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Arsenic and cadmium content in edible mushrooms from São Paulo, Brazil determined by INAA and GF AAS

V. A. Maihara,[1]* P. L. Moura,[1] M. G. Catharino,[1] L. P. Castro,[1] R. C. L. Figueira[2]

[1] *Instituto de Pesquisas Energéticas e Nucleares- IPEN/CNEN-SP, Av. Prof. Lineu Prestes 2242, CEP: 05508-000 São Paulo, Brasil*
[2] *Universidade Cruzeiro do Sul – São Paulo, Brasil*

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Arsenic and cadmium contents in eight edible mushroom species (*Agaricus bisporus*, *Agaricus sp*, *Pleurotus ostreatus*, *Pleorotus florida*, *Pleorotus eryngui*, *Pleurotus osteatus*, *Pleurotus salmoneostramineus*, *Lentinula edodes*) consumed by Brazilian population were determined by instrumental neutron activation analysis (INAA) and graphite furnace atomic absorption spectrometry (GF AAS), respectively. Arsenic concentrations varied from 0.009 mg/kg in *P. eryngui* to 0.210 mg/kg dry weight in *L. edodoes* and Cd from 0.011 g/kg in *P. eryngui* to 0.229 mg/kg dw in *P. salmoneostramineus*. The consumption of mushrooms in São Paulo-Brazil may be considered safe from a toxicological point of view as As and Cd presented levels of ingestion below the maximum levels recommended by the World Health Organization.

Introduction

Since the beginning of mankind, mushrooms have been a part of the human diet, especially in Asia. Presently, there are around 2,000 catalogued edible species, however, only 25 of them are consumed on a regular basis.[1]

Edible mushrooms can be saprophytes, symbiontes and parasites of different plants. All need organic matter to grow (heterotrophic organisms) but the most commonly used for controlled production are the saprophytes. These mushrooms secrete enzymes to digest surrounding foodstuffs and obtain their nourishment from organic matter. The growth compost, that can be a mixture of hay, straw, corn cobs, water cotton seed meal or nitrogen supplements or even wood logs, can influence the chemical composition and, as a consequence, the nutritional value of the cultivated mushrooms.[2]

Mushrooms are excellent nutritional sources since they provide proteins, fibers, vitamins and minerals, such as K, P, Fe. The mineral composition of these mushrooms, however, may also contain some toxic elements, like arsenic, cadmium or mercury.[3]

In several countries, studies have revealed high toxic element concentrations in various mushroom species, especially in European countries where mushroom consumption is high[4,5] and where families include mushroom cultivation as a domestic activity.[6]

The adverse health effects of arsenic have long been recognized. The acute toxicity of arsenic ranges from very toxic to completely non-toxic, inorganic arsenic being more toxic than organic arsenic compounds. The most toxic forms of arsenic are the inorganic arsenic(III) and (V) compounds. Methylated forms of arsenic have a low acute toxicity; arsenobetaine which is the principal arsenic form in fish and crustaceans is considered non-toxic.[7] Although natural soils contain arsenic mostly in inorganic forms, in mushroom mainly organic arsenic compounds are found. The arsenic accumulation in certain fungi has been observed.[3,8,9] BYRNE et al.[10] analyzed a number of mushrooms of different species and the main arsenic compound found was arsenobetaine.

Cadmium is known as a toxic element as well, since it can occur as an inhibitor in many life processes. In general, the two major sources of contamination are the production and utilization of cadmium and the disposal of wastes containing cadmium. Increases in soil cadmium content will result in the uptake of cadmium by plants. Edibles free-living food organisms such as shellfish, crustaceans and fungi are natural susceptible to increases in soil cadmium. Mushrooms, in particular, may be very rich in cadmium.[11–13]

In Brazil, mushroom consumption is still small since people know little about the nutritional and medicinal benefits of mushrooms. However, consumption is growing due to refined flavor, nutritional and medicinal values. From 1995 to 2005 the world's mushroom production increased more than 60%. In the last years, Brazilian mushroom production and commercialization has increased considerably, as well.[14]

The most cultivated species in Brazil is *Agaricus bisporus* but there are also other species such as *Pleurotus ostreatus* or *Lentinula edodes* that are now widely produced.[14]

In this study, two important toxic elements, arsenic and cadmium concentrations were determined in eight edible mushroom species cultivated in São Paulo state, Brazil. Arsenic was determined by instrumental neutron activation analysis (INAA) and cadmium by graphite furnace atomic absorption spectrometry (GF AAS).

* E-mail: vmaihara@ipen.br

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Experimental

Mushroom samples

Edible mushrooms were acquired in retail stores and directly from producers of various cities of São Paulo state. Eight fresh species were collected.

Sample preparation

All the samples were cleaned and submerged for 10 minutes in Milli-Q H_2O and were cut in small pieces with a plastic knife and then put in Petri dishes or plastic recipients. The samples were then freeze-dried for 10 to 15 hours in a Thermo Electron Corporat (Modulyo Model) freeze-dryer. After the freeze-drying process, the samples were ground and homogenized in a domestic blender with Ti blades. These mushroom samples were then stored in pre-cleaned polyethylene bottles.

Instrumental neutron activation analysis (INAA)

To determine the arsenic concentration, the instrumental neutron activation analysis methodology was applied. About 200 mg of freeze-dried edible mushroom were irradiated with As standard (2.3 μg As) for 8 hours under a thermal neutron flux of $4.5 \cdot 10^{12}$ $cm^{-2} \cdot s^{-1}$ at the IEA-R1 nuclear research reactor of IPEN/CNEN-SP.

After a decay period of 4 days, the mushroom samples and standard were counted in a Ge detector (Model POP TOP – EG&G ORTEC) with a resolution of 1.90 keV for the 1332.49 keV γ-ray peak of ^{60}Co. γ-ray spectrum was analyzed using the VISPECT 2 software.[15] Arsenic was determined by 559.1 keV photopeak.

Graphite furnace absorption atomic spectrometry (GF AAS)

Cadmium concentrations were determined by GF AAS. Approximately 300 mg of the dried sample were digested in 4 mL of concentrated HNO_3 and 1 mL of 30% H_2O_2 in closed PTFE vessels in a digestion block for 3 hours at 90 °C. The digest was diluted with Milli-Q water up to a volume of 25 mL.

A Perkin Elmer AAnalyst 800 atomic absorption spectrometer with Zeeman background correction at wavelengths of 228.8 nm for cadmium was used.

Results and discussion

The accuracy of the INAA and GF AAS methods was verified by certified reference materials. For validation of As determination by INAA the reference materials Mixed Polish Herbs INCT-MPH-2 and Tea Leaves INCT-TL-1 from the Polish Institute of Nuclear Chemistry and Technology were analyzed. The NIST reference materials Oyster Tissue (NIST-1566b) and Mussel Tissue (NIST - 2796) were used for Cd determination.

The methodologies were also assessed via participation in a proficiency test organized by the International Atomic Energy Agency under the Project IAEA INT/1/ 054 "Preparation of Reference Materials and Organization of Proficiency Test Rounds", for the certification of a mushroom reference material.[16] The results obtained showed good agreement with the certified values (Table 1).

The limit of detection for arsenic and cadmium were determined using the IUPAC criterion[17] and the values obtained were 0.007 mg/kg for Cd and 0.002 mg/kg for As.

Arsenic and cadmium were determined in almost all mushroom species analyzed. The results are presented in dry weight (dw) in Table 2.

The mean content of As in edible mushroom samples analyzed was 0.077 mg/kg dry weight, varied from 0.009 mg/kg in *P. eryngui* to 0.210 mg/kg dw in *L. edodoes*. According to VERTTER,[9] the As content in mushrooms varied from 0.19 to 1.5 mg/kg dw *(A. bisporus)*, 0.09–0.50 mg/kg (*P. ostreatus)* and 0.04–0.07 mg/kg (*L. edodes*). These values are in agreement with the results obtained in this paper.

Table 1. As and Cd determination in reference materials (in mg/kg)

Reference material	As		Cd	
	x ± s[a]	Certified value	x ± s[a]	Certified value
Mixed Polish Herb	0.195 ± 0.026	0.191 ± 0.023	0.195 ± 0.015	0.211 ± 0.021
Tea Leaves Polish	0.082 ± 0.007	0.106 ± 0.021	na	–
Oyster Tissue	na	–	2.46 ± 0.10	2.48 ± 0.08
Mussel Tissue	na	–	0.864 ± 0.060	0.82 ± 0.16
IAEA Mushroom	0.406 ± 0.029	(0.417 ± 0.057)[b]	2.37 ± 0.14	2.48 ± 0.27

[a] Mean value ± standard deviation ($n = 5$).
[b] Informative value.
na: Not analyzed.

Table 2. As and Cd concentrations of the analyzed mushroom samples (mean ± SD in mg/kg dry weight)*

Mushroom species	Local name	City	As	Cd
Pleurotus ostreatus	Shimeji escuro	São Paulo	0.027 ± 0.004	0.074 ± 0.002
Pleurotus florida	Shimeji branco	São Paulo	0.073 ± 0.018	0.220 ± 0.013
Pleurotus eryngui	Eryngui	São Paulo	0.009 ± 0.003	0.011 ± 0.003
Pleurotus osteatus	Hiratake	São Paulo	0.056 ± 0.004	0.117 ± 0.006
Pleurotus salmoneostramineus	Salmão rosa	São Paulo	0.043 ± 0.004	0.229 ± 0.004
Agaricus sp	Porto Bello	São Paulo	0.125 ± 0.014	<LD
Agaricus bisporus	Champignon	São Paulo	0.097 ± 0.024	<LD
Agaricus bisporus in conserve	Champignon	São Paulo	0.163 ± 0.015	<LD
Lentinula edodes	Shitake	São Paulo	0.210 ± 0.009	0.190 ± 0.011
		Suzano	0.020 ± 0.005	0.114 ± 0.012
		Mirandópolis	0.012 ± 0.002	0.130 ± 0.007
		Juquitiba	0.083 ± 0.006	0.195 ± 0.008

* Mean and standard deviation ($n = 3$).
LD: Limit of detection.

In this study the highest and lowest Cd concentration were 0.011 mg/kg dw in *P. eryingui* and 0.229 mg/kg dw in *P. salmoneostramineus*. All the *Agaricus* varities presented values are lower than the limit of detection. The specimens of the *Lentinula edodes* species collected in different regions have similar cadmium levels (0.114–0.195 mg/kg), whereas arsenic concentrations presented show higher variability (0.012–0.210 mg/kg) in this species.

Cadmium accumulation has been demonstrated in literature, and cadmium levels of mushroom samples have been reported in the range of 0.81–7.50 mg/kg,[11] 0.14–0.95 mg/kg,[12] 0.25–2.75 mg/kg.[13] The study performed by MATTILA et al.[18] showed that *L. edodes* is an effective Cd accumulator (10 µg/100 g).

The FAO/WHO provisional tolerable weekly intakes (PTWI) are 15 µg and 7 µg per kg of bodyweight for arsenic and cadmium, respectively. Thus, a 60 kg bodyweight person has to eat 18 kg of fresh mushroom in a week to reach the PTWI for Cd, which in turn, seems very unlikely to occur, and hence, the consumption of this foodstuff should be considered safe in Brazil from a toxicological point of view, according to the preliminary results presented in this study.

Conclusions

The results obtained in this study offer information about the concentration of two toxic elements in edible mushroom species. The As and Cd contents determined in edible mushroom samples cultivated in São Paulo were lower than the observed values in the literature. These data are important in view of toxicology, food chemistry and environmental protection.

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