2007 International Nuclear Atlantic Conference - INAC 2007
Santos, SP, Brazil, September 29 to October 5, 2007
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR – ABEN

^{137}Cs AND ^{40}K ESTIMATE IN EDIBLE MUSHROOMS IN SÃO PAULO, BRAZIL

Lilian Pavanelli de Castro[1], Vera A. Maihara[1], Patrícia L. C. Moura [1] and Rubens C. L. Figueira [2]

[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
Cep:05508-000 São Paulo, SP, Brasil
lilian.pavanelli@terra.com.br
vmaihara@ipen.br
patricialandim@ig.com.br

[2] Universidade Cruzeiro do Sul
Rua Dr° Ussiel Cirilo, 225, São Paulo,SP, Brasil
figueiraru@yahoo.com.br

ABSTRACT

After the Chernobyl accident in 1986, high levels of the radionuclide accumulation in different foodstuffs and the environment have being reported. The potential of mushrooms to accumulate fallout radionuclides in their fruit-bodies have been well recognized. Mushrooms can also accumulate toxic elements in general, including natural radionuclides. In Southern Hemisphere countries, especially in Latin America, there are a few studies on this subject. In Brazilian literature, there are no studies that determine the composition of natural and artificial radionuclides in edible mushrooms. The objective of this study was to measure of ^{137} Cs and ^{40}K activity in commercialized edible mushrooms in São Paulo, Brazil. The activity measurements were carried out by spectrometry gamma. The system detection efficiency was measured using the certified reference materials IAEA-300 Marine Sediment and IAEA-375 Soil. The activities of ^{137}Cs in the mushroom samples varied from 2.2 to 6.5 Bq kg^{-1} for *Pleurotus osteatus* and *Agaricus bisporus* respectively. The ^{40}K activities varied from 150 to 907 Bq kg^{-1} for *Pleurotus ostreatus* and *Lentinula edodes,* respectively.

1-INTRODUCTION

High radionuclide levels in mushrooms have being reported after the Chernobyl accident in 1986 [1]. In European countries an intensive research activity has been focused to verify the artificial radionuclide contamination levels due to this accident [2]. The environmental biomonitoring has demonstrated that diverse organisms such as crustaceans, fish and mushrooms are useful to evaluate the contamination and quality of the ecosystems [3-4].

Particularly, different species of mushrooms have a high capacity to retain radionuclides and toxic elements from the soil as reported by Giovani [5], Íngaro [6], Ruhm [7]. Several radionuclides can be accumulated in mushrooms, including ^{137}Cs and ^{40} K. ^{137}Cs is of specific interest in the environment due to its half life time (30.17 y), its easy migration in trofic chains and also to its biodisponibility [8]. Potassium is widely distributed in the nature, it is found in the soil, in all vegetable and animal tissues, presenting itself as an element of extreme importance for the brain and muscles. Approximately half the radioactivity found in humans comes from ^{40}K [9].

However, little attention has been given to the radioactivity content in mushrooms and the dose for the population due to its ingestion [10]. Currently, there are 2000 species of edible mushrooms known and about 25 are cultivated commercially [11]. In Brazil, the species more cultivated and consumed are: *Agaricus bisporus,* known as Champignon de Paris; *Lentinula edodes, as* Shitake; and *Pleurotus sp,* as Shimeji or Hiratake [12].

Mushroom ingestion in Brazil is very low, when compared to the European and Asian countries, where the consumption is high and the mushroom is one part of the eating habits. Studies have shown that these organisms have a significant nutritional value and as well as medicinal value acting as antitumoral, antiviral and reducing cholesterol agents [13].

In the Southern Hemisphere countries, specifically in Latin America, there are no studies on the natural and artificial radioactivity in mushrooms [14]. There is little information regarding the quality of the edible mushrooms cultivated by Brazilian producers. For this reason, it is important to investigate the contaminant levels present in edible mushrooms and verify the possible risks that this contamination can offer for consumers. The present study evaluated ^{137}Cs and ^{40}K content present in cultivated and consumed species of edible mushrooms in the state of São Paulo, Brazil.

2. MATERIALS AND METHODS

2.1 Sampling

The edible mushroom samples were acquired in different commercial points of São Paulo metropolitan region, specifically in Municipal Markets. Some samples were acquired directly from producers located in some cities as Mogi das Cruzes, Mirandópolis, Suzano and Juquitiba.

The sample acquisition period was from November/2006 to March /2007. About 400g were colleted for each edible species. The edible mushrooms collected were from *Agaricus sp, Pleurotus sp* and *Lentinula sp* species. The whole mushroom was analyzed and no distinction were made distinctions between the parts of the mushrooms.

2.2 Analytical Procedure

2.2.1. Sample preparation

All the samples were clean and left submerged for 10 minutes in Milli-Q H_2O. After this, the water was thrown away and the mushroom samples were cut in small pieces with a plastic knife and put in Petri plates or plastic recipients. The samples were then freeze-dried for 10 to 15 hours in the Thermo Electron Corporat (Moduly Model) freeze-dryer. After the lyophilization, the samples were ground and homogenized in a domestic blender with Ti blades. These mushroom samples were stored in pre-cleaned polyethylene bottles with 65 mm of diameter and 19 mm of height and stored per approximately 20 days until the respective counting.

2.2.2 Equipment

The ^{137}Cs and ^{40}K gamma activities were measured by gamma spectrometry. The equipment for analysis consisted of Hiperpure Germanium detector (model POP TOP – EG&G ORTEC) with 1.9 keV resolution for the 1332.2 keV of ^{60}Co, this system is connected to an electronic system.

2.2.3 ^{137}Cs and ^{40}K analysis

To determine the low ^{137}Cs levels the methodology developed by Figueira [15] was applied. Consequently, the same methodology was used for the ^{40}K analysis. The adopted procedures consisted, initially, in an accumulating counting of background radiation (BG) counting of the empty plastic pot in intervals of 25000s, from 100000s to 200000s. Later, the reference materials, that were placed in the same geometry bottle and stored up to 20 days, were submitted to the same counting procedure for the BG, in order to calculate the detector efficiency.

Linear regression fits were made for the activity by counting time (BG and reference materials). Then, the detector efficiency was determined by the equation (1):

$$\varepsilon = \frac{a_{RM} - a_{BG}}{m_{RM} . A_{RM}} \qquad (1)$$

Where,

ε = detector efficiency for the 661.6 keV for the ^{137}Cs photopeak and 1460.8 keV for the ^{40}K;
a_{RM}; a_{BG} = angular coefficient of the regression curve for the reference material and BG;
m_{RM} = mass of the reference material in kilograms;
A_{RM} = activity of the reference material (Bq kg^{-1}), adjusted to the date of the analysis.

The same accumulative method used for the reference materials was used for the sample counting. The activities were determined from the equation (2):

$$A = \frac{a_S - a_{BG}}{m_A . t . \varepsilon} \qquad (2)$$

A = sample activity in Bq kg^{-1}

a_S, a_{BG} = angular coefficient of the regression curve for the sample and BG
m_A = sample mass in kg;
t = counting time in second;
ε = efficiency for the 661.6 keV for the ^{137}Cs photopeak and 1460.8 keV for the ^{40}K

3. RESULTS AND DISCUSSION

The detector efficiency was obtained from measurements of reference materials: IAEA-300, and IAEA-375. The efficiency values were 2% for 661.6 keV of ^{137}Cs photopeak and 0.18% for 1460.8 keV of ^{40}K photopeak. The reference material data used for the efficiency determination are described in Table 1.

Table 1: IAEA reference material data

Reference Material	Reference Date for Decay Correction	Material	Certificated value (Bq kg $^{-1}$)	
			^{137}Cs	^{40}K
IAEA –300	01/01/1993	Marine sediment	1066,6 (1046 –1080)	1059 (1046 –1226)
IAEA -375	31/12/1991	Soil	5280 (5200-5360)	424 (417-432)

For analytical method validation, the following reference materials were analyzed: IAEA-414, and IAEA-Mushroom. The IAEA Mushroom material was certificated in an Interregional Project INT/1/ 054 "Preparation of reference materials and organization of proficiency test rounds" [16]. The ^{137}Cs and ^{40}K activities obtained are presented in Table 2.

The results obtained are in good agreement with the reference values, the relative errors were in the order of 10%. The minimum detection concentrations (MDC) (IAEA, 1989) were calculated to both radionuclides, the results were 1.18 Bq kg^{-1} for ^{137}Cs and 46.2 Bq kg^{-1} for ^{40}K.

The edible mushroom samples analyzed in this study were the following species: *Agaricus sp*, *Pleurotus sp* and *Lentinula sp*. The ^{137}Cs and ^{40}K activities in the edible mushroom samples are presented in Table 3.

The ^{137}Cs activities varied from 2.2 to 6.5 Bq kg^{-1} dw and ^{40}K activities ranged from 150 to1227 Bq kg^{-1} dw. However, the ^{137}Cs activity values were below the minimum detection concentration in 42,8% of the samples. In this way, only some fungi samples, have demonstrated a special capacity of ^{137}Cs uptake. The results obtained were compared to the literature results, as are shown in Table 4.

Table 2: ^{137}Cs and ^{40}K activities (Bq kg^{-1}) in reference materials.

	Mushroom-IAEA			IAEA-414		
	This study	Certified Value	R E (%)	This study	Certified Value	R E (%)
^{137}Cs	3083 ± 180	2899 (2740 – 3058)$^{(1)}$	6.3	6.5 ± 0.4	5.14 (5 – 5.27)$^{(1)}$	26
^{40}K	1009 ± 76	1136 (1046 – 1226)$^{(1)}$	11	496 ± 45	480 (461 – 498)$^{(1)}$	3.3

(1) confidence interval

Table 3: ^{137}Cs and ^{40}K activity values in edible mushroom samples in dry weight

Sample	Commercial Name	Origin	Species	^{137}Cs (Bq kg^{-1})	^{40}K (Bq kg^{-1})
1	Porto Belo	São Paulo-SP	*Agaricus sp*	6.5 ± 0.4	1227 ± 112
2	Campignon	São Paulo-SP	*Agaricus bisporus*	<1.8	760 ± 69
3	Shimeji escuro	São Paulo-SP	*Pleurotus ostreatus*	4.9 ± 0.3	841 ± 77
4	Eryngui	São Paulo-SP	*Pleurotus eryngui*	<1.8	766 ± 70
5	Eryngui	Suzano-SP	*Pleurotus eryngui*	2.4 ± 0.1	786 ± 72
6	Hiratake	São Paulo-SP	*Pleurotus osteatus*	<1.8	687 ± 63
7	Salmão	São Paulo-SP	*Pleurotus ostreatus*	<1.8	150 ± 14
8	Salmão	São Paulo-SP	*Pleurotus ostreatus*	2.2 ± 0.1	554 ± 42
9	Shitake	São Paulo-SP	*Lentinula edodes*	<1.8	817 ± 74
10	Shitake	Juquitiba - SP	*Lentinula edodes*	5.1 ± 0.3	798 ± 73
11	Shitake	Mirandópolis-SP	*Lentinula edodes*	2.2 ± 0.1	440 ± 40
12	Shitake	Mogi das Cruzes-SP	*Lentinula edodes*	<1.8	907 ± 83
13	Shitake	São Paulo-SP	*Lentinula edodes*	3.5 ± 0.2	716 ± 65
14	Shitake	São Paulo-SP	*Lentinula edodes*	2.3 ± 0.1	867 ± 79

The ^{40}K activities obtained presented a symmetric distribution similar to those found in other studies. In this study this radionuclide was detected in 100% of the samples. The results seem to indicate the ^{40}K uptake is self-regulated, and it can also be a nutritional requirement for these organisms [10]. It has been proposed that the large variation found to the ^{40}K activity values in this and other studies can be related to geology, sample cultivation location, culture age, among others [17].

Table 4: ^{137}Cs and ^{40}K activities obtained in mushroom samples from different countries.

Reference	Bq. kg $^{-1}$		Region
	^{137}Cs	^{40}K	
This study	**2.2- 6.5**	**150 - 1227**	**São Paulo - Brazil**
Vaszari, et al,1992 [18]	3 - 714	704 - 2234	Hungary
Marzano, et al, 2001 [3]	2 - 732	---	Italy
Kuwahara, et al, 2004 [17]	291-7950	999 – 2670	Mount Fuji - Japan
Kirchner, et al , 1998 [19]	2.5 - 2763	---	France
Baeaza, et al, 2003 [10]	0.61 -121.7	468 -2670	Spain
Gaso, et al , 2000 [20]	0.2 - 91	18 - 257	Mexico

However, the ^{137}Cs activities in mushrooms cultivate in São Paulo were much lower compared with other countries (Table 4) where there has been more influenced of radionuclide contamination by nuclear releases and Chernobyl accident. It can be verified in the work of [1], the ^{137}Cs levels in mushrooms were much higher than in other agricultural products, even ten years after the Chernobyl accident.

4. CONCLUSION

The employed methodology in this study showed adequate to determine ^{40}K and ^{137}Cs activities in biological samples. All the activities obtained for both radionuclides in edible mushrooms cultivate in São Paulo were according to expected values to environment and do not offer a risk to consumers. The ^{137}Cs levels are according to South Hemisphere radioactive fallout from nuclear atmosphere tests occurred in the past.

Acknowledgment: The authors wish to thank the FAPESP, CAPES and IPEN/CNEN-SP for financial support.

REFERENCES

1. H. Sugiyama, H.Terada, H. Shibata, Y. Morita and F. Kato, "Radiocesium concentration in wild mushrooms and characteristics of cesium accumulation by the edible mushrooms (*Pleurotus ostreatus*)," *J.Health Sc.,* **v. 46(5)**, pp. 370-375 (2000).
2. P. Kalac, L. Svoboda, "A review of trace element concentrations in edible mushrooms," F*ood Chem.* **v.69**, pp.273-281 (1999).
3. F. N. Marzano, P. G. Bracchi, P. Pizzetti, "Radioactive and conventional Pollutants accumulated by edible mushrooms (Boletus sp) are useful indicators of species origin," *Environ.Res.*, **v. 85,** pp. 260-264 (2001).

4. C. A. Spodatto, “Impacto ambiental indicators”. *Committee of Environment. Brazilian Society of the Science of the Harmful Plants*, http://www.cnpma.embrapa.br/herbicidas/ (2007).
5. C. Giovani, P. L. Nimis, and R. Padovani, “Investigation of the performance of macromycetes as bioindicators of radioactive contamination. In “ *Transfer of Radionuclides in Natural and Semi – natural Environments*,” Desmet, Nassimbei and Belli*, Eds*, pp. 485-491, Elsevier, London (1990).
6. G. Íngaro, P. Bwlloni, and G. P. Santaroni, “Mushrooms as biological monitors of trace elements in the environment,” *J.Radional. Nucl.Chem.*, **v.161**, pp.163-120 (1992).
7. W. Ruhm, L. Kammerer, L. Hiersche and E. Wirth, “The 137 Cs/ Cs-134 ratio in fungi as indicator of the major mycelium location in forest soil,” *J.Environ.Radioact.,* **v. 35**, pp.129-134 (1997).
8. E. Malinowska, P. Szefer and R. Bojanowski, “Radionuclides conent in Xerocomus badius and other commercial mushrooms from several regions of Poland,” *Food Chem.*, **v. 97,** pp. 19-24 (2005).
9. M. Sanchez, S. Landsberger and J. Braisted, “Evaluation of 40K en food by determining total potassium using neutron activation analysis,” *J.Radional.Nucl.Chem.,* **v.269**, n°2, pp. 487-490 (2006).
10. A. Baeza, S. Hernàndez, J. F.Guillèn, G. Moreno, L. J. Manjòn and R. Pascual, “Radiocesium and natural gamma emitters in mushrooms collected in Spain.” *Sci.Total Environ.,* **v.318,** pp.59-71 (2004).
11. L. N. Coutinho, “Cultivo de espécies de cogumelo comestíveis, http://www.geocities.com/esabio.geo/cogumelo/agaricus.htm (2007).
12. A. F. Urben, H. C. B. Oliveira, W. Vieira, M. J. Correia and A. H. Uriartt, "Mushrooms production by means of modified Chinese technology," Brasília: Embrapa, p.151 (2001)
13. L. M. Jansson and L. Kutti, “Micronutrients in edible mushrooms*,” Human Nut.*. **v.5,** pp.1-8**.** (2004).
14. F. L. Melquiedes and C. R. Appoloni, “Natural radiation levels in powdered milk samples,” *Ciênc.Tecnol.Aliment.*, **v. 24** , n° 4, pp.501-504 (2004).
15**. R. C.** Figueira, L. R. N. Silva, A. M. G. Figueiredo and I. I. L. CUNHA, “Instrumental analysis by gamma spectrometry of low level Cs –137 in marine sample. In: Goiânia, Ten Years later.” *IAEA*, pp.239 –327 (1998).
16. A. Rahman, N. Siddique, S. Ahmad and M. Rosswbach, “Report on the proficiency tests exercise for radionuclides in mushroom reference material” – *Prepared for IAEA under IAEA Interregional Project INT/1/054*,(2006).
17. C. Kuwahara, A. Fukumoto, A. Ohsone, N. Furuya, H. Shibata, H. Sugiyama and F. Kato, “Accumulation of radiocesium in wild mushrooms collected from a Japanese Forest and cesium uptake by microorganisms isolated from the mushroom-growing soils,” *Sci.Total Environ.,* **v.345**, n°1-3, pp.165-173 (2005).
18. E. E.Vaszari, V. Tóth and S. Tarján, “ Determination of ratioactivities of some species of higher fungi,” *J. Radioanal. Nucl. Chem*, **v165(6)**, pp. 345-350 (1992).
19. G. Kirchner and O. Daillant, “ Accumulation of ^{210}Pb , ^{226}Ra and radioactive cesium by fungi,” *Sci.Total Environ.,***v 222**, pp.63-70 (1998).
20. M. I. Gaso, N. Segovia, O. Morton, M. L. Cervantes, L. Godinez, P. Peña and E. Acosta, “Cs and relationships with major and trace elements in edible mushrooms from México.” *Sci. Total. Environ.*, **v 262**, pp.73-89 (2000).