



Metallic elements and metalloids in *Boletus luridus*, *B. magnificus* and *B. tomentipes* mushrooms from polymetallic soils from SW China



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ABSTRACT

Yunnan Province in China is known for its high biodiversity of mushrooms and a diverse geochemistry of soil bedrock and polymetallic soils, but our knowledge of mineral compositions of mushrooms from Yunnan is scarce. The metallic trace elements, Ag, Ba, Co, Cd, Cs, Cu, Cr, Hg, Li, Mn, Ni, Pb, Rb, Sr, V, Tl, U and Zn, and the metalloids, As and Sb, have been investigated using validated methods with a dynamic reactive cell by mass spectroscopy – inductive coupled plasma and cold vapour – atomic absorption spectroscopy on three popular species of *Boletus* mushrooms from Southwestern China. The trace mineral profiles in caps and stipes of *B. luridus* (24 individuals), *B. magnificus* (29 individuals) and *B. tomentipes* (38 individuals) have been evaluated. The interspecific differences in the content of several trace elements could be attributed to known differences in the geochemistry of soils in Yunnan, but for copper a difference was observed within species. The mean values of concentrations in composite samples of caps for *B. luridus*, *B. magnificus* and *B. tomentipes* from three to four locations were at the ranges (mg kg⁻¹ dry biomass): Ag (1.3–3.7), As (0.79–53), Ba (4.0–12), Co (0.68–1.2), Cd (0.79–2.2), Cs (0.67–55), Cu (37–77), Cr (5.0–7.6), Hg (2.1–5.4), Li (0.15–0.61), Mn (13–28), Ni (0.86–4.6), Pb (0.59–1.8), Rb (90–120), Sb (0.014–0.088), Sr (0.63–1.6), V (1.4–2.2), Tl (0.017–0.054), U (0.029–0.065) and Zn (130–180). Caps of *Boletus* mushrooms were richer in Ag, Cu, Hg and Zn than stipes, while other elements were distributed roughly equally between both morphological parts. *B. luridus*, *B. magnificus* and *B. tomentipes* grew in certain sites in Yunnan contained Ag, As, Ba, Cr, Hg, Ni, Sr or V at elevated concentration. A specific geochemistry of the soils type (latosols, lateritic red earths, and red and yellow earths in the Circum-Pacific Mercuriferous Belt of Southwestern China) can explain occurrence of some minerals at greater or elevated amount in mushrooms in Yunnan, while number of available research and data on mineral composition of mushrooms due to geochemical anomalies of soil parent material is so far little.

1. Introduction

Yunnan province of China has a large biodiversity of mushroom, plant and animal life. Its topography with a mild climate is also unique – with as much as 3000 m deep canyons and different types of forests. Consumption of mushrooms from the wild may be up to 24 kg *per capita* annually by certain locals in Yunnan, while their way of cooking is specific (using a wok). In addition, large volumes of mushrooms are exported from Yunnan to other regions of China and abroad (Falandysz and Borovička, 2013; Wang et al. 2014; Zhang et al. 2008, 2010). Yunnan is also diverse in the geochemistry of soil bedrock and forms a large part of the Circum-Pacific Mercuriferous Belt in China (Fan, 1991; He et al., 2004). Therefore, mushrooms from some regions in Yunnan

can be elevated in geogenic mercury (Falandysz et al., 2015a, 2015b, 2015c; Kojta et al., 2015). Although in the recent decade some data were published on mineral constituent composition of mushrooms from Yunnan, there is a need for more studies because of the high biodiversity of species and diverse soil geochemistry (Falandysz et al., 2015b; Fan, 1991; Li et al., 2011, 2016; Liu et al., 2012; Saniewski et al., 2016; Wang et al., 2015; Yin et al., 2012; Zhang et al. 2008, 2015; Zhu et al., 2011).

The objective of this study was to elucidate the accumulation potential, distribution and concentration levels of Ag, As, Ba, Co, Cd, Cs, Cu, Cr, Hg, Li, Mn, Ni, Pb, Rb, Sb, Sr, V, Tl, U and Zn in *Boletus* mushrooms such as *B. luridus*, *B. magnificus* *B. tomentipes* from the regions with a variable and often anomalous soil bedrock composition

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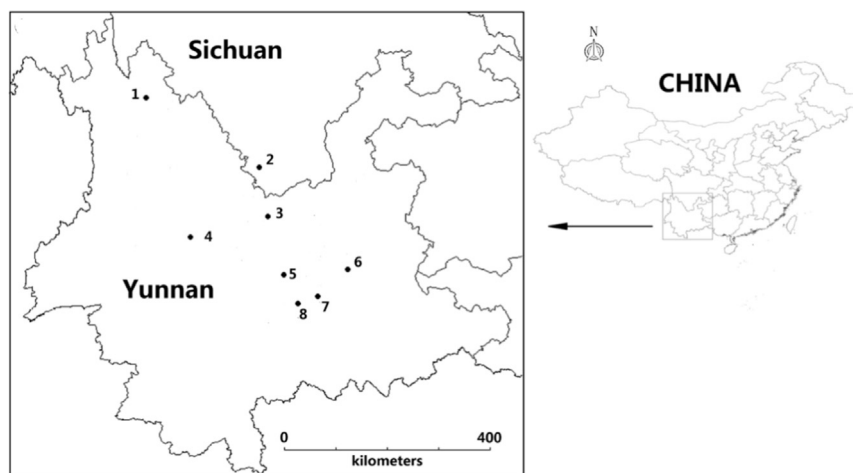


Fig. 1. Location of the sampling sites (1–8) for details see in Table 2. The figure was created by DIVA-GIS7.5 software.

due to high amount of certain hazardous minerals from Yunnan province in Southwestern China. *Boletus* mushrooms are highly popular as organic food and are widely consumed in Yunnan. This study for the first time presents data on 20 metallic and semi-metallic elements, which were determined using validated methods with a dynamic reactive cell (DRC) by mass spectroscopy – inductive coupled plasma (ICP-MS) and cold vapour – atomic absorption spectroscopy (CV-AAS) in a large collection of individuals for three *Boletus* species (*B. luridus*, *B. magnificus* and *B. tomentipes*) from Yunnan.

2. Materials and methods

2.1. Mushrooms

In total, 24 specimens *B. luridus* (Schaeff.) Murrill, 29 of *B. magnificus* (W.F. Chiu) Gelardi, Simonini & Vizzini and 38 of *B. tomentipes* (Earle) Murrill were collected from eight distantly distributed sites in Yunnan in 2011 and 2012 (Fig. 1). Fresh mushrooms were cleaned directly after picking, any visible plant vegetation and soil debris was removed with a ceramic knife and the bottom part of the stipe was cut off, and further rinsed with deionized water. Each individual fruit body was separated into cap and stipe, than they were prepared and pooled respectively. Pooled samples were examined, because it is possible to obtain a representative information on the content of a given chemical element accumulated in mushrooms based on a composite sample instead of the examination of many individual specimens, and also costs of analyses are highly reduced (Falandysz, 2014). Thereafter, the mushroom samples were placed into plastic trays of an electrically heated commercial dryer (dehydrator for vegetables etc.) model: Ultra FD1000 dehydrator, Ezidri, Australia, and dried at 65 °C to constant mass. Dried fungal materials were pulverized in a porcelain mortar that was cleaned by hand washing using a laboratory brush, deionized water and detergent and further rinsed with distilled water and dried in an electrically heated laboratory dryer at 105 °C, and finally kept in brand new sealed polyethylene bags under dry conditions (Wiejak et al., 2014). A number of pooled samples made per species and depending on a site of collection was from 3 to 4.

2.2. Elemental analysis

Before digestion, the samples were dried at 65 °C for 12 h using an electrically heated laboratory oven. Then, subsamples of dried and powdered mushrooms (~0.5000 g) were digested with 5 mL of 65% HNO₃ (Suprapure, Merck, Germany) under pressure in a microwave oven model Ethos One (Milestone Srl, Italy). The heating program was performed in one step: the power of the process was 1500 W, ramp time

20 min, temperature 200 °C and hold time 30 min. Reagent blank solutions were prepared in the same way. For every set of 10 mushroom samples digested, two blank samples were run. The digest was diluted to 10 mL using deionized water (TKA Smart2Pure, Niederelbert, Germany).

2.3. Instrumentation

The elements Li, V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Ag, Cd, Sb, Cs, Ba, Pb, Tl, U were determined using the ELAN DRC II ICP-MS Inductively Coupled Plasma Mass Spectrometer (PerkinElmer, SCIEX, Canada) equipped with a Meinhard concentric nebulizer, cyclonic spray chamber, dynamic reaction cell, Pt cones and a quadrupole mass analyzer. DRC was employed to remove spectral interferences. Typical instrument operating conditions for the ICP-MS spectrometer were: RF power – 1100 W; plasma Ar flow rate – 15 L min⁻¹; nebulizer Ar flow rate – 0.87 L min⁻¹ and auxiliary Ar flow rate – 1.2 L min⁻¹ and lens voltage – (7.5–9.0) V. Whilst tuning the ICP-MS, compromise conditions for maximum signal intensity of the analyte (²⁴Mg⁺, ¹¹⁵In⁺, ²³⁸U⁺) and minimum ratio of oxide (¹⁴⁰Ce¹⁶O⁺/¹⁴⁰Ce < 3%) and doubly charged ions (¹²⁸Ba²⁺/¹²⁸Ba⁺ < 3%) were found. The proper working conditions of ICP-MS working were checked by using a solution containing Mg, In, U at a concentration of 1 mg L⁻¹ and a Ba concentration of 10 mg L⁻¹ (Smart Tune Solution e Elan DRC II/plus, Atomic Spectroscopy Standard, Perkin Elmer Pure). For calibration curve construction, a mixed standard solution with contents of 10 mg L⁻¹ was used (Multielement Calibration Standard 3, Atomic Spectroscopy Standard, Perkin-Elmer Pure). Moreover, the isotopes of ⁴⁵Sc, ⁷⁴Ge, ¹⁰³Rh and ¹⁵⁹Tb prepared from individual solutions with contents of 1000 mg L⁻¹ were applied as internal standards in order to effectively correct temporal variations in signal intensity (ICP Standard CertiPUR, Merck, Germany). Calibration curves for elements were constructed in the range of 0.1 µg L⁻¹ to 50 µg L⁻¹. Argon with a purity of 99.999% was used as a nebulizer, auxiliary and plasma gas in a ICP-MS (Messer, Chorzów, Poland) (Drewnowska et al., 2017; Falandysz et al., 2017a, 2017b).

The determinations of total Hg content of fungal and soil samples was performed using cold-vapour atomic absorption spectroscopy (CV-AAS) by a direct sample thermal decomposition coupled with gold wool trap of Hg and its further desorption and quantitative measurement at a wavelength of 253.7 nm. The analytical instrument used was a mercury analyzer (MA-2000, Nippon Instruments Corporation, Takatsuki, Japan) equipped with auto sampler and operated respectively at low and high modes (Falandysz et al., 2012; Jarzyńska and Falandysz, 2011).

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