



## **RADIONUCLIDES AND OTHER ELEMENTS DISTRIBUTION IN THE CATALÃO I PHOSPHATE ORE ROCKS, BRAZIL, AND THEIR INDUSTRIAL (BY) PRODUCTS**

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### **ABSTRACT**

*This investigation focused the distribution of radionuclides and others elements in the Catalão I phosphate ore rocks, Brazil, and their industrial (by) products. The flotation-separation process causes the incorporation of no more than 10%, 15% and 30% of radionuclides, heavy metals and fluorine, respectively, into the concentrated phosphate. The radionuclides and heavy metals existent in phosphate fertilizers applied in Brazilian crops according to the recommended rates, do not raise their concentration in soils to harmful levels, consequently, not offering hazard to the ecosystem and animal or human health. The <sup>238</sup>U intake of raw phosphoric acid is higher than the guideline value proposed by Health Canada, whereas the maximum annual dose ingested through raw phosphoric acid consumption just represents 25% of the annual effective dose estimated due to food ingestion.*

### **RESUMO**

*Este trabalho enfocou a distribuição de radionuclídeos e outros elementos nas rochas fosfáticas de Catalão I e seus produtos industriais. O processo de flotação-separação ocasiona a incorporação de até 10%, 15% e 30% de radionuclídeos, metais pesados e flúor, respectivamente, no concentrado de fosfato. Os radionuclídeos e metais pesados existentes nos fertilizantes à base de fosfato aplicados na agricultura brasileira de acordo com as taxas recomendadas não ocasionam a elevação dos valores de concentração até níveis prejudiciais, portanto, não oferecendo risco ao ecossistema e saúde animal ou humana. A ingestão de <sup>238</sup>U presente no ácido fosfórico bruto é maior que o valor de referência proposto por Health Canada, enquanto que a máxima dose anual associada ao consumo de ácido fosfórico bruto representa apenas 25% da dose anual efetiva associada à ingestão de alimentos.*

## INTRODUCTION

The Catalão I phosphate deposit is an alkaline-carbonatite complex that developed a weathered profile with a well defined vertical mineral zonation and residual concentration of unweathered ore mineral (apatite) due to dissolution of carbonates (Oliveira & Imbernon, 1998). Its genesis, mineralogy and economic aspects have been extensively studied (Valarelli, 1971; Ulbrich & Gomes, 1981; Hirano *et al.*, 1987; Brod *et al.*, 2000, 2001; Junqueira-Brod *et al.*, 2005a, 2005b; Toledo *et al.*, 2002, 2004; Ribeiro *et al.*, 2001, 2005).

The Catalão I phosphate ore rocks are utilized to produce phosphate fertilizers, which are applied in soils and crops, where they are sources of macro (N, P, K, Ca, Mg and S), micronutrients (B, Cl, Co, Cu, Fe, Mn, Mo, Ni, Se, Si and Zn) and metals considered toxic (As, Al, Cd, Pb and Hg) (Camelo *et al.*, 1997; Mirlean *et al.*, 2001). The build up of toxic heavy metals and fluorine in soils as a result of continuous application of phosphate fertilizers has been evaluated in long term experiments carried out in many studies (Alloway, 1990; Kabata-Pendias & Pendias, 1984; Adriano, 1986; Mortvedt, 1987; Charter *et al.*, 1993; Kponblekou & Tabatabai, 1994; Malavolta, 1994; McLaughlin *et al.*, 1996; Gimeno-Garcia *et al.*, 1996; Camelo *et al.*, 1997; Abdel-Haleem *et al.*, 2001; Conceição & Bonotto, 2006a).

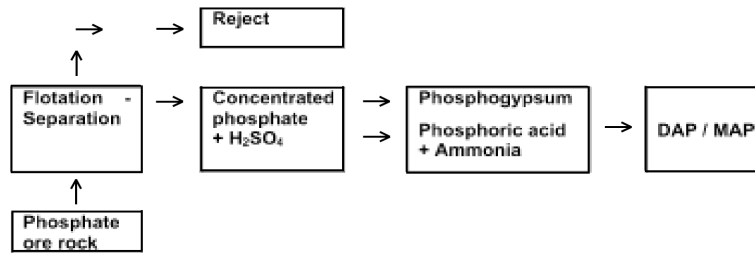
The phosphate ore rocks are also enriched in uranium, thorium and their daughters, as firstly reported in 1908 (Ring, 1977), and whose behavior has been described elsewhere (Menzel, 1968; Pfister *et al.*, 1976; Ring, 1977; Guimond, 1978; Rothbaum *et al.*, 1979; Mortvedt, 1986; Todorovsk & Kulev, 1993; 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, 2006a). Various authors have also studied the

behavior of radionuclides in phosphogypsum (Bolivar *et al.*, 1995; Rutherford *et al.*, 1995; Haridasan *et al.*, 2002) and in 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.*, 1998; Godoy, 1989; Mazzilli & Saueia, 1997; Mazzilli *et al.*, 2000).

The chemical and radionuclides composition in the fresh rocks and weathered horizons from Catalão I complex have been described by Conceição & Bonotto (2006b). This paper investigates the incidence and fractionation of radionuclides and other elements in the industrial (by) products of the Catalão I phosphate deposit as their long-continued application can redistribute and elevate the radionuclides, heavy metals and fluorine concentrations in soil profiles, and, consequently, their availability for plants and subsequent transfer to the human food chain (mainly in acid soils).

## MATERIALS AND METHODS

The first step to obtain the industrialized products derived from Catalão I phosphate ore rocks is the flotation-separation process, where the concentrated phosphate (apatite) is obtained and the other minerals compose the reject (Figure 1). The apatite is destroyed by action of H<sub>2</sub>SO<sub>4</sub> during the production of H<sub>3</sub>PO<sub>4</sub>, originating phosphogypsum (10CaSO<sub>4</sub> .2H<sub>2</sub>O) as by-product. The MAP (monoammonium phosphate) and DAP (diammonium phosphate) are obtained by H<sub>3</sub>PO<sub>4</sub> mixed with ammonium. Samples representing all steps were analyzed, i.e. phosphate ore rocks (CI-1 and CI-2), reject (CI-3 and CI-4), concentrated phosphate (CI-5 and CI-6), MAP (CI-7 and CI-8), DAP (CI-9 and CI-10), phosphogypsum (CI-11 and CI-12), and H<sub>3</sub>PO<sub>4</sub> (CI-13).



**Figure 1:** Simplified route of industrial (by) products derived from Catalão I complex.

The minerals identification was made by optical microscopy on undisturbed samples and X-ray diffractometry (Siemens, model D5000) on powdered samples. The major elements concentration (P<sub>2</sub>O<sub>5</sub>, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, MnO, TiO<sub>2</sub>, BaO and SrO) was measured by X-ray fluorescence (Phillips, model PW 2510) and the heavy metals concentration (Cr, Cd, Cu, Ni, Pb and Zn) through the use of AAS-atomic absorption spectrometry (Varian, model 240FS) in 0.5 g of crushed sample (200 mesh) digested with HCl (30 mL) + HNO<sub>3</sub> (10 mL). The lower AAS detection limits were: Cd= 1 ppm; Cr, Cu, Ni and Zn =2 ppm; Pb= 5 ppm. The upper AAS limit was 5000 ppm to all analyzed elements. The fluorine extraction of all samples was realized with 50 mL of 0.5 M citric acid (50 or 500 mg). Each sample and respective extractant solution was agitated, filtered (0.45 µm Millipore membrane) and the fluorine concentration determined by potentiometry (0.1 to 70 ± 0.02 mg/ ) with an Orion ion-selective electrode coupled into a digital meter.

Uranium concentration and <sup>234</sup>U/<sup>238</sup>U activity ratio of all samples were determined by the use of standard alpha spectrometric techniques (Osmond & Cowart, 1976; Ivanovich & Harmon, 1992; Bonotto, 1996), where <sup>232</sup>U was the spike utilized. About 1 g of each solid sample was crushed to 200 mesh, placed in an acid digestion bomb and brought into complete solution with HF, HNO<sub>3</sub>, and HCl (Bonotto, 1996). About 100 mL of phosphoric acid was dissolved in 10 L of distilled water and the uranium was co-precipitated with Fe(OH)<sub>3</sub>. 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 equal volume of isopropyl ether. The following steps corresponded to anion exchange, electrodeposition, and alpha spectrometry as described by Bonotto (1996).

The gamma spectrometry through NaI(Tl) scintillation detector was utilized to measure the <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K activity concentration in the samples. All solid samples (about 80 g) were dried, crushed and packed in aluminum boxes, whereas the samples of phosphoric acid (about 100 mL) were inserted in glass flasks. Both recipients were sealed to attain, in about 4 weeks, secular equilibrium between <sup>226</sup>Ra, <sup>232</sup>Th and their short-lived daughters. The data were obtained as reported by Duarte & Bonotto (2000).

Ra<sub>eq</sub> was evaluated from <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K activity concentrations according to the equation (Beretka & Mathew, 1985):

$$Ra_{eq} = A_{Ra} + 1.43 A_{Th} + 0.077 A_K$$

where: A<sub>Ra</sub>, A<sub>Th</sub> and A<sub>K</sub> are the specific activities of <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K in Bq/kg, respectively.

## RESULTS AND DISCUSSION

### Phosphate ore rocks and industrialized (by) products

The chemical composition of Catalão I phosphate ore rock and their industrial (by) products are shown in table 1 and figures. 2, 3 and 4. The Catalão I phosphate ore rocks are composed by apatite, quartz, goethite, magnetite, anatase, Al-phosphates

and barite. The Catalão I phosphate ore rocks exhibit 1 to 15% of P<sub>2</sub>O<sub>5</sub> and high concentration of major elements (CaO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, BaO and SrO) and F due to the presence of those minerals. Malavolta (1994) reported the following concentrations for phosphate rocks worldwide: Cd= 1-100 ppm, Cr= 7-500 ppm, Cu= 1-1000 ppm, Ni= 0-100 ppm, Pb= 0-10 ppm and Zn= 4- , 00 ppm. The rocks analyzed in this paper exhibit values of Cd, Cr, Cu and Zn concentration that are within the world range, whereas the Ni and Pb concentrations are higher.

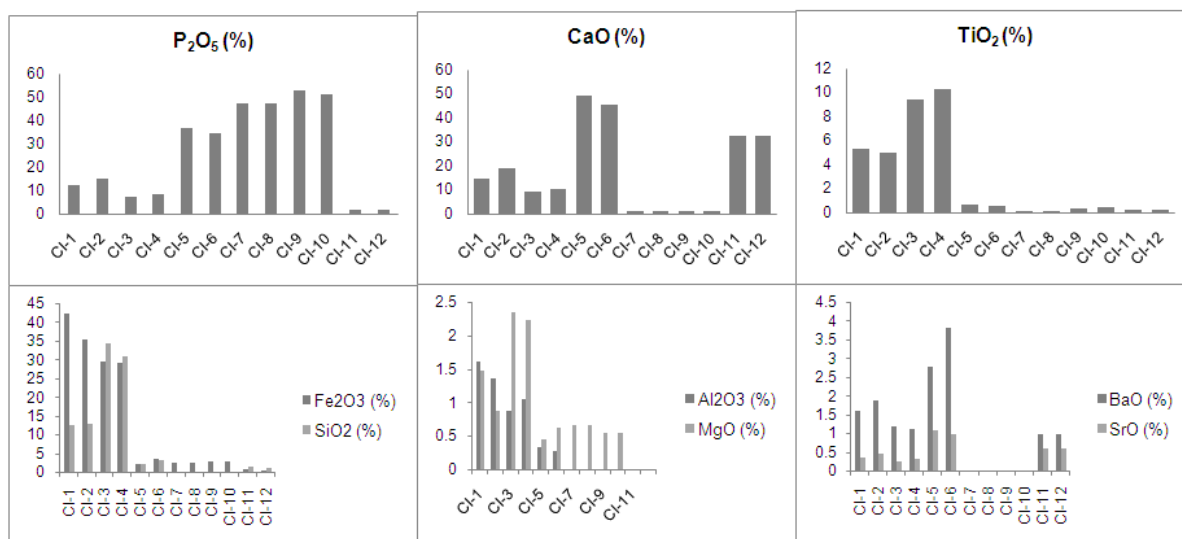
After the flotation-separation process, the concentrated phosphate gets enriched in P<sub>2</sub>O<sub>5</sub>, F, CaO, BaO and SrO in relation to Catalão I phosphate ore rocks

due to the presence of apatites and small amounts of Al-phosphates (gorceixite and goyazite). This phase is depleted in the other major elements, so the remaining minerals (quartz, goethite, magnetite, anatase and barite) are released to the reject. Table 2 and figure 5 show the heavy metals and fluorine concentration and <sup>238</sup>U, <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K activities concentrations in the Catalão I complex, considering the production in one year of phosphate ore rocks, reject and concentrated phosphate. The flotation-separation process fractionates about 83, 83, 54, 70, 82, 91, 65, 69, 87, 75 and 77% of Cd, Cr, Cu, Ni, Pb, Zn, F, <sup>238</sup>U, <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K to reject, respectively, reinforcing that these elements may be preferentially incorporated in minerals that are going to the reject.

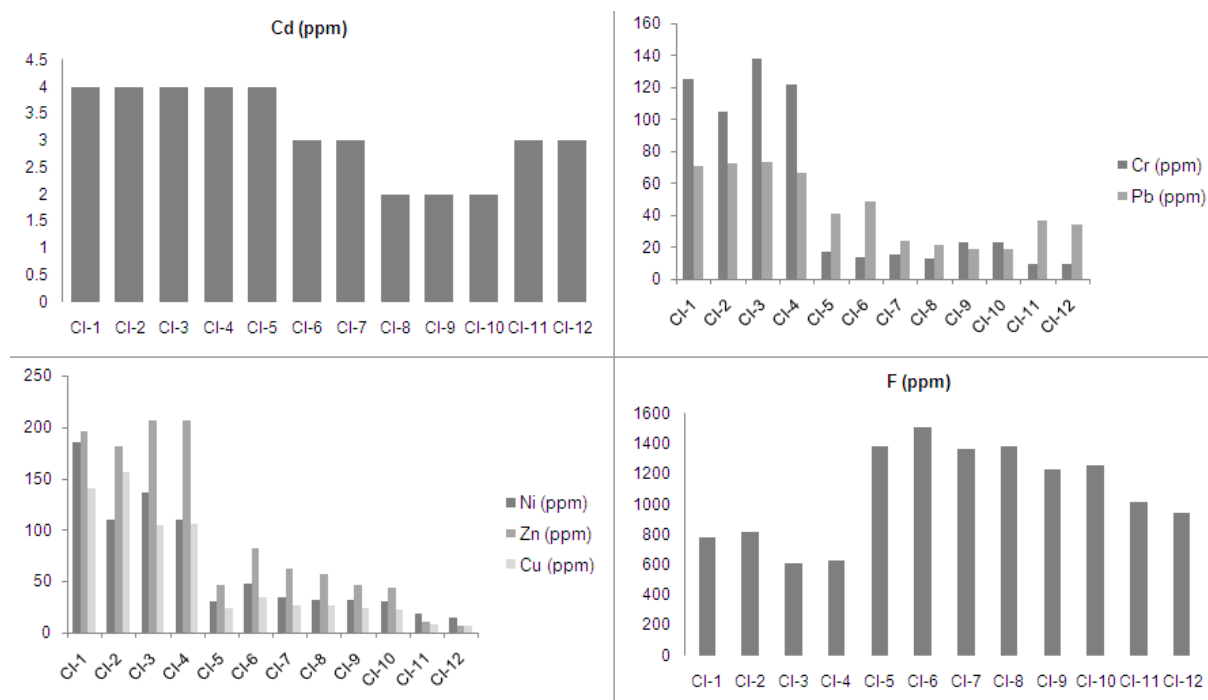
**Table 1:** Chemical composition in phosphate ore rocks and their industrial (by) products from Catalão I complex. CI-1 and CI-2= phosphate ore rock; CI-3 and CI-4= reject; CI-5 and CI-6= concentrated phosphate; CI-7 and CI-8= MAP; CI-9 and CI-10= DAP; CI-11 and CI-12= phosphogypsum; CI-13= H3PO4.

Sample	CI-1	CI-2	CI-3	CI-4	CI-5	CI-6	CI-7	CI-8	CI-9	CI-10	CI-11	CI-12	CI-13
<b>Major elements (%)</b>													
P <sub>2</sub> O <sub>5</sub>	12.00	15.20	7.30	8.26	36.80	34.30	47.30	47.10	52.50	51.00	1.56	1.42	
Na <sub>2</sub> O	0.04	0.04	0.09	0.08	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
K <sub>2</sub> O	0.06	0.06	0.11	0.12	0.02	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CaO	14.50	18.80	9.18	10.50	49.40	45.40	0.96	0.95	0.92	0.83	32.40	32.50	
SiO <sub>2</sub>	12.50	12.90	34.50	31.10	2.19	3.40	0.19	0.22	0.14	0.14	1.37	1.17	
Al <sub>2</sub> O <sub>3</sub>	1.62	1.38	0.88	1.07	0.35	0.29	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe <sub>2</sub> O <sub>3</sub>	42.40	35.50	29.50	29.20	2.00	3.66	2.29	2.32	2.64	2.82	0.53	0.49	
MgO	1.49	0.88	2.36	2.24	0.46	0.63	0.68	0.67	0.55	0.56	<0.01	<0.01	<0.01
MnO	0.39	0.35	0.40	0.42	0.04	0.06	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
TiO <sub>2</sub>	5.26	4.96	9.39	10.30	0.61	0.57	0.14	0.14	0.32	0.45	0.23	0.20	
BaO	1.62	1.89	1.20	1.14	2.79	3.85	<0.01	<0.01	<0.01	<0.01	0.97	0.99	
SrO	0.36	0.47	0.26	0.31	1.09	0.98	<0.01	<0.01	<0.01	<0.01	0.61	0.61	
LOI <sup>1</sup>	5.38	5.00	3.22	3.07	1.11	1.86					20.20	21.10	
<b>Heavy metals and fluorine (ppm)</b>													
Cd	4	4	4	4	4	3	3	2	2	2	3	3	
Cr	126	105	139	122	17	14	15	13	23	23	9	9	
Cu	141	157	105	106	24	35	27	26	24	22	8	6	
Ni	186	111	137	111	31	48	34	32	32	31	18	15	
Pb	71	73	74	67	41	49	24	21	19	19	37	34	
Zn	197	182	207	207	46	83	62	57	46	44	11	6	
F	784	822	614	632	1386	1506	1368	1386	1230	1254	1014	942	
<b>Radionuclides and Ra<sub>eq</sub> (Bq/kg)</b>													
<sup>238</sup> U <sup>2</sup>	1072	970	801	624	392	606	1849	1615	953	1398	321	234	157 <sup>3</sup>
<sup>234</sup> U <sup>2</sup>	1098	989	785	636	396	612	1849	1615	924	1440	321	229	160 <sup>3</sup>
<sup>226</sup> Ra <sup>2</sup>	342	339	364	297	130	215	11	11	11	11	292	213	24 <sup>3</sup>
<sup>232</sup> Th <sup>2</sup>	1232	1070	989	1081	385	520	65	41	42	34	172	151	158 <sup>3</sup>
<sup>40</sup> K <sup>2</sup>	282	291	276	255	143	134	<5	<5	<5	<5	53	48	<5 <sup>3</sup>
Ra <sub>eq</sub>	2125	1841	1799	1862	691	968	104	70	70	60	542	433	250 <sup>3</sup>
<b>Activity Ratio</b>													
<sup>234</sup> U/ <sup>238</sup> U	1.02	1.02	0.98	1.02	1.01	1.01	1.00	1.00	0.97	1.03	1.00	0.98	1.02
<sup>226</sup> Ra/ <sup>238</sup> U	0.32	0.35	0.45	0.47	0.33	0.35	<0.01	<0.01	<0.01	<0.01	0.91	0.91	0.15
<sup>232</sup> Th/ <sup>238</sup> U	1.15	1.10	1.24	1.73	0.98	0.86	0.04	0.03	0.04	0.02	0.54	0.64	1.00

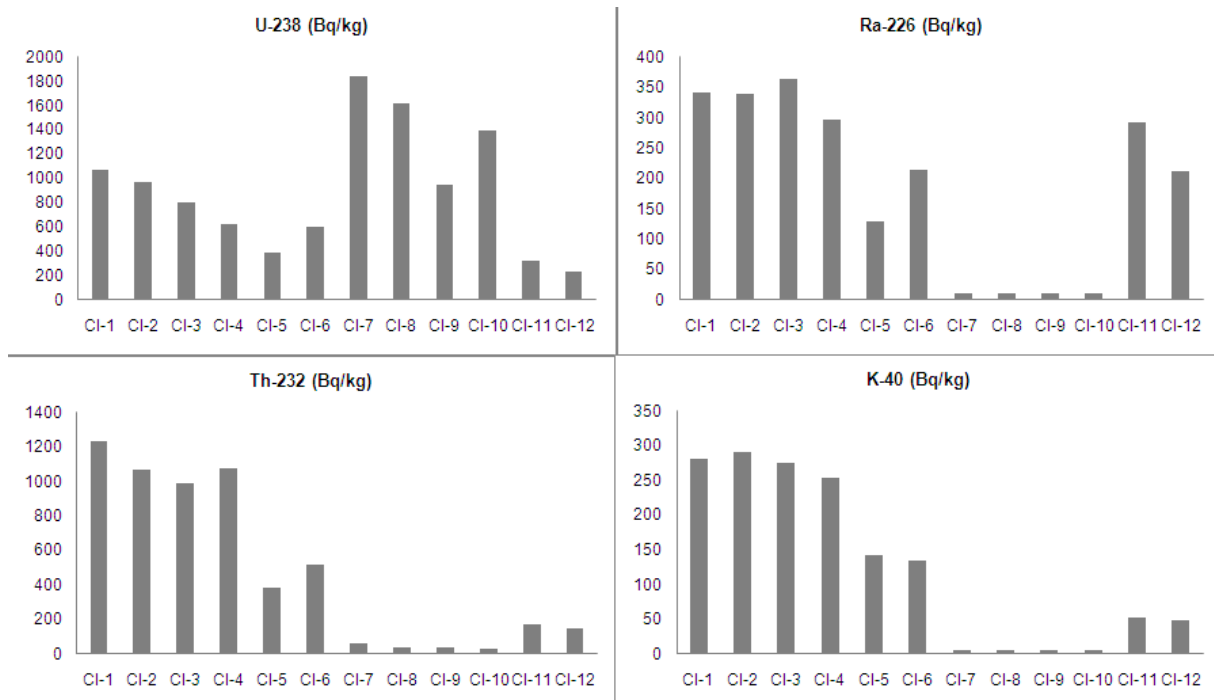
<sup>1</sup>Loss on ignition; <sup>2</sup>Analytical uncertainty ± 10% (1σ standard deviation); <sup>3</sup>Bq/L.



**Figure 2:** Major elements concentration in industrial (by) products from Catalão I complex. CI-1 and CI-2= phosphate ore rock; CI-3 and CI-4= reject; CI-5 and CI-6= concentrated phosphate; CI-7 and CI-8= MAP; CI-9 and CI-10= DAP; CI-11 and CI-12= phosphogypsum.



**Figure 3:** Heavy metals and fluorine concentration in industrial (by) products from Catalão I complex. CI-1 and CI-2= phosphate ore rock; CI-3 and CI-4= reject; CI-5 and CI-6= concentrated phosphate; CI-7 and CI-8= MAP; CI-9 and CI-10= DAP; CI-11 and CI-12= phosphogypsum.



**Figure 4:** Radionuclides activity concentration in industrial (by) products from Catalão I complex. CI-1 and CI-2= phosphate ore rock; CI-3 and CI-4= reject; CI-5 and CI-6= concentrated phosphate; CI-7 and CI-8= MAP; CI-9 and CI-10= DAP; CI-11 and CI-12= phosphogypsum.

Mazzilli *et al.* (2000) found that 90% of  $^{226}\text{Ra}$  and 80% of  $^{232}\text{Th}$  of the total incorporated in Brazilian phosphate ore rocks are fractionated into phosphogypsum, with  $^{238}\text{U}$  being predominantly incorporated in phosphoric acid during the industrial processing of these rocks. However, no more than 31% of radionuclides are incorporated into the Catalão I concentrated phosphate through the flotation-separation process, as shown in table 2 and figure 5. The differences may be justified by the fact that Mazzilli *et al.* (2000) only considered the phosphogypsum and phosphate rocks in the mass-balance calculations.

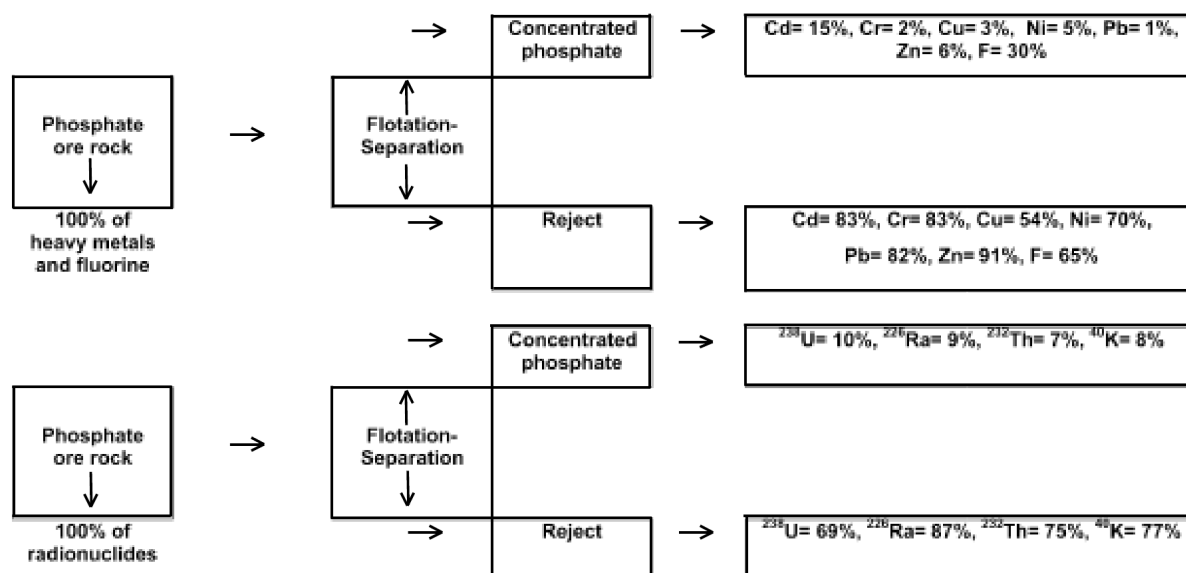
The  $\text{P}_2\text{O}_5$  concentration in MAP and DAP is higher than in concentrated phosphate (Table 1). The F concentration follows the tendency MAP > DAP > phosphogypsum. The CaO, BaO and SrO, after the initial acid attack (Figure 1) go to phosphogypsum, suggesting a similar chemical behavior among these elements. The Cd, Cu, Ni, Pb, Zn and F concentrations decreased in MAP,

DAP and phosphogypsum in relation to concentrated phosphate. The heavy metals concentration in MAP and DAP are within the worldwide range for phosphate fertilizers (Charter *et al.*, 1993; Kponblekou & Tabatabai, 1994; Malavolta, 1994; Gimeno-García *et al.*, 1996; Camelo *et al.*, 1997; Abdel-Haleem *et al.*, 2001).

The radionuclides activity concentration in MAP and DAP is within the range of values obtained worldwide for phosphate fertilizers (Menzel, 1968; Pfister *et al.*, 1976; Ring, 1977; Guimond, 1978; Rothbaum *et al.*, 1979; Mortvedt, 1985; Todorovsky & Kulev, 1993; Bolivar *et al.*, 1995; Alam *et al.*, 1997; Ioannides *et al.*, 1997; Ibrahim, 1998; Khan *et al.*, 1998; Conceição & Bonotto, 2006a). The average annual effective dose from natural sources corresponding to 2.4 mSv per year (UNSCEAR, 1993) may be attained by  $\text{Raeq} = 544 \text{ Bq/kg}$ , that is a value not exceeded by MAP, DAP and phosphogypsum.

**Table 2:** Heavy metals and fluorine concentration and radionuclides activity concentration in phosphate ore rock and (by) products obtained by the flotation-separation process in one year.

Sample	Production	Cd	Cr	Cu	Ni	Pb	Zn	F	<sup>238</sup> U	<sup>226</sup> Ra	<sup>232</sup> Th	<sup>40</sup> K
									( $\times 10^6$ kg/yr)			
Phosphate ore rock	6 $\times 10^6$ ton	24	783	984	891	432	1137	4818	52.0	18.9	69.1	17.2
Reject	5 $\times 10^6$ ton	20	653	528	620	353	1035	3115	35.6	16.5	51.8	13.3
Concentrated phosphate	1 $\times 10^6$ ton	3.5	16	30	40	45	65	1446	4.99	1.7	4.5	1.4



**Figure 5:** Distribution of heavy metals, fluorine and radionuclides caused by flotation-separation processes at Catalão I phosphate rocks.

The <sup>238</sup>U activity concentration in MAP and DAP is higher than in the concentrated phosphate (Table 1), the same behavior observed by P<sub>2</sub>O<sub>5</sub>. This fact may suggest that the most important uranyl complexes are formed with phosphate. However, as shown by Langmuir (1978), this situation is only possible under near-neutral pH conditions, a situation not favored by the initial attack with H<sub>2</sub>SO<sub>4</sub> (Figure 1). Thus, the <sup>238</sup>U incorporation in phosphate fertilizers occurs as [(UO<sub>2</sub>)SO<sub>4</sub>] and [U(SO<sub>4</sub>)<sub>2</sub>] that are water soluble, as demonstrated by Rothbaum *et al.* (1979). The <sup>226</sup>Ra relatively to <sup>238</sup>U activity concentration increased from concentrated phosphate to phosphogypsum, suggesting the occurrence of fractionation between <sup>238</sup>U and <sup>226</sup>Ra, as indicated by <sup>226</sup>Ra/<sup>238</sup>U activity ratio in these phases (Table 1). The <sup>226</sup>Ra possesses chemical behavior similar to calcium, possibly occurring as 10CaSO<sub>4</sub>·2H<sub>2</sub>O (phosphogypsum) (Roessler, 1990) or (Ca,Ba,Sr)SO<sub>4</sub> (radiobarite) (Rutherford *et al.*, 1995). The

<sup>232</sup>Th and <sup>40</sup>K activity concentrations decreased in MAP, DAP and phosphogypsum in relation to concentrated phosphate (Table 1).

**Industrialized (by) products and their environmental hazards**

Micronutrients as Cu, Ni and Zn are essential for plant life, without evidencing hazards to the human health. Cd, Cr and Pb are not essential elements and according to their concentrations can be classified as toxic to plants. The Brazilian soils are normally acid, with low content of organic matter and deficient in micronutrients, which cause decreasing of the agricultural productivity in Brazilian crops. The addition of phosphate fertilizers aims to correct this, also reducing the production costs, making the agricultural products cheaper in the international market and, consequently, more competitive for exportation with improvement in the quality of the agricultural products (Malavolta, 1994).

The phosphate fertilizers have been utilized in many parts of world, being generally applied at rates of 600 kg/ha (1 ha= 10,000 m<sup>2</sup>) per year in Brazil (Malavolta, 1994). The maximum average annual addition of heavy metals and fluorine distributed per unit arable land corresponds to 1.8 (MAP), 13.8 (DAP), 16.2 (MAP), 19.8 (MAP), 13.8 (MAP), 36 (MAP) and 826 (MAP) g/ha for

Cd, Cr, Cu, Ni, Pb, Zn and F, respectively (Table 3).

The high F inputs can be responsible for pollution in freshwater and groundwater (Mirlean *et al.*, 2001) and the addition of 826 g/ha of F, under favorable geochemical conditions, may pollute 590 m<sup>3</sup> of water if it is assumed a tolerance limit of 1.4 mg/L (CONAMA, 2005).

**Table 3:** Mean concentration and distribution of heavy metals and fluorine in phosphate fertilizers produced by Catalão I complex.

Sample	Cd	Cr	Cu	Ni	Pb	Zn	F							
								Cd	Cr	Cu	Ni	Pb	Zn	F
				(ppm)										
MAP	3	14	27	33	23	60	1377	1.8	8.4	16.2	19.8	13.8	36.0	826
DAP	2	23	23	32	19	45	1242	1.2	13.8	13.8	19.2	11.4	27.0	745

Table 4 exhibits a comparison of the maximum allowable release of heavy metal into Brazilian and British soils. The Brazilian limits are higher than the British ones, except for Pb, because they refer to the addition of sewage mud into soils. The heavy metals addition is greatly lower than the annual tolerance limits. The number of years of continuous application for the maximum annual tolerance limits to be reached ranged from 1087 (Pb) to 10556 (Cd) years (Table 4). Therefore, the heavy metals (micronutrients or not) determined in phosphate fertilizers and applied in Brazilian crops according to the recommended rates

do not raise their concentration in soils to harmful levels in short and medium periods of time. Such a finding is supported by various studies (Mulla *et al.*, 1980; Mortvedt, 1985, 1987; Alcorido & Reicheigl, 1993; Malavolta, 1994), indicating that the increasing concern about the entry of heavy metals, specially Cd, Pb and Ni into the human food chain (McLaughlin *et al.*, 1996) must not be associated with phosphate fertilizers (the contribution is less than 1% of the heavy metals load to the soil, according to Malavolta, 1994), but to others anthropogenic sources (domestic and industrial residues/wastes and pesticides).

**Table 4:** Tolerance limit, estimated annual addition of heavy metals and number of expected years for reaching the allowable limit.

Element	Annual allowable limit (UK) <sup>1</sup> (kg/ha)	Annual allowable limit (Brazil) <sup>2</sup> (kg/ha)	Annual addition (kg/ha)	Number of years (UK)	Number of years (Brazil)
Cd	0.166	1.9	0.0018	92	10556
Cr	33.33	-	0.0138	2415	-
Cu	9.33	75.0	0.0162	576	4629
Ni	2.33	21.0	0.0198	118	1061
Pb	33.33	15.0	0.0138	2415	1087
Zn	18.66	140.0	0.0360	518	3889

<sup>1</sup>Davies (1980) and Adriano (1986); <sup>2</sup>CETESB (1999).

The maximum annual average addition of radionuclides distributed per unit arable land corresponds to 104, <1, 3 and <1 Bq/m<sup>2</sup> for <sup>238</sup>U, <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K in MAP, respectively (Table 5). 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, 1999; Sam *et al.*, 1999; Khater *et al.*, 2001). 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 10 cm of soils with assumed apparent density of 1.5 g/cm<sup>3</sup>, a maximum MAP increase in about 0.69, <0.01, 0.02 and <0.01 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 (Table 5). The <sup>238</sup>U added does not reach 3% of the normal <sup>238</sup>U content in an undisturbed soil (world average of 25 Bq/kg, according to

Ibrahim, 1998). Table 5 shows that the maximum additional external radiation exposure caused by phosphate fertilizers used in Brazilian crops is 0.01 nGy/h (MAP and DAP) 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).

**Table 5:** Addition, increase and exposure rate (ER – estimated using DRCF= 0.0414, 0.623 and 0.461 nGy/h per Bq/kg to <sup>40</sup>K, <sup>232</sup>Th and <sup>226</sup>Ra, respectively) per unit arable land originated from phosphate fertilizers produced at Catalão I complex.

Sample	<sup>238</sup> U	<sup>234</sup> U	<sup>226</sup> Ra	<sup>232</sup> Th	<sup>40</sup> K	<sup>238</sup> U	<sup>234</sup> U	<sup>226</sup> Ra	<sup>232</sup> Th	<sup>40</sup> K	ER (nGy/h)
	(Bq/m <sup>2</sup> )					(Bq/kg)					
MAP	104	104	<1	3	<1	0.69	0.69	<0.01	0.02	<0.01	0.01
DAP	71	71	<1	2	<1	0.47	0.47	<0.01	0.01	<0.01	0.01

A phosphoric acid consumption rate of 1 L/yr is expected for adult inhabitants in Brazil, which is used in water and effluent treatment plants, as well by food, beverage and pharmaceutical industries. On average, 90 µg of uranium exist in the human body, with 66% found in the skeleton, 16% in the liver, 8% in the kidneys and 10% in other tissues. The <sup>238</sup>U intake (430 mBq/day) due to raw phosphoric acid is higher than the proposed limit of 32 mBq/day (Health Canada, 1999) or 50 mBq/day (Holtzman, 1980). These values were based in limits derived from renal toxicity for soluble uranium compounds and from radiation exposure for insoluble uranium compounds. The results here reported suggest that this

consumption can cause problems to human health, such as decreasing the glomerular filtration rate, nephritis and other biochemical effects and histopathological changes in the kidneys, liver, thyroid and aorta (Mirto *et al.*, 1999). On the other hand, using the dose coefficients proposed by ICRP (1996), it is possible estimate the maximum annual dose ingested through raw phosphoric acid consumption as about 58 µSv (Table 6), a value that represents 25% of the annual effective dose estimated due to food ingestion (0.23 mSv/yr, according to UNSCEAR, 1993). Therefore, depending on the guideline reference values adopted, different conclusions may be attained.

**Table 6:** 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)
<sup>238</sup> U	157	1	157	0.045	7.06
<sup>234</sup> U	160	1	160	0.049	7.84
<sup>226</sup> Ra	24	1	24	0.280	6.72
<sup>232</sup> Th	158	1	158	0.230	36.34
<b>Total</b>					<b>57.96</b>

<sup>1</sup>ICRP (1996).

## CONCLUSION

The heavy metals concentration and radionuclides activities concentrations in Catalão I phosphate ore rocks, MAP and DAP are within the worldwide range for these rock types and phosphate fertilizers. The flotation-separation process causes the incorporation of no more than 15% of heavy metals, 30% of fluorine and 10% of radionuclides into the

concentrated phosphate. The  $^{238}\text{U}$  activity concentration in MAP and DAP is higher than in the concentrated phosphate. The  $^{226}\text{Ra}$  relatively to  $^{238}\text{U}$  activity concentration increased from the concentrated phosphate to phosphogypsum, suggesting the occurrence of fractionation between  $^{238}\text{U}$  and  $^{226}\text{Ra}$ . The  $^{232}\text{Th}$  and  $^{40}\text{K}$  activity concentration decrease in MAP, DAP and phosphogypsum in relation to concentrated phosphate. The addition of inorganic phosphate fertilizers 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 and, consequently, the possible increase of a) radon flux from the soil, b) uptake by plants and c) natural alpha activity of food products must be minimal. The expected consumption of 1 L of raw phosphoric acids contained into food, beverage and pharmaceutical industries does not offer hazards to human health in relation to annual dose ingestion due to the radionuclides analyzed. However, the intake of this raw acid can cause problems to human health if different guideline values are adopted on the comparison.

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