# LOCALIZATION AND BIOAVAILABILITY OF MERCURY AND SELENIUM IN EDIBLE MUSHROOMS *BOLETUS EDULIS* AND *SCUTIGER PES CAPRAE*

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## Introduction

Mushrooms are able to accumulate several essential as well as hazardous metals (Hg, Cd), metalloids (As), non-metal (Se), and other elements (Ag, Au, Cs, Rb, V, Zn), especially when grown at metal-polluted sites. *Boletus edulis* (King Bolete) and *Scutiger (Albatrellus) pes caprae* (Goat's foot) are edible mushrooms which form mycorrhizal associations with hardwoods and conifers. They are known Se- and Hg-accumulators (Falandysz and Borovička, 2013), both elements are known to accumulate in caps of fruiting bodies, largely in inorganic form (more than 80% and up to 99%) (Miklavčič et al., 2013; Slejkovec et al., 2000); but, the accessibility and bioavailability of Hg and Se remains largely unknown.

The aim of this study was to determine localization and speciation of Hg in caps of *B. edulis* and *S. pes caprae* by using high-throughput imaging methods as Laser Ablation - Inductively Coupled Plasma - Mass Spectroscopy (LA-ICP-MS), Synchrotron-X-ray Fluorescence (SR-XRF) and X-ray Absorption Spectroscopy (XAS). Bioavailability of Hg was determined by feeding mushrooms to the slugs (*Arion* spp.).

## Methods

Mushrooms were sampled in September 2014 at a non-polluted site in the suburbs of Ljubljana and at a Hg-polluted area near a former Hg mine, Idrija (Table 1). For LA-ICP-MS and SR-XRF analyses the caps were sliced to 2 mm cross-cuttings, wrapped in Al foil, frozen in propane cooled by liquid nitrogen, and freeze-dried for three days (Alpha 2-4, Christ). The remaining cap and the stalks were frozen and freeze-dried for bulk analysis (ICP-MS) and feeding the slugs. SR-XRF and XAFS analyses were performed at the XRF beamline, Elettra, Synchrotron Trieste. Freeze-dried and pelletized mushrooms were fed to the slug snails for two weeks. Hg and Se concentrations in hepatopancreas and muscle tissues were determined by ICP-MS. Malondialdehide (MDA) test (Hodges et al., 1999) was performed in order to determine the level of


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lipid peroxidation in hepatopancreas tissues. Bioavailability was calculated as the ratio between the elemental content (mg) in hepatopancreas and the elemental content (mg) in ingested food.

**Results**

Hg and Se mainly accumulated in the spore forming part of the mushroom cap (Fig. 1). Hg concentrations of mushrooms collected in Idrija were approximately 10-times higher than of those from the background environment (Table 1). Mushrooms contained distinct amounts of Hg and Se in bioavailable form. Feeding mushrooms to the snails induced lipid peroxidation in hepatopancreas (Table 1).

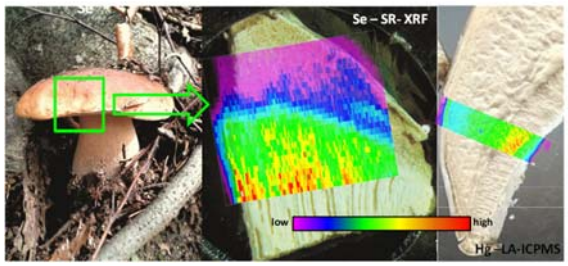


**Figure 1.** Figure 1. Selenium and mercury distribution in the edible mushroom *Boletus edulis* recorded by SR-XRF and LA-ICP-MS.

**Table 1.** Hg and Se concentrations in the mushrooms, Hg and Se bioavailability and the level of MDA in snail hepatopancreas. In all cases statistically significant differences are given (Duncan's test, $p<0.05$, $n=5$). Hepatopancreas (HP), bioavailability (BA).

| Mushroom/ location/mushroom part | Hg (mg/ kg) dry weight | Se (mg/ kg) dry weight | Hg -BA-HP (%) | Se -BA-HP (%) | MDA in HP (as % of control fed with lettuce) |
|---|---|---|---|---|---|
| *B. edulis*/ Idrija/ cap | 98.9 ± 5.1a | 13.9 ± 2.1a | 16.7% ± 1.9a | 7.2% ± 1.2% ab | 220% ± 13% a |
| *B.edulis*/ Ljubljana sub./ cap | 7.85 ± 1.2b | 14.1 ± 1.1a | 12.8% ± 1.1a | 5.3% ± 0.2% bc | 193% ± 14% ab |
| *B. edulis*/ Ljubljana sub./ stalk | 3.75 ± 0.7b | 30.0 ± 2.3a | 18.1% ± 5.5a | 9.3% ± 1.1% a | 168% ± 11% b |
| *S.pes caprae*/ Ljubljana sub./ whole | 39.6 ± 3.6ab | 246 ± 17b | 3.9% ± 0.5b | 4.6% ± 0.5% c | 158% ± 10% b |

**Conclusion**

Hg and Se are present in mushrooms in bioavailable form: therefore consumption of limited amounts is recommended in order not to exceed the allowed daily intake of 2 µg Hg/ kg bodyweight according to WHO.

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