**Research Article**

**Content and Bioaccumulation of Nine Mineral Elements in Ten Mushroom Species of the Genus *Boletus***

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Concentrations and bioconcentration potential of nine elements (Ca, Cu, Fe, K, Mg, Mn, Na, P, and Zn) in ten species of wild edible *Boletus* and the corresponding underlying soils were analyzed. The analyses were performed using inductively coupled plasma atomic emission spectrophotometer. *Boletus* showed relative abundant contents of P, K, Fe, Mg, Ca, and Na and less of Zn, Cu, and Mn. Caps compared to stalks were enriched in P, K, Cu, Mg, and Zn, while stalks were enriched in Mn. The elements such as P and K were accumulated (BCF > 1), while Ca, Fe, Mg, Mn, and Na were excluded (BCF < 1) in the fruiting bodies. The correlation analysis indicated high correlations between Cu, Mn, Ca, and Fe in the mushrooms as compared to the corresponding soils. Significant correlations were also obtained between Cu-P (r = 0.775), Fe-P (r = 0.728), and Zn-P (r = 0.76) for caps and Cu-Mg (r = 0.721), Fe-Mg (r = 0.719), Zn-Mg (r = 0.824), and Zn-P (r = 0.818) for stalks. The results of this study imply that ability of fungus to accumulate elements from substrate could be influenced by mushroom species and underlying soil substrates.

1. Introduction

Mushrooms are traditionally recognized as a valued source of nutrients and a popular delicacy in many countries for their rich contents in proteins, essential minerals, and low energy levels [1]. Edible wild-grown mushrooms consumption has been preferred to cultivated species for their indisputable flavor, texture, and medicinal properties [2, 3]. Proteins of wild edible mushrooms are usually high, commonly ranging between 10% and 60%, which were calculated using the conversion factor of 4.38 [1]. Mushroom gathering has been a very popular leisure and commercial activity in many European and Asian countries [4].

Macromycetes in nature play a major role in biogeochemical transformation of macro- and microelements essential to humans [5]. Wild mushrooms can absorb large amounts of water and minerals within a relatively short period due to large area of mycelium overgrowing the surface layer of soil [6]. Abundance of minerals such as P, K, Ca, Mg, Na, Fe, Mn, Zn, and Cu desired in human nutrition has been reported in edible wild-grown mushrooms; meanwhile, undesired high levels of toxic elements including As, Hg, Cd, and Pb were also found in previous studies [5]. Bioconcentration factor (BCF) is the ratio of the element content in fruiting body (cap or stalk) to the content in underlying substrate, which can express the ability of fungi to accumulate elements from substrate [7]. If BCF exceeds unity (BCF > 1) it indicates the accumulation of elements in fungus, and if BCF is below unity (BCF < 1) it excludes bioaccumulation [8]. Bioaccumulation capacity of mushroom is usually affected by fungal lifestyle, age of fruiting body, specific species and element, and environment such as pH, organic matter, and pollution [5].

Rich resources of wild edible fungi are distributed in Yunnan province (southwest of China) due to the mild and rainy climate. Laterite, lateritic red loam, red soil, yellow soil, and brown soil are the main agrotypes in Yunnan [9]. Contents of elements such as Cu, Fe, Pb, Cd, Co, Se, Ni, V, Ti, Sc, and Ti in soil are rather high, which would be the primary sources of elements to fungi [10]. More than 880 species of wild-grown mushrooms were identified as edible in Yunnan province, which account for 80% in China and 40% in the world [11]. Export volume of wild edible mushrooms in Yunnan was
105000 and 135000 tons, and the exports were 1.21 and 1.43 million dollars in 2010 and 2011, respectively. Species of the genus *Boletus* and *Tricholoma matsutake* are the main export varieties, which account for 90% of the total export in Yunnan [12].

Species of the genus *Boletus* are a popular food throughout the world because of their particular aroma, sensory qualities, texture, and biologically active compounds. Flavor of the favorite dried species such as *Boletus edulis*, *Boletus aereus*, and *Boletus badius* includes odor and marvelous taste of nuttiness, earthiness, and meatiness [13]. 199 species of Boletales were identified as edible in China, among which 144 species were distributed in Yunnan province [14]. *Boletus is* abundant in proteins, carbohydrates, vitamins, and essential elements required in the human body. Furthermore, its history of traditional use in oriental therapies and modern clinical practice has been reported such as for its anti-inflammatory, antimicrobial, antioxidant, antiviral, antioxidant, and immunomodulatory activities and its use for reduction of blood glucose levels [15]. However, species such as *Boletus edulis*, *Boletus badius*, *Boletus griseus*, and *Boletus pinophilus* contained high contents of toxic Cd, Hg, As, and Pb [5,16,17]. Also undesired Ag and Sb can be elevated in some wild-grown mushrooms [18,19].

There was little information available about bioaccumulation ability of elements in *Boletus* family in China. Since these mushrooms have been traditionally used for consumption by local people and trading, the aim of this study was to determine the contents of nine elements (Ca, Cu, Fe, K, Mg, Mn, Na, P, and Zn) in ten species of edible *Boletus* and the underlying soil to investigate the relationship between fruiting body and habitat.

### 2. Materials and Methods

#### 2.1. Sampling

Mature fruiting bodies of ten edible species of the genus *Boletus* were collected from Yunnan province (southwest of China) during summer and autumn in 2012. The species, habitat, and number of fruiting bodies are given in Table 1. The underlying surface layers (0 to 10 cm) were collected after removing the superficial layer of litter and organic detritus.

#### 2.2. Digestion Process

Dried mushroom samples were weighed as 0.3 g accurately and placed into the polytetrafluoroethylene (PTFE) pressure vessels. 4 mL HNO₃ (65%) and 2 mL H₂O₂ (30%) were added to the vessel and digested under pressure in an automatic microwave digestion system, Ethos One (Milestone, Italy). The extract was further diluted to 25 mL using deionized water.

Soil samples (0.1 g) were placed into the polytetrafluoroethylene beaker and digested and mixed with 6 mL HNO₃ (65%) and 1 mL HClO₄ (72%) on an electric hot plate at 170°C, removing and cooling the samples when they turned into paste. Then the paste was dissolved in 10 mL HF (40%) and 0.5 mL HClO₄ (72%) and heated again at 210–220°C until the acid evaporated completely. Further, 10 mL HCl (38%) was added and heated until dissolved and diluted with distilled water up to 25 mL.

#### 2.3. Analytical Determination

All elements (Ca, Cu, Fe, K, Mg, Mn, Na, P, and Zn) contents in dry weight (dw) of mushrooms and soils samples were determined using inductively coupled plasma atomic emission spectrophotometer (ICP–AES, 9000, Shimadzu, Japan). The repeatability for all determined elements was less than 5%. Limits of quantitation (LOQ) for Ca, Cu, Fe, K, Mg, Mn, Na, P, and Zn were 0.04, 0.17, 0.18, 2.16, 0.04, 0.01, 1.53, 0.44, and 0.05 mg/kg dw, respectively. The efficiency of the process was validated with 94–107% recovery success using certified reference materials, namely, tea leaves (GBW07605) and soils (GBW07406), both produced by the Institute of Geophysical and Geochemical Exploration in Beijing, China.

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**Table 1: Families, habitat, and number of analyzed fruiting bodies.**

| Species                        | Habitat                     | Number |
|--------------------------------|-----------------------------|--------|
| *Boletus speciosus* Frost      | On mixed woods ground       | 10     |
| *Boletus griseus* Frost        | On needles, oak, and chestnut forest ground | 10     |
| *Boletus luridus* Schaeff.     | On broadleaf or mixed woods ground | 8      |
| *Boletus umbriniporus* Hongo   | On forest ground            | 8      |
| *Boletus tomentipes* Earle     | On needles and broadleaf forest ground | 7      |
| *Boletus edulis* Bull.         | On mixed coniferous and broadleaf forest ground | 10     |
| *Boletus pallidus* Frost       | On shaw ground              | 9      |
| *Boletus brunneissimus* W.F. Chiu | On mixed pine tree and katue forest ground | 9      |
| *Boletus rubellus* Krombh.     | On broadleaf or mixed woods ground | 7      |
| *Boletus aereus* Bull.         | On oak forest ground        | 7      |
3. Results and Discussion

3.1. Element Concentrations. The element contents in fruiting bodies of Boletus (cap and stalk) and underlying soil samples are presented in Table 2. As previously reported, fruiting bodies of Boletus can be considered as rich in P, K, Na, Ca, and Mg and also abundant in trace elements such as Cu, Zn, and Mn. Among the minerals determined in this study, K, P, Fe, Mg, and Ca exhibited higher concentrations than Na, Zn, Cu, and Mn, which is in accordance with the literature [7]. While Boletus collected from Yunnan contained lower levels of K, Na, Ca, Mg, Fe, and Mn than other reports [20], significant differences were obtained not only among various Boletus species but also within different part of fruiting body (Table 2). Similarly to previous studies, the ranges of concentrations spread over one to two orders of magnitude often occurred [21, 22].

Among the mushroom species analyzed, the greatest contents of Cu, K, Mg, Na, and P were quantified in the caps and stalks of Boletus pallidus, and Mn and Zn were found in Boletus luridus and Boletus rubellus. Highest Ca and Fe contents were found in the caps of Boletus brunneimimus and stipes of Boletus edulis, namely, 669 and 4200 mg/kg dw, respectively. In the study by Zhou and Yin (2008) [23], Boletus edulis showed higher contents of K, Na, Ca, Mg, and Fe than Boletus speciosus and Boletus aereus. In our early study, values of 13.6, 121, 248, and 20.3 mg/kg dw for Cu, Fe, Mg, and Zn were determined in Boletus tomentipes, respectively, which are lower than the present results [24]. Similarly, contents of K, Ca, Fe, Mg, and Zn for Boletus speciosus and Boletus griseum collected from Yunnan province in 2009 were lower than the data in Table 2 [25].

K contents in caps and stalks of Boletus edulis (cap: 29000 mg/kg, stalk: 20000 mg/kg dw) and Boletus subumentosus (cap: 46000 mg/kg, stalk: 43000 mg/kg dw) from Poland were much higher than the values in our study (cap: 9017–18968 mg/kg, stalk: 4865–15325 mg/kg dw) [8, 26]. P contents were found at the ranges of 4942–10611 mg/kg dw and 2176–5621 mg/kg dw for caps and stalks of Boletus, respectively. Higher values were found to be 8700–16000 mg/kg dw in caps and 4100–7500 mg/kg dw in stalks of Macroepiota procera.
and lower values of 640–4490 mg/kg dw were for the fruiting body of thirty macrofungi species from Turkey [27, 28].

The range of Fe contents in this study was 376–1600 in caps and 357–4200 mg/kg dw in stalks, which are much higher than the values previously reported [8, 29]. Similar values were found to be 150–1741 mg/kg dw, and a particularly higher value was 11460 mg/kg dw for Lepista nuda [30, 31]. Reported Ca contents in Boletus edulis, Boletus speciosus, and Boletus tomentipes were 913.9, 1147.6, and 1097.4 mg/kg dw, which are higher than the values observed in this study [32].

Mg and Zn concentrations in different Boletus were in the ranges of 386–1239 and 45–223 mg/kg dw for caps and 279–935 and 33–131 mg/kg dw for stalks, respectively, which coincide with the literature reports [5]. Cu and Mn contents in Boletus badius, Boletus luridus, and Boletus edulis were found to be lower than the results in our study, which is 33–78 and 17–67 mg/kg dw for caps and 16–39 and 26–85 mg/kg dw for stalks, respectively [5, 33, 34]. Other species such as Macrolepiota procera and Lepista nuda contained higher content of Cu (236.5 mg/kg dw) and Mn (480 mg/kg dw) [6, 31]. The range of Na contents in caps was 105–601 mg/kg dw and 90–500 mg/kg dw in stalks, which are lower than values in species such as Boletus submontosus (77–1200 mg/kg dw), Pleurotus ostreatus (220–1400 mg/kg dw), and Agaricus bisporus (16000–25000 mg/kg dw) [26, 35, 36].

Uneven distribution of elements between caps and stalks is shown in Table 2. The caps of Boletus contained higher contents of K, P, Cu, Mg, and Zn and lower contents of Mn when compared to stalks. Reports also suggested similar results for these elements in Boletus edulis, Boletus submontosus, and Boletus scaber [26, 37, 38]. However, the contents of Ca, Fe, and Na between caps and stalks have no certain regularity (Table 2). Contents of Cu, P, and Zn in caps are approximately twice or even three higher than in stalks, and similar findings were obtained in the review of Falandysz and Borovička [5]. As can be seen from Table 2, both caps and stalks can be considered as abundant in P, K, Fe, Mg, Zn, and Ca, and Boletus could be considered potential dietary sources of these essential elements to humans.

According to the EU Scientific Committee, 60 kg of body weight was used for intake calculations. For intake calculations, usually a 300 g portion of fresh mushrooms per meal is assumed, which contains 30 g of dry matter [39]. The elements intakes by a normal (60 kg) consumer in mg per serving for all studied fruiting bodies are presented in Table 3.

### 3.2. Bioconcentration Factor (BCF). Bioconcentration factor (BCF) values in caps and stalks of Boletus are summarized in Table 4. Among the elements determined, P and K exhibit BCF > 1, except for BCF for stalk of Boletus edulis (Table 4), while Ca, Fe, Mg, Mn, and Na are bioexcluded (BCF < 1) by the Boletus species studied. Although a certain element in the soil is abundant and could accumulate to relatively high contents in the mushroom, BCF below 1 may be obtained, which was reported for Ca, Fe, Mg, Mn, and Na in a recent study [8].

Wild mushrooms such as Pholiota nameko, Tricholoma quercicolor, and Ramaria flava collected from Sichuan province (China) showed lower BCF values for potassium, that is, 0.84, 0.48, and 0.5, respectively [40]. Higher BCF values for K, Na, Zn, Cu, P, and Mg were found in Boletus submontosus, namely, 4400, 340, 110, 77, 40, and 21 for caps and 3900, 310, 67, 27, 18, and 11 for stalks, respectively [26]. Boletus edulis collected from Poland also showed higher levels of BCF values for Cu and Zn, that is, 3.6–31 for caps and 1.7–16 for

### Table 3: Daily metal intakes by a normal, 60 kg consumer in mg/serving.

| Species               | Cap       | Stipe    |
|-----------------------|-----------|----------|
| Boletus speciosus     | 5.16 ± 1.08 | 4.23 ± 2.73 |
| Boletus griseus       | 16.1 ± 1.68 | 15.4 ± 0.96 |
| Boletus luridus       | 14.3 ± 0.87 | 11.9 ± 4.95 |
| Boletus umbriniporus  | 4.98 ± 0.99 | 2.85 ± 0.36 |
| Boletus tomentipes    | 2.97 ± 1.35 | 3.39 ± 1.02 |
| Boletus edulis        | 9.6 ± 0.78  | 9.5 ± 0.99 |
| Boletus pallidus      | 10.3 ± 0.72 | 11.3 ± 1.68 |
| Boletus brunneissimus | 20.1 ± 1.02 | 4.62 ± 2.34 |
| Boletus rubellus      | 8.55 ± 2.01 | 19.0 ± 1.05 |
| Boletus acreus        | 4.2 ± 0.63  | 4.17 ± 0.18 |

Ca, Cu, Mg, Mn, Na, P, Zn
Correlation Analysis. Matrices of correlation coefficients among elements concentrations of the fruiting body (caps and stalks) and underlying soils are presented in Tables 5 and 6. Cu (r = 0.556) and Mn (r = 0.431) had significant correlations in caps, and high correlation were seen between Ca (r = 0.727), Cu (r = 0.6), and Fe (r = 0.569) in stalks. Similar results were obtained for Cu (r = 0.478), Mn (r = 0.389), and Fe (r = 0.417) in Verpa conica, Tricholoma terreum, and Boletus radialis, respectively [44]. Meanwhile, significant correlations were also found between Ca-Fe (r = 0.681), Cu-P (r = 0.775), Fe-P (r = 0.728), Mn-P (r = 0.667), Zn-K (r = 0.673), Zn-Mg (r = 0.675), and Zn-P (r = 0.76) for caps. For stalks, significant correlations were found between Cu-Mg (r = 0.721), Cu-P (r = 0.659), Fe-Mg (r = 0.719), Fe-P (r = 0.693), Zn-Mg (r = 0.824), Zn-P (r = 0.684), and Zn-P (r = 0.818).

4. Conclusion

The present study gives an overview for the levels of elements accumulation, determined in caps and stalks of ten species of Boletus from Yunnan province, southwest of China. From the nutritional point of view, these Boletus could be considered as a potential dietary source of essential elements such as...
P, K, Mg, Cu, Zn, Mn, and Fe. Elements K, P, Cu, Mg, and Zn are preferably accumulated in the cap of *Boletus*, while Mn is preferably accumulated in stalk. Depending on the environmental conditions and mushroom species, the values of BCF varied highly depending on chemical element and were >1 for P and K, while they were <1 for Ca, Fe, Mg, Mn, and Na. The correlation analysis showed that Cu, Mn, Ca, and Fe contents were highly correlated in the mushrooms as compared to the corresponding soils. Significant correlations were also obtained between Cu-P (r = 0.775), Fe-P (r = 0.728), and Zn-P (r = 0.76) for caps and Cu-Mg (r = 0.721), Fe-Mg (r = 0.719), Zn-Mg (r = 0.824), and Zn-P (r = 0.818) for stalks.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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