Research Article

Variations in Element Levels Accumulated in Different Parts of *Boletus edulis* Collected from Central Yunnan Province, China

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ICP-AES and microwave assisted digestion were applied to determine P, Mg, Ca, Zn, Na, Cu, Ba, Ni, V, Cd, Sr, Co, and Li in the caps and stipes of *Boletus edulis* collected from six spatially distant sites in Yunnan province, China. Fruiting bodies of King Bolete are abundant in P, Mg, Ca, Zn, Cu, and Na, followed by Ba, Cd, Ni, V, Li, Sr, and Co. Contents of P, Mg, Zn, and Cu are more abundant in caps than in stipes of King Bolete. However, elements such as Na, Ba, Cd, Ni, V, Li, Sr, and Co prefer to accumulate in stipes of mushrooms from Yaoan, Chuxiong. The results of this study indicate that spatial variations of elements between caps and stipes are mainly related to different bedrock soil geochemistry and enrichment capability for various elements.

1. Introduction

Edible wild-grown mushrooms are traditionally consumed as delicacy in lots of countries and many are also used in traditional Chinese medicine [1–4]. This would be due to the abundant sources of protein, carbohydrates, dietary fibre and certain vitamins, and minerals as well as bioactive components [5–7]. Reports suggested that edible wild-grown mushrooms have many pharmacological effects such as antioxidant, anti-tumor, and hypoglycaemic effect and boosting the immune system [8, 9]. In Yunnan province, the main wild edible and medicinal fungi are *Boletus*, *Tricholoma*, *Termitomyces*, *Aphyllaphorales*, and *Tuber* [10].

King Bolete (*Boletus edulis* Bull. Fr.) is famous for its nutrition, flavor, taste, appearances, and medicinal value worldwide [11]. In China, they are mainly distributed in Yunnan, Sichuan, Fujian, Shanxi, and Guizhou province and usually grow up under the pine forest and broad-leaved forest [12]. Some alkaloid substances such as adenine, choline, and putrescine are produced by King Bolete, which are one of the ingredients of traditional Chinese medicine—Shujin Pill [11]. Besides, studies have indicated that inhibition rate of King Bolete extract for Sarcoma-180 is 100% and 90% for ehrlich

ascites carcinoma [13, 14]. These functional characteristics are, as suggested by Qi et al., mainly due to the type and content of trace element but other active compounds seem also to take part [15].

Edible wild-grown mushrooms have a very effective mechanism to accumulate extremely high concentrations of macro- and microelements from soil [16–19]. Recognized factors influencing the bioaccumulation of trace elements in fungi are bedrock geochemistry, fungal lifestyle, environmental pollution, specific species, and element [20–24]. Fruiting bodies of King Bolete are naturally abundant in certain essential elements including P, K, Ca, Mg, Zn, Fe, Cu, and Se, but also in Hg, Cd, Pb, Ag, and Ni which are hazardous to human [25–29].

Central Yunnan province is one of the most wild edible mushrooms resource-rich and largest production regions in China. The main species are *Boletus*, *Leccinum*, *Xerocomus*, *Tricholoma matsutake*, *Termitomyces*, and *Thelephora ganbajun* [10]. Data published on element concentration of King Bolete did indicate the considerable variation between the sites, years, and reports [30, 31]. There is scarcity of data on minerals composition variation of King Bolete collected from China. In addition, due to the presence of hymenophore with

FIGURE 1: Localization of the sampling sites (dot) of *Boletus edulis* in central Yunnan, China.

generative spores in caps, distribution of elements is unevenly within the fruiting body of mushroom [32]. It is necessary to ascertain elements variation of King Bolete in China through knowledge of the concentrations of many essential and toxic elements. The objective was to examine and evaluate the distribution disparity in elements concentration (P, Mg, Ca, Zn, Na, Cu, Ba, Ni, V, Cd, Sr, Co, and Li) of caps and stipes of King Bolete collected from central Yunnan province, China.

2. Materials and Methods

2.1. Mushrooms Sampling. King Bolete (*Boletus edulis* Bull.: Fr.) samples were collected during summer and autumn in 2011 from six spatially distant sites in central Yunnan province, China (Figure 1). The specific site and number of specimens used in this study are given in Table 1. Fresh fruiting bodies were cleaned up with a plastic knife from visible plant or substrate debris and next separated to two parts (cap and stipe). Each sample was washed with deionized water and dried in an electrically heated oven at 65°C to constant weight. Dried samples were pulverized with a muller and stored in sealed polyethylene bag in dry condition for analysis.

2.2. Reagents and Apparatus. Deionized water and nitric acid solution were used to prepare all aqueous solutions and clean or soak the glassware. Nitric acid solution (HNO₃ 65%) and hydrogen peroxide (H₂O₂ 30%) were used for digestion of samples in automatic microwave digestion system. The contents of the minerals in King Bolete were determined using inductively coupled plasma atomic emission spectrophotometer (ICP-9000, Shimadzu, Japan).

2.3. Analysis. 0.5 g of dried and powdered sample was mixed with 4 mL HNO₃ (65%), 2 mL H₂O₂ (30%), and 3 mL deionized water in polytetrafluoroethylene (PTFE) pressure vessels and digested in microwave digestion system. Ultimate digest was transferred to 25 mL colorimetric cylinder using deionized water for constant volume and subjected to instrumental analysis. Concentration of all elements in caps and stipes was

TABLE 1: Locations and numbers of *Boletus edulis* samples collected from central Yunnan in 2011.

Code	Location	Number of samples
BE1	Baofeng, Jinning, and Kunming	11
BE2	Yulu, Nanhua, and Chuxiong	7
BE3	Pubei, Yimen, and Yuxi	12
BE4	Longchuan, Nanhua, and Chuxiong	10
BE5	Qianchang, Yaoan, and Chuxiong	8
BT6	Shaqiao, Nanhua, and Chuxiong	8

determined using inductively coupled plasma atomic emission spectrophotometer and for blank solutions and certified reference material (GBW07605) as well. Discrepancies between certified values and concentrations quantified were all below 10%.

3. Results and Discussion

Data on the parameters determined for caps and stipes of King Bolete are presented in Table 2. The element concentrations vary significantly not only among the collection sites but also within morphological parts of a particular fruiting body. Samples of King Bolete collected from different sites show rich content in P, Mg, Ca, Zn, Cu, and Na which accumulate both in cap and in stipe, followed by Ba, Cd, Ni, V, Li, Co, and Sr. Meanwhile, prominent differences in the concentrations of these elements are also found in the caps and in the stipes of King Bolete.

Qc/s value is a quotient between the minerals concentrations in caps and stipes, which is used to express the elements distribution within the fruiting body of the mushrooms. Significant differences have been suggested in loads of accumulated elements between caps and stipes, and some were caused by the site or year of mushroom collection [30, 31, 33]. In this study, multivariate Qc/s values are obtained between the elements and collection sites (Table 2). Minerals such as P, Mg, Zn, and Cu prefer to accumulate in the cap of King Bolete collected of all sites in this study. Except for the prevailing elements P, Mg, Zn, Ca, and Cu, Qc/s values for other elements in King Bolete collected from BE5 are <1. Consequently, these different distributions of elements between caps and stipes are mainly related to different bedrock soil geochemistry and ability to accumulate various elements.

3.1. Essential Elements: P, Mg, Ca, Zn, Na, Cu, Ni, and Co. P is the essential element that nearly participates in all physiological chemical reactions such as forming the bones, teeth, and nucleic acid, maintaining balance of ATP metabolism, and regulating acid-base balance. Rich concentrations are found in King Bolete and with the range of 4356–9013 mg kg⁻¹ and 2150–3891 mg kg⁻¹ dm for cap and stipe, respectively. So contents in caps are higher than in stipes, and Qc/s values vary between 1.62 and 2.57 (Table 2). King Bolete collected from mountain area of Liaoning province in China with 4995 mg kg⁻¹ dm agreed with this study [11]. P value

TABLE 2: Elements content of *Boletus edulis* collected from central part of Yunnan province in 2011 (mg/kg dm, mean, SD, range).

Elements	BE1	BE2	BE3	BE4	BE5	BE6
P						
Cap	5523 ± 1070 1429–13588	9013 ± 2328 11620–13010	5528 ± 705 4451–6406	6021 ± 1044 3970–7381	4356 ± 1146 1285–5655	5420 ± 1410 2339–7256
Stipe	3022 ± 535 1614–6086	3891 ± 965 2635–5008	2150 ± 406 1595–2794	3616 ± 1577 1679–7179	2668 ± 668 1285–3435	3348 ± 1229 3966–5730
Qc/s	1.83	2.32	2.57	1.67	1.63	1.62
Mg						
Cap	1221 ± 64 332–3071	1447 ± 137 2116–2334	935 ± 184 737–1404	1138 ± 185 782–1416	1028 ± 163 365–1397	918 ± 173 580–1136
Stipe	705 ± 42 406–1771	710 ± 143 462–889	442 ± 59 339–523	939 ± 261 607–1393	620 ± 48 653–645	636 ± 156 761–942
Qc/s	1.73	2.04	2.12	1.21	1.66	1.44
Ca						
Cap	212 ± 15 34–260	249 ± 64 303–476	656 ± 126 199–2435	635 ± 114 353–1118	339 ± 104 189–487	367 ± 149 204–924
Stipe	209 ± 11 26–279	236 ± 72 115–338	239 ± 68 125–349	952 ± 202 151–1632	144 ± 59 67–259	373 ± 121 170–750
Qc/s	1.01	1.06	2.74	0.67	2.35	0.98
Zn						
Cap	128 ± 69 29–299	534 ± 122 426–1370	204 ± 72 102–652	113 ± 26 79–167	54 ± 16.6 16–71	86 ± 21 38–103
Stipe	65 ± 13 38–134	332 ± 82 61–512	60 ± 24 39–120	66 ± 12 27–176	35 ± 9.3 16–45	47 ± 23 26–84
Qc/s	1.97	1.61	3.4	1.71	1.54	1.83
Na						
Cap	19.3 ± 5.8 5.8–57.2	35.2 ± 16.7 5.2–134	15.3 ± 9.9 3.8–89	100 ± 21 38–156	63 ± 6.7 55–74	2.9 ± 0.4 1.3–5.8
Stipe	19.6 ± 6.2 3.9–73.0	27.5 ± 5 2.1–41.1	23.5 ± 8.1 5.8–102	129 ± 34 69–202	95 ± 17 62–143	148 ± 47 16–242
Qc/s	0.98	1.28	0.65	0.77	0.66	0.02
Cu						
Cap	33.6 ± 1.8 11.5–81.3	884 ± 63 57–3025	40.3 ± 17 22–79	53.4 ± 44 19–202	17 ± 5.7 5.4–23.5	26.8 ± 8 17.3–41
Stipe	19.2 ± 2.3 10.6–52.3	703 ± 49 24–1496	20.4 ± 11 9–54	32 ± 21 14–87	8.6 ± 2.7 5.4–13	13.9 ± 3.8 9–20
Qc/s	1.75	1.26	1.98	1.67	1.98	1.93
Ni						
Cap	2.7 ± 0.8 1.27–4.33	5.2 ± 1.1 3–9.9	2.1 ± 0.35 1.5–2.6	5.2 ± 1.8 2.1–7.9	2.4 ± 0.7 1.2–3.2	63.7 ± 14 49–83
Stipe	1.7 ± 0.6 1.05–2.66	2.3 ± 0.42 1.86–2.96	1.1 ± 0.22 0.77–1.54	5.1 ± 3.1 2.3–15.2	16.7 ± 8 1.2–25.7	42.9 ± 16 25–62
Qc/s	1.59	2.26	1.91	1.02	0.14	1.48
Co						
Cap	1.0 ± 0.34 0.53–1.61	0.8 ± 0.36 0.29–1.64	1.1 ± 0.39 0.55–1.79	0.9 ± 0.21 0.54–1.36	0.4 ± 0.1 0.19–0.49	8.4 ± 2.7 4–13.6
Stipe	0.9 ± 0.25 0.34–2.13	0.5 ± 0.15 0.27–0.67	1.0 ± 0.61 0.38–2.04	0.8 ± 0.18 0.31–2.56	4.6 ± 1.7 0.39–5.9	6.3 ± 2.4 2.5–8.7
Qc/s	1.11	1.6	1.1	1.13	0.09	1.33
Ba						
Cap	8.1 ± 1.1 2.59–12.0	9.7 ± 3.4 3.96–20.3	6.6 ± 1.9 3.44–9.13	9.9 ± 4 4.5–18.2	4.8 ± 1.5 2.7–6.9	66.7 ± 32 26–136
Stipe	5.3 ± 0.58 3.27–7.81	4.4 ± 1.37 2.62–6.85	2.7 ± 0.7 1.78–3.84	9.6 ± 3.4 5.4–25.1	65.5 ± 20 3.4–73	41.1 ± 13 25–63
Qc/s	1.53	2.2	2.44	1.03	0.07	1.62

TABLE 2: Continued.

Elements	BE1	BE2	BE3	BE4	BE5	BE6
V						
Cap	1.7 ± 0.56 0.6–2.85	3.9 ± 0.86 1.24–8.75	1.2 ± 0.34 0.65–1.64	3.7 ± 0.8 0.98–7.29	1.6 ± 0.7 0.7–2.82	27.3 ± 10.5 12.5–46.6
Stipe	1.1 ± 0.34 0.45–1.93	1.4 ± 0.41 1.02–2.11	0.5 ± 0.02 0.33–0.92	3.4 ± 1.1 1.5–11.1	15.3 ± 4.8 0.9–23.9	15.8 ± 7.5 8–30
Qc/s	1.55	2.79	2.4	1.09	0.1	1.73
Cd						
Cap	2.1 ± 0.3 0.48–5.37	5.3 ± 1.9 1.2–13	1.2 ± 0.35 0.74–2.05	1.4 ± 0.67 0.76–2.99	1.6 ± 0.6 0.41–2.6	24.8 ± 5.6 11.8–36.5
Stipe	0.9 ± 0.25 0.35–1.95	1.5 ± 0.03 0.96–2.23	0.5 ± 0.1 0.31–0.82	0.9 ± 0.72 0.19–4.45	5.1 ± 1.9 0.5–9.1	10.1 ± 2.3 4–16.5
Qc/s	2.33	3.53	2.4	1.56	0.31	2.46
Sr						
Cap	4.4 ± 0.32 0.5–23.5	1.5 ± 0.1 0.45–3.34	1.5 ± 0.4 0.92–2.5	2.1 ± 0.57 1.13–2.89	0.9 ± 0.3 0.56–1.54	11.5 ± 5.9 6.7–24.8
Stipe	1.4 ± 0.5 0.78–2.14	0.9 ± 0.2 0.59–1.09	1.0 ± 0.37 0.64–1.82	1.9 ± 1 0.53–4.26	9.7 ± 3.1 0.59–15.4	9.9 ± 2.6 6.8–12.9
Qc/s	3.14	1.67	1.5	1.11	0.09	1.16
Li						
Cap	0.6 ± 0.03 0.37–1.02	1.6 ± 0.2 0.57–3.68	0.3 ± 0.05 0.18–0.36	1.6 ± 0.85 0.29–3.27	1.2 ± 0.45 0.7–2.1	5.9 ± 1.3 1.2–8.7
Stipe	0.4 ± 0.02 0.06–0.91	0.6 ± 0.17 0.42–0.88	0.2 ± 0.08 0.07–0.33	1.4 ± 1.1 0.57–3.96	3.1 ± 1.13 0.87–4.1	4.3 ± 1.26 0.3–3.89
Qc/s	1.5	2.67	1.5	1.14	0.39	1.37

Qc/s is the ratio of the element concentration in cap to stipe.

in fruiting body (cap and stipe) and Qc/s of King Bolete is insufficient.

Caps of King Bolete contain Mg at 918–1447 mg kg⁻¹ dm, which are higher than for stipes (442–939 mg kg⁻¹ dm). Lower values of 590–960 mg kg⁻¹ dm were obtained for caps of King Bolete collected from Poland [31, 33, 34]. However, in the study by Liu et al. [23], elevated contents of Mg (1100–1500 mg kg⁻¹ dm) were got in wild-grown mushroom such as *Catathelasma ventricosum*, *Laccaria amethystina*, and *Stropharia rugoso-annulata*.

Ca is the activator of more than 200 kinds of enzymes in the human body, which can make each organ function well. Na concentration values distribution in King Bolete varies depending on the sites (Table 2). Qc/s values for Ca vary between 0.67 and 2.74, and contents of stipes for BE4 (0.67) exceed that of caps, and opposite feature could be observed for BE3 (2.74) and BE5 (2.35), while they are similar for BE1 (1.01), BE2 (1.06), and BE6 (0.98).

Zinc contents were reported at between 28 and 140 mg kg⁻¹ dm for edible wild-grown mushrooms collected from China [7]. Meanwhile, higher concentration was also reported showing its physiological importance to mushroom. The examples are as follows: 190 mg kg⁻¹ dm (cap) [34], 240 mg kg⁻¹ dm (cap) [35], and 580 mg kg⁻¹ dm (whole fruiting body) [30]. As shown in Table 2, stipes of King Bolete are half or even less than caps in essential Zn, and value of Qc/s for Zn in this study is 1.54–3.4, which extremely agrees with literature data previously reported [16]. Nevertheless, a higher value (Qc/s = 4.6) was reported in fruiting body

of King Bolete collected from Xichang in Sichuan province, China [36].

Na content for caps is between 2.9 and 100 mg kg⁻¹ dm and for stipes between 19.6 and 148 mg kg⁻¹ dm. Higher values were determined in cultivated and some preserved mushrooms and content was 860, 1000, and 16000–25000 mg kg⁻¹ dm for *Agaricus bisporus* (whole), *Lentinula edodes*, and *Agaricus bisporus* (preserved), respectively [37–39]. Na is present higher in concentrations in stipes than in caps, except for samples collected from BE2 (Yulu, Nanhua) with the value of 1.28 (Table 2). Published data in stipes of King Bolete are about twice more abundant in Na than the caps [16]. Report also suggested the similar Qc/s value (0.45) for sodium in parasol mushroom *Macrolepiota procera* [40].

Cu is an essential element, and a large variation of values is noted; they ranged, respectively, between 17–884 and 8.6–703 mg kg⁻¹ dm for caps and stipes (Table 2). Cu in this study is more abundant in caps than stipes of King Bolete, and Qc/s value varies between 1.26 and 1.98. Higher Qc/s value of 2.8 was obtained for King Bolete collected from Pbocka Dale in Poland [34]. In addition, Cu contents in caps of *Leccinum* mushrooms from Poland were half or even less than in stipes [41].

Published data on Ni and Co in caps and stipes of King Bolete is few and relatively insufficient. Ni content of King Bolete at six sites varied between 2.1 and 63.7 mg kg⁻¹ dm in caps and between 1.1 and 42.9 mg kg⁻¹ dm in stipes. The mean Co concentrations were 0.4–8.4 and 0.5–6.4 mg kg⁻¹ for caps and stipes, respectively. Published data on Co contents were

usually below or around 0.5 mg/kg DM, which were lower than the results in this study [42]. Contents in caps are somewhat higher than those in stipes except sample collected from BE5; that is, Qc/s value is 1.02–2.26 and 1.1–1.6 for Ni and Co, respectively.

3.2. Ba, V, Cd, Sr, and Li. As shown in Table 2, Ba, V, Cd, Sr, and Li contents in samples from BE6 are obviously higher than those from other regions, which is most probably depending on the geological bedrock in this site. Arithmetic mean of Qc/s for these elements is 1.03–3.53; nevertheless, for certain site (BE5) the Qc/s value is <1.

Ba content is in the range of 4.8–66.7 and 2.7–65.5 for caps and stipes, respectively, and these values are particularly higher than the reference data previously reported, which were 0.2–1.5 mg kg⁻¹ dm for caps and 0.36–1.4 mg kg⁻¹ dm for stipes [30, 31, 33, 34].

Reports on V contents on King Bolete were very few, and literature data were 0.02–0.09 mg kg⁻¹ dm in caps, 0.03 mg kg⁻¹ dm in stipes, and 1.27 mg kg⁻¹ dm in whole fruiting body [27, 31]. King Bolete in this study contains V at elevated concentrations; for caps it is 1.2–27.3 mg kg⁻¹ dm and for stipes at 0.5 to 15.8 mg kg⁻¹ dm, Qc/s value is 0.1–2.79.

Cd is toxic metallic element is found in edible mushrooms and can leach out of fruiting bodies during boiling. Tolerance limit is 2 µg/g dm for cultivated mushroom, and no such tolerances exist for edible wild-grown fungi [43]. Apart from the highest value (24.8 mg kg⁻¹ dm) of cap from EB6, other values are relatively low, which is consistent with the results of earlier studies [16].

King Bolete contains Sr at 0.9–11.5 mg kg⁻¹ dm in caps and at 0.9–9.9 mg kg⁻¹ dm in stipes, which is higher value than for samples from Poland. Most of the sites surveyed caps, when compared to stipes containing higher content of Sr, and opposite feature was found in earlier reports [30, 31, 33, 34].

The lithium salt, Li₂CO₃, is considered as a therapeutic for neurodisorders. Li is a trace element in fungi, and content is relatively low [16]. Li content of King Bolete from Italy was between 0.04 and 0.9 mg kg⁻¹ dm [44]. Higher results are determined in present study: mean value of Li is from 0.3 to 5.9 mg kg⁻¹ dm in caps and from 0.2 to 4.3 mg kg⁻¹ dm in stipes.

4. Conclusion

King Bolete collected from central Yunnan province contained high content of elements such as P, Mg, Ca, Zn, Na, and Cu, next for Ba, Ni, V, Cd, and Sr, and the least for Co and Li. Distribution of elements in different parts of King Bolete was unevenly, mainly depending on the hymenophore in the caps. In addition, spatial variations of Qc/s value were noted for King Bolete from different sites, which seem to be due to variations in local soil substrate geochemistry. Our results indicated that there is a close relationship between element concentrations and hymenophore in cap and bedrock soil geochemistry.

Conflict of Interests

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

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