Macro- and Microelement Contents of Fruiting Bodies of Wild-Edible Mushrooms Growing in the East Black Sea Region of Turkey

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ABSTRACT

Eleven different wild-edible mushroom species growing in the Black Sea region of Turkey were analysed for their element content. Specimens of mushrooms were gathered in Trabzon, Giresun and Ordu and analyzed for 31 elements by ICP-OES, four of which (Be, Sb, Te and Ti) were not detected. Whereas some minerals including Ag, As, Cd, La, Mo, Pb, Se, Y and Zr were detected in just a few mushroom species, another 18 minerals were found in all 11 species. All element concentrations were expressed on a dry weight basis (d.w.). With regard to nutritionally important amounts of essential and trace minerals, the element content (µg/g d.w.) of mushroom samples ranged from 21800 - 39800 for K, 2590 - 14000 for P, 268 - 1600 for Ca, 561 - 1210 for Mg, 561 - 1210 for Fe, 11.2 - 321 for Cu, 36.2 - 241 for Zn, 14.1 - 76.5 for Mn and 0.13 - 2.85 for Co. Small amounts of toxic metals such as As, Cd and Pb were found in all 11 mushroom species. Laccaria laccata contained a large amount of As (145 µg/g d.w.). These results show that the investigated mushrooms can be a useful component for human diets because of their high content of many essential minerals and trace elements and low content of toxic metals.

Keywords: Wild-Edible Mushrooms, Mineral Content, Toxic Metals, Trace Elements, Turkey

1. Introduction

Hunger has increased in the world over the past several years due to rising food prices and food scarcity caused in part by the diversion of farmland from the production of foods to the generation of ethanol for motor vehicles. These circumstances have led populations in many parts of the world to search for alternative food sources that would contribute to satisfying their nutritional needs. In this regard, many people worldwide collect wild-edible mushrooms to supplement their diets. However, since in many cases our knowledge of the mineral composition of wild-edible mushrooms is incomplete, there is a need for studies that will provide this information.

Mushrooms are an important class of organisms in nature and can be found almost everywhere on the earth. The macrofungi that includes numerous wild-edible and cultivated species do not normally constitute a large portion of the human diet; however, interest in the consumption of wild and cultivated mushrooms is increasing in many countries due to awareness of their high content of various essential nutrients, including trace minerals [1-10]. In this respect, the fact that wild mushrooms accumulate large amounts of both macro- and trace minerals has prompted researchers to analyze them for their metal contents, especially since many mushrooms accumulate high levels of heavy metals such as cadmium, mercury, lead, copper and arsenic [3,11] that can have severe toxicological effects on humans, even at very low levels.

Several factors may affect the accumulation and content of trace elements and heavy metals in mushrooms. During the past two decades, in addition to reporting on heavy metals in mushrooms, many studies have also investigated the contents of both nutritionally significant major and trace minerals in macrofungi in the northern hemisphere [1-8,12-19]. Some of these studies were conducted in the Black Sea region of Turkey, where numer-
ous mushroom species grow in the country that spans the continents of Europe and Asia, [5,12-15,17-19,20-23]. The region of Turkey where the mushroom species reported herein were collected has a rich macrofungal flora [13]. In eastern Turkey, the climate is mild and rainy and all four seasons are normally wet with mild temperatures. The climate throughout the year, but especially in spring and autumn, is ideal for fungal growth. People who live in this region of the country often include mushrooms in their diet. However, data related to nutrients of wild edible mushrooms of the region are scarce. In the present study, 11 mushrooms in the Black Sea region of Turkey were analysed for their content of micronutrients. To our knowledge, no previous work on the mineral content of these mushroom species has been reported either from the region or from other habitats around. The present study reports the mineral content of fruiting bodies of 11 wild-edible macrofungi samples collected from the Black Sea region of Turkey determined using an inductively coupled plasma-optical emission spectrometer (ICP-OES).

2. Materials and Methods

2.1. Collection of Mushrooms

Fruiting bodies of 11 wild-edible mushrooms (Laccaria laccata, Leucopaxillus giganteus, Russula rosea, Cantharellus cibarius, Tricholoma saponaceum var. saponaceum, Agaricus arvensis, Boletus edulis, Clavulina rugosa, Hydnum repandum, Cantharellus tubaeformis, Lepista nuda), belonging to 8 different families were collected during field trips to the provinces of Trabzon, Giresun and Ordu between 2002 and 2005. At each collecting site the ecological and morphological properties of the specimens were recorded (Table 1). The specimens were then taken directly to the laboratory and examined microscopically using Nikon research microscopes. After spore prints were made to determine the color of the spores, the spores were then subjected to various measurements. The specimens were grouped according to taxa, lyophilized to a constant weight, and reduced to a fine powder (20 mesh) for further chemical analysis.

Taxonomic identification was made according to criteria described elsewhere [24,25] and representative voucher specimens were deposited at a personal fungarium of Faculty of Fatih Education at the Karadeniz Technical University in Trabzon, Turkey. All extractions and determinations were performed in triplicate and the results are expressed plus or minus one standard deviation and dry weight basis (d.w.), as means.

2.2. Mineral Analysis

The lyophilized and milled samples were dried for seven days in a vacuum desiccator until a constant weight. Triplicate portions (approx. 0.2 g) of each specimen were weighed into 125 mL Phillips beakers and digested with 20 mL of concentrated nitric acid and 1 mL of perchloric acid. The samples were covered with watch glasses and let stand for 1 hour at room temperature on a hot plate. The temperature was ramped at 50 C/15 min to 150 C where they were left to reflux for 24 hours. The watch-glass covers were removed and the samples were taken to near dryness at the same temperature. The samples were cooled to room temperature and dissolved in 10.0 ml of 4% nitric acid/1% perchloric acid. The solutions were analyzed for their mineral and trace metal content by ICP-OES. This digestion technique does not dissolve any siliceous material present in the samples. The results are expressed as μg/g dry weight (d.w.).

2.3. Statistical Analysis

Data are the three separate extractions and determinations of completely random experimental design. Duncan’s Multiple Range Test was used to determine the statistical significance of differences among the means (SAS Institute Inc., Cary, NC, USA). Means were compared within each row of the data. For comparisons among the means analysis of variance was used.

3. Results and Discussion

The families of mushroom species used in this study, their habitat and geographical locations are given in Table 1 and all element concentrations are given in Table 2. Thirty one minerals were scanned; however, since detectable levels of Be, Sb, Te and Tl were not found in the samples, these metals were excluded from the tables. The element concentrations varied significantly not only among the mushroom species but also within a particular genus (Table 2, p < 0.05). The limit of detection and average values for each element are also given in Table 2. Amounts of Ag, Cd, Co, Li, Mo, Se, Y and Zr for some mushroom species were below the limit of detection. The detection limits of the method for Ag, Cd, Co, Li, Mo, Y and Zr were 0.34, 0.05, 0.06, 0.01, 0.09, 0.86, 0.10, and 0.25 μg/g, respectively (see the end note of Table 2).

According to the results shown in Table 2, the highest K concentration was found in T. saponaceum var. saponaceum (39800 μg/g), whereas L. laccata and C. rugosa had average K contents that were slightly lower at (30200 μg/g and 28900 μg/g, respectively). The second most abundant element among 11 mushroom species was P and its content varied between 2590 and 14000 μg/g, being remarkably high in L. giganteus and L. nuda. Comparatively high Ca concentrations (1600 μg/g) were found in C. tubaeformis followed by L. laccata (10500 μg/g).
A high and remarkably changing level was noted in Mg. The Mg content (mean 870 μg/g) ranged from 561 and 1210 μg/g, and was highest in A. arvensis and L. nuda (1210 and 1200 μg/g) and lowest in C. tubaeformis (561 μg/g). The average concentration of Na was 492 μg/g and its content was the highest in C. tubaeformis (669 μg/g) and lowest in C. rugosa (336 μg/g).

As revealed by ANOVA analysis, the majority of the mushroom species differed in significantly among these species in terms of macroelement concentrations (Table 2). In general, the range of macroelement concentrations in the mushrooms we studied concurs with the literature values (μg/g d.w.) for K (2421 - 45200), P (1200 - 10600), Ca (34 - 5300), Na (28 - 400) and Mg (58 - 1800) [4,6,10,16]. Recently, Ouzouni et al. [26] reported a higher content of Mg for C. cibarius (866.3 μg/g) and a lower content of Mg for L. nuda (949.8 μg/g d.w.) than those reported in the present study (815 and 1200 μg/g, respectively).

The contents of Co, La, Li, Mo, V, Y and Zr averaged between 0.2 and 0.8 μg/g. The amounts of others (Ag, Ba, Cd, Cr, Ni, Pb, Se, Sr and Ti) ranged from 1.3 to 11 μg/g, being the highest for Se. Among the elements, no satisfied biological roles for Ag, Ba, Sr, Ti, Y and Zr have been reported so far.

The Cd and Pb contents of the tested mushrooms were comparatively low (mean: 1.46 and 1.78 μg/g). Measurable Pb was found only in one sample, namely L. laccata (1.78 μg/g). Lead is especially toxic to the growing brain and can affect the behavioral development of children, even at low concentrations. Organic lead compounds are fat-soluble and are more toxic than inorganic forms, and can pass through the placenta and thus affect a growing fetus [8,20]. The highest Cd concentration was 10.6 μg/g for A. arvensis and the lowest concentration was 0.14 μg/g for C. tubaeformis. Cadmium is known to be toxic and inhibitory of many critical life processes [27]. It can be taken up directly from water and food and it has a tendency to accumulate in plants and animals [8]. Mushrooms may contain large amounts of Cd [8]. The ability to accumulate Cd is a characteristic of mushrooms [16] and is closely correlated with the presence of a genetically-determined binding compound [8,27]. The Cd values reported in the literature for a wide range of mushroom species were between 0.02 and 5 μg/g d.w.

The highest (1320 μg/g) and the lowest (93.5 μg/g) amounts of Al were found in C. rugosa and B. edulis, respectively. In the present study, Al was detected in only two samples of macrofungi, namely, L. laccata and L. giganteus, 145 and 10.4 μg/g, respectively. The highest amount of Cu (321 μg/g) was found in C. rugosa and the lowest was found in H. repandum (11.2 μg/g). The mean Cu content of all mushrooms we studied was 70.4 μg/g d.w. In the present study Cu levels for H. repandum were lower than those reported in the literature (24.3 and 89.5 μg/g) [8,13]. In previous studies, Cu values reported for H. repandum ranged between 5.15 and 16.3 μg/g [13,20]. The published Cu values for mushrooms reported in the literature ranged from 3.8 to 107 μg/g [4-6,8,10,14,15,18,19,26]. A similar amount of Cu (75.1 μg/g) was reported for L. nuda by Ouzouni et al. [26]. Kalac and Svoboda [3] maintains that Cu levels in the

Table 1. Characterization of wild-edible mushrooms collected from the East Black Sea region of Turkey.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Herbarium number</th>
<th>Family</th>
<th>Species</th>
<th>Habitat, geographical location and collection date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SES 2192</td>
<td>Hydnangiaceae</td>
<td>Laccaria laccata (Scop) Cooke</td>
<td>In mixed wood in Giresun-Kesap-Alatas, 10.08.2003</td>
</tr>
<tr>
<td>2</td>
<td>SES 2564</td>
<td>Tricholomataceae</td>
<td>Leucopaxillus giganteus (Sowerby) Singer</td>
<td>Amongst grass in pastures, Trabzon-Macka Sevino 10.09.2002</td>
</tr>
<tr>
<td>4</td>
<td>SES 2020</td>
<td>Cantharellaceae</td>
<td>Cantharellus cibarus Fr. var. cibarus</td>
<td>Under Carpinus orientalis in Rize-Kalkandere-Zeyno, 30.08.2004</td>
</tr>
<tr>
<td>5</td>
<td>SES 2291</td>
<td>Tricholomataceae</td>
<td>Tricholoma saponaceum (Fr.) P. Kumm. var. saponaceum</td>
<td>In hardwood forest in Gümüşhane- Yirmezne 13.08.2002</td>
</tr>
<tr>
<td>6</td>
<td>SES 2222</td>
<td>Agaricaceae</td>
<td>Agaricus arvensis Schaeff</td>
<td>Amongst grass in pastures in Trabzon-Akcaabat-Hidirnebi, 12.10.2002</td>
</tr>
<tr>
<td>7</td>
<td>SES 2141</td>
<td>Boletaceae</td>
<td>Boletus edulis Bull. Fr.</td>
<td>Under Picea in Trabzon-Sürmene-Perdos, 03.10.2004</td>
</tr>
<tr>
<td>8</td>
<td>SES 2107</td>
<td>Clavulinaceae</td>
<td>Clavulina rugosa (Bull.) J. Schröt</td>
<td>Under Picea orientalis in Giresun-Kesap-Dokuztepe, 09.08.2003</td>
</tr>
<tr>
<td>9</td>
<td>SES 2021</td>
<td>Hydnaceae</td>
<td>Hydnum repandum L.</td>
<td>Under Picea orientalis in Ordu-Aybasti, 26.10.2005</td>
</tr>
<tr>
<td>10</td>
<td>SES 2110</td>
<td>Cantharellaceae</td>
<td>Cantharellus tubaeformis (Bull.) Fr.</td>
<td>Under Picea orientalis in Artvin-Yusufeli-Hadozor, 07.09.2005</td>
</tr>
<tr>
<td>11</td>
<td>SES 2145</td>
<td>Tricholomataceae</td>
<td>Lepista nuda (Bull.) Cooke</td>
<td>In garden in Trabzon-Of-Saracli, 08.09.2002</td>
</tr>
</tbody>
</table>

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100 - 300 mg/kg d.w. range should not be considered a human health risk. In the present study, the highest amounts of Cu (321 µg/g) was found in *C. rugosa*. Our Cu values agree well with the data reported for *L. nuda* (75.1 µg/g) and *C. cibarius* (32.5 µg/g) in the literature [26]. The levels of Cu we measured in mushrooms are not considered a health risk. The recommended dietary allowances (RDA) for adults is 0.90 mg Cu/day [29].

The levels of Fe we measured in the 11 mushroom species ranged from 74 to 829 µg/g, being the highest in *C. rugosa* and the lowest in *B. edulis*, and the average Fe content was 256 µg/g. In the present study, iron was determined as the second most abundant of the trace elements after Al, and its content was the highest in *C. rugosa* (829 µg/g) and lowest in *B. edulis* (74 µg/g). Iron content of mushroom samples in the literature has been reported to be in the 8 to 3904 µg/g range [4-6,8,10,14,16,18,19]. For *H. repandum*, the values reported in the literature are 33.5, 125, 50 and 250 and 317 µg/g [12,13,19,20].

The Mn content in the present study averaged 41.2 µg/g. The Mn level found in previous studies of wild-growing mushrooms varied between 1.2 - 329 µg/g d.w. [4-6,8,10,14-16,18,19]. The Mn contents of all 11 mush-
All 11 mushroom species we tested were good sources of Zn. The lowest (36.2 μg/g) and highest (241 μg/g) zinc contents were found in H. repandum and L. laccata, respectively. The range of Zn content reported for a number of different mushrooms in the literature was 5.5-253 μg/g. [4,6,8,10,14-16,18,19,26]. More recently, the Zn content of H. repandum from the same region but from a different habitat in Turkey was reported to be 55.0 μg/kg d.w. [19], which is much higher than the lower limit cited in the literature (37.8 μg/g d.w.) [4], whereas the Zn content reported for C. cibarius (149 mg/kg d.w.) [19] was lower than that of the upper limit reported by Sanme and associates (253 μg/g d.w.) [4] and Ouzouni et al. (54.3 μg/g d.w.) [26]. We found a lower Zn content in L. nuda (86.20 μg/g) than that reported by Ouzouni et al. [26] for the same species from Greece (99.0 and 35.9 μg/g). The average Zn content was 97.5 μg/g for the 11 mushrooms we studied. The uptake of metal ions in mushrooms differs in many respects from that in plants and soil content [1,6,28]. Thus, the differences in the mineral contents of mushrooms reported in various studies can be attributed to the ecosystems in which they were grown and by environmental factors such as climate, growing conditions and soil content [1,6,28].

From the above results, it is apparent that all of the mushrooms we collected from three sites in the East Black Sea region should be regarded as important sources of many essential elements (e.g., K, P, Ca, Mg) and trace minerals (e.g., Fe, Cu, Zn, Mn, Co) C. rugosa seems to be especially efficient in concentrating certain minerals, including Al, Cu, Fe, Mn and Ni. Noteworthy
is the fact that the Ca content of all 11 mushroom species was low relative to many other foods, especially green leafy vegetables. The highest contents of Al (145 μg/g d.w.), Cu (321 μg/g d.w.) and Fe (829 μg/g d.w.) were found in *C. rugosa*. The highest As content (145 μg/g d.w.) was found in *L. laccata*. All 11 of the mushroom specimens contained significant amounts of Mg, Fe, Mn, and Zn.

4. Conclusion

All 11 of the mushroom species we studied appear to be good sources of many minerals and trace elements that are essential for humans. *C. rugosa* is an effective heavy metal accumulator for Al (1320 μg/g d.w.), followed by Fe and Cu (Table 2). Also, with the exception of *L. laccata*, the content of toxic metals such as Pb, Cd and As was low. In general, these wild-edible mushroom species can be consumed unreservedly without any health risk. With the exception of *L. laccata*, the Pb level in the mushrooms we analyzed was below the level of detection.

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