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SEQUENTIAL DETERMINATION of U and Th ISOTOPES, ^{226}Ra, ^{228}Ra, ^{210}Pb, and ^{210}Po in MUSHROOM

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ABSTRACT

For this study, mushroom samples were collected in Brazil at the São Paulo Metropolitan Region and at the Poços de Caldas Plateau (PC; a region of elevated natural radioactivity, which houses the first Brazilian uranium mine). This paper discusses a sequential methodology to determine natural series radionuclides in mushrooms, such as uranium (^{238}U and ^{234}U) and thorium (^{232}Th, ^{230}Th, and ^{228}Th) isotopes, radium-226, radium-228, as well as lead-210 and polonium-210; using Alpha Spectrometry, Gamma Spectrometry, and Total Alpha and Beta Counting. The method involves total sample dissolution in a closed system in order to avoid loss of Polonium and employment of specific chromatographic resins for radionuclide purification. A subsequent interpretation of the results can provide information on pollutants present in mushrooms and infer possible contamination in the areas sampled as well as allow an association of measured concentrations to radioactive anomalies in the Plateau.

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1. INTRODUCTION

Mushrooms have significant nutritional and medicinal value acting as antitumoral, antiviral, and as a reducing cholesterol agent. This foodstuff can accumulate toxic elements in general, including natural radionuclides, so that different mushroom species have different capacities to retain radionuclides. They may be employed as environmental biomonitoring indicators in order to evaluate contamination and quality of ecosystems [1, 2].

So far, little attention has been given to radioactivity content in mushrooms and the dose for the population due to ingestion.

The Poços de Caldas Plateau is located in Minas Gerais State, Brazil. It is an example of tectonic process in which an alkaline intrusion of more than 1 000 km^2 was elevated to a

height of 400 to 500 m above the adjacent granite substrate. The remaining of the intrusion is now shaped as a circular area of approximately 35 km in diameter.

An almost complete and deep decomposition of rocks, under sub-tropical conditions, along with weathering conditions, produced around 70 areas of radioactive anomaly. In contrast to metamorphic granites from coastal mountains, uranium and thorium are found separately in the Plateau; with uranium associated to zirconium and thorium associated to iron and manganese oxides.

The Plateau surface is composed of smooth elevations covered with vegetation. The region is used for pasture, and some cultures of potatoes, corn, beans, carrots and eucalypt trees. Annual precipitation at the Plateau is 1 700 mm, with 80% concentrated during the rainy season [3].

Several studies were conducted in this area regarding incorporation of radionuclides in agricultural products produced in the region and their risk associated with consumption, mainly in areas under the influence of mining activities, which have the ability to re-mobilize radionuclides and other pollutants such as heavy metals, making them available in the environment.

The first Brazilian uranium mining and milling plant (INB), which is being decommissioned, is located in the Plateau. Studies were conducted to evaluate transference of radionuclides to potatoes, beans, green leaves, and other products under INB influence. ^{226}Ra and ^{210}Pb concentrations were found to be similar to those in the North Hemisphere or at most 10 times higher.

Extensive research has been carried out since the 1970's regarding the content of essential trace elements and toxic elements in mushroom. After Chernobyl accident, determination of radionuclides in mushrooms was intensified, especially in Europe, since radionuclides accumulated in the fructification body of these fungi.

Kirchner & Daillant [4] verified the potential for mushroom to accumulate radionuclides, as well as heavy metal species; Szanto et al [5] verified that plant incorporation and soil/plant transference factors were elevated.

Analyses of mushrooms in different sampling locations revealed its possible use as monitors for biosphere contamination and its role in biogenic migration of radionuclides in soils and transfer through the food chain [6].

Mushrooms typically grow in forests and fields. However, almost all ecosystems (including deserts and tundra) will favor their growth in the correct substrate. A particular growth medium may consist, for example, of a tree portion in decomposition, open grasslands, animal fecal material, or areas under trees. Mushrooms can be divided into three groups: saprofits, which live and metabolize organic matter; parasites, which live in other species in a non-symbiotic relationship; and symbiotic, that lives through the use of underground mycorrhiza (symbiosis between certain fungi and plant roots) [7].

In terms of forest ecosystems, mushroom species have important functions in decomposition of plant materials and ability to accumulate and retain limiting/trace components from the soil [8, 9].

The potential of a mushroom to accumulate long lived radionuclides from fallout, such as ^{137}Cs, and in smaller extension ^{90}Sr, as well as heavy metal species, is well known. Since the 1960's, it is known that several mushroom species can accumulate radioactive cesium, silver, ruthenium, and natural potassium. However, little is known about transference of natural radionuclides to mushrooms, such as uranium and thorium, along with their decay products.

The objective of this study was to determine activity concentrations of ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{228}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb, and ^{210}Po in mushroom samples collected at the Poços de Caldas Plateau.

2. MATERIALS AND METHODS

2.1. Collection of mushroom samples

Samples of a wild mushroom species were collected and named PC samples. Their size was relatively small, 5 cm long, shaped like a hat. The samples were found in a humid area under some trees, nearby the CNEN/LAPOC Laboratory.

The second set of samples, named SP samples, was collected in a Greenhouse from São Paulo Metropolitan region, also relatively small (approximately 3 cm long). These samples were of an edible species.

2.2. Preparation of mushroom samples

Samples were washed with tap water and then deionized water to eliminate impurities that were collected along with the samples. They were dried in a hood with air circulation at 50 ºC during 48 hours. After drying, samples were grinded, sieved and stored in plastic flasks.

Figures 1 and 2 present pictures of mushroom samples and their preparation in the Laboratory.

Figure 1. Picture of mushrooms collected in the Poços de Caldas Plateau.

Figure 2. Preparation of mushroom samples collected in the Poços de Caldas Plateau.

2.3. Determination of Uranium and Thorium Isotopes

Uranium and thorium in mushroom samples were separated through specific resins Dowex 1 X 2 (strongly anionic) and UTEVA (from Eichrom Technologies; recovered by a tri-butyl-phosphate layer, TBP, which extracts uranium with formation of ionic bonds). ^{232}U and ^{229}Th were employed to monitor chemical recovery and correct results for better precision and accuracy. Samples were digested by means of an open digestion system and dissolved in 8M nitric acid medium.

The Dowex 1 X 2 resin was pre-conditioned with 8M HNO_3 to remove non-retained ions. Samples were percolated through the column with more addition of nitric acid. Thorium was eluted with concentrated hydrochloric acid. The solutions were then dried and electrodeposited for Alpha Spectrometry determination.

The UTEVA resin was pre-conditioned with 3M HNO_3. Eluates obtained through the Dowex resin separation were then percolated through a column containing the UTEVA resin. 9M HCl was employed to wash away thorium residues. Uranium elution was done with 0.01M HCl. The solutions were dried and electrodeposited.

2.4. Uranium and Thorium Electrodeposition

Both eluates obtained were evaporated and electrodeposited in polished silver planchets, under 1.0 A and 1.2 A current, for thorium and uranium, respectively.

Quantification of uranium and thorium isotopes were carried out by Alpha Spectrometry, with detector efficiency being determined through a certified alpha emitting source mixture from Analytics Inc. (Model SRS 63997-121).

2.5. Determination of ^{210}Po Activity

Polonium analyses were done according to the procedure described by Vadja et al [9]. Samples were digested in a closed digestion system with nitric acid. A standard ^{209}Po solution was added to correct for Polonium loss during the analysis. The final residue was dissolved in 1.5M HCl and 1.0 g of ascorbic acid was added to avoid interference of Iron ions. Polonium in an acid and reducing medium was spontaneously deposited in silver planchets, at an 80-90 ºC temperature range, during 4 hours under constant agitation. Alpha Spectrometry was then employed to determine ^{210}Po in mushroom samples.

2.6. Determination of ^{226}Ra, ^{228}Ra, and ^{210}Pb

Radium and Lead were subjected to a radiochemical separation procedure. ^{133}Ba was used as a carrier to determine Radium losses during the procedure. A known amount of stable Lead Nitrate was added at the beginning of determination to control ^{210}Pb losses.

Samples were digested in a closed digestion system with nitric acid and dissolved in acid medium, followed by simple precipitation with pH change. Radium was co-precipitated through a suspension of barium sulfate (seeding suspension). The micro-precipitate, $Ba(Ra)SO_4$, was filtered through a 0.45 µm millipore membrane. Lead was precipitated as $PbCrO_4$. Determinations were carried out through a Gas Flow Proportional Counting System, by Total Alpha and Beta Counting, for Radium and Lead, respectively.

2.7. Nuclear and Analytical Techniques

An Alpha Spectrometry System (Alpha Analyst from Canberra) was employed, with surface barrier detectors. For alpha and beta emitting radionuclides, a Gas Flow Proportional Counting System, Tennelec S5XLB from Canberra was employed.

An ICP/OES Inductively Coupled Plasma, from Varian, Model Liberty R2, was employed to determine ^{133}Ba, which was necessary in order to evaluate the recovery of Radium isotopes.

3. RESULTS AND DISCUSSION

Table 1 presents the results obtained for uranium and thorium isotopes, ^{226}Ra, ^{228}Ra, ^{210}Pb, and ^{210}Po in mushroom samples collected at the Poços de Caldas Plateau and São Paulo State. Chemical recovery values for all radionuclides were between 74 and 98%. As it can be observed, radionuclide content in mushroom samples collected at the Poços de Caldas Plateau (PC) was much larger than the content found in São Paulo (SP) samples. They are at a minimum 10 times higher than SP activity concentrations, for each radionuclide. Preliminary results indicated that mushrooms are probably appropriate bioindicators for radioactivity levels in areas with elevated natural radioactivity. However, it is necessary to collect a larger number of PC and SP samples to prove this trend.

^{234}U and ^{238}U activity concentrations are an average of 17 times greater than ^{235}U concentrations and U isotopes found in SP samples. ^{230}Th concentrations in PC samples are approximately 20 times greater than SP mushroom samples. ^{226}Ra concentration in PC samples was found to be three times greater than SP concentrations. ^{228}Ra concentration in PC samples was at least 3 times higher than SP samples. ^{210}Pb found in PC samples, was 6 times greater than concentration in SP samples, as well as ^{210}Po. ^{210}Pb and ^{210}Po were considered to be in equilibrium for PC and SP samples.

Table 1. Results for Radionuclides in Mushroom

Radionuclide	Mushroom samples from PC Plateau (Bq kg^{-1})	Mushroom samples from SP (Bq kg^{-1})
^{234}U	18.8 ± 5.5	< 0.27
^{235}U	0.72 ± 0.28	< 0.06
^{238}U	16.7 ± 4.6	< 0.02
^{228}Th	20.4 ± 1.4	1.1 ± 0.4
^{230}Th	10.5 ± 0.8	< 0.15
^{232}Th	11.7 ± 0.9	< 0.12
^{226}Ra	42.0 ± 6.0	16 ± 4
^{228}Ra	34.0 ± 4.0	<10
^{210}Pb	57.0 ± 6.0	9 ± 1
^{210}Po	48.6 ± 7.6	8.02 ± 0.99

A study conducted by Baeza et al (2006) [1] reported ^{234}U and ^{238}U activity concentration levels of less than 3 Bq kg^{-1}, which was inferior to the activity concentrations found for PC mushroom samples in this study. Soils were also analyzed and it was verified that almost all Uranium and thorium were transferred from the soil to the fruiting mushroom body. ^{230}Th activity concentration levels were inferior to 3 Bq kg^{-1} [1], which were also inferior to those levels found for PC samples, in this study.

A French study reported ^{210}Pb concentrations in the range of 1.76 to 36.5 Bq kg^{-1} [4], which was inferior to the concentration found in PC samples. Lead uptake in mushrooms mainly originates from direct uptake of ^{210}Pb present in the soil.

Skwarzec & Jakusik (2003) [2] reported ^{210}Po activity concentration levels of 17 Bq kg^{-1}, almost 3 times inferior to levels found in mushroom PC samples. No reference was found for ^{226}Ra levels in mushrooms.

4. CONCLUSIONS

Preliminary results showed that radionuclide levels found in mushroom samples collected at the Poços de Caldas Plateau were always superior to the levels found in São Paulo State mushroom samples. This finding can be employed as a bio-monitoring tool to identify natural radioactive anomaly areas. The mushrooms from the PC Plateau can be considered as adequate bio-indicators, since they are wild species, offering an easy material to collect, prepare, and process.

It is important to mention that the fraction of radionuclides capable of transfer to fruiting mushroom bodies would be that fraction not strongly bound to the soil particles, present in the exchangeable and dilute-acid soil fractions. Further radionuclide analysis in PC and SP soils will be performed to enrich this study.

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REFERENCES

1. A. Baeza; F. J. Guillén; A. Salas; J.L Manjon. “Distribution of radionuclides in different parts of a mushroom: Influence of the degree of maturity”. *Science of the Total Environment*. **Vol. 359**. pp. 255-266 (2006).

2. B. Skwarzec; A. Jakusik. “210Po bioaccumulation by mushrooms from Poland”. *J. Environ. Monitoring*. **Vol.** 5. pp. 791-794 (2003).

3. L. M. H. Vasconcellos; E. C. S. Amaral; M. E. Vianna; E. P. Franca. "Uptake of ^{226}Ra and ^{210}Pb by food crops cultivated in a region of high natural radioactivity in Brazil". *J. Environ. Radioactivity*. **Vol. 5.** pp. 287-302 (1987).

4. G. Kirchner; O. Daillant. "Accumulation of ^{210}Pb, ^{226}Ra, and radioactive cesium by fungi". *Science of the Total Environment*. **Vol. 222**, pp. 263-270 (1998).

5. Z. Szanto; M. Hult; M.Watjen; T. Altzitzoglou. "Current radioactivity content of wild edible mushrooms: a candidate for an environmental reference material". *Journal of Radioanalytical and Nuclear Chemistry*. **Vol. 273**. Nº 1, pp. 167-170 (2007).

6. G. Winkelmann; D. R.Winge. "Transition metal ion uptake in yeasts and filamentous fungi – accumulantion of radionuclides in fungi". *Mental Ions in Fungi*. CRC Press. **Vol. II**. pp. 259-272 (1994).

7. M. C. Duff; M. L. Ramsey. "Accumulation of Radiocesium by mushrooms in the environment: a literature review". *Journal of Environment Radioactivity*. **Vol. 99**, pp. 912-932 (2008).

8. T. Ban-Nai; Y. Muramatsu; S.Yoshida; S. Uchida; S. Shibata; S. Ambe; F. Ambe; A. Suzuki. "Multitracer studies on the accumulation of radionuclides in mushrooms". *J. Radiat*. **Vol. 38**. pp. 213-218 (1997).

9. N. Vadja; J. L. Rosa; R. Zeisler; P. Danesi; G. Kis-Benedek. "A Novel Technique for the Simultaneous determination of ^{210}Pb and ^{210}Po Using a Crown Ether". *J. Environ. Radioactivity*. **Vol. 37.** No.3. pp.355-372 (1997).