Macroelement and Microelement Contents in Wild Edible Mushroom Species from the Southern Regions of China

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Macroelement (P, Na, K, Ca, Mg) and microelement (Zn, Fe, Mn, Cd, Cr, Pb) contents in 8 different wild-growing edible mushroom species collected from the southern regions of China were determined by flame and graphite furnace atomic absorption spectrometry. All element concentrations were determined on a dry weight basis. The highest mean concentration of macroelements was found for K (22.2 g/kg), followed by P (5.15 g/kg), Ca (2.66 g/kg), Mg (1.23 g/kg) and Na (1.18 g/kg). The ranges of macroelement concentrations for K, P, Ca, Mg and Na were 11.6-34.2, 3.42-8.02, 0.85-3.83, 0.57-1.90 and 0.77-1.43 g/kg, respectively. The mean microelement concentrations, across all tested fungi, were in the following order: Fe > Zn > Mn > Cd > Pb > Cr. The ranges of microelement concentrations for Fe, Zn, Mn, Cd, Pb and Cr were 471.3-2906, 82.8-274.2, 21.3-283, 0.4-91.8, 2.0-10.8 and 0.2-4.6 mg/kg, respectively. Levels of heavy metals (Cd, Pb) in *Russula vinosa*, *Russula virescens* and *Lyophyllum decastses* can be considered as low when compared with European statutory limits. Therefore, the three wild mushrooms can be used in well-balanced diets due to their contents of functional minerals.

Key Words: Wild edible mushrooms, China, Trace metals, Atomic absorption spectrometry.

INTRODUCTION

Mushrooms are valuable health foods, low in calories and high in vegetable proteins, vitamins, chitin, fibers and minerals[1-4]. The trace elements in mushrooms are of great biochemical interests and having nutritional and important medicinal attributes, including anticancer, antiviral, immunopotenhancing, hypolipidemic activities[5]. The content of metals is generally assumed to the species-dependent, collecting site of the sample, age of fruiting bodies and mycelium and distance from sources of pollution[6]. Heavy metal concentrations in mushrooms are also considerably higher than those in agricultural crop plants, vegetables and fruits. This suggests that mushrooms possess a very effective mechanism that enables them readily to concentrate certain heavy metals from the ecosystem, compared to green plants growing in similar conditions[7]. According to Stije and Besson[8], the mechanism by which some heavy metals are accumulated is somewhat obscure although it seems to be associated with a chelation reaction with sulfhydryl groups of protein and especially with methionine.

About 2,500 species of edible mushrooms exist in nature, with nearly 1,000 species showing various degrees of edibility in China[9]. The southern areas in China have a mild and rainy climate in summer and autumn, providing nearly ideal conditions for fungal growth, with temperatures ranging between 20 ºC and 30 ºC. People who live in this region of China have widely consumed wild edible mushrooms because of their delicate flavor and texture as well as their high content of trace minerals. However, certain forms of some metals can also be toxic, even at very low concentrations and therefore pose a risk to the health of animals and people. Therefore, it is necessary to investigate the metal content in wild species, given the fact that many of them are known to accumulate high levels of heavy metals, such as cadmium, mercury, lead and copper[10].

In China, as in many other countries, fungi collection is very popular, particularly in summer and autumn. Thus, some people collect fungi in such quantities that they can make a substantial contribution to food intake. However, few studies have been reported on the trace element concentrations of wild-growing edible mushrooms in southern areas of China. The purpose of this study is to (1) evaluate macroelement and microelement contents in fruiting bodies of wild grown, mostly edible fungi collected from the south forest region of China and (2) search for edible species which accumulate high levels of toxic metals, in order to assess the possible dietary risk to human health.

EXPERIMENTAL

Samples of mushrooms were collected from southern areas of China in summer and autumn 2008. The habitat, edibility and the families of mushroom species are given in Table-1. The collected samples were washed with distilled water and placed on trays. Each sample was oven-dried at 60 ºC to constant weight and then powdered to pass through a 40 mesh sieve.

TABLE-1
FAMILIES, HABITAT AND EDIBILITY OF MUSHROOM SPECIES

Class, family and species of mushrooms	Habitat	Edibility
Russula vinosa Lindbl.	Under beech	Edible
Russula virescens (schaeff. ex Zanted) Fr.	Amongst grass under broad leafed trees	Edible
Russula albida Peck	In woodland	Edible
Lyophyllum decastses (Fr.) Sing	Under broad leafed trees or conifers	Edible
Cantharellus cibarius Fr.	In mixed woodland	Edible
Calvatia craniiformis (Schw.) Fr.	In woodland	Edible (only when young)
Agaricus silvaticus Schaeff.: Fr.	Under broad leafed trees or conifers	Edible
Macrolepiota crustosa Shao et Siang	Under deciduous trees	Edible

One gram of sample was placed in a porcelain crucible and ashed in an oven at 420-450 ºC for 15-24 h. Ashed material was dissolved in 2 mL concentrated HNO_3, evaporated to dryness, heated again to 450 ºC for 3 h, dissolved in 1 mL conc. H_2SO_4 and 2 mL conc. HNO_3 and diluted with distilled water up to 25 mL. A blank digest was carried out in the same way. For the element analyses, a Hitachi Z-8000 atomic absorption spectrometer was used in this study. Phosphorus content was measured by phosphorus molybdenum blue spectrophotometry. Pb and Cd levels in samples were determined by a HGA graphite furnace, using argon as inert gas. Other measurements were carried out in an air/acetylene flame. The instrumental parameters and operating conditions are given in Table-2.

TABLE-2
INSTRUMENTAL ANALYTICAL CONDITIONS OF ELEMENT ANALYSES

Element	Acetylene (l/min)	Air (l/min)	Wavelength (nm)	Slit width (nm)	Lamp current (mA)
Mg	2.0	17.0	283.3	0.5	4
K	2.0	17.0	766.5	0.5	5
Na	2.0	17.0	589.0	0.5	6
Ca	2.0	17.0	422.5	0.5	4
Fe	2.0	17.0	248.3	0.2	30
Mn	2.0	17.0	279.5	0.2	20
Zn	2.0	17.0	213.9	0.7	15
Cr	2.5	17.0	357.9	0.7	25
Pb	2.0	17.0	283.3	0.7	30
Cd	2.0	17.0	228.8	0.7	4

In order to validate the method for accuracy and precision, certified reference materials, namely spinach CRM 10015 (National Institute of Standards and Technology) were analyzed for corresponding elements. A control sample was digested and analyzed with each analytical batch of samples to check the effectiveness of our digestion procedure. Each time its concentration deviated more than 10 % from the certified value the calibration curve was reconstructed.

RESULTS AND DISCUSSION

The results of the analysis of the CRM show good agreement with the certified levels, as shown in Table-3.

Mineral contents appeared to be dependent on type of the mushrooms analyzed. The mean concentrations for each analyzed macroelement in the whole fruiting body are shown in Table-4.

The highest mean concentration, on a dry weight basis, was found for K (22.2 g/kg), followed by P(5.15 g/kg), Ca(2.66 g/kg) Mg(1.23 g/kg) and Na(1.18 g/kg). The contents of K were high in comparison to Na and Na/K ratio is very low, which is considered to be an advantage from the nutritional point of view. The highest K concentration was measured in *Macrolepiota crustosa* (34.2 g/kg) and the lowest was found in *Lyophyllum decastses* (11.6 g/kg). The Na contents (mean 1.18 g/kg) are, however, higher in the present study than in previous studies[11,12]. But there are no great differences among the species. *Macrolepiota crustosa* had the highest P content (8.02 g/kg). The lowest content of P was found in *Russula vinosa* (3.42 g/kg). The P results of all mushroom species are in agreement with those found in the literature[13]. Comparatively high Ca concentrations (3.83 g/kg) were measured in *Lyophyllum decastses*, *Russula vinosa* contained relatively less Ca (0.85 g/kg). The Ca levels obtained in the present study are generally higher than those obtained previously[11,13]. Magnesium levels were similar in all the mushrooms analyzed and were of levels similar to those generally found in vegetables. The highest (1.90 g/kg) Mg content was found in *Calvatia craniiformis* and the lowest (0.57 g/kg) was found in *Russula vinosa*. Magnesium contents obtained in this study are generally in accordance with previous publications[11,14].

TABLE-3
VALUES DETERMINED FOR THE MEASURED METALS USING CERTIFIED REFERENCE MATERIAL (SPINACH) AS SAMPLE

Metals	Certified value (µg/g)	Determined (µg/g)[a]	Recovery (%)
Na	15000 ± 600	14850 ± 522	99
K	24900 ± 1100	25000 ± 265	100
Mg	5520 ± 150	5355 ± 99	97
Ca	6600 ± 300	6300 ± 56	95
Fe	540 ± 20	535 ± 15	99
Mn	410 ± 3	415 ± 27	101
Zn	35.3 ± 1.5	33.5 ± 1.4	95
Cr	1.4 ± 0.2	1.35 ± 0.1	96
Pb	11.1 ± 0.9	11.0 ± 1.13	99
Cd	0.15 ± 0.025	0.14 ± 0.021	93

[a]Average of three separate digestions.

TABLE-4
MACROELEMENT CONCENTRATIONS (g/Kg, DRY WEIGHT) IN THE FRUITING BODIES OF EIGHT FUNGAL SPECIES FROM THE SOUTHERN REGIONS OF CHINA

Mushroom samples	P	K	Na	Ca	Mg
Russula vinosa	3.42 ± 0.2	19.8 ± 0.5	1.34 ± 0.09	0.85 ± 0.18	0.57 ± 0.04
Russula virescens	4.94 ± 0.5	21.9 ± 1.7	1.41 ± 0.14	3.40 ± 0.70	1.05 ± 0.04
Russula albida	5.05 ± 0.4	21.8 ± 0.8	1.10 ± 0.26	2.91 ± 0.93	0.85 ± 0.11
Lyophyllum decastses	3.92 ± 0.2	11.6 ± 0.8	1.41 ± 0.25	3.83 ± 0.42	1.20 ± 0.04
Cantharellus cibarius	4.18 ± 0.7	28.9 ± 1.2	1.43 ± 0.32	3.38 ± 0.20	1.28 ± 0.20
Calvatia craniiformis	5.98 ± 1.0	16.3 ± 1.3	1.05 ± 0.33	2.40 ± 0.63	1.90 ± 0.47
Agaricus silvaticus	5.70 ± 0.3	22.7 ± 2.4	0.77 ± 0.08	1.09 ± 0.14	1.31 ± 0.15
Macrolepiota crustosa	8.02 ± 0.9	34.2 ± 1.6	0.93 ± 0.21	3.41 ±1.18	1.65 ± 0.11
mean	5.15 ± 0.5	22.2 ± 1.3	1.18 ± 0.21	2.66 ± 0.55	1.23 ± 0.15

Results represent means of three replicates ± standard deviation.

The mean concentrations of microelements in the entire fruiting body are shown in Table-5. The mean microelement concentrations, across all tested fungi, were in the order: Fe > Zn > Mn > Cd > Pb > Cr. The highest Fe content (2906 mg/kg) was found in *Cantharellus cibarius* whereas the lowest Fe content (471.3 mg/kg) was found in *Macrolepiota crustosa*. Fe contents given in the literature[13-15] are much lower than those of found in present study.

TABLE-5
MICROELEMENT CONCENTRATIONS (mg/kg, DRY WEIGHT) IN THE FRUITING BODIES OF EIGHT FUNGAL SPECIES FROM THE SOUTHERN REGIONS OF CHINA

Mushroom samples	Fe	Mn	Zn	Cr	Pb	Cd
Russula vinosa	503.7±35.7	23.3±1.5	88.2±7.7	2.8±1.8	2.7±0.7	0.9±0.1
Russula virescens	1758.5±51.9	41.0±5.3	96.6±7.9	3.9±1.2	2.0±0.3	0.4±0.1
Russula albida	761.1±41.7	21.3±2.5	121.6±16.4	ND[a]	9.6±0.8	3.0±0.5
Lyophyllum decastses	1065.3±40.3	283±12.3	145±14.9	0.2±0.1	3.0±0.4	1.6±0.2
Cantharellus cibarius	2906±91.4	55.2±7.1	82.8±4.3	3.2±0.9	4.6±0.4	0.9±0.2
Calvatia craniiformis	1751.3±39.1	47.5±8.4	209.5±9.3	3.7±1.4	10.8±1.4	9.1±0.8
Agaricus silvaticus	812.7±40.6	36.3±1.5	213.1±13.2	4.6±2.6	9.3±0.7	51.9±4.1
Macrolepiota crustosa	471.3±34.3	59.7±3.5	274.2±26.7	1.7±0.4	7.4±0.9	91.8±9.0
Mean	1253.7±46.9	70.9±5.3	153.9±12.6	2.5±1.1	6.2±0.7	20.0±1.9

Results represent means of three replicates ± standard deviation.
[a]ND: Not determined.

Minimum and maximum values of Zn in the present study were 82.8 and 274.2 mg/kg. The highest and lowest levels were found in *Macrolepiota crustosa* and *Cantharellus cibarius*, respectively. Hence, Zn contents in mushrooms are in agreement with the previous studies[10,12,16]. Zinc is widespread among living organisms due to its biological significance. The highest Mn content was 283 mg/kg, for the species *Lyophyllum decastses*, whereas the lowest Mn content was 21.3 mg/kg, for the species *Russula albida*. Manganese contents in mushrooms are in good agreement with previous studies[11,14,17].

The highest concentration of Cr was found in *Agaricus silvaticus* (4.6 mg/kg). Chromium content was not determined in *Russula albida*. Chromium results in mushrooms are close to those found in the literature[3,14,18].

The highest Pb content in mushroom samples investigated (10.8 mg/kg) was found in *Calvatia craniiformis* whereas the lowest Pb content (2.0 mg/kg) was found in *Russula virescens*. The Pb concentrations of previous studies were between 0.1 and 40 mg/kg[19,20]. Lead is especially toxic to the growing brain and can affect the behavioral development of youngsters, even at low concentrations. Organic lead compounds are fat soluble and are more toxic than other forms. Such forms of lead can pass through the placenta and thus affect a growing fetus[11].

The highest Cd content (91.8 mg/kg) was found in *Macrolepiota crustosa* whereas the lowest Cd content (0.4 mg/kg) was found in *Russula virescens*. Cadmium contents of *Agaricus silvaticus*, *Calvatia craniiformis* and *Macrolepiota crustosa* are higher than the most of literature values[3,17,18]. Cadmium is known as a principal toxic metal, since it inhibits many life processes[21]. It can be taken up directly from water and *via* food and it has a tendency to accumulate in plants and animals[11,22].

A linear regression correlation test was performed to investigate correlations between metal concentrations. The values of correlation coefficients between metal concentrations are given in Table-6. There are good correlations between P-Na, P-Zn, P-Cd, Na-Zn, Na-Pb, Na-Cd, Mg-Zn, Mn-Cr and Zn-Cd pairs. The other correlations between metals are not significant. There are positive correlations of P-Zn, P-Cd, Mg-Zn and Zn-Cd pairs. Negative correlations were found between P-Na, Na-Zn, Na-Pb, Na-Cd and Mn-Cr pairs.

TABLE-6
METAL-TO-METAL CORRELATION COEFFICIENT MATRIX
FOR MUSHROOM SAMPLES

	P	K	Na	Ca	Mg	Fe	Mn	Zn	Cr	Pb	Cd
P	1.000										
K	0.572	1.000									
Na	–0.737*	–0.293	1.000								
Ca	0.165	0.112	0.401	1.000							
Mg	0.703	0.173	–0.449	0.295	1.000						
Fe	–0.260	0.058	0.485	0.388	0.263	1.000					
Mn	–0.253	–0.524	0.354	0.498	0.099	–0.017	1.000				
Zn	0.883**	0.275	–0.821*	–0.019	0.744*	–0.417	0.023	1.000			
Cr	0.082	0.182	–0.343	–0.536	0.042	0.279	–0.815*	–0.069	1.000		
Pb	0.590	0.118	–0.820*	–0.216	0.541	–0.157	–0.355	0.626	0.375	1.000	
Cd	0.856**	0.644	–0.747*	–0.048	0.475	–0.459	–0.142	0.859**	–0.043	0.379	1.000

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

The occurrence and distribution of different macroelements and microelements in fruiting bodies of certain mushrooms is not only an important problem for physiology and ecology of fungi, but also has practical environmental and toxicological aspects[21]. Therefore, the investigation of the biological mechanisms of uptake and accumulation could play an important role in the future. As harvesting of mushrooms in forests, either commercially or recreationally, is increasing, it is important to ensure that mushroom resource is safe and the toxic element contents are kept within limits safe for human health.

The maximum level for certain contaminants in foodstuffs established by the Commission of the European Communities[23] is set at about 0.2 and 0.3 mg/kg for wet samples of Cd and Pb, respectively, in cultivated fungi. For intake calculations, usually a 300 g portion of fresh mushrooms per meal is assumed, which contains 30 g of dry matter[7,10]. The tolerance limits for dry material will be 2.0 and 3.0 mg/kg dry weight for Cd and Pb, respectively.

The present results show that samples of *Russula albida*, *Calvatia craniiformis*, *Agaricus silvaticus* and *Macrolepiota crustosa* from the southern regions of China have elevated Cd and Pb concentrations and exceed the European tolerance limits set for dried mushrooms.

Conclusion

Basic documentation of metal levels in the southern regions of China has an important application, given the increasing popularity of wild sporocarps as cuisine in China. Extensive studies on this issue have been undertaken in countries, such as many of the nations in eastern Europe. In contrast, only a few studies on trace element concentrations in wild edible fungi have been conducted in China. Basic documentation of metal levels in fungi would be in the public interest. From the above results it can be seen that the four wild edible fungi examined in this study, *Russula albida*, *Calvatia craniiformis*, *Agaricus silvaticus* and *Macrolepiota crustosa*, from southern regions of China should be consumed with caution when monitoring Cd and Pb intake. The collected samples, *Russula vinosa*, *Russula virescens* and *Lyophyllum decastses*, can be used in well-balanced diets due to their contents of functional minerals and low toxic metal contents.

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