2009 International Nuclear Atlantic Conference - INAC 2009
Rio de Janeiro,RJ, Brazil, September27 to October 2, 2009
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
***ISBN:* 978-85-99141-03-8**

DETERMINATION OF REE AND U IN AGRICULTURAL SOILS FROM JAGUARI RIVER BASIN, SÃO PAULO, BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Uranium has the highest atomic weight of the naturally occurring elements. It is weakly radioactive and occurs naturally in low concentrations (a few parts per million) in soil, rock and water. The rare earth elements (REE) form the largest chemically coherent group in the periodic table. The versatility and specificity of the REE have given them a level of technological, environmental, and economic importance considerably greater than might be expected. The objective of this work was to determine the concentration of the lanthanides (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu), and U, considering the soil use and occupation from the Jaguari river basin, São Paulo. Instrumental Neutron Activation Analysis (INAA) was used for the REE and U analysis The study area is located in a traditional agricultural area which is nowadays one of the main industrial regions of Brazil. In order to evaluate the quality of these soils in relation to lanthanides and U levels, the obtained concentrations were compared to guiding values reported by environmental protection agencies. The 75th percentile for U in agricultural soils (2.76 mg kg^{-1}) was higher than in the control areas (1.61 mg kg^{-1}), but much lower than the maximum allowed concentration for soils in The Netherlands (28.3 mg kg^{-1}). The lanthanides presented concentration levels higher than the guiding values of the *RIVM - -National Institute for Public Health and the Environment* guidelines.

1. INTRODUCTION

Uranium has the highest atomic weight of the naturally occurring elements. It is weakly radioactive and occurs naturally in low concentrations (a few parts per million) in soil, rock and water. The rare earth elements (REE) form the largest chemically coherent group in the periodic table. Though generally unfamiliar, the REE are essential for many hundreds of applications. The versatility and specificity of the REE have given them a level of technological, environmental, and economic importance considerably greater than might be expected. Rare earth elements metals are a collection of seventeen chemical elements in the periodic table, namely scandium, yttrium, and the fifteen lanthanides.

Some of the lanthanides have established a solid footing in technology. For example, as components of alloys, Sm, Pr and Ce are used in magnetic materials, and La and Y serve as components of modern high-temperature superconductors. Others are used as catalysts for chemical reactions, or they are needed for the production of laser crystals. La, Ce and Nd are used in car catalysts, stabilizing the catalyst support (a γ-alumina based honeycomb) as they enhance the oxidation of pollutants. However, this increased industrial use also means that the lanthanides are present in higher levels in the environment. In China, one of the greatest

ISBN: 978-85-99141-03-8

producers of REE in the world, lanthanides have been used as fertilizers in agriculture since the 70 's [1], although the essentiality of these elements to mankind, plants and other living organisms are not yet well established. Investigations on the increasing concentration of lanthanides and uranium in the environment caused by industrial emissions and/or agriculture deposition (phosphate fertilizers) have generated toxicological essays to provide guide levels in soils and plants aiming to prevent impacts of these elements in the food chain [2].

Uranium presence in fertilizers is a consequence of the natural occurrence of this element in phosphate rocks usually employed as a source of phosphorous in phosphate fertilizer production. The fate of the uranium added to the agricultural soil by routine applications of phosphate fertilizers is not well known yet. However, continuous utilization of this type of fertilizer results in adsorption of a certain amount of minerals by plants, and therefore, this is a source of uranium in the human diet. The uranium concentration in Brazilian phosphate fertilizers ranges from 5.17 to 54.3 mg kg^{-1} [3].

There is no maximum concentration allowed for lanthanides and uranium in Brazilian soils. The National Institute of Public Health and the Environment - RIVM from The Netherlands has established maximum permissible concentrations of some REE [4] and uranium [5]. The objective of this work was to determine the concentration of the lanthanides (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu), and U, considering the soil use and occupation from the Jaguari river basin, São Paulo. Instrumental Neutron Activation Analysis (INAA) was used for the REE and U analysis. The study area is located in a traditional agricultural area which is nowadays one of the main industrial regions of Brazil.

2. MATERIALS AND METHODS

2.1 Sampling Strategy

The soils were divided in two groups: agricultural soils and pristine soils (control areas). Soil samples from agricultural (n=29) and pristine (n=20) areas were collected at the 0-20 cm depth, grinded, homogenized and placed in containers previously cleaned with 10% nitric acid and washed with deionized water. Each sampling point comprised a 10.000 m^2 area, which was selected by using a 15 km x 15 km matrix. A total of 10 sub-samples were collected from each area to give one (1) sample composite. The study area is located in Jaguari river basin, a tributary of the Piracicaba river in the State of São Paulo including the municipalities: Joanopolis, Piracaia, Vargem, Bragança Paulista, Pedra Bela, Pinhalzinho, Tuiuti, Amparo, Monte Alegre do Sul, Morungaba, Campinas, Moji Mirim, Santo Antonio da Posse, Jaguariuna, Cosmópolis, Limeira, Arthur Nogueira, Americana and Engenheiro Coelho. The soils samples belong to argisols and oxisols (Fig. 1).

ISBN: 978-85-99141-03-8

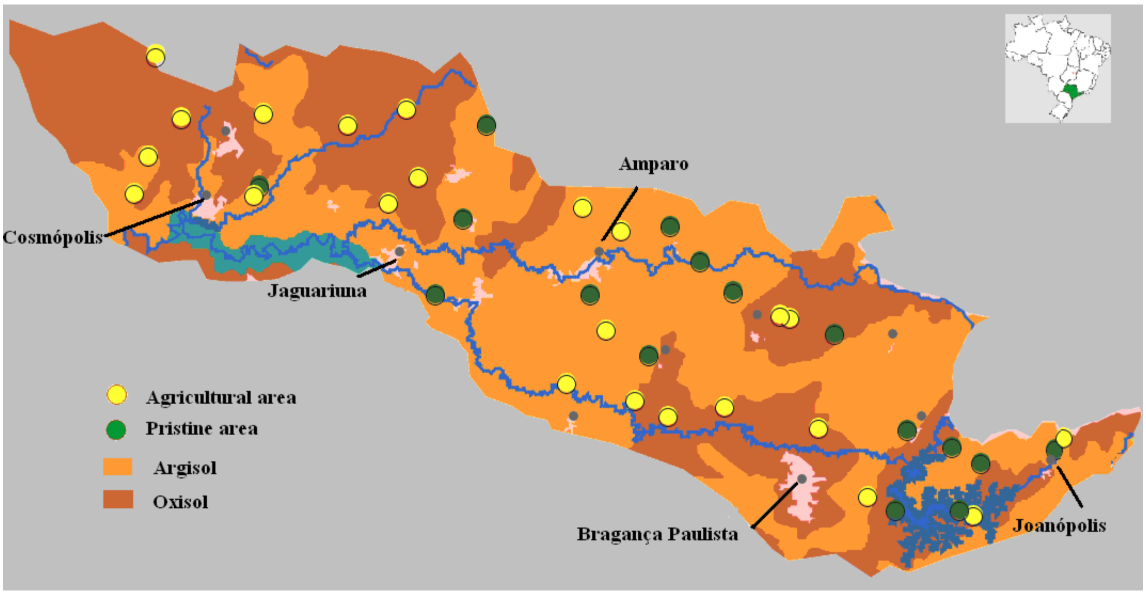

Figure 1. Soil samples location in Jaguari river basin.

2.2 Analytical procedure

For INAA, the samples and the certificate reference materials granite GS-N and basalt BE-N (mass approximately 100 mg) were packed in plastic bags, inserted in aluminum containers and irradiated for 8 hours at a thermal neutron flux of 10^{13} n cm^{-2} s^{-1} at the nuclear reactor IEA-R1 of the Instituto de Pesquisas Energéticas e Nucleares IPEN-CNEN/SP. The measurements of the induced gamma-ray activity were performed in an hyperpure Ge detector GX2020 CANBERRA, connected to a S-100 multichannel analyzer and to a personal computer. The resolution of the system was 1.90 keV for the 1332 keV gamma-ray of ^{60}Co. The gamma-ray spectra were processed using VISPECT software. Two series of counting were performed, the first one five days after irradiation, for the determination of La, Sm, Nd and Lu and the second one twenty days after irradiation, for the determination of Ce, Eu, Tb, Yb and U. The counting times were about 2 hours. The quality control of the results was made by analyses of the geological reference material Soil-7 (IAEA). The results showed good accuracy (relative errors to certified values < 5%) and good precision (relative standard deviations < 10%).

3. RESULTS AND DISCUSSION

The statistical comparison between the two groups of soils showed significant differences (Kruskal-Wallis p<0,05) for the concentrations of U, indicating that there is an increase in U levels in the studied agricultural soils (Tab.1), which may be associated to phosphate fertilizers. The 75th percentile for U in agricultural soils (2.76 mg kg^{-1}) was higher than in the control areas (1.61 mg kg^{-1}), but much lower than the maximum allowed concentration for soils in Netherlands (28.3 mg kg^{-1}).

ISBN: **978-85-99141-03-8**

There was no statistical difference for the lanthanides, thus indicating that there was no quality change in the agricultural soils for these elements. For Ce, the median concentrations in agriculture soils was of 81.64mg kg^{-1}, and in the control area was of 95.54 mg kg^{-1}, which were comparable to agricultural Chinese soils (mean 86 mg kg^{-1}) [6]. The maximum concentration allowed for Ce in soils, according to the *RIVM* guidelines is of 53 mg kg^{-1}. The *background* values for La (5.0 mg kg^{-1}), Ce (9.0 mg kg^{-1}), Sm (0.7 mg kg^{-1}), Eu (0.1 mg kg^{-1}), Tb (0.1 mg kg^{-1}), Yb (0.6 mg kg^{-1}) and Lu (0.11 mg kg^{-1}) in Dutch soils are lower than the ones obtained in the control area.

Table 1. REE concentration for pristine and agriculture soils in Jaguari river basin

Descriptive Statistics	Soil group	La	Lu	Ce	Nd	Eu	Sm	Tb	Yb	U
		................mg kg^{-1}..................								
maximum	Pristine	89,6	0,76	432,88	180,93	3,39	9,75	1,66	5,95	3,45
	agricultural	78,59	0,49	270,58	102,63	3,30	8,96	1,65	3,63	5,81
minimum	Pristine	5,5	0,13	27,82	7,44	0,34	0,92	0,2	0,66	0,24
	agricultural	3,34	0,12	25,75	2,63	0,19	0,6	0,24	0,66	0,5
median	Pristine	22,19	0,20	95,54	32,25	1,2	2,92	0,68	1,36	1,27
	agricultural	15,63	0,25	81,64	17,87	0,81	1,96	0,43	1,61	1,91
75 th	Pristine	28,80	0,3	140,43	55,86	1,9	4,41	0,96	1,8	1,61
	agricultural	26,89	0,3	131,4	32,79	1,19	3,5	1,06	1,94	2,76

4. CONCLUSIONS

The concentration for U in agricultural soils was higher than in the control areas, suggesting an influence of phosphate fertilizers. The lanthanides presented concentration levels higher than the guiding values of the *RIVM*. Despite the low increase of uranium in agricultural soils in the study area, more studies in other agricultural areas are necessary for the establishment of standards for soil quality in relation to uranium levels.

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