27	451±23	644±65	297±20	283±14	<45	879
Industry C							
PR	344±94	352±19	666±142	246±17	255±14	87±30	710
PA	ND	8±1	<19	ND	<3.0	<45	
PG	61±7	350±42	353±31	69±4	130±16	<45	452
MAP	283±32	17±2	37±12	231±16	40±4	118±21	356
DAP	374±35	<5.0	<19	120±8	44±3	<45	175
NPK	380±41	425±22	741±82	307±21	240±12	<45	867
Industry D							
PR	14±6	53±4	<19	56±4	57±5	<45	136
PA	ND	<5.0	<19	ND	<3.0	63±11	
PG	<2	24±3	66±25	19±2	29±3	<45	55
DCP	<2	14±1	<19	10±1	17±2	148±17	40

ND – not determined

Errors correspond to propagation errors of the measurement