

Concentration of Radioactive Elements (U, Th and K) Derived from Phosphatic Fertilizers in Cultivated Soils

Valter Antonio Becegato^{1*}, Francisco José Fonseca Ferreira², William César Pollonio Machado³

¹Departamento de Engenharia Ambiental; Universidade do Estado de Santa Catarina; C.P.: 281; becegato@cav.udesc.br; 88520-000; Lages - SC - Brasil. ²Laboratório de Geofísica Aplicada; Universidade Federal do Paraná; C.P.: 19001; francisco.ferreira@ufpr.br; Curitiba - PR - Brasil. ³Instituto Ambiental do Paraná; Rua Guarani, 1002; wcpm@mail.crea-pr.org.br; 85501058; Pato Branco - PR - Brasil

ABSTRACT

Gamma spectrometric measurements were obtained for the agricultural soils aiming at characterizing the spatial distribution of radionuclide concentrations (K, eU and eTh), as well for the samples of phosphatic fertilizers and agricultural gypsum. In the study areas, three types of soils occurred: Eutrophic Red Nitosol (Alfisol), Eutroferic Red Latosol of clayey texture (Oxisoil) and Dystrophic Red Latosol of medium texture (Oxisoil). The results showed that the radionuclide concentrations in more clayey soils were higher than in more sandy soils, mainly as a function of a higher adsorption capacity of the former. For the area where human activity predominated, the average contents of K, eU and eTh were respectively 54.75; 10.22 and 7.27 Bq/Kg, significantly higher than those for the area where no fertilizers were used (34.15 Bq/Kg K; 1.69 Bq/Kg eU, and 5.36 Bq/Kg eTh). Variations in the radionuclide concentrations were also observed in various fertilizer formula used in soybean and wheat crops.

Key words: Gamma-rays spectrometry, soils, fertilizers

INTRODUCTION

Modern agriculture applies high technology, aiming at increasing the productivity. Cultures such as soybean and wheat adopt cultivars with high genetic potential that, together with chemical fertilizers, result in high productivity. In the last 20 years, the Brazilian agriculture would not have been possible without the application of large volumes of fertilizers. However, the presence of radionuclides in phosphatic fertilizers (Guimond and Hardin, 1989; Khan et al., 1998; Zielinski, et al., 2000; San Miguel et al., 2003; Becegato et al.,

2008) interferes in the environment and the consequences are still unknown.

Recent research in Brazil with radioactive elements derived from different fertilizer compositions has triggered the interest of the Brazilian scientific community regarding their environmental implications.

Gypsum, a secondary product of the production of acidified fertilizers, has been recently used. Agricultural gypsum, derived from the phosphoric acid, is composed of calcium, sulfur and water in varied concentrations. This product is used in order to supply calcium and sulfur to the deeper

* Author for correspondence

soil horizons, enabling the development of the plant root system and thus exploring a larger volume of soils in the search of nutrients and water (Nuernberg et al., 2002).

The fertilizers commercialized in Brazil contain radioactive elements (*e.g.* Mazzilli et al., 2000; Yamazaki and Geraldo, 2003; Saueia et al., 2004). Their contents depend on the source rock. In the case of phosphatic fertilizers, there are several trademarks and commercial compositions, with varying nitrogen, phosphorus and potassium contents. Pfister et al., (1976) observed that the high uranium concentration in triple superphosphate, in relation to the simple superphosphate, depends on the mode of production. In the first case, the rock undergoes a phosphoric acid attack, holding uranium as a dissolved uranyl complex. In relation to the monoammonia and diammonia phosphates, these are obtained combining phosphoric acid and ammonia.

Brazilian soils, mostly situated in the tropical zone, are in general poor as a consequence of constant losses by leaching (Andrello et al., 2003) of certain elements such as nitrogen, phosphorus and potassium (Santos Júnior et al., 2005), which are essential to the cultures such as soybean, wheat and sugar cane. The present practice of replacing nutrients in the soils and consequently supplying substances in order to reach high productivity is by the application of chemical fertilizers, mostly compounds commercially named NPK. Their formula vary widely and the concentrations are chosen according to the need of each soil and culture.

Soils differ in their capacity of cation retention. The cation exchange capacity (CEC) depends on the texture, physical properties, and clay and organic matter contents. More clay soils retain more cations; the opposite happens with sandy soils, where percolation of water is made easy by their high macroporosity, resulting in leaching of chemical elements that remain in solution in the soil.

The research on radionuclides in arable soils is still incipient in Brazil. This work shows the application of gamma spectrometry in an area where soybean is planted in the summer and wheat in the winter and where high technology is used, in order to reach maximum grain productivity.

MATERIALS AND METHODS

The study area is located close to Maringá in the State of Paraná, considered an regional agriculture pole. The area has been used for soybean plantation in the summer and wheat in the winter. The climate, according to the Paraná climatic chart (Iapar, 1978) and following Köeppen's classification, is Cfa, or mesothermal humid subtropical, with hot summers; rainfalls tend to concentrate in the summer, with an average annual values of 1200 mm (Rufino et al., 1993). Situated on the Third Paranaense Planalt, the area is inserted in the Cauiá Group, more specifically the Goio-Erê Formation (Fernandes and Coimbra, 2000), in transitional contact with the Serra Geral Formation (basalts).

A portable GS-512 gamma spectrometer from Geofyzika (Czech Republic), represented by Scintrex (Canada), designed to operate with 512 channels in a 0.1 to 3 MeV interval and pertaining to the Research Laboratory of Applied Geophysics – LPGA/UFPR, was used for data collection in the field. The GS-512 spectrometer is a probe (45 cm in length; 12.5 cm in diameter, weighing 4.6 kg), containing a 76 x 76 mm NaI(Tl) crystal, a detection circuit, and a reference radioactive source (^{137}Cs). Another module (23.5 x 23.0 x 9.0 cm) stores and processes the data obtained.

The natural occurring elements that produce gamma rays of intensity and energy enough to be measured by gamma spectrometry are potassium, uranium and thorium. Potassium is identified and quantified by means of the absorption of the 1.46 MeV energy, which corresponds to a sole natural isotope (^{40}K) that represents 0.012 % of total K (the other isotopes, ^{39}K and ^{41}K , are not radioactive and represent respectively 93.26 % and 6.73 % of total K). The natural isotopes of the uranium series constitute a mixture of ^{238}U (99.3 %) and ^{235}U (0.7 %), representative of complex decay chains that end with the stable isotopes ^{206}Pb and ^{207}Pb , respectively. Uranium is detected by the 1.76 MeV energy that corresponds to the absorption of ^{214}Bi of the ^{238}U series, used to identify and quantify natural uranium. Natural thorium is composed of the ^{232}Th isotope and its decay products, representing 100 % of total Th. It is identified by the ^{208}Tl peak, which corresponds to the 2.62 MeV absorption energy. Therefore, the

uranium and thorium concentrations are determined indirectly by gamma spectrometry. This is the reason why these concentrations are named uranium equivalent (eU) and thorium equivalent (eTh) respectively.

The gamma-spectrometric data were obtained in situ from a georeferenced grid on agricultural soils, totaling 77 points, and from two native forest areas, one characterized by a clayey and other by a sandy-clayey soil; 20 points were sampled in each area. Additionally, 20 points in piles of agricultural gypsum were sampled. Soil textures were determined in the laboratory.

The gamma spectrometer calibration

The instrument was calibrated by the Institute of Radioprotection and Dosimetry (IRD) of the Brazilian Nuclear Energy Commission (CNEN) on 23rd February 2003, according the procedures described in Ferreira et al., (2003). The calibration system (Barretto et al. 1986) was constituted by eight concrete cylindrical blocks or pads (3.0 m of diameter and 0.5 m of thickness, with density of 2.1 g/cm^3 and volume of 3.53 m^3 , weighing 7.41 tons), lying around a circle of 20 m of diameter in the IRD/CNEN gardens (0.5 m above sea level). Weather and atmospheric radon variations can influence the measurements with time; however, during the visual inspection, no fractures or significant modifications due to the weather were observed on the surface of the pads. To monitor the cosmic radiation, radon and instrumental background, a reservoir in the center of the circle with 4 m of diameter and 0.7 m of thickness was filled with the water.

The radiation sources were intermingled with

concrete, resulting from a 1:2:3 mixture of cement, crushed granite and sand. The aggregate grain-size was less than 1 cm, to make the mixture and homogenization with radioactive material easy. All the sources, excepting the background (BKG), were contaminated with the radioactive material in several proportions and combinations (Barretto et al., 1986). Table 1 shows K (%), U (ppm) and Th (ppm) concentrations obtained for the sources, derived from a large number (1266 valid determinations among 2180) of chemical analyses and by neutron activation, according to Barretto et al., (1986), and considering secular equilibrium. The uncertainties were indicated in terms of the standard deviation from the average (Ribeiro et al., 2005) and the number of determinations. The concentrations were also monitored by gamma spectrometers during the preparation of the sources, resulting K, U and Th contents as recommended by Barretto et al., (1986). For uranium, the differences in relation to Table 1 came from BKG (0.50 ± 0.01 ppm) and pads U1 and UTh2 (56.9 ± 1.15 and 38.95 ± 0.81 ppm, respectively). Regarding thorium, the recommended content for pad U2 was 45.57 ± 0.57 ppm. Such differences were suggested by Barretto et al., (1986) to compensate the effects of possible disequilibria in the uranium series. Ribeiro et al. (2005) stated that, the radiometric data, it was not clearly whether disequilibrium totally justified the corrections proposed. They mentioned that the majority of radiometric determinations fell in an interval twice the standard deviations around the values obtained by means of the chemical analyses and by neutron activation.

Table 1 – Radioelement concentrations in the IRD/CNEN pads, determined by chemical analyses and neutron activation, according to Barretto et al., (1986). The uncertainties correspond to standard deviation estimates and the number of determinations is indicated in brackets.

<i>Pads</i>	K Concentration (%)	U Concentration (ppm)	Th Concentration (ppm)
BKG	0.08 ± 0.01 (95)	0.82 ± 0.01 (70)	1.75 ± 0.12 (28)
K1	6.74 ± 0.06 (25)	2.00 ± 0.07 (62)	20.90 ± 0.81 (23)
K2	4.43 ± 0.08 (64)	2.97 ± 0.06 (79)	29.72 ± 1.39 (22)
U1	3.47 ± 0.04 (39)	69.92 ± 0.67 (85)	50.13 ± 0.99 (44)
U2	3.43 ± 0.08 (39)	19.45 ± 0.14 (58)	53.06 ± 1.68 (34)
Th1	3.54 ± 0.07 (52)	11.63 ± 0.15 (37)	255.97 ± 5.25 (47)
UTh1	3.64 ± 0.03 (64)	12.10 ± 0.24 (78)	71.59 ± 1.76 (48)
UTh2	3.65 ± 0.03 (27)	44.47 ± 0.63 (91)	152.39 ± 4.76 (55)

The calibration readings were taken every 10 minutes in pads K1, U1, Th1, BKG. The cosmic radiation (more than 3.000 KeV) was automatically monitored by GS-512. It was known that countings measured in the calibration *pads* from the K- (^{40}K – 1.46 Mev), U- (^{214}Bi – 1.76 Mev) and Th- (^{208}Tl – 2.62 Mev) windows were in linear relation with the source concentrations. Subtracting BKG from the countings, three equations with three unknowns derive for each window. According to the manual (Geofyzika, 1998), a 3 x 3 concentration matrix [Q], calculated by the representative parameters for the contents of the K1, U1 and Th1 sources and a geometric factor (which, for a cylindrical *pad* is given by $G = 1 - h/r$, where h (m) is the height of the detector in relation to the source surface and r is the pad radius; during the calibration process the sensor

was placed directly on the center of the sources, thus $G = 1$), is related to a equivalent counting matrix [n], calculated from the *pad* measurements and BKG taken on the water level, and with the calibration matrix [C] composed by some calibration constants, resulting the following matrix equation:

$$[Q] = [C] \times [n], \text{ or } [C] = [Q]/[n]$$

Once the instrument was calibrated, readings in all eight pads were taken for three minutes, time considered satisfactory for routine fieldwork. Tables 2, 3 and 4 show K (%), eU (ppm) and eTh (ppm) concentrations respectively, after subtracting BKG, according to Barretto et al., (1986), modified by Ribeiro et al., (2005), Ferreira et al., (2003) and Ribeiro et al., (2005).

Table 2 – Comparison between K concentrations (%) from IRD/CNEN *pads* determined by chemical analyses and neutron activation by Barretto et al., (1986), modified by Ribeiro et al., (2005)¹, and calculated by Ferreira et al., (2003)² and Ribeiro et al., (2005)³.

<i>Pads</i>	K Concentration (%) ¹	K Concentration (%) ²	K Concentration (%) ³
K1	6.66 ± 0.32	6.53	6.50 ± 0.16
K2	4.35 ± 0.65	4.89	4.63 ± 0.13
U1	3.39 ± 0.27	3.35	3.40 ± 0.13
U2	3.35 ± 0.51	3.41	3.42 ± 0.13
Th1	3.46 ± 0.52	3.62	3.51 ± 0.22
UTh1	3.56 ± 0.26	3.49	3.55 ± 0.11
UTh2	3.57 ± 0.19	3.47	3.43 ± 0.19

The comparison of Tables 2 and 4 showed that K and Th determinations, calculated by Ferreira et al. (2003), agreed with Barretto et al. (1986)'s data, modified by Ribeiro et al., (2005). In relation to the U contents of pad U1 (Table 3), differences were found out of the interval defined by the standard deviation around the average concentrations values, also signaled by Ribeiro et al., (2005). Insignificant contrasts were found in pads U2 and UTh2 (Table 3). On the other hand, the comparison between results for potassium by Ferreira et al. (2003) and Ribeiro et al., (2005) was satisfactory, excepting a small modification in pad K2 (Table 2). For uranium, a difference around 1 ppm in pad U1 was detected, whereas variations in

pads U2 and UTh2 were insignificant (Table 3). Regarding thorium, the following values were obtained by Ferreira et al., (2003) *versus* the minimum indices calculated by Ribeiro et al., (2005) for pads K1, K2, Th1, UTh1 and UTh2, respectively: 15.93 x 16.5; 28.81 x 29.2; 248.63 x 261; 68.81 x 71; 162.11 x 167.6 (Table 4).

The gamma-spectrometric data were obtained from cultivated soils, as well as soils under native forest (not contaminated by the human activity) and samples of fertilizers and gypsum. In the soils, 90% of the gamma rays come from superficial layers up to a maximum depth of 45 cm (Wilford et al., 1997).

Table 3 – Comparison between U concentrations (ppm) from IRD/CNEN *pads* determined by chemical analyses and neutron activation by Barretto et al., (1986), modified by Ribeiro et al., (2005)¹ and calculated by Ferreira et al., (2003)² and Ribeiro et al., (2005)³.

<i>Pads</i>	U Concentration (ppm) ¹	eU Concentration (ppm) ²	eU Concentration (ppm) ³
K1	1.18 ± 0.56	1.70	1.69 ± 0.45
K2	2.15 ± 0.54	1.89	2.11 ± 0.55
U1	69.10 ± 6.20	55.89	57.90 ± 3.20
U2	18.63 ± 1.10	20.04	21.10 ± 1.30
Th1	10.81 ± 0.91	10.82	11.4 ± 1.60
UTh1	11.28 ± 2.10	10.91	10.67 ± 0.94
UTh2	43.65 ± 6.00	37.44	39.90 ± 2.10

Table 4 – Comparison between Th concentrations (ppm) from IRD/CNEN *pads* determined by chemical analyses e neutron activation by Barretto et al. (1986), modified by Ribeiro et al., (2005)¹, and calculated by Ferreira et al., (2003)² and Ribeiro et al., (2005)³.

<i>Pads</i>	Th Concentration (ppm) ¹	eTh Concentration (ppm) ²	eTh Concentration (ppm) ³
K1	19.15 ± 4.00	15.93	17.60 ± 1.10
K2	27.97 ± 6.50	28.81	30.80 ± 1.60
U1	48.30 ± 6.60	45.62	45.10 ± 2.10
U2	51.31 ± 9.80	44.14	46.00 ± 2.10
Th1	254.22 ± 36.00	248.63	271.00 ± 10.00
UTh1	69.84 ± 12.00	68.81	74.10 ± 3.10
UTh2	150.62 ± 35.00	162.11	174.20 ± 6.60

RESULTS AND DISCUSSION

In the study area, three types of soil were identified and mapped (Fig. 1): Eutrophic Red Nitosol of clayey texture, derived from the basaltic rocks, which were spatially distributed closer to the drainage channels, where the relief was steeper; Eutroferic Red Latosol was a deeper,

older soil comparatively to the former, of clayey texture, also derived from basaltic rocks and corresponding to undulated smooth to almost plane relief, and Dystrophic Red Latosol, resultant from reworking of the Serra Geral and Goio-Erê formations, with clay contents between 16 and 35%, of medium texture and spatially distributed on an almost plane relief.

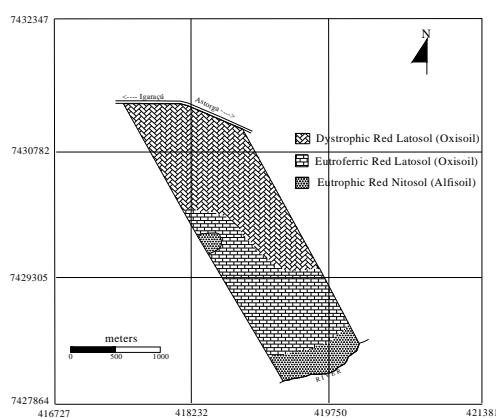


Figure 1 - Map of soils

The average radionuclide values for the 77 sampled points were 54.75 Bq/Kg for K, 10.22 Bq/Kg for eU, and 7.25 Bq/Kg for eTh (Table 5). Souza (1998) found values of 86.1 Bq/Kg U in clayey soils in Araras (State of São Paulo), whereas Kumru and Bakaç (2003) found average indices of 135 Bq/Kg U and 17.05 Bq/Kg Th. Kannan et al., (2002), studying radionuclides in India soils, found U values from 16 to 359.65 Bq/Kg.

Taking into consideration the soils analyzed and their textures, the clayey ones (Eutroferic Red Latosol-Oxisoil and Eutrophic Red Nitosol-Alfisoil) presented U average values of 14.9 Bg

Kg⁻¹, whereas the sandy-clayey soils (Dystrophic Red Latosol-Oxisoil) yielded an average concentration of 7.03 Bq/Kg (Tables 6 and 7). The U content was twice these values in the clayey soils, for which the variation coefficient was 19.92%, representing a less dispersion of the data, when compared with the 48.4% for the whole area (Table 5). The average K content for the sandy-clayey soil was 57.28 Bq/Kg, slightly higher than that for the clayey soils, where the average was 51 Bq/Kg. Thorium average concentration was 9.03 Bq/Kg in the sandy-clayey soil, therefore, higher than 4.61 Bq/Kg for the clayey soils.

Table 5 – Statistics of the gamma spectrometric data and the clay contents of the total area, without taking into account the types of soils.

	K	eU	eTh	Clay (%)	
				Depth (cm)	
				0-20	20-40
		Bq/Kg			
Minimum	0	2.46	0.41	14	14
Maximum	124	20.91	17.1	88	92
Average	54.75	10.22	7.25	39.3	44.7
Median	62	8.4	7.73	26	31
Standard Deviation	23	4.94	4.35	23.38	25.7
Variation Coefficient (%)	42	48.4	60	60	57.4
Skewness	0.4	0.26	0.15	0.60	0.53
Kurtosis	1.18	-1.20	-0.87	-1.26	-1.36

Table 6 - Descriptive statistics of the geophysical data and the clay contents for the sandy-clayey soil.

	Potassium	Uranium	Thorium	Clay
				(%)
		Bq/Kg		
Minimum	31	2.46	0.81	14
Maximum	124	14.76	17.09	47
Average	57.28	7.03	9.03	25.20
Standard Deviation	22.61	3.10	3.83	7.40
Variation Coefficient (%)	39.47	44.10	42.41	29.36
Skewness	1.77	0.29	-0.39	2.14
Kurtosis	0.96	0.91	-0.05	1.43

Table 7 - Descriptive statistics of the geophysical data and the clay contents for the clayey soils.

	Potassium	Uranium	Thorium	Clay
				(%)
		Bq/Kg		
Minimum	0.00	8.61	0.41	46.00
Maximum	93.00	20.91	13.43	92.00
Average	51.00	14.96	4.61	73.58
Standard Deviation	23.40	2.98	3.74	12.40
Variation Coefficient (%)	45.88	19.92	81.13	16.85
Skewness	0.03	-0.43	-0.37	-0.66
Kurtosis	-0.28	-0.35	0.80	-0.42

For the areas with no agricultural activity, where the soils underlied a native vegetation constituted by fragments of forests (national parks), 20 gamma spectrometric measurements were taken with three repetitions at each point. The average of three measurements and the statistic summary are presented in Table 8. Similarly, the clayey soils were discriminated from the sandy-clayey ones, for comparison with the arable area. Thus the average K, eU and eTh values for the clayey soils of the arable area (Table 8), which were respectively 51.0, 14.9 and 4.61 Bq/Kg, higher than the respective average concentrations for the soils of the virgin areas: 26.4, 1.41 and 1.81 Bq/Kg. Such strong differences could be explained by the fertilizers and statistically proven by the Student's t test. Similar behavior also occurred with the sandy-clayey soil, when the results for the cultivated area were compared with the correspondent ones for the virgin area, except for the fact that there was no significant difference between the eTh averages for both the areas, as

indicated by the same letters in the respective averages (Table 8).

In the virgin area where the sandy-clayey soil dominated, the average eU value was 1.97 Bq/Kg, which was higher than that for the clayey soils 1.41 Bq/Kg. On the other hand, K and eTh for the former area were respectively 41.9 and 8.91 Bq/Kg, higher than the averages for the clayey soils: 26.4 and 1.81 Bq/Kg. A possible explanation was the age and mineral composition of these soils. The clayey soils that developed on the Serra Geral Formation were older, weathered and consequently more leached, allowing K and eTh percolation along the soil profile. In soils of mixed texture that resulted from reworking of the Serra Geral and Goio-Erê formations, the latter of sandy texture, a contribution of minerals with higher K and Th contents might have occurred during the sedimentation, with higher K and Th contents corresponding to the Goio-Erê Formation source areas.

Table 8 – Statistics of the radionuclides measured in soils underlying native forest (n = 20).

	Texture					
	Sandy-clayey			Clayey		
	K	eU	eTh	K	eU	eTh
	Bq/Kg					
Minimum	0	0	7.32	0	0	0.4
Maximum	93	6.15	11.8	62	2.46	3.66
Average (*)	41.9a	1.97c	8.91e	26.4f	1.41h	1.81j
Average (**)	57.28b	7.03d	9.03e	51.0g	14.9i	4.61k
Median	31	1.85	8.5	31	1.23	1.63
Standard deviation	23.1	1.71	1.19	23.1	0.92	0.9
Variation coefficient (%)	55.2	86.9	13.4	87.7	64.8	49.8
Skewness	0.15	0.81	0.87	0.25	-0.25	0.39
Kurtosis	0.08	0.47	0.47	-1.04	-1.04	-0.59

Averages followed by the same letters do not differ considerably 5% by the t Test. (*) average of three measurements, (**) average of the sandy-clayey and clayey soils respectively.

The spatial distribution of the radionuclides is represented in Figures 2, 3 and 4. Figure 2 showed that the highest concentration of uranium occurred in the most clayey parts, corresponding to Eutrophic Red Nitisols (Alfisol) and Eutroferic Red Latosols (Oxisol) (Fig. 1).

Thorium distribution, on the contrary (Fig. 3), largely coincided with the exposition of Dystrophic Red Latosol (Fig. 1), probably because of the presence of residual minerals. The map of

potassium distribution (Fig. 8) showed that the most radioactive part was concentrated in the area where the soil had a more sandy texture, reflecting a possible presence of potassium-bearing minerals, as corroborated by Nascimento (2003).

Figures 5, 6 and 7 show the distribution of radionuclides along vertical sections of the three types of soils. The measurements were taken directly along the soil profiles every 20 cm.

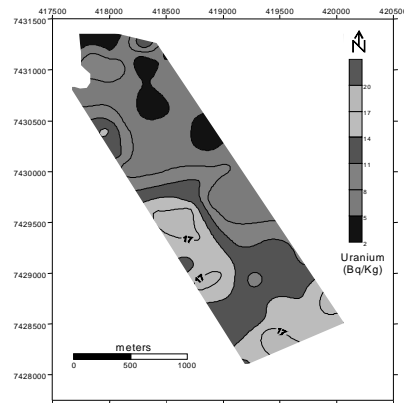


Figure 2 – Uranium spatial distribution (eU).

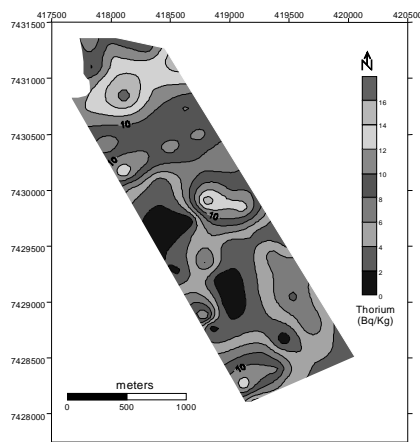


Figure 3 - Thorium spatial distribution (eTh).

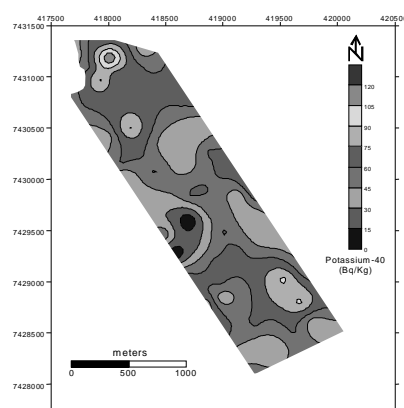


Figure 4 – Potassium spatial distribution.

The radionuclide concentrations along the Dystrophic Red Latosol of sandy-clayey texture (Fig. 5) were practically constant along the first 20

cm, with progressively increasing K contents down to 60 cm, which was approximately what was with uranium and thorium. Between 60 and 80

cm K contents decrease, whereas eU and eTh remained practically constant. From 80 cm to the end of the sampling, K indices tended to slightly increase to values similar to those of the first 20

cm of the profile. However, eU and eTh values tended to decrease with the depth, especially the latter, denoting more retention of these radioelements in relation to the surface.

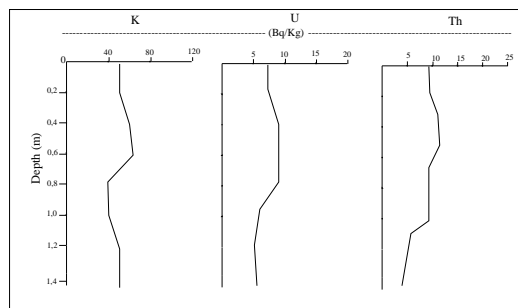


Figure 5 - Variations of radionuclide contents along the Dystrophic Red Latosol (Oxisoil) profile.

For the Eutrophic Red Nitosol soil profile (Fig. 6), eU and eTh contents increased down to the first 0.4 m, remained constant to 0.8 m, and progressively decreased to 1.6 m, when from this level on, the concentrations increased towards horizon C, reaching the material that originated these soils, denoting eU and eTh depletion from the source-rock to the surface. Similar behavior was observed in the potassium profile: from 1.6 m, K contents gradually increased towards horizon C.

The distribution of radioelements in the Eutroferic Red Latosol with depth (Fig. 7) was similar, with enrichment from a depth of 2.2 m to horizon C.

Dickson and Scott (1997) observed significant changes in radiogenic elements in the soils formed from mafic rocks in Australia. Clay soils originating from basalt showed losses up to 50% K and increase in U and Th close to the felsic rocks contents. According to these authors, in the areas dominated by strongly weathered, deeper soils, also derived from the basaltic rocks, depletion of K occurred and the U and Th were similar to those obtained for sandy soils derived from felsic rocks. Such distribution pattern differed from the behavior of the radionuclides in the soil sections studied here, possibly for their position in the subtropical humid region, with average rainfalls of 1,492 mm/year (Rufino et al., 1993), plus the physical/chemical weathering, mainly of the deeper and older Eutroferic Red Latosol, contrasting to drier climates, as in Australia, leading to the retention of radioelements in the soils profiles.

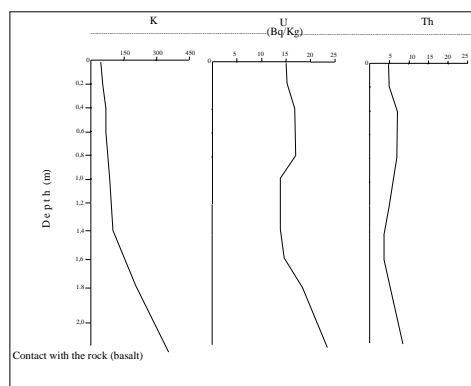


Figure 6 - Variations of radionuclide contents along the Eutrophic Red Nitosol (Alfisol) profile.

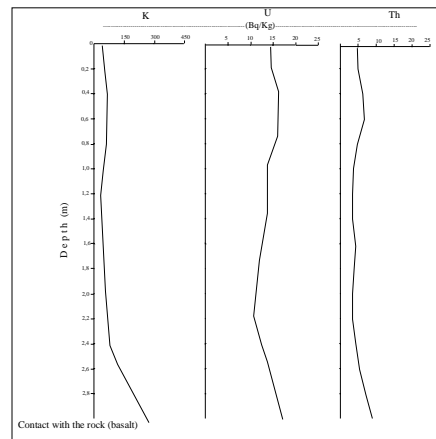


Figure 7 - Variations of radionuclide contents along the Eutroferric Red Latosol (Oxisoil) profile.

Australian climatic condition is similar to some parts of the Brazilian northeastern region, where certain soils accumulate high concentrations of salts in sub-surface by capillarity. Dowdall and O'Dea (2002), studying the radioactivity along the organic soil profiles in Ireland, observed that there was an increase in U along the profiles where the oxidation of organic matter was significantly reduced. Starting from a depth of approximately 0.15-0.20 m, where the lack of oxygen leads to a predominantly reducing environment, the decomposition of organic matter by

microorganisms is reduced and consequently the capacity of cation exchange is increased, which would increase U retention in such soils.

A statistical summary of the radionuclide contents taken from random sampling of phosphatic fertilizers (two formulas) and gypsum piles, totaling 20 determinations, is presented in Table 9. Results showed that the concentrations varied largely, mainly in fertilizers. Thus, K, eU and eTh variations were from 603.0 to 522.4; from 647.6 to 58.0, and from 753.9 to 10.82 Bq Kg⁻¹ respectively, with averages of 562.7, 352.8 and 382.3 Bq/Kg.

Table 9 - Statistics for radionuclide contents in samples (n = 20) of fertilizers and gypsum.

	Fertilizers/formulas (N-P-K)			K	0 - 16 - 25		K	Gypsum	
	5 - 25 - 25	eU	eTh		eU	eTh		eU	eTh
	Bq/Kg								
Minimum	341	385.0	567.36	403	51.66	5.3	0	552.27	155.8
Maximum	992	911.43	985.3	651	63.97	14.65	93	656.82	183.96
Average	603	647.60	753.90	522.4	58.0	10.82	51.1	607.31	170.33
Median	573.4	634.06	758.85	527.0	57.8	11.40	62	609.47	170.13
Standard Deviation	185.6	144.3	88.48	69.88	3.89	2.62	32.2	31.47	8.25
Variation Coefficient (%)	30.78	22.29	11.74	13.38	6.7	24.16	63.0	5.19	4.8
Skewness	0.65	-0.06	0.05	0.33	0.05	-0.45	-0.13	-0.25	0.20
Kurtosis	-0.12	-0.27	2.68	-0.44	-1.22	-0.6	-1.07	-0.71	-0.85

Paschoa et al., (1984) analyzed U concentrations in samples of various types of fertilizers and obtained an average of 1,044.26 Bq/Kg; Yamazaki

and Geraldo (2003), studying U contents in samples of NPK fertilizers from several Brazilian manufacturers, determined variations between

63.59 and 667.89 Bq/Kg and average of 333.25 Bq/Kg.

According to Pfister et al., (1976), the differences in radioactivity concentrations in various products are mainly due to the mode of fractioning during the chemical reaction in the acidulation phase of the phosphoric acid production. Products such as MAP (monoammonia phosphate) show that radium concentrations are ten times higher than those of uranium, due to the production process of such fertilizer, which uses ammonia, which in turn does not react with the phosphatic rock, which is the opposite of what happens with the U-rich phosphoric acid. Apatites in the phosphatic concentrates are destroyed by sulfuric acid during the production of superphosphates. However, uranium remains as uranyl and uranous sulfates, both soluble in water. Lacking organic matter and in sandy soils, U is usually mobile and is transported as a hexavalent carbonate complex or as a divalent uranyl ion (Rothbaum et al.1979).

The radionuclide average contents found in the gypsum samples were 51.1; 607.31 and 170.33 Bq/Kg respectively of K, eU and eTh (Table 5). Bolivar et al., (1995) indicated an average activity of 600 Bq/Kg U in the gypsum deposits, whereas Aguirre et al. (1995) cited 4.3 to 502 Bq/Kg U and 2.4 to 156 Bq/Kg Th intervals in river sediments close to the fertilizer factories. Mazzili et al., (2000) analyzed the gypsum samples from four manufacturers and were obtained average values of 17.75; 27.75 and 128 Bq/Kg respectively of K, U and Th.

CONCLUSIONS

The Eutrophic Red Nitosol and Eutroferic Red Latosol of clayey texture retained more radionuclides than the Dystrophic Red Latosol of mixed texture.

The radionuclide contents were lower in the area of native forest, when compared with the areas of agricultural activity, denoting the contribution of phosphatic fertilizers and gypsum in the cultivated soil.

The gamma-spectrometric measurements revealed differences in the radionuclide contents corresponding to the formula of the fertilizers.

At the present, there was no cause for environmental alarm concerning the U, Th and K contents detected in the soils studied in this work.

RESUMO

Medições gamaespectrométricas foram obtidas em solos agrícolas objetivando caracterizar a distribuição espacial das concentrações de radionuclídeos (K, eU e eTh), bem como em amostras de fertilizantes fosfatados e gesso agrícola. Na área ocorrem três tipos de solos: Nitossolo Vermelho Eutrófico, Latossolo Vermelho Eutroférrico textura argilosa e Latossolo Vermelho Distrófico textura média. Constatou-se que as concentrações de radionuclídeos nos solos mais argilosos foram maiores do que nos solos mais arenosos, em função, principalmente, da maior adsorção pelos primeiros. Os teores médios em Bq/Kg de K, eU e eTh na área com atividade antrópica foram respectivamente de 54,75; 10,22 e 7,27, significativamente maiores do que em áreas virgens sem aplicação de fertilizantes (34,15 de K; 1,69 de eU e 5,36 de eTh). Foram também observadas variações nas concentrações de radionuclídeos em diferentes formulações de adubos utilizados nas culturas de soja e trigo.

REFERENCES

- Aguirre, A. M.; León, M. G. and Ivanovich, M. (1995), U and Th speciation in river sediments. *The Science of the Total Environment*, 173/174, 203-209.
- Andrello, A. C.; Guimarães, M. F.; Appoloni, C. R. and Nascimento Filho, V. F. (2003), Use of Cesium-137 Methodology in the Evaluation of Superficial Erosive Processes. *Brazilian Archives of Biology and Technology*, **46**(3), 307-314.
- Barretto, P. M. C.; Austerlitz, C.; Malheiros, T. and Lovborg, L. (1986), *Radioactive concrete sources at IRD/CNEN, Brazil, for the calibration of uranium exploration and environmental field instruments*. Relatório IRD/DEX-3/CNEN, 66.
- Becegato, V. A; Ferreira, F. J. F; Cabral, J. B. P and Neto, S. L. R. (2008), Gamma-ray Spectrometry Sensor and Geochemical Prospecting in an Area of Sugar Cane Plantation. *Brazilian Archives of Biology and Technology*, **51**(1), 1-10.
- Bolivar, J. P.; Tenório, R. G. and León, G. (1995), Fluxes and distribution of natural radionuclides in the production and use of fertilizers. *Appl. Radiat. Isot.* Vol.46, n.6/7, pp.717-718.
- Dickson, B. L. and Scott. (1997), K. M. Interpretation of aerial gamma-ray surveys – adding the geochemical factors. *AGSO Journal of Australian Geology and Geophysics*, Austrália, v.17, n. 2, p.187-200.

- Dowdall, M. and O'Dea, J. (2002), $^{226}\text{Ra}/^{238}\text{U}$ disequilibrium in an upland organic soil exhibiting elevated natural radioactivity. *Journal of Environmental Radioactivity*, v. 59 p. 91-104.
- Fernandes, L. A. and Coimbra, A. M. (2000), Revisão estratigráfica da parte oriental da bacia Bauru (Neocretáceo). *Revista Brasileira de Geociências* 30 (4), 723-734.
- Ferreira, F. J. F., Flexor, J. M. and Guimarães, G. B. (2003), Síntese da calibração do gamaespectrômetro GS-512 do LPA/UFPT no IRD-CNEN 12p. (relatório inédito).
- Guimond, R. J. and Hardin, J. M. (1989), Radioactivity released from phosphate containing fertilizers and from gypsum. *J. Radiat. Appl. Instrum. Radiat. Phys. Chem.*, v.34, n.2, p. 369-315.
- IAPAR. (1978), Cartas climáticas básicas do Estado do Paraná. Londrina, 41 p.
- Khan, K.; Khan, H.M.; Tufail, M.; Khatibeh, A.J.A.H. and Ahmad, N. (1998), Radiometric Analysis of Hazara Phosphate Rock and Fertilizers in Pakistan. *J. of Environ. Radioactivity*, v. 38 n. 1, pp. 77-84.
- Kannan, V.; Rajan, M. P., Iengar, M. A. A. R. and Ramesh, R. (2002), Distribution of natural and anthropogenic radionuclides in soil and beach samples of Kalpakkam (Índia) using hyper pure germanium (HPGe) gamma ray spectrometry. *Appl. Radiat. Isot.* 57:109-119.
- Kumru, M. N. and Bakaç, M. (2003), R-mode factor analysis applied to the distribution of elements in soils from the Aydin basin, Turkey. *J. of Geoch. Exploration* 77, 81-91.
- Mazzilli, B.P.; Palmiro, V., Saueia, C.H. and Nisti, M.B. (2000), Radiochemical characterization of Brazilian phosphogypsum. *J. of Environ. Radioactivity*, 49:113-122.
- Nascimento, C. T. C. (2003), Resistividade elétrica e radiação gama natural no estudo de solos sob cerrado nativo. Tese de Doutorado, Universidade de Brasília, 111p.
- Nuernberg, N. J.; Rech, T. D. and Basso, C. (2002), *Usos do gesso agrícola*. Florianópolis: Epagri, 31p. Boletim Técnico, 122.
- Paschoa, A. S., Mafra, O. Y., Cardoso, D. O. and Rocha, A.C.S. (1984), Application of SSNTD to the Brazilian phosphate fertilizer industry to determine uranium concentrations. *Nuclear Tracks and Radiation Measurements*, v.8, n. 1-4, p.469-472.
- Pfister, H.; Philipp, G. and Paul, Y.H. (1976), Population dose from natural radionuclides in phosphate fertilizers. *Radiation and Environmental Biophysics*, v. 13, p. 247-261.
- Ribeiro, F. B., Carlos, D. U., Hiodo, F. Y and Strobino, E.F. (2005), A Least squares procedure for calculating the calibration constants of a portable gamma-ray spectrometer. *Radiation Protection Dosimetry*, v. 113, no. 3, 251-256.
- Rothbaum, H. P.; McGaveston, D. A.; Wall, T.; Johnston, A. E. and Mattingly, G. E. G. (1979), Uranium accumulation in soils from long-continued applications of superphosphate. *Journal of Soil Science*, v.30, n.1, 147-153.
- Rufino, R. L.; Biscaia, R. C. M.; and Merten, G. H. (1993), Determinação do potencial erosivo da chuva do estado do Paraná, através de pluviometria: Terceira aproximação. *Revista brasileira de Ciência do Solo*, Campinas, v.17, p.439-444.
- SanMiguel, Pérez-Moreno, J. P.; Bolívar, J. P and García-Tenório, R. (2003), Validation of isotope signatures in sediments affected by anthropogenic inputs from uranium series radionuclides. *Environmental Pollution*, 123:125-130.
- Santos Júnior, J. A.; Cardoso, J. J. R. F.; Silva, C. M.; Silveira, S. V. and Amaral, R. S. (2005), Analysis of the ^{40}K Levels in Soil using Gamma Spectrometry. *Brazilian Archives of Biology and Technology.*, 48, (Special), 221-228.
- Saueia, C. H.; Mazzilli, B. P. and Fávaro, D. I. T. (2004), Natural radioactivity in phosphate rock, phosphogypsum and phosphate fertilizers in Brazil. *Journal of Radioanalytical and Chemistry*, v. 264, no.2 445-448.
- Souza, J. L. (1998), Anomalias aerogamaespectrométricas (K, U e Th) da quadrícula de Araras (SP) e sua relações com processos pedogenéticos e fertilizantes fosfatados. Curitiba, Dissertação de Mestrado – Universidade Federal do Paraná.
- Yamazaki, I. M. and Geraldo, L. P. (2003), Uranium content in phosphate fertilizers commercially produced in Brazil. *Appl. Radiat. Isot.* 59:133-136.
- Zielinski, R. A.; Simmons, K. R. and Orem, W. H. (2000), Use of ^{234}U and ^{238}U isotopes to identify fertilizer-derived uranium in the Florida Everglades. *Appl. Geochemistry* 15:360-383.
- Wilford, J. R.; Bierwirth, P. N. and Craig M. A. (1997), Application of airborne gamma-ray spectrometry in soil/rigolity mapping applied geomorfology. *AGSO. J. Austral. Geol. Geophy.*, 17:201-216.

Received: November 21, 2006;

Revised: December 28, 2007;

Accepted: June 17, 2008.