E3S Web of Conferences 1, 04005 (2013)
DOI: 10.1051/e3sconf/20130104005

Distribution of potentially toxic elements in the Brazilian phosphogypsum and phosphate fertilizers

C. H. R. Saueia[1,2], B. P. Mazzilli[1], F. M. Le Bourlegat[1] and G. J. L. Costa[2]

[1] Laboratório de Radiometria Ambiental, Instituto de Pesquisas Energéticas e Nucleares, Av Lineu Prestes 2242 CEP05508-000 São Paulo, Brazil, chsaueia@ipen.br, mazzilli@ipen.br, fe_melo@hotmail.com
[2] Universidade Nove de Julho, Av. Dr. Adolpho Pinto, 109 Barra Funda, Brazil, glcosta@ipen.br

Abstract. 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) as by-product. Phosphoric acid is the raw material for the production of phosphate fertilizers (SSP, TSP, MAP and DAP). Phosphogypsum waste is stored in stacks, since its level of impurities (metals and radionuclides among others) prevent its safe reutilization. However, part of this waste is used to improve fertility of agricultural soils. The main aim of this paper is to determine the levels of potentially toxic elements in phosphate fertilizers and phosphogypsum produced in Brazil. The elements Co and Cr were analyzed by instrumental neutron activation analysis and As, Cd, Cu, Hg, Ni, Pb, Se and Zn were analyzed by ICP-OES. The results obtained are lower than the limits established by the Brazilian regulatory agency for metals in fertilizers and soil conditioner.

Key words: Phosphogypsum, phosphate fertilizers, metals

Introduction

Phosphate fertilizers produced in Brazil are obtained by wet reaction of the igneous phosphate rock with concentrated sulphuric acid, giving as final product phosphoric acid and dehydrated calcium sulphate (phosphogypsum) as by-product. Phosphoric acid is the basic material for the production of phosphate fertilizers triple superphosphate (TSP), single superphosphate (SSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP).

Phosphogypsum (PG) waste is stored in stacks, since its level of impurities (metals and radionuclides among others) prevent its safe reutilization.

The presence of natural radionuclides in the Brazilian phosphate mineral ores and their redistribution in products and by-products is well known (Mazzilli et al., 2000; Saueia & Mazzilli, 2006; Mazzilli et al., 2011). However, few data is available concerning the distribution of metals in the phosphate industry (Saueia et al., 2012).

Fertilizer industries generated about $170x10^3$ tons worldwide of PG annually and all the countries that produce phosphate fertilizers by wet process are facing the same problem of finding solutions for the safe application of PG, in order to minimize the impact caused by the disposal of large amounts of this by-product.

In Brazil the phosphate industry generates about 5.5 10^6 ton of PG per year; part of this waste has been used to improve fertility of agricultural systems. Therefore, it is important to analyse the concentration of metals in the phosphate fertilizers and phosphogypsum.

Some trace elements such as copper (Cu) and zinc (Zn) are essential to plant growth and are called micronutrients. However, these elements can be toxic in high concentrations. Cobalt (Co) and selenium (Se) are not essential to plant growth but are required by animals and humans. Cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), mercury (Hg) and arsenic (As) are considered as toxic elements and are reported to cause contamination of soil, water and food chains (He et al., 2005).

Although fertilizers provide nutrients to crops, they can contain also elements, such as toxic metals, that are potentially harmful for the environment.

In recent years, some countries have set tolerance limits for some elements in fertilizers and supplements, e.g., Canada has limited maximum contents for several heavy metals (Canadian Food Inspection Agency, 1997), some states of US have adopted the same threshold values (U.S. EPA, 1999) and in Brazil, maximum metal concentrations in fertilizers and soil conditioner are regulated by the Brazilian regulatory agency (MAPA - Instrução Normativa, 2006).

In the international literature several papers reported the presence of heavy metals in P fertilizers and the input into agricultural systems (López et al., 2007; Al-Masri et al. 2004; He et al., 2005).

The main aim of this paper is to evaluate the distribution of metals in phosphate fertilizers and PG produced in Brazil, by the three main industries, named A, B and C. The elements Co and Cr were analyzed by instrumental neutron activation analysis (INAA) and As, Cd, Cu, Hg, Ni, Pb, Se and Zn were analyzed by ICP-OES.

Materials and Methods

INAA is based on the reaction between neutrons and a target nucleus. The neutron is captured by the nucleus and produces a radioactive nucleus. This excited nucleus decays according to its half-life time and emits gamma-radiation which can be detected by gamma spectrometry. The spectrometer used was a hyper-pure germanium detector from Eurisys Measures, with resolution of 1.8 keV for the 1332 keV ^{60}Co photopeak and 15% efficiency.

The determination of the elements was carried out by irradiation of approximately 150 mg of each sample, during 16 hours at a neutron flux of 10^{12} n.cm^{-2}s^{-1}, at Instituto de Pesquisas Energéticas e Nucleares (IPEN) nuclear research reactor IEA-R1.

For the determination of the elements As, Cd, Cu, Hg, Ni, Pb, Se and Zn the samples were treated following the USEPA 3052 method, which consist of a strong acid attack in a microwave and measurement of the concentrations using ICP-OES. The standard reference materials Soil-7 (IAEA) and SRM 2709 – San Joaquin Soil (NIST) were used to evaluate the precision and accuracy of both methodologies.

Results and Discussion

The concentration obtained for the elements Co, Cd, Cr, Cu, Ni, Pb and Zn are presented in Table 1. The concentration of As, Hg and Se were below the detection limits, with values <0.9 for As, < 1.2 for Hg and < 0.2 for Se.

Accuracy and precision were evaluated and the results are presented in Table 2 for the reference materials analyses by INAA and ICP-OES. In general, relative standard deviation and relative error were lower than 10% proving the precision and accuracy of the techniques used.

Table 1. Concentration of the elements in samples of phosphate fertilizers and phosphogypsum (μg g^{-1}).

Elements	Co	Cr	Cd	Cu	Ni	Pb	Zn
TSP A	23.8±0.9	38±2	17.8 ± 0.3	81.8 ± 1.8	83.9 ± 10.4	70.0 ± 2.4	78.8 ± 2.8
SSP A	11.7±0.5	48±3	11.7 ± 0.7	47.4 ± 1.0	51.9 ± 6.7	53.3 ± 4.2	42.2 ± 1.4
PG A	0.8±0.03	37±3	< 1.5	12.5 ± 0.3	9.4 ± 2.6	14.0 ± 1.6	11.6 ± 0.3
TSP B	9.9±0.3	28±3	5.5 ± 0.3	16.7 ± 0.4	18.2 ± 1.8	60.6 ± 2.2	30.5 ± 1.0
MAP B	13.5±0.4	17±2	1.8 ± 0.1	24.9 ± 0.5	16.1 ± 1.9	20.8 ± 1.3	43.3 ± 1.5
PG B	1.0±0.03	37±3	< 1.5	9.8 ± 0.3	11.2 ± 2.3	19.4 ± 1.3	13.8 ± 0.4
MAP C	16.6±0.5	41±3	5.2 ± 0.3	53.3 ± 1.1	65.1 ± 7.1	45.1 ± 1.6	58.9 ± 2.0
DAP C	14.9±0.6	14.9±0.6	5.6 ± 0.3	34.6 ± 0.7	45.3 ± 5.2	51.6 ± 2.0	48.8 ± 1.7
PG C	1.7±0.05	56±4	< 1.5	13.7 ± 0.4	15.5 ± 1.9	23.3 ± 1.2	15.1 ± 0.5

Table 2. Relative standard deviation (RSD) and relative error (RE) for standard reference material Soil-7using INAA and for standard reference material SRM 2709 using ICP-OES.

Element	Certified Values (µg g^{-1})	Calculated Values (µg g^{-1})	RSD (%)	RE (%)
Soil-7 (IAEA)				
Co	8.9±0.9	8.3±0.2	2.4	6.7
Cr	60±13	65.8±6.7	10	9.6
SRM 2709 – San Joaquin Soil				
Cd	0.38±0.01	<1.5	-	-
Cu	34.6±0.7	37.5±0.2	0.53	8.4
Ni	88±5	88.2±1.4	1.6	0.2
Pb	18.9±0.5	18.3±1.4	7.6	3.1
Zn	106±3	106.8±3.8	3.5	0.7

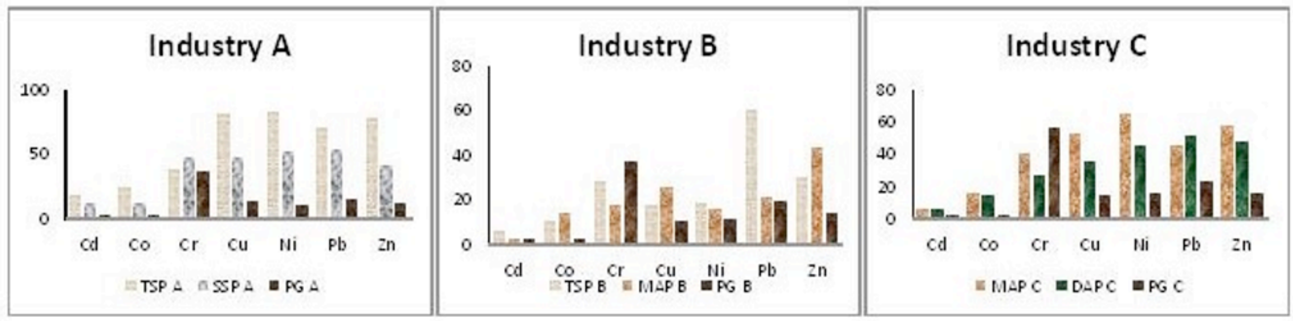

Fig. 1. Concentration of metals in samples of phosphogypsum and phosphate fertilizers (SSP, TSP, MAP, DAP) in µg g^{-1}.

The distribution of the metals concentration in the phosphate fertilizers and phosphogypsum are presented in Figure 1.

The concentration of the metals studied was higher for all the fertilizers, particularly in SSP and TSP compared with PG. One exception is chromium which presents concentrations of the same order of magnitude in phosphate fertilizers and PG. The Brazilian regulatory agency (MAPA - Instrução Normativa, 2006), established maximum limits for metals in fertilizers: 10 µg g^{-1} for As, 20 µg g^{-1} for Cd, 200 µg g^{-1} for Cr, 0.2 µg g^{-1} for Hg and 100 µg g^{-1} for Pb, and in soil conditioner 20 µg g^{-1} for As, 8 µg g^{-1} for Cd, 500 µg g^{-1} for Cr, 2.5 µg g^{-1} for Hg, 175 µg g^{-1} for Ni, 80 µg g^{-1} for Se and 300 µg g^{-1} for Pb. The results obtained are lower than the limits established by MAPA for all fertilizers and PG studied.

Conclusion

The results obtained in this paper for the metals concentration in PG showed that its utilization is safe. The concentrations found in the PG are of the same order of magnitude of the results observed in the phosphate fertilizers and therefore it can be used as soil amendment without additional risk.

However, the long term contribution of metals concentration to agricultural lands is not easily quantified, since the quantity of metals spread along with fertilizers and PG in the agricultural fields depends upon the quantity of fertilizers and PG used, the type of crop and soil and the number of applications per year. Therefore, the data presented here can be used for studies of different scenarios of the application of Brazilian phosphate fertilizers and PG in agriculture.

Acknowledgements

The authors thank the financial support provided by CNPq grants nº 300835/95-7 and 150935/2010-2.

References

Al-Masri MS, Amin Y, Ibrahim S, Al-Bich F. Distribution of some trace metals in Syrian phosphogypsum. Applied Geochemistry. 2004; 19 :747-753.

Canadian Food Inspection Agency, Trade Memorandum, T-4-93. Standards for metals in fertilizers and supplements 1997.

He ZL, Yang X E, Stoffella PJ. Trace elements in agroecosystems and impacts on the environment. J.

Trace Elements in Medicine and Biology 2005; 19:125-140.
Instrução Normativa DAS 27, 05 de junho de 2006. Publicada no D.O.U do dia 09/06/2006, nº 110, seção 1, páginas 15 e 16. Anexo II referente a limites máximos de metais pesados tóxicos admitidos para fertilizantes minerais com nitrogênio, potássio, macronutrientes secundários, para os com até 5% de P_20_5 e para os demais não especificados no Anexo 1.
López RP, Valero AM, Nieto JM. Changes in mobility of toxic elements during the production of phosphoric acid in the fertilizer industry of Huelva (Spain) and environmental impact of phosphogypsum wastes. J Hazardous Materials 2007;148:745-750.
Mazzilli BP, Palmiro V, Saueia CHR, Nisti MB. Radiochemical characterization of Brazilian phosphogypsum. J. Environ. Radioact 2000; 49: 113-122.
Mazzilli B P, Saueia CH R, Jacomino V M F, Mello J W V. Natural radionuclides and metals intake into soya, corn and lettuce grown on soil amended with phosphogypsum. Int J Environ Anal Chem 2011; DOI:10.1080/03067319.2010.549339
Otero N, Vitória L, Soler A, Canals A. Fertilizer characterisation: Major, trace and rare earth elements. Applied Geochemistry 2005; 20: 1473-1488.
Saueia CHR, Mazzilli BP. Distribution of Natural Radionuclides in the Production and Use of Phosphate Fertilizers in Brazil. J. Environ. Radioact 2006; 89: 229-239.
Saueia CHR, Bourlegat FM, Mazzilli BP, Fávaro DIT. Availability of metals and radionuclides present in phosphogypsum and phosphate fertilizers used in Brazil 2012; J Radioanl Nucl Chem. in press.
U.S. E.P.A. Background report on fertiliser use, contaminants and regulations, EPA 747-R-98-003, 1999. Office of Pollution Prevention and Toxics, Washington (DC).