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Cadmium in edible mushrooms from NW Spain: Bioconcentration factors and consumer health implications

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ABSTRACT

Mushrooms do not constitute a significant portion of the human diet, but the consumption of wild and cultivated mushrooms has become increasingly in recent years. Some species accumulate high levels of toxic metals, both in unpolluted and polluted areas. In this study, we examined the accumulation capacity of cadmium in edible mushrooms in relation to certain factors and their possible toxicological implications. Cadmium concentrations were determined by an ICP-MS spectrometer in 238 samples of the fruiting bodies of 28 wild and cultivated growing edible mushrooms species and the underlying soil. The hymenophore (H) and the rest of the fruiting body (RFB) were analysed separately. The highest mean cadmium concentration (mg/kg dry weight) was found in *Agaricus macrosporus* (52.9 in H and 28.3 in RFB). All mushroom species accumulated cadmium in relation to the underlying soils. There were statistically significant differences between the hymenophore and the rest of the fruiting body ($p < 0.001$). Cadmium concentrations were compared to data in the literature and to levels set by legislation. It was concluded that consumption of our studied mushrooms is not a toxicological risk as far as cadmium content is concerned, although the species *A. macrosporus* should not be consumed.

1. Introduction

Some species of mushrooms can survive, grow and reproduce within contaminated soils, and can accumulate in their flesh high concentrations of certain metals and metalloids, e.g. Ag, As, Cd, Hg, Pb (Kojta et al., 2012; Melgar et al., 1998). Many mushrooms that emerge in background areas due to species-specific features can also absorb and sequester in their fruiting bodies certain metals and metalloids to high concentrations (Falandysz et al., 2007, 2008a, 2008b; Gucia et al., 2012). The capacity of mushrooms (*Macromycetes*) to absorb and sequester metallic elements or metalloids in their fruiting body can be assessed by the bioconcentration factor (BCF) values of the elements (García et al., 2009, 2013; Kojta et al., 2012; Melgar et al., 2009, 2014; Falandysz et al., 2015).

Mushrooms have a very effective mechanism to accumulate metals from the environment. Therefore, mushrooms are generally used for the evaluation of the level of environmental pollution (Kula et al., 2011; Şen et al., 2012). Fruiting bodies are appreciated, not only for texture and flavour but also for their chemical and nutritional properties (Manzi et al., 2001), although researches during the last three decades found that mushroom species accumulate several trace elements, mainly mercury, cadmium, and lead, and metalloids, namely arsenic and radionuclides (Doğan et al., 2006; Falandysz et al., 2008b; García et al., 2015; Mendil et al., 2005; Uzun et al., 2011).

It has been reported that as mushrooms are therapeutic foods, they are taken into an account to prevent diseases such as hypertension, hypercholesterolemia and cancer owing to their chemical compositions (Kula et al., 2011; Sarikurkcu et al., 2011).

Biosorption of cadmium has been observed in brown macroalgae and its uptake was dependent on the pH value (Gutiérrez et al., 2015). In contrast to green plants, mushrooms consist of large concentrations of some metals such as Cd, Pb, and Hg, so for the evaluation of a possible hazard to human health due to the ingestion of mushrooms, a great effort should be made (Kalač and Svoboda, 2000; Kula et al., 2011; Peña-Fernández et al., 2014). In order to find metal contents in the fruiting bodies of a large number of species of edible mushrooms, many studies have been done (Cocchi et al., 2006; Falandysz et al., 2007, 2008a; Kalač, 2010; Li et al., 2011; Mendil et al., 2004; Svoboda et al., 2006; Yamaç et al., 2007; Zhu et al., 2011).

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As results from numerous papers indicate, the content of many trace elements, especially cadmium and mercury, increases in mushrooms from polluted areas as compared with those from unpolluted rural sites, which have been taken as background values. However, the relationship between the substrate contamination by a trace element and its content in a mushroom is not tight enough to enable on universal usage of each mushroom species as a reliable bioindicator (Kalač, 2010). In recent studies by using many populations and sampling sites some species showed bioindication potential for heavy metals, e.g. the mushroom *Boletus edulis* showed bioindication potential for cadmium in topsoil with low Cadmium concentration (Falandysz et al., 2011), and *Leccinum* spp. for mercury (Falandysz et al., 2015).

Most heavy metals are chemically stable and accumulated in the surface layers of soils. Thus, the elements tend to bioaccumulate, and the fruiting bodies, mainly of ectomycorrhizal macrofungi, can contain extremely high levels of heavy metals. Cadmium is intensively accumulated by fungi, and relatively high copper and zinc concentrations (bioaccumulation values higher than 1) in certain species of wild growing species of fungi are also reported (Alonso et al., 2003; Sarikurkcu et al., 2011; Severoglu et al., 2013; Venturella et al., 2014; Vinichuk, 2013). Mycelium accumulates Cd and fruiting bodies may contain much higher cadmium content than most plants. Consequently, the consumption of fruiting bodies of edible fungi with high Cd contents represents an important pathway by which Cd enters the human food system (Vinichuk, 2013). Considering that Cadmium is a multitarget toxicant, with special emphasis on oxidative stress mechanism, currently, the protective role of some plant extracts in the toxic effect induced by metal cadmium is being investigated using *in vivo* and *in vitro* (isolated hepatocytes) assays (Dewanjee et al., 2013; Dua et al., 2015).

The present paper investigates the accumulation capacity (concentration or exclusion) of cadmium in the fruiting bodies of some edible mushrooms (wild and cultivated species) in relation to various factors, including the growth substrate (metal content, acidity and organic matter content), the species and ecology (mycorrhizal and saprophytic) and the morphological part (hymenophore and the rest of the fruiting body). We also calculated the cadmium bioconcentration factor (BCF) and evaluated how much of our daily intake of cadmium is from the consumption of these mushrooms.

2. Materials and methods

2.1. Sampling

The study was carried out in the province of Lugo (Galicia, NW Spain) in three different areas: urban-pastureland, rural-pastureland, and forest areas during the years 2011 and 2012. The mushroom species were selected according to their culinary quality, commercialisation and availability in the areas of study.

The upper soil horizons (0–10 cm, after removing the superficial layer of organic detritus) were also collected from appropriate sampling places.

In total, 238 samples of edible mushrooms from 28 species of *Basidiomycetes* fungi were collected: 13 saprophytes [terrestrial: *Agaricus campestris* L., *Agaricus macrosporus* (F.H. Møller & Jul. Schäff.) Pilát = *Agaricus urinascens* (Jul. Schäff. & F.H. Møller) Singer, *Agaricus sylvicola* (Vittad.) Peck, *Calvatia utriformis* (Bull.) Jaap, *Clitocybe nebularis* (Batsch) P. Kumm., *Coprinus comatus* (O.F. Müll.) Pers., *Lepista nuda* (Bull.) Cooke, *Macrolepiota procera* (Scop.) Singer and *Marasmius oreades* (Bolton) Fr.; cultivated: *Agaricus bisporus* (J.E. Lange) Imbach and *Pleurotus ostreatus* (Jacq.) P. Kumm.; wood decaying: *Fistulina hepatica* (Schaeff.) With. and *Agrocybe cylindracea* (DC.) Maire] and 15 mycorrhizals [*Amanita rubescens* Pers., *Boletus aereus* Bull., *Boletus aestivalis* (Paulet) Fr., *B. edulis* Bull., *Boletus pinophilus* Pilát & Dermek, *Cantharellus cibarius* Fr., *Hydnum repandum* L., *Lactarius deliciosus* L. (Gray), *Leccinum scabrum* (Bull.) Gray, *Russula cyanoxantha* (Schaeff.) Fr., *Tricholoma columbetta* (Fr.) P. Kumm., *Tricholoma equestre* (L.) P. Kumm., *Tricholoma portentosum* (Fr.) Quél., *Xerocomus badius* (Fr.) E.-J. Gilbert, and *Xerocomus chrysenteron* (Bull.) Quél.]. *T. equestre* (L.) P. Kumm. was included as an edible mushroom, but Bedry et al. (2001) observed that this species could cause rhabdomyolysis; in Spain, its commercialisation is forbidden according to Royal Decree 30/2009 (BOE, 2009).

These samples were cleaned (not washed), cut and separated into two parts (Hawksworth et al., 1995): the hymenophore (H) and the rest of the fruiting body (RFB) (comprised of the cap, minus the hymenophore, and the stipe); both anatomical parts were analysed separately, in order to compare the amount of mercury accumulated in the fertile part (H) with regard to the sterile part (RFB).

The fresh mushrooms, after being cleaned, cut and separated into the H and the RFB parts, were air-dried for several days and further dried in an oven at 50 °C (approximately 40 h), until the samples reached a constant weight. They were then pulverised in an agate mortar. Sub-samples (between 0.3 and 0.5 g) of powdered mushrooms were wet-digested with 8 ml of concentrated nitric acid (Suprapur, Merck) in closed PTFE vessels inside a microwave oven (ETHOS 20, Milestone). The digested samples were filled to 50 ml with deionised water. All samples were run in triplicate.

The soil substrate samples were dried at room temperature for several weeks and then sieved through a pore size of 2 mm. A representative sample of up to 0.5 g was digested in 10 ml of concentrated nitric acid (Suprapur, Merck) for 10 min in a closed PTFE vessel inside a microwave oven (ETHOS 20, Milestone). The extract obtained after filtering through Whatmann No. 42 filter paper into a volumetric flask was brought to a volume of 50 ml with deionised water (US EPA method 3051, 1994).

2.2. Analysis

Samples were analysed by an ICP-MS spectrometer, Varian 820. The sensitivity of this method was determined according to the detection limits established for this spectrometer, which was 0.2 ng/l (ppt) for cadmium. To assess the precision of the method, the coefficient of variation (CV) of the average of 15 replicates of a sample solution was determined. The calculated CV was 2.25%.The accuracy of our analytical method was determined using the certified reference material "CS-M-1: As, Cd, Cu, Hg, Pb, Se and Zn in dried mushroom powder, Cow Bolete (*Suillus bovinus*)", which is certified by the Institute of Nuclear Chemistry and Technology, Warsaw, Poland. The referenced value is reported as 0.273 ± 0.093 and the value obtained with our analytical method is 0.267 ± 0.022 (97.93%).

2.3. Soil pH and organic matter

Distilled water (25 ml) was added to 10 g of air-dried soil sample, and the mixture was left at 25 °C for 1 h. The pH was determined using a pH meter (GLP 21. CRISON). The organic matter content of the soil was determined gravimetrically after the combustion of the organic matter within the soil sample (2 g air-dried) at 550 °C for 16 h in a furnace horn (Select-Horn. SELECTA) (Melgar et al., 2009).

2.4. Statistical analysis

Variances in the metal levels of mushrooms depending on the species, ecology and anatomical parts of the various mushroom