

RADIOMETRIC CHARACTERIZATION OF PHOSPHORIC ACIDS AND THEIR INDUSTRIAL PRODUCTS

Fabiano Tomazini da CONCEIÇÃO¹ & Daniel Marcos BONOTTO²

(1) Departamento de Planejamento Territorial e Geoprocessamento, Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista / UNESP, Avenida 24-A, 1515 – Bela Vista. CEP 13506-900. Rio Claro, SP.

Endereço eletrônico: ftomazini@rc.unesp.br

(2) Departamento de Petrologia e Metalogenia, Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista / UNESP, Avenida 24-A, 1515 – Bela Vista. CEP 13506-900. Rio Claro, SP.

Endereço eletrônico: dbonotto@rc.unesp.br

Introduction
Sampling and Analytical Techniques
Results
Discussion
 Filtration Cake and Its Environmental Hazards
 Phosphoric Acids and Their Environmental Hazards
Conclusion
Bibliographic References

ABSTRACT – The addition of phosphoric acids and their (by)products became a common practice in areas like metal treatment, detergent production, water and effluent treatment, as well by food, beverage and pharmaceutical industries. The phosphoric acids exhibit different radionuclides activity concentration, being important to evaluate the implications for the human and animal health. The ²³⁸U concentration in almost all raw acid phosphoric are within the worldwide range and the mean exposure rate for the filtration cake is 10 nGy/h, which is mainly attributed to ⁴⁰K. The results obtained for total and (bio)available uranium concentration in filtration cake indicate that only 40% is (bio)available for plants. The radionuclides present in phosphoric acid food grade and filtration cake do not raise their concentration in human food chain or soils to harmful levels, consequently, not offering hazard to the ecosystem and animal or human health.

Keywords: Radionuclides, phosphoric acids and (by) products, environmental hazards.

RESUMO – *F.T. da Conceição & D.M. Bonotto - Caracterização radiométrica de ácidos fosfóricos e seus produtos industriais.* A adição de ácidos fosfóricos e seus produtos derivados tornou-se uma prática comum em várias áreas como tratamento de metais, produção de detergentes, tratamento de águas e efluentes, bem como em indústrias alimentícias, de bebidas e farmacêuticas. Os radionuclídeos nos ácidos fosfóricos estão presentes em diferentes concentrações atividade, de maneira que é importante avaliar as implicações para a saúde humana e animal. A atividade de ²³⁸U no ácido fosfórico bruto praticamente está inserida no intervalo de variação global e a taxa de exposição média associada ao material filtrado corresponde a 10 nGy/h, a qual é atribuída principalmente ao ⁴⁰K. Os resultados obtidos para a concentração total e biodisponível de urânio no material filtrado indicam que apenas 40% encontra-se disponível para as plantas. Os radionuclídeos presentes no ácido fosfórico de grau alimentar e material filtrado não contribuem para a elevação da radioatividade na cadeia alimentar humana ou solos até níveis perigosos, portanto, não oferecem riscos ao ecossistema e saúde humana e animal.

Palavras-chave: Radionuclídeos, ácidos fosfóricos e produtos derivados, danos ambientais.

INTRODUCTION

In Brazil, the Alto Paranaíba igneous province is composed by alkaline-carbonatite complexes (Figure 1) that have resulted of Late Cretaceous ultrapotassic magmatism (Ulbrich & Gomes, 1981). The climatic actions led to the development of thick weathering profiles, which exhibit a well-developed vertical mineral zonation with residual concentration of unweathered ore minerals due to dissolution of carbonates (Oliveira & Imbernon, 1998). Phosphate fertilizers are manufactured from these complexes and, according to their origin, may contain uranium, thorium and their daughter, being this presence firstly reported in 1908

(Ring, 1977), whose behavior has been described worldwide (Menzel, 1968; Pfister et al., 1976; Ring, 1977; Guimond, 1990; Rothbaum et al., 1979; Mortvedt, 1986; Todorovsky & Kulev, 1993; Sam & Holm, 1995; Hull & Burnett, 1996; Alam et al., 1997; Ioannides et al., 1997; Ibrahim, 1998; Khan et al., 1998; Sam et al., 1999; Khater et al., 2001; Conceição & Bonotto, 2006).

The first step to obtain the phosphate fertilizers is the flotation-separation process, where the apatites are concentrated (Figure 2A). The apatite is destroyed by action of H₂SO₄ during the production of SPP (simple superphosphate) and H₃PO₄, originating H₂SiF₆ and

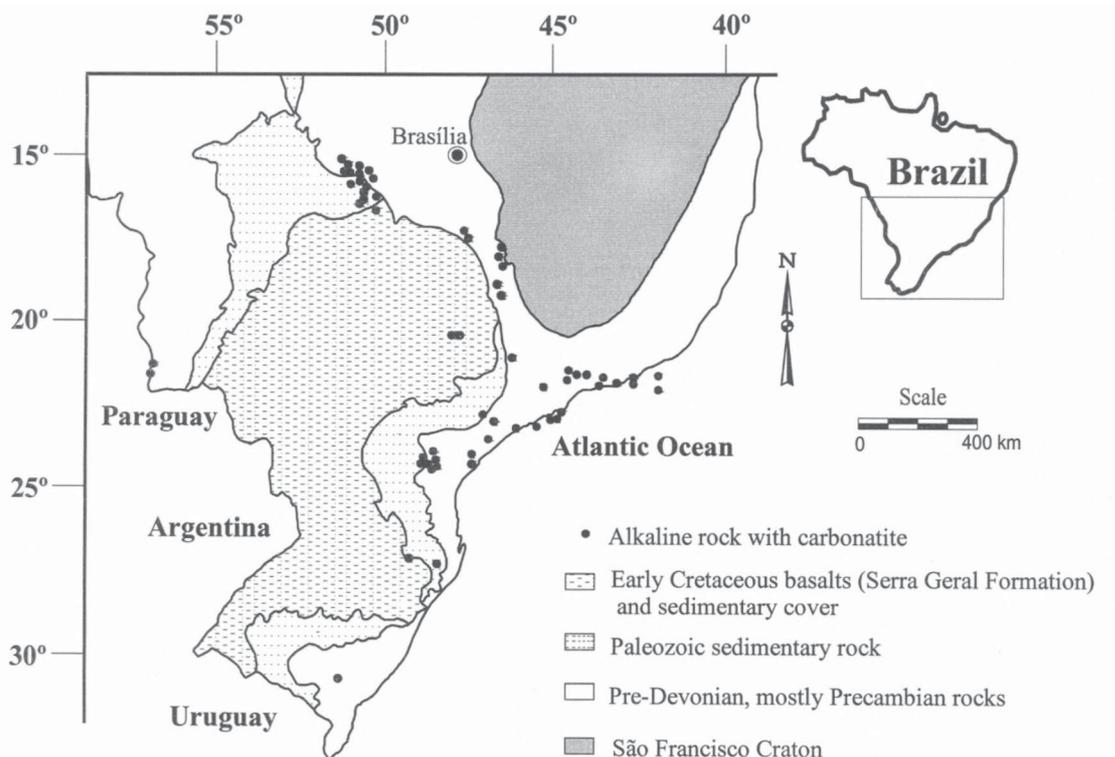


FIGURE 1. Distribution of alkaline complexes in Brazil (modified from Ulbrich & Gomes, 1981).

phosphogypsum as by-products. The TSP (triple superphosphate) is obtained with the concentrated phosphate being attacked by H_3PO_4 and the MAP (monoammonium phosphate) and DAP (diammonium phosphate) by H_3PO_4 mixed with ammonium. Various authors have also studied the behavior of radionuclides in phosphogypsum (Bolívar et al., 1995; Rutherford et al., 1995; Haridasan et al., 2002) and phosphoric acid (Singh et al., 2001) that are by-products of the fertilizers industry. In Brazil, most of the studies have emphasized the presence of radionuclides in phosphate rocks and phosphogypsum (Paschoa et al., 1984; Pessenda et al., 1988; Godoy, 1989; Mazzilli & Saueia, 1997; Mazzili et al., 2000; Santos et al., 2002).

The use of phosphoric acid without purification may elevate the radionuclides transfer to the human

food chain, being important to know the proportion of such a transfer due to the implications for the human and animal health. In Brazil, there is a producer of purified phosphoric acid that has been used in areas like metal treatment, detergent production, water and effluent treatment as well by food, beverage and pharmaceutical industries. The purification processes (liquid-liquid extraction) allow that the raw acid will be manufactured to phosphoric acid in food grade, being the filtration cake and the reject their by-products (Figure 2B). Thus, the objective of this paper was to perform the radiometric characterization of phosphoric acids and their industrial (by) products used in Brazil. Moreover, a contamination index has been applied to provide a basis for comparison of potential radionuclides hazards.

SAMPLING AND ANALYTICAL TECHNIQUES

The phosphoric acid samples were collected in all purification steps, i. e. raw acid (named A, B, C and D, where A and B are Brazilian producers), reject and the phosphoric acid food grade. The radiometric characterization of the filtration cake (Figure 2b) was performed for 27 samples (3 kg each) collected in different positions and depths from 10 drillings conducted in waste piles.

The gamma spectrometry was utilized to measure the ^{226}Ra , ^{232}Th and ^{40}K activity concentration in all samples. Duarte & Bonotto (2000) described the method applied to all solid samples (about 80g) that were dried, crushed, and packed in aluminum boxes as well to the samples of phosphoric acid (about 100 mL) that were inserted in glass flasks. The readings were performed in about 4 weeks for ^{226}Ra and ^{232}Th and

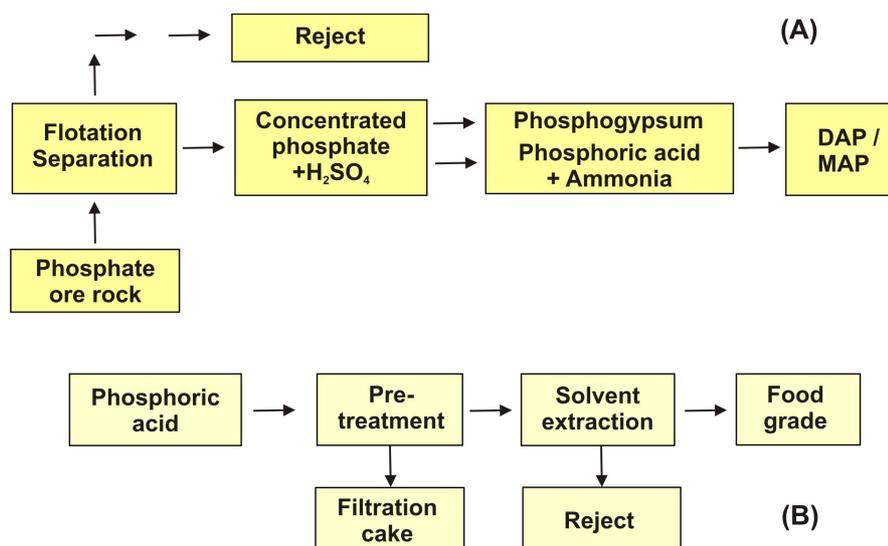


FIGURE 2. Simplified route of industrial (by) products derived from (A) phosphate rocks and (B) phosphoric acid.

their short-lived daughters to reach the condition of secular radioactive equilibrium. After this quantification, the gamma exposure rate was obtained using dose rate conversion factors (DRCF = 0.0414, 0.623 and 0.461 nGy/h per Bq/kg to ^{40}K , ^{232}Th and ^{226}Ra , respectively) adopted by UNSCEAR (1993).

The total and (bio)available uranium activity concentration and the $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR) of five samples of the filtration cake (Figure 2b) and all samples of phosphoric acid (and their industrial by-products) were determined by the use of standard alpha spectrometric techniques (Osmond & Cowart, 1976; Ivanovich & Harmon, 1992; Bonotto, 1986), where ^{232}U was the spike utilized. About 0.5 g of each solid sample was crushed to 200 mesh, placed in an acid digestion bomb, and brought into complete solution with HNO_3 and HCl (Bonotto, 1996). The (bio) available uranium was evaluated on transferring 2.5 g to a 100 mL beaker and adding 0.1 M HCl (50 mL); after

shaking during 2 hours, the mixture was filtered and the liquid phase recovered for isotopic extraction (Santos et al., 2002). About 100 mL of phosphoric acid (and their industrial by-products) were dissolved in 10 L of distilled water and the uranium was co-precipitated with $\text{Fe}(\text{OH})_3$. The solutions resulting from solid and liquid samples were heated to dryness, the residue was dissolved in 8 M HCl , and the iron extracted with isopropyl ether. Uranium was separated from Th and other elements by anion exchange resin. The aliquot containing U was transferred to an electrodeposition cell, and U was deposited on a stainless steel planchet after 3 hours at a current density of 1 Acm^{-2} (Bonotto, 1996). The alpha counting was performed with a $\text{Si}(\text{Au})$ surface barrier detector. The uranium concentration was calculated by isotope dilution from the counting rates of ^{238}U and ^{232}U peaks, and the $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR) was calculated from the counting rates of ^{238}U and ^{234}U peaks.

RESULTS

The ^{238}U concentration in almost all raw acid phosphoric are within the range of 0.005-0.05g of $\text{U}_3\text{O}_8/\text{L}$ as reported by Singh et al. (2001). The lower values for ^{238}U were obtained to raw acid (producer A) and acid food grade (Table 1). All acids possess low ^{226}Ra , ^{232}Th and ^{40}K activity concentration, reflecting ^{238}U enrichment in relation to ^{226}Ra and ^{232}Th , as also indicated the $^{226}\text{Ra}/^{238}\text{U}$ and $^{232}\text{Th}/^{238}\text{U}$ activity ratios

(Table 1). These results are equivalent to those obtained by Conceição & Bonotto (2006) that ^{226}Ra and ^{232}Th are incorporated preferentially to ^{238}U in several phases during the phosphate ore rock processing, such as SSP, MAP, DAP and phosphogypsum (Fig. 2a). The $^{234}\text{U}/^{238}\text{U}$ activity ratio shows the secular equilibrium condition for all samples (Table 1). The phosphoric acid used in the industrial process during the sampling was

TABLE 1. Radionuclides activity concentration and isotopic composition of phosphoric acid samples.

Sample	²³⁸ U (µg/L)	²³⁸ U (Bq/L)	²²⁶ Ra (Bq/L)	²³² Th (Bq/L)	⁴⁰ K (Bq/L)	²³⁴ U/ ²³⁸ U	²²⁶ Ra/ ²³⁸ U	²³² Th/ ²³⁸ U
Raw acid – producer A	733	9	2	2	55	0.98	0.22	0.22
Raw acid – producer B	21,585	264	3	3	26	1.00	0.01	0.01
Raw acid – producer C	71,018	869	3	1	5	0.99	<0.01	<0.01
Raw acid – producer D	75,819	928	6	4	40	0.98	<0.01	<0.01
Reject	94,643	1,158	<1	4	<1	1.00	-	<0.01
Acid food grade	187	2	<1	<1	<1	1.01	-	-

Analytical uncertainty ±10% (1σ standard deviation)

the raw acid derived from producer B; data in Table 1 indicate that the acid food grade possesses purification level of about 99.1%, remaining the most of uranium in the reject of the phosphoric acid purification.

The mean exposure rate for the filtration cake is 10 nGy/h (Table 2), that is mainly attributed to ⁴⁰K. The frequency distribution (Figure 3) indicates that 37.1% of the observed values are between 5 and 10 nGy/h. The results obtained for total and (bio) available uranium concentration and ²³⁴U/²³⁸U, ²²⁶Ra/²³⁸U and ²³²Th/²³⁸U isotopic composition of the filtration cake deposit samples are given in Table 3 and Figure 4. These samples were chosen due to their different P₂O₅ concentration values. The mean uranium concentration

is 32.06 µg/g, the mean ²³⁴U/²³⁸U activity ratio is practically 1 (1.06), indicating secular equilibrium. About 40% of total uranium is (bio) available. Utilizing the value of 30,464 ton of material contained in the filtration cake pile (Geofocus, 2006), it is possible estimate an uranium content of 977 kg in this deposit, so that only 391 kg can be available for plants.

Another aspect observed is the poor relationship (r = 0.14) between the exposure rate and P₂O₅ concentration and the elevated positive relationship (r = 0.95) between uranium and phosphorous in the filtration cake (Figure 5). This relationship indicates that uranium is probably linked to phosphorous, as reported by Langmuir (1978).

DISCUSSION

FILTRATION CAKE AND ITS ENVIRONMENTAL HAZARDS

The Brazilian soils are normally acid, with low content of organic matter and deficient in micronutrients that may cause decreasing of the agricultural productivity in Brazilian crops. The possible use of filtration cake can be as phosphate fertilizers in the agriculture, for improving the quality of the products (Malavolta, 1994). Thus, it is convenient a comparison of the values obtained in this work with those of phosphate rocks utilized as phosphate fertilizers worldwide (Table 4).

The ²³⁸U activity concentration in filtration cake is within the range of 37 – 4900 Bq/kg reported to phosphate rocks (Menzel, 1968). A comparison of the analyzed phosphate rocks with different phosphate deposits (Table 4) shows ²³⁸U activity concentration exceeding that reported in Kola (Russia) and Cajati (Brazil). The ²²⁶Ra activity concentration in filtration

cake is lower than the range of 100-10,000 Bq/kg reported by Roessler (1990) to other phosphate deposits worldwide (Table 4). The ⁴⁰K activity concentration in filtration cake is higher than that in Kola, Morocco, Sudan, Egypt, among others (Table 4). The ²³²Th activity concentration is lower than the mean value reported for phosphate rocks (74Bq/kg, according to Menzel, 1968).

The exposure rate considers the radiation effects in the air above 1m of any area (UNSCEAR, 1993) and, if the obtained mean radionuclide activity concentration in filtration cake is considered, then, an exposure rate corresponding to 10 nGy/h can be estimated (Table 2), value that just represents 18% of the world average outdoor exposure due to terrestrial gamma radiation (55 nGyh⁻¹, according to UNSCEAR, 1993). This may be explained because of its origin, i.e. it is a reject of phosphoric acid food grade production,

TABLE 2. Drilling, sampling depth, P₂O₅ concentration, ²²⁶Ra, ²³²Th and ⁴⁰K activity concentration and exposure rate (ER) for all samples of the filtration cake.

Drilling	Depth ¹ (m)	P ₂ O ₅ ¹ (%)	²²⁶ Ra ² (Bq/kg)	²³² Th ² (Bq/kg)	⁴⁰ K ² (Bq/kg)	ER (nGy/h)
1	0 – 2.5	19.5	40	<1	105	23
2	0 – 4	18.7	40	<1	45	20
3	0 – 3	18.2	1	<1	67	4
3	3 – 6	17.2	10	<1	169	12
3	6 – 8.2	21.1	1	<1	22	2
4	0 – 3	14.0	9	<1	260	15
4	3 – 6	20.6	1	<1	60	4
4	6 – 9	18.3	11	<1	62	8
4	9 – 10	12.6	2	<1	50	4
5	0 – 3	17.3	26	<1	189	20
5	3 – 6	20.6	4	<1	163	9
5	6 – 9	21.3	1	<1	146	7
5	9 – 12	17.4	1	<1	118	6
5	12 – 13.7	11.8	7	<1	113	8
6	0 – 3	20.9	4	<1	119	7
6	3 – 6	22.5	6	<1	92	7
6	6 – 9	16.9	1	<1	25	2
6	9 – 11.3	19.0	6	<1	52	5
7	0 – 3	20.1	29	<1	76	17
7	3 – 6	22.0	1	<1	20	2
8	0 – 3	13.5	1	<1	182	9
8	3 – 6	16.4	1	<1	99	5
8	6 – 8	22.7	21	<1	31	11
9	0 – 3	17.1	31	<1	34	16
9	3 – 6.3	24.7	35	<1	160	21
10	0 – 3	19.0	1	<1	49	3
10	3 – 4	21.6	35	<1	84	20
Mean		18.7	12	<1	96	10

¹Geofocus (2006); ²Analytical uncertainty ±10% (1σ standard deviation)

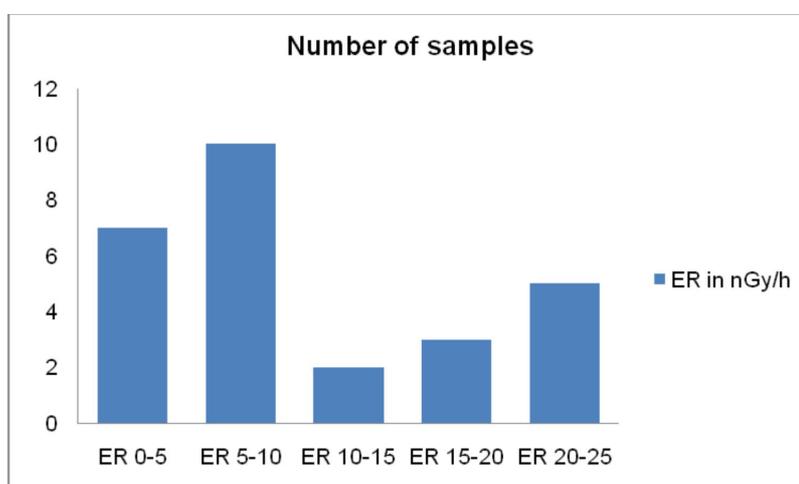


FIGURE 3. Frequency of the exposure rate in the filtration cake samples.

TABLE 3. Total and (bio)available uranium concentration and $^{234}\text{U}/^{238}\text{U}$ activity ratio in filtration cake samples.

Sample	Depth (m)	P ₂ O ₅ (%)	²³⁸ U – Total (µg/g)	²³⁸ U – (bio)available (µg/g)	²³⁴ U/ ²³⁸ U
4	0 – 3	14.0	15.47	5.64 (38%)	1.06
5	9 – 12	17.4	15.17	6.26 (41%)	1.08
6	6 – 9	16.9	22.51	9.86 (44%)	1.07
8	6 – 8	22.7	53.84	20.89 (39%)	1.06
9	3 – 6.3	24.7	53.33	21.45 (40%)	1.06
Mean			32.06	12.82 (40%)	1.06

Analytical uncertainty ±10% (1σ standard deviation)

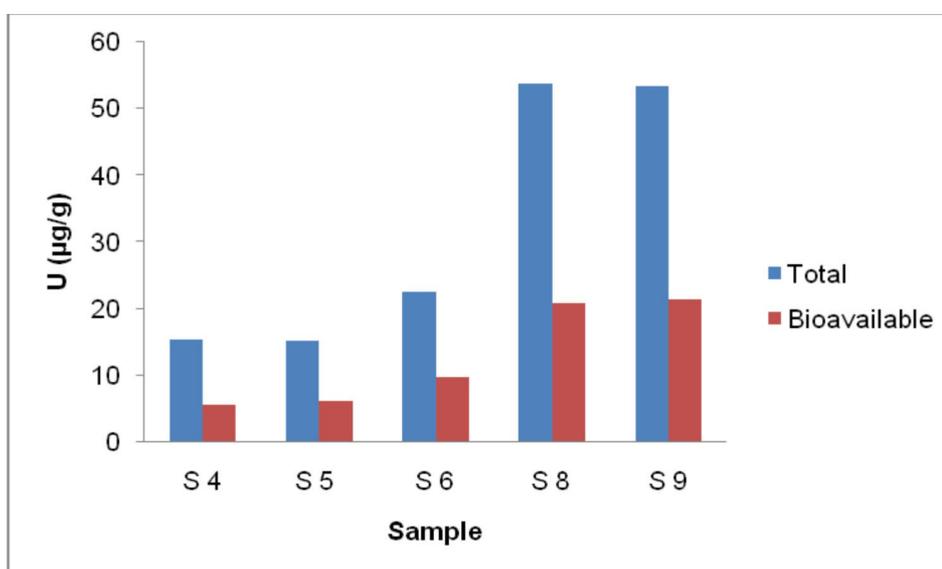


FIGURE 4. Total and (bio)available uranium concentration in some filtration cake samples.

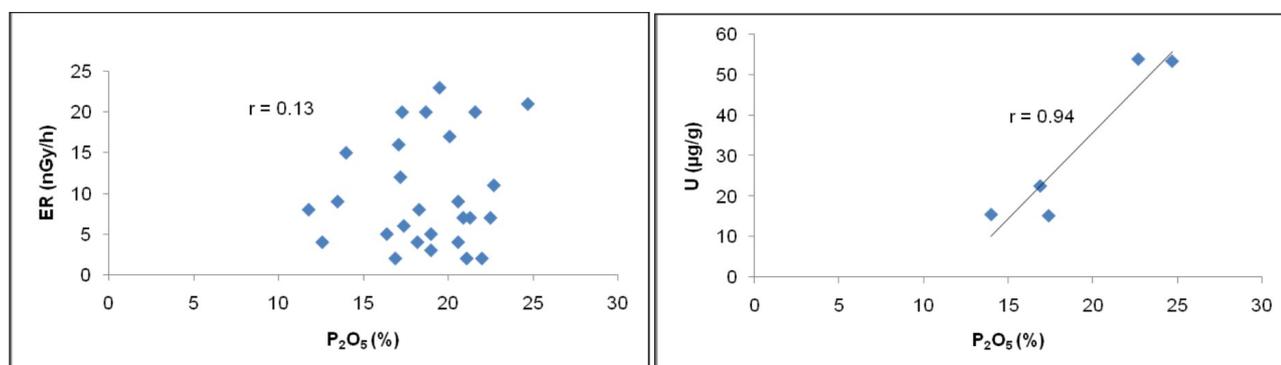


FIGURE 5. Relationships between exposure rate and P₂O₅ concentration and ^{238}U and P₂O₅ concentration in the filtration cake samples.

TABLE 4. Activity concentration of radionuclides (Bq/kg) and exposure rate – ER (nGy/h) in phosphate rocks from different countries.

Country	²³⁸ U	²²⁶ Ra	²³² Th	⁴⁰ K	ER	Reference
Filtration cake	396	12	<1	96	10	This work
Brazil (Catalão)	868	316	1151	287	874	Conceição & Bonotto (2006)
Brazil (Tapira)	1313	256	3238	1201	2184	Conceição & Bonotto (2006)
Brazil (Araxá)	1849	-	-	-	-	Cullen & Pachoa (1978)
Brazil (Cajati)	370	-	-	-	-	Lapido-Loureiro (1986)
Russia (Kola)	40	30	80	40	65	Guimond (1990)
Morocco	1700	1600	20	10	750	Guimond (1990)
Sudan (Uro)	2598	2263	2.5	51.7	1047	Sam & Holm (1995)
Sudan (Kurun)	684	555	0.83	23	257	Sam & Holm (1995)
Egypt (Abu-Tartor)	408	287	23.7	21.4	148	Khater et al. (2001)
USA (North Florida)	474	648	-	-	298	Roessler (1990)
Tanzania (Arusha)	4641	5022	717	286	2772	Makweba & Holm (1993)
Israel	1726	1852	11	4	860	Olszewska-Wasiolę (1995)
Tunisia	580	821	29	32	397	Olszewska-Wasiolę (1995)
Algeria	1627	619	64	22	326	Olszewska-Wasiolę (1995)
Jordan	1837	1044	2	8	482	Olszewska-Wasiolę (1995)

which utilized phosphoric acid (reject of phosphate fertilizers production). As a consequence, the radionuclides are incorporated in various phases during two industrial processes (Figure 2) and, consequently, the activity concentration in filtration cake is lower than the other phosphate deposits worldwide.

The phosphate fertilizers have been utilized in many parts of world, being generally applied at rates of 600kg/ha (1 ha = 10,000m²) per year in Brazil (Malavolta, 1994). Assuming this application rate to filtration cake, the maximum average annual addition of radionuclides distributed per unit arable land corresponds to 23.8, 0.72, <0.06 and 5.76 Bq/m² of ²³⁸U, ²²⁶Ra, ²³²Th and ⁴⁰K, respectively. These values are lower than those reported in many parts of the world where untreated ground phosphate rocks have been used as plant fertilizers (Makweba & Holm, 1993; Sam et al., 1999; Khater et al., 2001; Conceição & Bonotto, 2006). Considering these annual additions of ²³⁸U, ²²⁶Ra, ²³²Th and ⁴⁰K, and since these radionuclides should be homogeneously distributed in

the upper 10cm of soils with assumed apparent density of 1.5 g/cm³, a maximum increase in about 0.16, 0.01, <0.01 and 0.04 Bq/kg of soil is found for ²³⁸U, ²²⁶Ra, ²³²Th and ⁴⁰K, respectively. The ²³⁸U added does not reach 0.64% of the normal ²³⁸U content in an undisturbed soil (world average of 25 Bq/kg, according to Ibrahim, 1998). In relation to exposure rate, the maximum additional external radiation exposure caused by filtration cake that will be used in brazilian crops is 0.01 nGy/h at 1 m above the ground level, value that just represents 0.02% of the world average outdoor exposure due to terrestrial gamma radiation (55 nGy/h, according to UNSCEAR, 1993).

PHOSPHORIC ACIDS AND THEIR ENVIRONMENTAL HAZARDS

The suggested daily U intake is 32mBq/day (Health Canada, 1999) due to food (25 mBq/day) and water (7 mBq/day), or 40mBq/day for a 60kg person (NCPR, 1987). The World Health Organization (WHO, 1998) recommends a maximum U intake of 6 mBq per kg of

TABLE 5. Radionuclides intake through phosphoric acid by the adult population and associated annual effective doses.

Radionuclide	Activity (Bq/L)	Consumption (L/year)	Intake (Bq/year)	Dose coefficient ¹ (μSv/Bq)	Dose (μSv/year)
Raw acid – Producer A					
²³⁸ U	9	1	9	0.045	0.41
²³⁴ U	9	1	9	0.049	0.44
²²⁶ Ra	3	1	3	0.280	0.84
²³² Th	2	1	2	0.230	0.46
Total					2.15
Raw acid – Producer B					
²³⁸ U	264	1	264	0.045	11.88
²³⁴ U	264	1	264	0.049	12.94
²²⁶ Ra	3	1	3	0.280	0.84
²³² Th	3	1	3	0.230	0.69
Total					26.35
Raw acid – Producer C					
²³⁸ U	869	1	869	0.045	39.11
²³⁴ U	860	1	860	0.049	42.14
²²⁶ Ra	3	1	3	0.280	0.84
²³² Th	1	1	1	0.230	0.23
Total					82.32
Raw acid – Producer D					
²³⁸ U	928	1	928	0.045	41.76
²³⁴ U	909	1	909	0.049	44.54
²²⁶ Ra	6	1	6	0.280	1.68
²³² Th	4	1	4	0.230	0.92
Total					88.90
Reject					
²³⁸ U	1158	1	1158	0.045	52.11
²³⁴ U	1158	1	1158	0.049	56.74
²²⁶ Ra	2	1	2	0.280	0.56
²³² Th	1	1	1	0.230	0.23
Total					109.64
Acid food grade					
²³⁸ U	2	1	2	0.045	0.09
²³⁴ U	2	1	2	0.049	0.10
²²⁶ Ra	<1	1	<1	0.280	0.28
²³² Th	<1	1	<1	0.230	0.23
Total					0.70

¹ICRP (1996)

body weight. This value was based in limits derived from renal toxicity for soluble uranium compounds and from radiation exposure for insoluble uranium compounds. On average, 90 µg of uranium exist in the human body, with 66% found in skeleton, 16% in the liver, 8% in the kidneys and 10% in other tissues. Uranium is considered a toxic element, like tungsten, mercury, lead and cadmium, affecting the kidneys (decreasing the glomerular filtration rate) and, consequently, causing nephritis and other biochemical effects and histopathological changes in the kidneys, liver, thyroid and aorta (Mirto et al., 1999; Zarkadas et al., 2001). Approximately 90% of the U solubilized in blood is excreted in urine, over a period of three days (Zarkadas et al., 2001).

If it is assumed an intake of 1 L of phosphoric acid per year by person, a ^{238}U activity concentration of 25, 723, 2,381, 2,542, 3,173 and 5 mBq/day can be found to raw phosphoric acid derived by producer A, B, C and D, reject and acid food grade, respectively (Table 5). Despite other problems to human health, these values indicate that the products with non-purified phosphoric acid can also cause problems due to uranium intake. However, the products with acid food grade do not present hazards to human health due to their low amount of uranium (just 16% of the value

recommended by Health Canada, 1999). Additionally, the ^{226}Ra , ^{232}Th and ^{40}K activity concentration in acid food grade was lower than the detection limit of the measuring techniques utilized in this work. The values obtained were lower than those found in vegetables, cereals, potatoes, eggs, milk, fruits, meats and poultries analyzed worldwide (England – Smith-Briggs & Bradley, 1984; USA – Fisenne et al., 1987; Japan – Shiraishi et al., 1992; Ukraine – Shiraishi et al., 1997; Taiwan – Kuo et al., 1997; Nigeria – Akinloye et al., 1999; Canada – van Netten et al., 2000; Poland – Pietrzak-Flis et al., 2001; India – Singh et al., 2001; Brazil – Santos et al., 2002).

The world mean annual effective dose due to intake of radionuclides through the food is 0.23 mSv (UNSCEAR, 1993). The human body is affected by different exposure rates (Heneine, 1984). Using the dose coefficients proposed by ICRP (1996), it is possible estimate the maximum annual dose due to a hypothetical ingestion of 1L of phosphoric acid. The values are 2.15, 26.35, 82.32, 88.90, 109.64 and 0.70 µSv/year (Table 5), which represent 0.93, 11.46, 35.79, 38.65, 47.67 and 0.30% of the annual effective dose estimated due to food ingestion (0.23 mSv, according to UNSCEAR, 1993), respectively, to raw phosphoric acid derived by producer A, B, C and D, reject and acid food grade.

CONCLUSION

The acid food grade possesses a purification level of about 99%, remaining the most of uranium in the reject of the phosphoric acid purification. The mean exposure rate for the filtration cake (reject) is 10 nGy/h, that is mainly attributed to ^{40}K . The mean uranium concentration in filtration cake is 32 µg/g, with only 40% being (bio)available by plants.

The addition of filtration cake to soils and crops has become a common practice in agriculture and

the results show that the additional external radiation exposure for the farmers due to phosphate fertilizers is insignificant if compared to the average annual effective dose from other natural sources. Besides, the hypothetical consumption of 1L of phosphoric acid and their industrial (by)products do not offer hazards to human health in relation to annual dose ingestion, in point of view of the radionuclides analyzed.

BIBLIOGRAPHICS REFERENCES

1. ALAM, M.N.; CHOWDHURY, M.; KAMAL, S.; GHOSE, S.; BANU, H.; CHAKRABORTY, D. Radioactivity in chemical fertilizers used in Bangladesh. **Applied Radiation and Isotopes**, v. 8, p. 1165-1168, 1997.
2. AKINLOYE, M.K.; OLOMO, J.B.; OLUBUNMI, P.A. Meat and poultry consumption contribution to the natural radionuclide intake of the inhabitants of the Obafemi Awolowo University, Ile-Ife, Nigeria. **Nuclear Instruments and Methods in Physics Research A**, v. 422, p. 95-800, 1999.
3. BOLÍVAR, J.P.; GARCÍA-TENÓRIO, R.; GARCÍA-LÉON, M. Enhancement of natural radioactivity in soils and sand-marshes surrounding a non-nuclear industrial complex. **The Science of the Total Environment**, v. 173/174, p. 125-136, 1995.
4. BONOTTO, D.M. **Aplicações hidrogeoquímicas dos isótopos naturais das séries do U (4n+2) e Th (4n) no Morro do Ferro, Poços de Caldas (MG)**. São Paulo, 1986. 378 p. Tese (Doutorado em Geofísica) – Instituto Astronômico e Geofísico, Universidade de São Paulo.
5. BONOTTO, D.M. **Comportamento hidrogeoquímico do ^{222}Rn e isótopos de urânio ^{238}U e ^{234}U sob condições controladas de laboratório e em sistemas naturais**. Rio Claro, 1996. 223 p. Tese (Livro-Docência em Geoquímica) – Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista.
6. CONCEIÇÃO, F.T. & BONOTTO, D.M. Radionuclides, heavy metals and fluorine incidence at Tapira phosphate rocks,

- Brazil, and their (by)products. **Environmental Pollution**, v. 139, p. 232-243, 2006.
7. CULLEN, T.L. & PASCHOA, A.S. Radioactivity in certain products in Brazil - Radioactivity in Consumer Products. Washington: **US Nuclear Regulatory Commission**, p. 376-379, 1978.
 8. DUARTE, C.R. & BONOTTO, D.M. Calibração em energia e concentração de espectrômetro gama para análise de U, Th e K. **Geociências**, v. 19, p. 313-319, 2000.
 9. FISENNE, I.M.; PERRY, P.M.; DECKER, K.W.; KELLER, H.W. The daily intake of $^{234,235,238}\text{U}$, $^{228,230,232}\text{Th}$ and $^{226,228}\text{Ra}$ by New York City residents. **Health Physics**, v. 53, n. 4, p. 35, 1978.
 10. GEOFOCUS. Modelo digital e avaliação química e volumétrica do depósito de "land fill". Cajati: **Relatório Final**, 2006.
 11. GODOY, J.M. Determination of ^{226}Ra and ^{228}Ra in gypsum. **Ciência e Cultura**, v. 41, n. 1, p. 86-87, 1989.
 12. GUIMOND, R.J. **Radium in fertilizers**. Vienna: International Atomic Energy Agency (IAEA), Technical Report No. 310, Environmental behavior of radium, p. 113-128, 1990.
 13. HARIDASAN, P.P.; MANIYAN, C.G.; PILLAI, P.M.B.; KHAN, A.H. Dissolution characteristics of ^{226}Ra from phosphogypsum. **Journal of Environmental Radioactivity**, v. 62, p. 287-294, 2002.
 14. HEALTH CANADA. Uranium in drinking water. Montreal: **Federal-Provincial Subcommittee on drinking water**, p. 1-26, 1999.
 15. HENEINE, I.F. **Biofísica básica**. São Paulo: Livraria Atheneu, 385 p., 1984.
 16. HULL, C.D. & BURNETT, W.C. Radiochemistry of Florida phosphogypsum. **Journal of Environmental Radioactivity**, v. 32, n. 3, p. 213-238, 1996.
 17. ICRP – INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION. **Age-dependent doses to members of the public from intake of radionuclides: Part 5. Compilation of ingestion and inhalation dose coefficients**. Oxford: Pergamon Press, ICRP Publication 72, 94 p., 1996.
 18. IBRAHIM, N., Determination of natural radioactivity in fertilizers by gamma ray spectroscopy. **Radiation Physics and Chemistry**, v. 51, n. 4-6, p. 62, 1998.
 19. IOANNIDES, K.G.; MERTZIMEKIS, T.J.; PAPA-CHRISTODOULOU, C.A.; TZIALLA, C.E. Measurements of natural radioactivity in phosphate fertilizers. **The Science of the Total Environment**, v. 196, p. 63-67, 1997.
 20. IVANOVICH, M. & HARMON, R.D. **Uranium series disequilibrium: Applications to earth, marine and environmental sciences**. Oxford: Clarendon Press, 910 p., 1992.
 21. KHAN, K.; KHAN, H.M.; TUFAIL, M.; KHATIBEH, A.J.A.H.; AHMAD, N. Radiometric analysis of Hazara Phosphate rock and fertilizers in Pakistan. **Journal of Environmental Radioactivity**, v. 38, n. 1, p. 7-84, 1998.
 22. KHATER, A.E.M.; HIGGY, R.H.; PIMPL, M. Radiological impacts of natural radioactivity in Abu-Tartor phosphate deposits, Egypt. **Journal of Environmental Radioactivity**, v. 55, p. 255-26, 2001.
 23. KUO, C.; LAI, Y.; HUANG, C.; LIN, M. Activity concentrations and population dose from Radium-226 in food and drinking water in Taiwan. **Applied Radiation and Isotopes**, v. 48, n. 9, p. 1245-1249, 1997.
 24. LANGMUIR, D. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. **Geochimica et Cosmochimica Acta**, v. 42, p. 547-569, 1978.
 25. LAPIDO-LOUREIRO, F.E. Alkaline rocks and carbonatites. In: CORDANI, U.G. (Ed.), **Correlation of uranium geology between South America and Africa**. Vienna: International Atomic Energy Agency (IAEA), Technical Reports Series, n. 270, p. 345-415, 1986.
 26. MAKWEBA, M.M. & HOLM, E. The natural radioactivity of the rock phosphate, phosphatic products and their environmental implications. **The Science of the Total Environment**, v. 133, p. 99-110, 1993.
 27. MALAVOLTA, E. **Fertilizantes e seu impacto ambiental**. São Paulo: Produquímica, 153 p., 1994.
 28. MAZZILLI, B.; PALMIRO, V.; SAUEIA, C.; NISTI, M.B. Radiochemical characterization of Brazilian phosphogypsum. **Journal of Environmental Radioactivity**, v. 49, p. 113-122, 2000.
 29. MAZZILLI, B. & SAUEIA, C. Implicações radiológicas da utilização de fosfogesso como material de construção. **Ambiente Construído**, v. 1, n. 2, p. 17-22, 1997.
 30. MENZEL, R.G. Uranium, radium, and thorium content in phosphate rocks and their possible radiation hazard. **Journal of Agricultural and Food Chemistry**, v. 16, p. 231-284, 1968.
 31. MIRTO, H.; BARROULLET, M.P.; HENGE-NAPOLI, M.H.; ANSOBORLO, E.; FOURNIER, M.; CAMBAR, J. Uranium-induced vasoreactivity in isolated glomeruli and cultured rat mesangial cells. **Toxicology in Vitro**, v. 13, p. 707-711, 1999.
 32. MORTVEDT, J.J. Effects of calcium silicate slag application on radium-226 concentrations in plants tissues. **Communications in Soil Science and Plant Analysis**, v. 17, p. 75-84, 1986.
 33. NCPR – NATIONAL COUNCIL ON RADIATION PROTECTION. **Ionizing radiation exposure of the population of the United States**. Washington: NCPR, Rep. DOE/NBB-037, 1975.
 34. OLIVEIRA, S.M.B. & IMBERNON, R.A.L. Weathering alteration and related REE concentration in the Catalão I carbonatite complex, central Brazil. **Journal of South American Earth Sciences**, v. 11, n. 4, p. 379-388, 1998.
 35. OLSZEWSKA-WASIOLE, M. Estimates of the occupational radiological hazard in phosphate fertilizers industry in Poland. **Journal of Radiation Protection Dosimetry**, v. 58, p. 269-276, 1995.
 36. OSMOND, J.K. & COWART, J.B. The theory and uses of natural uranium isotopic variations in hydrology. **Atomic Energy Review**, v. 14, p. 621-679, 1976.
 37. PASCHOA, A.S.; MAFRA, O.Y.; CARDOSO, D.O.; ROCHA, A.C.S. Applications 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, 1984.
 38. PESSENDA, L.C.R.; NASCIMENTO FILHO, V.F.; DE NADAI, E.A.; FERRAZ, E.S.B. Determinação de Ra-226 e Th-232 em amostras de fosfatos naturais, gessos industriais e solos superficiais por espectrometria gama. In: CONGRESSO GERAL DA ENERGIA NUCLEAR, 2, 1988, Rio de Janeiro. **Proceedings...** Rio de Janeiro: Associação Brasileira de Energia Nuclear, 1988, p. 403-407.
 39. PFISTER, R.J.; PHILLIP, G.; PAULY, H. Population dose from natural radionuclides in phosphate fertilizers. **Radiation and Environmental Biophysics**, v. 13, p. 247-261, 1976.
 40. PIETRZAK-FLIS, Z.; ROSIAK, L.; SUPLINSKA, M.M.; CHRZANOWSKI, E.; DEMBINSKA, S. Daily intakes of ^{238}U , ^{234}U , ^{232}Th , ^{230}Th , ^{228}Th and ^{226}Ra in the adult population of central Poland. **The Science of the Total Environment**, v. 273, p. 163-169, 2001.
 41. RING, R.J. Recovery of byproduct uranium from manufacture of phosphate fertilizers. **Atomic Energy**, p. 12-20, 1977.

42. ROESSLER, C.E. Control of radium in phosphate mining, beneficiation and chemical processing. Vienna: International Atomic Energy Agency (IAEA), **The environmental Behavior of Radium**, v. 2, p. 270-279, 1990.
43. ROTHBAUM, H.P.; McGAVESTON, D.A.; WALL, T.; JOHNSTON, A.E.; MATTINGLY, G.E.G. Uranium accumulation in soils from long-continued applications of superphosphate. **Journal of Soil Science**, v. 30, n. 1, p. 147-153, 1979.
44. RUTHERFORD, P.M.; DUDAS, M.J.; SAMEK, R.A. Environmental impacts of phosphogypsum. **The Science of the Total Environment**, v. 149, p. 1-38, 1995.
45. SAM, A.K.; AHAMED, M.M.O.; KHANGI, F.A.; NIGUMI, Y.O.; HOLM, E. Radiological and chemical assessment of Uro and Kurun rock phosphate. **Journal of Environmental Radioactivity**, v. 42, p. 66-75, 1999.
46. SAM, A.K. & HOLM, E. The natural radioactivity in phosphate deposits from Sudan. **The Science of Total Environment**, v. 162, p. 173-178, 1995.
47. SANTOS, E.E.; LAURIA, D.C.; AMARAL, E.C.S.; ROCHEDO, E.R. Daily ingestion of ²³²Th, ²³⁸U, ²²⁶Ra, ²²⁸Ra and ²¹⁰Pb in vegetables by inhabitants of Rio de Janeiro City. **Journal of Environmental Radioactivity**, v. 62, p. 5-86, 2002.
48. SHIRAIISHI, K.; IGARASI, Y.; TAKAKU, Y. Daily intakes of ²³²Th and ²³⁸U in Japanese males. **Health Physics**, v. 63, p. 187-191, 1992.
49. SHIRAIISHI, K.; TAGAMI, K.; BAN-NAI, T. Daily Intakes of ¹³⁴Cs, ¹³⁷Cs, ⁴⁰K, ²³²Th and ²³⁸U in Ukrainian adults males. **Health Physics**, v. 73, p. 814-819, 1997.
50. SINGH, S.; MALHOTRA, R.; KUMAR, J.; SINGH, B.; SINGH, L. Uranium analysis of geological samples, water and plants from Kulu Area, Himachal Pradesh, India. **Radiation Measurements**, v. 34, p. 427-431, 2001.
51. SMITH-BRIGGES, J.L. & BRADLEY, E.J. Measurement of natural radionuclides in UK diet. **The Science of the Total Environment**, v. 35, p. 431-440, 1984.
52. TODOROVSKY, D. & KULEV, I. On the uranium content in some technogenic products potential environmental pollutants. **Journal of Radioanalytical and Nuclear Chemistry**, v. 5, p. 405-413, 1993.
53. ULBRICH, H.H.G.J. & GOMES, C.B. Alkaline rocks from continental Brazil. **Earth Sciences Reviews**, v. 17, p. 135-154, 1981.
54. UNSCEAR – UNITED NATIONS SCIENTIFIC COMMITTEE ON THE EFFECTS OF ATOMIC RADIATION. **Sources and effects of ionizing radiation**. New York: United Nations, UNSCEAR, 922 p., 1993.
55. VAN NETTEN, C.; HOPTION CANN, S.A.; MORLEY, D.R.; VAN NETTEN, J.P. Elemental and radioactive analysis of commercially available seaweed. **The Science of the Total Environment**, v. 255, p. 169-175, 2000.
56. WHO – WORLD HEALTH ORGANIZATION. **Guidelines for drinking water quality**. Geneva: WHO. Health Criteria and Other Supporting Information, 2 ed., addendum to v. 2, WHO/EOS/98.1, 36 p., 1998.
57. ZARKADAS, C.H.; KARYDAS, A.G.; PARADELLIS, T. Determination of uranium in human urine by total reflection X-ray fluorescence. **Spectrochimica Acta Part B**, v. 56, p. 2505-2511, 2001.

*Manuscrito Recebido em: 10 de janeiro de 2011
Revisado e Aceito em: 27 de abril de 2011*