

# RADIOMETRIC CHARACTERIZATION OF PHOSPHORIC ACIDS AND THEIR INDUSTRIAL PRODUCTS

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**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 <sup>238</sup>U 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 <sup>40</sup>K. 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 <sup>238</sup>U 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 <sup>40</sup>K. 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 H<sub>2</sub>SO<sub>4</sub> during the production of SPP (simple superphosphate) and H<sub>3</sub>PO<sub>4</sub>, originating H<sub>2</sub>SiF<sub>6</sub> and

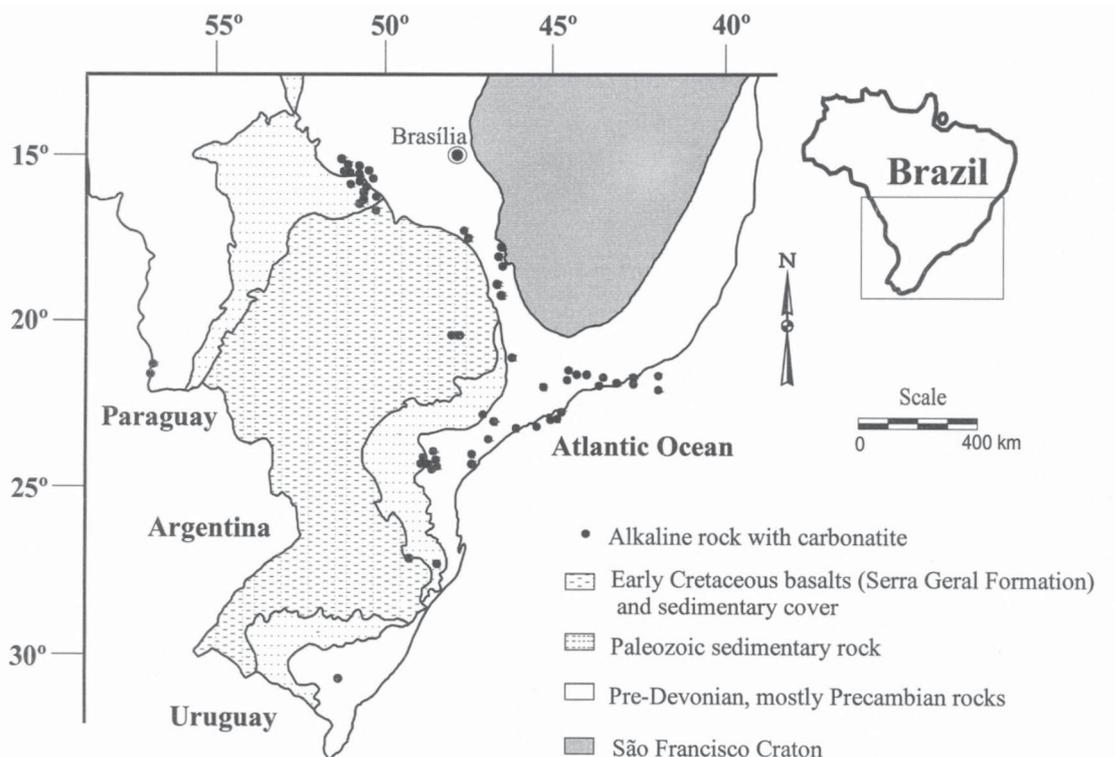


FIGURE 1. Distribution of alkaline complexes in Brazil (modified from Ulbrich & Gomes, 1981).

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).

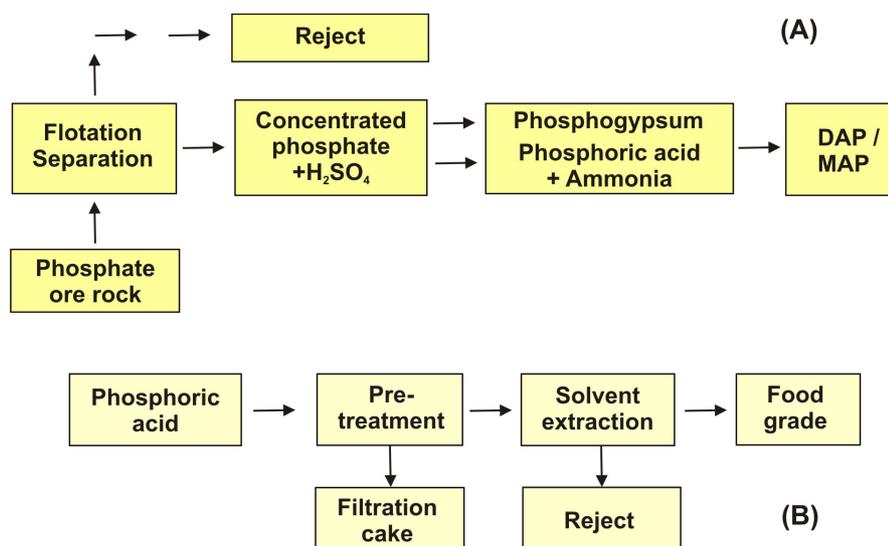
The use of phosphoric acid without purification may elevate the radionuclides transfer to the human

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  $^{40}\text{K}$ ,  $^{232}\text{Th}$  and  $^{226}\text{Ra}$ , 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  $^{232}\text{U}$  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  $\text{HNO}_3$  and  $\text{HCl}$  (Bonotto, 1996). The (bio) available uranium was evaluated on transferring 2.5 g to a 100 mL beaker and adding 0.1 M  $\text{HCl}$  (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  $\text{HCl}$ , 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  $1 \text{ Acm}^{-2}$  (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  $^{238}\text{U}$  and  $^{232}\text{U}$  peaks, and the  $^{234}\text{U}/^{238}\text{U}$  activity ratio (AR) was calculated from the counting rates of  $^{238}\text{U}$  and  $^{234}\text{U}$  peaks.

## RESULTS

The  $^{238}\text{U}$  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  $^{238}\text{U}$  were obtained to raw acid (producer A) and acid food grade (Table 1). All acids possess low  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  activity concentration, reflecting  $^{238}\text{U}$  enrichment in relation to  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ , 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  $^{226}\text{Ra}$  and  $^{232}\text{Th}$  are incorporated preferentially to  $^{238}\text{U}$  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	<sup>238</sup> U (µg/L)	<sup>238</sup> U (Bq/L)	<sup>226</sup> Ra (Bq/L)	<sup>232</sup> Th (Bq/L)	<sup>40</sup> K (Bq/L)	<sup>234</sup> U/ <sup>238</sup> U	<sup>226</sup> Ra/ <sup>238</sup> U	<sup>232</sup> Th/ <sup>238</sup> 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 <sup>40</sup>K. 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 <sup>234</sup>U/<sup>238</sup>U, <sup>226</sup>Ra/<sup>238</sup>U and <sup>232</sup>Th/<sup>238</sup>U isotopic composition of the filtration cake deposit samples are given in Table 3 and Figure 4. These samples were chosen due to their different P<sub>2</sub>O<sub>5</sub> concentration values. The mean uranium concentration

is 32.06 µg/g, the mean <sup>234</sup>U/<sup>238</sup>U 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 P<sub>2</sub>O<sub>5</sub> 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 <sup>238</sup>U 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 <sup>238</sup>U activity concentration exceeding that reported in Kola (Russia) and Cajati (Brazil). The <sup>226</sup>Ra activity concentration in filtration

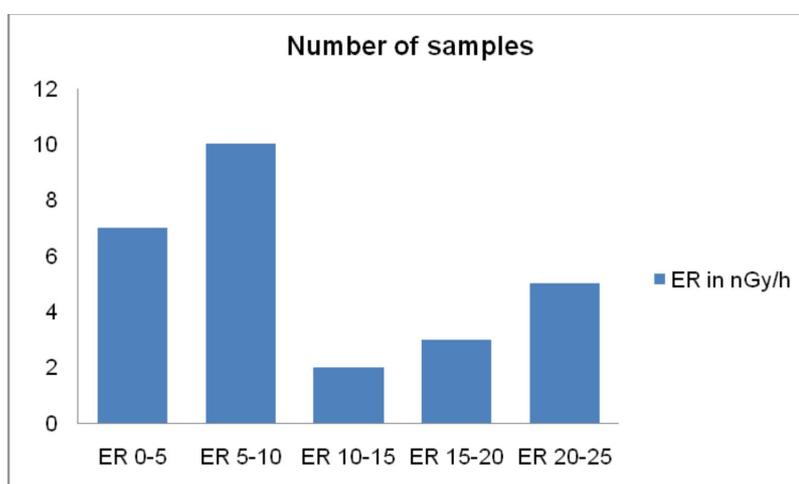
cake is lower than the range of 100-10,000 Bq/kg reported by Roessler (1990) to other phosphate deposits worldwide (Table 4). The <sup>40</sup>K activity concentration in filtration cake is higher than that in Kola, Morocco, Sudan, Egypt, among others (Table 4). The <sup>232</sup>Th activity concentration 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<sup>-1</sup>, 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, P<sub>2</sub>O<sub>5</sub> concentration, <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K activity concentration and exposure rate (ER) for all samples of the filtration cake.

Drilling	Depth <sup>1</sup> (m)	P <sub>2</sub> O <sub>5</sub> <sup>1</sup> (%)	<sup>226</sup> Ra <sup>2</sup> (Bq/kg)	<sup>232</sup> Th <sup>2</sup> (Bq/kg)	<sup>40</sup> K <sup>2</sup> (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
<b>Mean</b>		<b>18.7</b>	<b>12</b>	<b>&lt;1</b>	<b>96</b>	<b>10</b>

<sup>1</sup>Geofocus (2006); <sup>2</sup>Analytical uncertainty ±10% (1σ standard deviation)

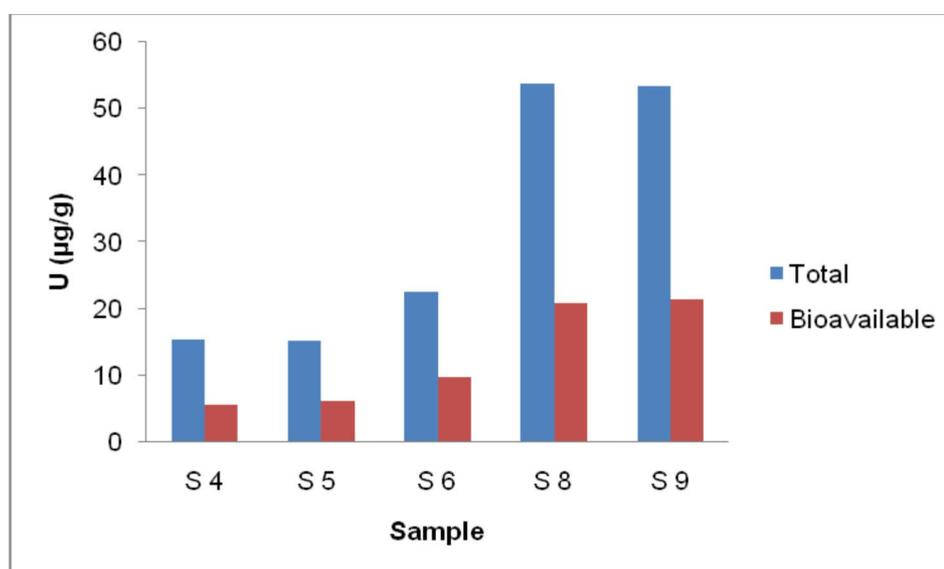


**FIGURE 3.** Frequency of the exposure rate in the filtration cake samples.

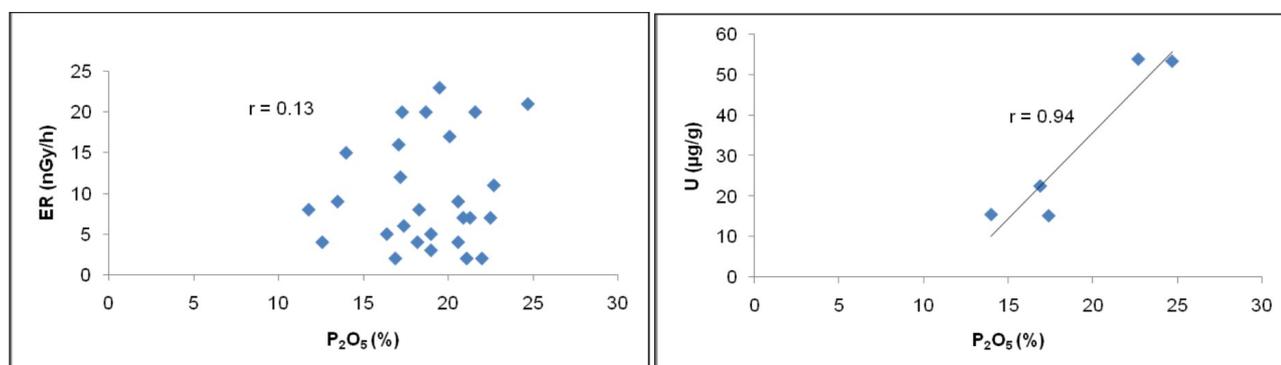
**TABLE 3.** Total and (bio)available uranium concentration and  $^{234}\text{U}/^{238}\text{U}$  activity ratio in filtration cake samples.

Sample	Depth (m)	P <sub>2</sub> O <sub>5</sub> (%)	<sup>238</sup> U – Total (µg/g)	<sup>238</sup> U – (bio)available (µg/g)	<sup>234</sup> U/ <sup>238</sup> 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
<b>Mean</b>			<b>32.06</b>	<b>12.82 (40%)</b>	<b>1.06</b>

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 P<sub>2</sub>O<sub>5</sub> concentration and <sup>238</sup>U and P<sub>2</sub>O<sub>5</sub> 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	<sup>238</sup> U	<sup>226</sup> Ra	<sup>232</sup> Th	<sup>40</sup> 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 = 10,000m<sup>2</sup>) 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/m<sup>2</sup> of <sup>238</sup>U, <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K, 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 <sup>238</sup>U, <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K, and since these radionuclides should be homogeneously distributed in

the upper 10cm of soils with assumed apparent density of 1.5 g/cm<sup>3</sup>, a maximum increase in about 0.16, 0.01, <0.01 and 0.04 Bq/kg of soil is found for <sup>238</sup>U, <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K, respectively. The <sup>238</sup>U added does not reach 0.64% of the normal <sup>238</sup>U 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 <sup>1</sup> (μSv/Bq)	Dose (μSv/year)
<b>Raw acid – Producer A</b>					
<sup>238</sup> U	9	1	9	0.045	0.41
<sup>234</sup> U	9	1	9	0.049	0.44
<sup>226</sup> Ra	3	1	3	0.280	0.84
<sup>232</sup> Th	2	1	2	0.230	0.46
<b>Total</b>					<b>2.15</b>
<b>Raw acid – Producer B</b>					
<sup>238</sup> U	264	1	264	0.045	11.88
<sup>234</sup> U	264	1	264	0.049	12.94
<sup>226</sup> Ra	3	1	3	0.280	0.84
<sup>232</sup> Th	3	1	3	0.230	0.69
<b>Total</b>					<b>26.35</b>
<b>Raw acid – Producer C</b>					
<sup>238</sup> U	869	1	869	0.045	39.11
<sup>234</sup> U	860	1	860	0.049	42.14
<sup>226</sup> Ra	3	1	3	0.280	0.84
<sup>232</sup> Th	1	1	1	0.230	0.23
<b>Total</b>					<b>82.32</b>
<b>Raw acid – Producer D</b>					
<sup>238</sup> U	928	1	928	0.045	41.76
<sup>234</sup> U	909	1	909	0.049	44.54
<sup>226</sup> Ra	6	1	6	0.280	1.68
<sup>232</sup> Th	4	1	4	0.230	0.92
<b>Total</b>					<b>88.90</b>
<b>Reject</b>					
<sup>238</sup> U	1158	1	1158	0.045	52.11
<sup>234</sup> U	1158	1	1158	0.049	56.74
<sup>226</sup> Ra	2	1	2	0.280	0.56
<sup>232</sup> Th	1	1	1	0.230	0.23
<b>Total</b>					<b>109.64</b>
<b>Acid food grade</b>					
<sup>238</sup> U	2	1	2	0.045	0.09
<sup>234</sup> U	2	1	2	0.049	0.10
<sup>226</sup> Ra	<1	1	<1	0.280	0.28
<sup>232</sup> Th	<1	1	<1	0.230	0.23
<b>Total</b>					<b>0.70</b>

<sup>1</sup>ICRP (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  $^{238}\text{U}$  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  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  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  $^{40}\text{K}$ . 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.

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