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Trace metal contents in wild edible mushrooms growing on serpentine and volcanic soils on the island of Lesvos, Greece

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ABSTRACT

The objectives of this survey were (1) to assess for the first time the Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn contents in wild edible mushrooms (*Russula delica*, *Lactarius sanguifluus*, *Lactarius semisanguifluus*, *Lactarius deliciosus*, *Suillus bellinii*) from the island of Lesvos, (2) to investigate the metals' variability among the species, as well as in relation to the chemical composition of the underlying soil, comparing mushrooms collected from volcanic and serpentine substrates and (3) to estimate metal intake by the consumption of the mushrooms under consideration. The trace metals in 139 samples were determined by flame or flameless atomic absorption spectroscopy. The median metal concentrations were as follows: Cd: 0.14; Cr: 0.10; Cu: 8.51; Fe: 30.3; Mn: 5.26; Ni: 0.34; Pb: 0.093 and Zn: 64.50, all in mg kg^{-1} dry weight. The observed concentrations are among the lowest reported for mushrooms from Europe or Turkey, while Pb and Cd values did not exceed the limits set by the European Union. Significant species- and substrate-related differences in the metal contents were found, but the variability did not follow a uniform pattern for all the metals in all mushroom species. As a general trend, the mushrooms growing in serpentine sites contained higher Cd, Cr and Ni than those from volcanic sites. The calculated bioconcentration factors (BCFs) showed that none of the mushrooms can be regarded as a metal bioaccumulator, although BCF values slightly above unity were found for Zn in the three *Lactarius* species, and for Cu in *R. delica*.

The studied mushrooms could supply considerable amounts of essential metals such as Zn and Cr. On the other hand, the consumption of *R. delica* collected from volcanic soils could provide 12% of the Cd daily tolerable intake and as high as 53% when collected from serpentine soils. Nonetheless, our results indicate that the regular consumption of wild edible mushrooms from Lesvos is quite safe for human health.

1. Introduction

Mushrooms are valuable health foods, both for their texture and flavor as well as for their low energy content, high proportion of indigestible fiber, specific b-glucans and antioxidant constituents (Kalač, 2009). In addition they contain significant amounts of vitamins, minerals and trace elements like Fe, Zn, Se, K (Elmastaş et al., 2007; Kalač, 2009). The chemical composition of mushrooms is the main cause for their therapeutic properties in preventing diseases such as hypertension (Talpur et al., 2002), hypercholesterolemia (Jeong et al., 2010) and several types of cancer (Lavi et al., 2006; Sullivan et al., 2006). Various wild edible mushroom species exhibit significant antioxidant activity, and therefore, can be used as an easily accessible source of natural antioxidants, as a potential food supplement, or in the pharmaceutical industry (Elmastaş et al., 2007).

The consumption of wild growing mushrooms has been preferred over that of cultivated ones in many countries of central and eastern Europe, and is considered to be increasing, even in the developed world (Agrahar-Murugkar and Subbulakshmi, 2005). The collection of mushrooms in Greece, although more restricted than in some other European countries such as Poland, France or Italy, is part of the national tradition and they have been an important ingredient in both traditional cuisine and gastronomy (Keltemidis, 2005).

From an ecological point of view, mushrooms exert a major influence on biogeochemical processes involving soil, rock and mineral surfaces, and the plant root–soil interface, and play a key role in the cycling of elements and the transformation of both organic and inorganic substrates. These processes can affect plant

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productivity and the mobility of toxic elements and substances, with socioeconomic consequences even on human health (Gadd, 2007). Furthermore, ectomycorrhizal fungi may increase plant tolerance to heavy metals, as for example in plants growing on Ni and Cr rich serpentine soils (Aggangan et al., 1998).

Compared to green plants, mushrooms can accumulate large amounts of some toxic heavy metals, such as Pb and Cd (Sesli and Tuzen, 1999; Demirbaş, 2001; Alonso et al., 2003; Falandysz et al., 2007; Konuk et al., 2007; Chudzyjski and Falandysz, 2008; Brzostowski et al., 2011a, 2011b; Falandysz et al., 2011; García et al., 2009; Gucia et al., in press; Jarzyńska et al., 2011). A well documented example is the high accumulative capacity of *Agaricus macrosporus* and other *Agaricus* species for Cd, and of *Coprinus comatus* for Pb (García et al., 1998 and references therein; Melgar et al., 1998 and references therein). Many other metals are essential for fungal growth and metabolism (e.g. Ca, Cu, Fe, Mg, K, Na and Zn). Both essential and non-essential metals can cause toxic effects to living organisms, including fungi, when present above certain threshold concentrations (Gadd, 1993). Metals exert toxic effects in many ways, e.g. by causing breakdown of cellular and organelle membranes, blocking operational groups of significant biological molecules such as enzymes or interacting with systems, which normally protect against harmful effects of free radicals generated during normal metabolism (Gadd, 2007). Nevertheless many fungi have developed a variety of mechanisms, both active and incidental, which allow them to survive, grow and flourish on substrates with high metal levels (Branco, 2010). Serpentine soils are typically inhospitable for many plants because of their soil chemistry, with high levels of potentially phytotoxic elements like Ni, Cr, Co and sometimes Mn and/or Cu (Chiarucci and Baker 2007; Branco, 2010; Kazakou et al., 2010). These stressful environmental conditions result in limited flora diversity along with high endemism and ecotypic specialization (Branco, 2010 and references therein; Kazakou et al., 2010). However, there is strong evidence that this general trend is not followed by ectomycorrhizal fungi, which show no specialization to edaphic chemical composition. On the contrary, it appears that serpentine soils support higher fungal diversity than non-serpentine ones (Branco, 2010).

On the island of Lesvos, Greece, about 60 species of mushrooms have been identified up to now in the herbarium of the Agricultural University of Athens (Dimou and Polemis, personal communication) but no studies on their heavy metal content have been undertaken. In this study we assess the concentrations of Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn in five mushroom species from the island of Lesvos (*Russula delica*, *Lactarius sanguifluus*, *Lactarius semisanguifluus*, *Lactarius deliciosus*, *Suillus bellinii*), all of which are common and frequently consumed by the local population. In addition, we examine the impact of species identity and of the geochemical composition of the substrate on trace metal variability by comparing the metal concentrations of mushrooms originating from serpentine and non-serpentine soils. Finally, we undertake an estimation of the dietary metal intakes by the consumption of the wild mushrooms concerned.

2. Materials and methods

2.1. Sampling

Mushroom samples of five of the most common wild growing species, namely *Russula delica*, *Lactarius sanguifluus*, *Lactarius semisanguifluus*, *Lactarius deliciosus* and *Suillus bellinii* (Table 1), were collected on the island of Lesvos, NE Aegean, Greece, in November 2009. Each species was collected from two different sites: *R. delica*, *L. sanguifluus* and *S. bellinii* were collected from one site on serpentine soils and one on volcanic, while *L. semisanguifluus* and *L. delicious* were collected from two sites, both located on volcanic soils (Fig. 1). Sampling from serpentine soils was based on the geological map of Lesvos (Hecht, 1972–1975) and confirmed by the presence of *Alyssum lesbiacum*, a serpentine endemic species (Kramer et al., 1997). Metal concentrations in the serpentine and non-serpentine soils were obtained from the survey of Kazakou et al. (2010). Ten to fifteen individuals of each species were collected from each site, adding up to a total of 139 samples. Both types of sampling sites were in sparse pine forest and were distant from human activities so that they could be considered as unpolluted. Identification of each species was based on standard reference books (Phillips, 1981; Konstantinidis, 2009).

2.2. Analytical procedures

The fruiting bodies of the fungi were thoroughly cleaned with a soft tissue from soil and substrate debris, chopped into pieces using plastic knifes and weighed within 24 h after collection. This was followed by freeze-drying for 48 h (to constant weight) and, finally, pulverization in an agate mortar. Freeze drying was conducted in samples pre-frozen at $-50\,^{\circ}C$ overnight, using a Labconco FreeZone 4.5 laboratory apparatus. Operating conditions were set at $-40\,^{\circ}C$ collector temperature and at <5 mBar vacuum level. Water content was calculated on the basis of water loss during freeze-drying. The pulverized samples were digested with conc. HNO_3 in a Mars Xpress system (CEM), according to the US EPA's Method 3051A (2007). Metal determinations were performed in a

Table 1
Mushroom species collected with corresponding family, habitat and edibility according to the literature.

Species	Family	Habitat	Edibility	Reference
Lactarius deliciosus	*Russulaceae*	Associated with *Pinus*, mostly on neutral and calcareous soils	Good	Basso (1999)
Lactarius sanguifluus	*Russulaceae*	Associated with *Pinus* on calcareous soils	Excellent	Basso (1999)
Lactarius semisanguifluus	*Russulaceae*	Associated with *Pinus*, mostly at grazed sites on calcareous soil	Excellent	Basso (1999)
Russula delica	*Russulaceae*	Deciduous and coniferous woods, and forests on calcareous soils	Good	Galli (2003)
Suillus bellinii	*Suillaceae*	Coastal pine forests of Mediterranean Europe	Moderate	Galli (2000)

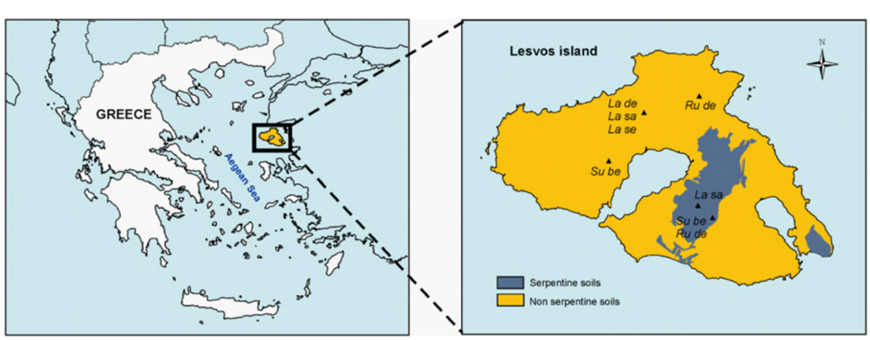

Fig. 1. Mushroom sampling sites on the island of Lesvos (Ru de=*R. delica*; La de=*L. deliciosus*; La sa=*L. sanguifluus*; La se=*L. semisanguifluus*; Su be=*S. bellinii*).