

# Availability of metals and radionuclides present in phosphogypsum and phosphate fertilizers used in Brazil

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Received: 23 November 2012  
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**Abstract** Phosphogypsum (PG) is a by-product of the phosphate fertilizer industry. In Brazil, three main phosphate industries are responsible for the production of  $5.5 \times 10^6$  metric tons of PG per year, which is stored in stacks. Part of this by-product can be reused to improve fertility of agricultural soils. For its safe application, it is necessary to characterize the impurities (metals and radionuclides) present in PG and to evaluate their availability to the environment. The main objectives of this paper are: to determine the total concentration of radionuclides ( $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{210}\text{Pb}$ ) and metals (As, Cd, Cr, Co, Cu, Hg, Ni, Pb, Se, Zn) in the Brazilian PG samples using different methodologies, to evaluate the available fraction of these elements in the PG samples using a methodology with mild leaching with EDTA, to compare the results obtained for PG samples with those obtained for the most used phosphate fertilizers. The total concentration obtained for the metals using methodologies with different initial digestion (strong attack with acids and HF and mild attack with nitric acid) are slightly different. The results obtained using the methodology with mild leaching showed that the metals and radionuclides are not available to the environment, giving evidence that the application of PG in agriculture is safe as far as contamination by such elements. PG presented metals concentration lower than the phosphate fertilizers. The results obtained for the PG samples, for As, Cd, Cr, Hg, Ni, Pb and Se, are below the limits established by the Brazilian Regulatory Agency.

**Keywords** Metals · Radionuclides · Phosphogypsum · Fertilizers

## Introduction

The Brazilian phosphate fertilizer is obtained by wet reaction of the igneous phosphate rock with concentrated sulphuric acid, giving as final product, phosphoric acid, and dehydrated calcium sulphate (phosphogypsum (PG)) as by-product. Phosphoric acid is the starting material for the most utilized Brazilian fertilizers: triple superphosphate (TSP), single superphosphate (SSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). The world consumption of  $\text{P}_2\text{O}_5$  in 2011 was estimated to be 145 million tons [1]. In Brazil, the  $\text{P}_2\text{O}_5$  consumption in 2010 was estimated as 2.6 million tons [2]. The main phosphate industries in Brazil are responsible for the production of  $5.5 \times 10^6$  metric tons of PG annually [3], which is stored in stacks. The level of impurities (metals and radionuclides, among others) present in PG makes its disposal or reutilization an environmental concern. PG can be considered as a technologically enhanced naturally occurring radioactive material (TENORM), depending upon its content of natural radionuclides. In Brazil TENORM industries are subjected to the recommendations given by Comissão Nacional de Energia Nuclear (CNEN), which include compliance with the radiological protection regulations [4, 5].

Santos et al. [6] performed the characterization of natural radionuclides of the U and Th series in the stockpiled PG waste in Brazil, and according to the Brazilian regulation [5], PG stockpiled is classified as category III (activity concentration below  $10 \text{ Bq g}^{-1}$ ), which means

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that the industry is obliged to perform an environmental radiological monitoring surveillance in its surrounding, in order to evaluate the degree of radiological contamination.

It is known that part of this waste can be reused to improve fertility of agricultural soils [7–10]. In Brazil, PG has been used for many years in agriculture, as a soil amendment. For its safe long term application, it is necessary to characterize the impurities (metals and radionuclides) present in PG and to study their mobility and bioavailability in the environment. This study is important since such impurities can migrate to agricultural products and enter in the food chain or to contaminate the draining water soil. To assure a safe utilization of PG it is important to determine not only the total concentration levels of the impurities but also to evaluate their fraction which is really available to the environment. To accomplish this task, the content of the labile elements were determined following a procedure adopted by European Commission [11], which includes an initial attack of the samples with EDTA prepared as an ammonium salt. This procedure intends to represent on a more realistic way the leaching of metals and radionuclides from PG to soil and agricultural products.

The concentration of metals in fertilizers and soil conditioners are controlled by environmental and agriculture regulation agencies in Brazil. According to the national agriculture regulation agency (Ministério da Agricultura, Pecuária e Abastecimento—MAPA) [12], the concentration of the metals As, Cd, Cr, Hg, Ni, Pb and Se in fertilizers and soil conditioner cannot exceed the limits presented in Table 1. The State Environmental Agency, (Companhia Ambiental do Estado de São Paulo CETESB) [13], established also values for soil prevention level for the following elements As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se and Zn. However, for an adequate application of these limits, the regulatory body should recommend specific methodologies for the determination of the total concentration of these elements in fertilizers. It is well known that, depending upon the methodology chosen, which may include attack with strong acids and HF on microwave or a mild attack with only HNO<sub>3</sub>, the leaching of the metals will be slightly different [14].

The main objectives of this paper are: to determine the total concentration of radionuclides (<sup>226</sup>Ra, <sup>228</sup>Ra and <sup>210</sup>Pb) and metals (As, Cd, Cr, Co, Cu, Hg, Ni, Pb, Se, Zn) in the Brazilian PG samples using different methodologies; to evaluate the available fraction of these elements in the PG samples using a methodology with mild leaching (EDTA); to compare the results obtained for PG samples with those obtained for the most used phosphate fertilizers (single super phosphate—SSP, triple superphosphate—TSP, monoammonium phosphate—MAP and diammonium phosphate—DAP); and finally to compare the results obtained with the limits adopted in Brazil.

## Experimental

### Metals determination

The metals Cd, Cu, Ni, Pb and Zn were determined using the methodology from United States Environmental Protection Agency, EPA 3052 [15], which includes a drastic attack of the samples with HF in a microwave oven and atomic absorption technique (AAS). The accuracy and precision were determined by the application of the same methodology in reference material Buffalo River Sediment from National Institute of Standards and Technology, NIST-2704. The relative accuracy achieved was 7.5 % (Cd), 8.4 % (Cu), 0.2 % (Ni), 3.3 % (Pb) and 0.7 % (Zn). The relative precision achieved was 6.8 % (Cd), 0.75 % (Cu), 1.6 % (Ni), 7.7 % (Pb) and 3.6 % (Zn).

The same elements and As, Se and Hg were determined using the methodology EPA 3050B [16], recommended by the Brazilian regulatory body [12] which includes a mild attack with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> and determination by atomic absorption spectrometry (AAS) and/or inductively coupled plasma atomic emission spectroscopy (ICP-AES). The accuracy and precision was performed by measuring the Standard Reference Material SRM 2709 San Joaquim, giving results ranging from 8.0 to 10 % for relative accuracy and from 3.5 to 11 % for relative precision.

The total concentration of Co and Cr were determined by instrumental neutron activation analysis (INAA), comparative method. The determination was carried out by irradiation of approximately 150 mg of each sample and 150 mg of reference materials as standards, during 16 h at a neutron flux of 10<sup>12</sup> n cm<sup>-2</sup> s<sup>-1</sup>, at Instituto de Pesquisas Energéticas e Nucleares (IPEN) research reactor IEA-R1. Gamma spectrometry was measured with a Ge-hyperpure detector, Inter technique, with 2.1 keV resolution for the 1,332 keV <sup>60</sup>Co photo peak. The accuracy and precision was performed by measuring the reference materials Buffalo River Sediment, NIST-2704 and International Atomic Energy Agency, IAEA-Soil 7. The relative accuracy obtained was 0.4 % for Co and 8.8 % for Cr; and the relative precision was 1.3 % for Co and 8.3 % for Cr.

### Radionuclides determination

The radionuclides <sup>226</sup>Ra, <sup>228</sup>Ra and <sup>210</sup>Pb were measured in PG samples using high-resolution gamma spectrometry, with a hyper-pure germanium detector, EGNC 150-190 R, from Eurisys Measures, with resolution of 1.8 keV for the 1,332 keV <sup>60</sup>Co photoppeak and 15 % relative efficiency. The detector was calibrated using natural soil, rock and water spiked with radionuclides certified by Amersham. Samples were packed in 100 cm<sup>3</sup> cans and sealed for about 4 weeks prior to the measurement in order to ensure that

**Table 1** Metals concentration and labile fraction ( $\text{mg kg}^{-1}$ ) (mean value  $\pm$  expanded uncertainty) in phosphogypsum (PG) and phosphate fertilizers (MAP, DAP, TSP and SSP), maximum limits for fertilizer and soil conditioner from MAPA, soil quality reference and prevention level values from CETESB

Element	Copebrás				Ultrafertil				Fosfertil				MAPA maximum limit		CETESB Soil prevention level		
	SSP		TSP		PG		MAP		DAP		PG		TSP			Fertilizer	Soil conditioner
	SSP	TSP	PG	PG	MAP	DAP	PG	PG	MAP	TSP	PG	TSP	Fertilizer	Soil conditioner			
As																	
b	2.3 ± 0.2	4.9 ± 0.5	<0.9	<0.9	6.6 ± 0.7	5.2 ± 0.5	<0.9	<0.9	8.2 ± 0.7	8.2 ± 0.8	<0.9	8.2 ± 0.7	8.2 ± 0.8	10	20	15	
d	2.6 ± 0.3	3.5 ± 0.3	<0.3	<0.3	4.8 ± 0.3	6.9 ± 0.7	<0.3	<0.3	4.6 ± 0.4	4.9 ± 0.5	<0.3	4.6 ± 0.4	4.9 ± 0.5				
Cd																	
a	11.7 ± 0.7	17.8 ± 0.3	<1.5	<1.5	5.2 ± 0.3	5.6 ± 0.3	<1.5	<1.5	1.8 ± 0.1	5.5 ± 0.3	<1.5	1.8 ± 0.1	5.5 ± 0.3	20	8	1.3	
b	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5				
d	<0.3	<0.4	<0.2	<0.2	0.10 ± 0.01	0.11 ± 0.01	<0.2	<0.2	<0.1	<0.4	<0.1	<0.1	<0.4				
Co																	
c	11.7 ± 0.5	23.8 ± 0.9	0.8 ± 0.03	0.8 ± 0.03	16.6 ± 0.5	14.9 ± 0.6	1.7 ± 0.05	1.7 ± 0.05	13.5 ± 0.4	9.9 ± 0.3	1.0 ± 0.03	13.5 ± 0.4	9.9 ± 0.3	-	-	25	
d	9.0 ± 1.0	13.6 ± 1.4	<0.2	<0.2	8.4 ± 0.7	4.9 ± 0.5	0.31 ± 0.03	0.31 ± 0.03	7.1 ± 0.8	6.4 ± 0.5	0.61 ± 0.05	7.1 ± 0.8	6.4 ± 0.5				
Cr																	
c	48 ± 3	38 ± 2	37 ± 3	37 ± 3	41 ± 3	27 ± 2	56 ± 4	56 ± 4	17 ± 2	28 ± 3 c	37 ± 3	17 ± 2	28 ± 3 c	200	500	150	
d	5.3 ± 0.5	7.0 ± 0.7	<0.3	<0.3	8.5 ± 0.7	8.3 ± 0.8	<0.3	<0.3	7.8 ± 0.8	5.8 ± 0.6	<0.2	7.8 ± 0.8	5.8 ± 0.6				
Cu																	
a	47.4 ± 1.0	81.1 ± 1.8	12.5 ± 0.3	12.5 ± 0.3	53.3 ± 1.1	34.6 ± 0.7	13.7 ± 0.4	13.7 ± 0.4	24.9 ± 0.5	16.7 ± 0.4	9.8 ± 0.3	24.9 ± 0.5	16.7 ± 0.4	-	-	60	
b	47.2 ± 2.0	94.5 ± 4.0	8.6 ± 1.1	8.6 ± 1.1	49.8 ± 2.1	33.8 ± 2.6	10.0 ± 1.0	10.0 ± 1.0	18.9 ± 0.8	20.4 ± 1.0	6.5 ± 1.2	18.9 ± 0.8	20.4 ± 1.0				
d	55 ± 5	97.8 ± 10	<0.9	<0.9	31.3 ± 5	25.1 ± 2	1.0 ± 0.1	1.0 ± 0.1	9.8 ± 0.8	10.6 ± 0.9	0.9 ± 0.1	9.8 ± 0.8	10.6 ± 0.9				
Hg																	
b	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.20	2.5	0.5	
Ni																	
a	51.9 ± 6.7	83.9 ± 10.4	9.4 ± 2.6	9.4 ± 2.6	65.1 ± 7.1	45.3 ± 5.2	15.5 ± 1.9	15.5 ± 1.9	16.1 ± 1.9	18.2 ± 1.8	11.2 ± 2.3	16.1 ± 1.9	18.2 ± 1.8	-	175	30	
b	30.5 ± 3.1	49.6 ± 6.7	8.2 ± 2.8	8.2 ± 2.8	42.6 ± 5.4	34.1 ± 3.7	17.6 ± 1.8	17.6 ± 1.8	11.6 ± 2.3	14.5 ± 2.0	13.0 ± 2.1	11.6 ± 2.3	14.5 ± 2.0				
d	15.2 ± 1.4	21.2 ± 2.5	<0.3	<0.3	25 ± 3	12.1 ± 1.2	0.8 ± 0.1	0.8 ± 0.1	7.3 ± 0.6	6.9 ± 0.7	0.6 ± 0.1	7.3 ± 0.6	6.9 ± 0.7				
Pb																	
a	53.3 ± 4.2	70.0 ± 2.4	14.0 ± 1.6	14.0 ± 1.6	45.1 ± 1.6	51.6 ± 2.0	23.3 ± 1.2	23.3 ± 1.2	20.8 ± 1.3	60.6 ± 2.2	19.4 ± 1.3	20.8 ± 1.3	60.6 ± 2.2	100	300	180	
b	13.4 ± 1.6	14.5 ± 1.6	7.9 ± 1.9	7.9 ± 1.9	9.7 ± 1.8	10.5 ± 1.8	10.6 ± 1.8	10.6 ± 1.8	9.3 ± 1.9	11.7 ± 1.7	9.8 ± 1.8	9.3 ± 1.9	11.7 ± 1.7				
d	17.9 ± 1.8	21.6 ± 2.0	1.0 ± 0.1	1.0 ± 0.1	2.6 ± 0.3	7.7 ± 0.8	1.8 ± 0.2	1.8 ± 0.2	2.3 ± 0.2	7.3 ± 0.6	3.7 ± 0.4	2.3 ± 0.2	7.3 ± 0.6				
Se																	
b	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	-	80	5	
d	<0.6	<0.8	<0.3	<0.3	<0.2	<0.1	<0.3	<0.3	<0.1	<0.8	<0.2	<0.1	<0.8				
Zn																	
a	42.2 ± 1.4	78.8 ± 2.8	11.6 ± 0.3	11.6 ± 0.3	58.9 ± 2.0	48.8 ± 1.7	15.1 ± 0.5	15.1 ± 0.5	43.3 ± 1.5	30.5 ± 1.0	13.8 ± 0.4	43.3 ± 1.5	30.5 ± 1.0	-	-	300	
b	39.8 ± 1.3	69.6 ± 2.4	10.7 ± 0.3	10.7 ± 0.3	73.6 ± 2.6	58.0 ± 2.0	9.3 ± 0.3	9.3 ± 0.3	40.2 ± 1.4	34.0 ± 1.1	8.2 ± 0.2	40.2 ± 1.4	34.0 ± 1.1				
d	39.7 ± 4.1	61.2 ± 5.9	<1.5	<1.5	64.3 ± 6.1	55 ± 5	0.7 ± 0.1	0.7 ± 0.1	27.9 ± 3.1	25.2 ± 2.5	0.9 ± 0.1	27.9 ± 3.1	25.2 ± 2.5				

a = EPA 3052; b = EPA 3050B; c = INAA; d = BCR-700

equilibrium has been reached between  $^{226}\text{Ra}$  and its decay products of short half-life. The  $^{226}\text{Ra}$  activities were determined by taking the mean activity of its daughter nuclides:  $^{214}\text{Pb}$  at 295 keV and 352 keV, and  $^{214}\text{Bi}$  at 609 keV. The  $^{228}\text{Ra}$  was determined by measuring the 911 and 968 keV gamma-ray peaks from  $^{228}\text{Ac}$ . The concentration of  $^{210}\text{Pb}$  was determined by measuring the intensity of the 46.5 keV peak. Self-absorption correction was applied to  $^{210}\text{Pb}$  since the attenuation for low energy gamma rays is highly dependent upon sample composition. The approach used was suggested by Cutshall et al. [17].

The total concentration of the radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{210}\text{Pb}$  in the leaching solution, obtained with mild extraction with EDTA [11], was determined by the measurement of the gross alpha and beta counting after a radiochemical separation of the elements of interest. The chemical procedure consists in an initial precipitation of Ra and Pb with 3 M  $\text{H}_2\text{SO}_4$ , dissolution of the precipitate with nitrilotriacetic acid at basic pH, precipitation of  $\text{Ba}(\text{Ra})\text{SO}_4$  with ammonium sulphate and precipitation of  $^{210}\text{PbCrO}_4$  with 30 % sodium chromate. The  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  concentrations were determined by measuring the gross alpha and beta activity of the precipitate  $\text{Ba}(\text{Ra})\text{SO}_4$  and the concentration of  $^{210}\text{Pb}$  was determined through its decay product  $^{210}\text{Bi}$ , by measuring the gross beta activity of the precipitate of  $^{210}\text{PbCrO}_4$ . Both radionuclides were measured in a low background gas flow proportional detector for 200 min. The activity concentration of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  were measured after 21 days of the radium precipitation and the concentration of  $^{210}\text{Pb}$  after 10 days of the precipitation of Pb as chromate. The measurement accuracy and precision were assessed by measuring the reference material of International Atomic Energy Agency, IAEA-326 radionuclides in soil. The relative accuracy achieved was 2.2 % ( $^{226}\text{Ra}$ ), 4.7 % ( $^{228}\text{Ra}$ ) and 6.6 % ( $^{210}\text{Pb}$ ). The relative precision achieved was 3.4 % ( $^{226}\text{Ra}$ ), 7.6 % ( $^{228}\text{Ra}$ ) and 5.6 % ( $^{210}\text{Pb}$ ).

#### Availability of metals and radionuclides

In order to evaluate the availability of the elements and radionuclides present in the PG and fertilizers to the soil, the mild extraction with EDTA [11] was applied to the samples. This methodology is based on a mild leaching of the elements with EDTA as ammonium salt solution at pH 7. The final leaching solution was filtered and used for the determination of the elements and radionuclides, according to the procedures already described.

## Results and discussion

The samples analyzed in this study come from the three main fertilizers producers, Copebras, Ultrafertil and

Fosfertil. The results obtained for the total concentration and available fraction of metals in PG and fertilizers samples are presented in Table 1 and Fig. 1, together with the maximum limits established by MAPA and soil prevention level values suggested by CETESB.

The total concentrations of Hg and Se observed in the PG samples and fertilizers were always below the detection limits of the methodology used. The concentration of As in the PG samples were below the detection limits of the methodology used, for the fertilizers the results were below the maximum limit for fertilizers ( $10 \text{ mg kg}^{-1}$ ).

Similar behavior was found for Cd and Pb, the concentrations obtained by using the methodologies EPA3050B and mild extraction with EDTA are similar for all the samples analyzed and very low (Fig. 1), giving evidence that these elements are not available to the environment. The total concentrations obtained by using the methodology EPA 3052, drastic attack with HF, was higher for all the fertilizers compared with PG, particularly Cd content in the fertilizers TSP and SSP from Copebras, which results are above the limit established by MAPA for this metal in soil conditioner.

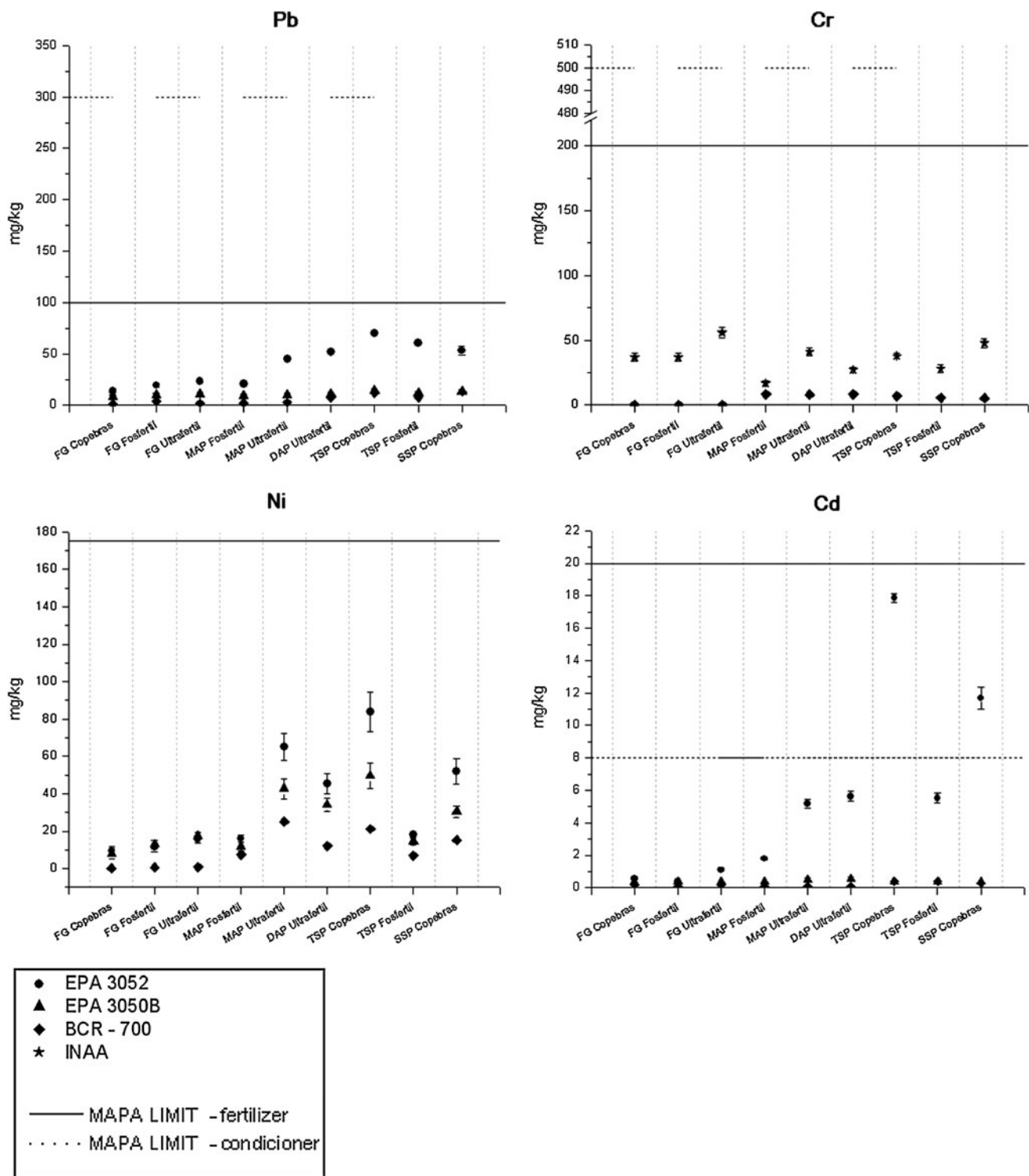
The differences observed in the total concentration of Cd, Cr, Ni and Pb obtained by using the methodologies EPA 3052 and EPA 3050B, (Fig. 1) especially in the fertilizers TSP and SSP, can be explained by the chemical industrial process, which involves an attack of the phosphate rock with sulfuric acid. Small amount of the phosphate rock, which did not react with the sulphuric acid, is still present in the fertilizers. The metals present in this phosphate rock are only dissolved with the drastic digestion (HF on a microwave) compared with the mild acid attack aperture.

Cu is considered as an essential element, important in the photosynthesis of plants. In all the samples analyzed, this metal presented similar concentrations, for all the methodologies used (EPA 3052, EPA 3050B and mild extraction with EDTA), confirming the high solubility of this element. The only exception was the fertilizer TSP from Copebras, which presented concentration above the soil prevention level from CETESB.

The concentrations of Co obtained in the PG samples using the mild extraction with EDTA were the same as the total concentration, whereas, for the fertilizers samples the results were slightly lower, indicating that such element, although present in the fertilizers, is not completely available to soil. The element Co is more enriched in the fertilizers than in the PG samples.

The results obtained for the Cr concentration using the mild leaching was lower than the total concentration for PG and fertilizers, therefore, this element although present in the samples analyzed is not available to the environment.

The low concentration observed for Ni, in PG and fertilizers, using the leaching with EDTA showed that this



**Fig. 1** Concentration (mean value ± expanded uncertainty) of Pb, Cr, Ni and Cd obtained by different methodologies and maximum limit for fertilizer and soil conditioner from MAPA

element is slightly available to the soil. The concentrations are below the maximum limit established by MAPA and the soil prevention level suggested by CETESB. The total

Ni concentration, obtained for the fertilizers from Ultrafertil (MAP and DAP) and from Copebras (TSP and SSP) are above the soil prevention level suggested by CETESB.

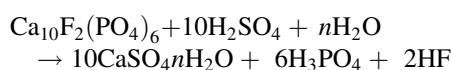
**Table 2** Radionuclides concentration and labile fraction (Bq kg<sup>-1</sup>) (mean value ± expanded uncertainty) in phosphogypsum (PG) and phosphate fertilizers (MAP, DAP, TSP and SSP)

Radionuclides	Copebrás A			Ultrafértil C			Fosfertil B		
	SSP	TSP	PG	MAP	DAP	PG	MAP	TSP	PG
Ra-226									
e	720 ± 96	546 ± 10	744 ± 138	9 ± 1	5 ± 1	344 ± 65	10 ± 4	105 ± 28	186 ± 46
d	11 ± 0.4	99 ± 3	16 ± 0.7	<0.02	<0.02	4.2 ± 0.2	<0.02	2.6 ± 0.2	1.5 ± 0.2
Ra-228									
e	196 ± 33	157 ± 24	242 ± 23	126 ± 11	48 ± 5	219 ± 40	293 ± 74	189 ± 13	151 ± 27
d	9.2 ± 0.1	72 ± 6	45 ± 4	20 ± 2	17 ± 1	16 ± 2	25 ± 4	24 ± 3	22 ± 4
Pb-210									
e	1084 ± 106	904 ± 60	1061 ± 132	40 ± 2	<19	347 ± 44	<19	175 ± 54	182 ± 46
d	75 ± 2	316 ± 04	26 ± 1	<0.05	<0.05	17 ± 1	<0.05	29 ± 1	12 ± 1

*d* BCR-700, *e* gamma spectrometry

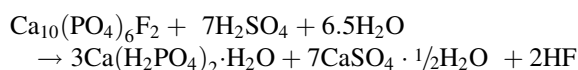
The Zn concentrations obtained in all the samples analyzed, by using the three methodologies, are similar, indicating that this element is completely available to the environment.

The results obtained for the total concentration and available fraction of the radionuclides in PG and fertilizers samples are presented in Table 2. The results obtained for the total concentration of <sup>226</sup>Ra, <sup>228</sup>Ra and <sup>210</sup>Pb show that these radionuclides are present in higher concentrations only in the PG and fertilizers SSP and TSP. The production of phosphoric acid can be described by the following reaction:

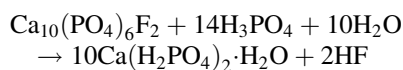


Since Ra isotopes and Pb form insoluble compounds with sulphates, they will concentrate in the final product of the reaction: calcium sulphate (PG).

During the chemical attack of the phosphate rock, different compounds can be formed, depending upon the experimental conditions and the stoichiometry of the reaction. SSP is formed by reacting sulphuric acid with phosphate rock, according to the reaction:



In the production of TSP, phosphoric acid reacts with apatite, according to the reaction:



In both cases, most of Ra and Pb will be present in the SSP and TSP.

The concentration of <sup>226</sup>Ra, <sup>228</sup>Ra and <sup>210</sup>Pb found in the labile fraction, on the other hand, is less than 10 % of the total available content of these radionuclides in PG.

A possible explanation for such behavior is that the radium and Pb in the PG precipitate with barium sulfate instead of calcium sulfate in the chemical reaction, forming insoluble compounds. Similar behavior was observed by Santos et al. [18], who performed a sequential extraction of Brazilian PG and found that most of the radium and lead are located in water insoluble (non-CaSO<sub>4</sub>) fraction. In the case of the fertilizers SSP and TSP, the concentration found for the radionuclides in the labile fraction presented slightly higher values, indicating that in these samples the radionuclides are more available to the environment. The concentration of <sup>226</sup>Ra, <sup>228</sup>Ra and <sup>210</sup>Pb found in the labile fraction of the fertilizers MAP and DAP is negligible.

## Conclusion

In general, the total concentration obtained for the metals using methodologies with different initial digestion (strong attack with acids and HF and mild attack with nitric acid) are slightly different. The results obtained using the methodology with mild leaching showed that the metals and radionuclides are not available to the environment, giving evidence that the application of PG in agriculture is safe as far as contamination by such elements is concerned. In all the cases, PG presented metals concentration lower than the phosphate fertilizers. The results obtained for the PG samples using all the methodologies are below the limits established by MAPA for As, Cd, Cr, Hg, Ni, Pb and Se; and below the soil prevention values suggested by CETESB.

The concentrations of As, Cd, Cu, Ni, Pb and Zn in PG were lower than the ones observed in the phosphate fertilizers most used in Brazil.

The fertilizers from Copebras (TSP and SSP) presented higher Cd concentrations (above the limits adopted for soil



conditioners), when the samples were treated with strong attack and HF.

The methodologies used gave different results for the total metals concentration in the PG and fertilizer samples, depending upon the initial attack of the samples, showing the necessity of establishing a specific methodology for the analysis of this type of samples.

The radionuclides, although present in the PG and the fertilizers SSP and TSP are not available to the environment.

The Brazilian PG has been used as soil conditioner since a long time. The results obtained in this paper for the metals and radionuclides concentration in PG showed that its utilization is safe. However, for an adequate application of the limits adopted, it is necessary to establish specific methodologies for the determination of the total concentration and the labile fraction of the elements in PG and fertilizers samples; since the results obtained are strongly affected by the methodology chosen.

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