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Analysis of heavy metals in some wild-grown edible mushrooms from the middle black sea region, Turkey

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Abstract

Concentrations of heavy metals (Cu, Cd, Pb, Zn, Mn, Fe, Cr and Ni) were determined in wild-grown edible mushrooms. The mushroom samples were collected from Tokat in the Middle Black Sea region of Turkey. The analyses were performed using a Perkin–Elmer Analyst 700 Atomic Absorption Spectrometer. The results indicated that the levels of heavy metals in mushrooms were high in some species. The level of Cu was the highest in *Agaricus bisporus* as 107 ± 8.5 μg/g. The levels of Cd, Pb, Zn and Mn conformed to the FAO/WHO (1976) standards. Fe content was higher than other metals in all mushroom species. The concentrations of Cr were highest in *Marasmius oreades*, *Armillaria mellea* and *Morchella elata* in this study. The highest Ni contents were observed in *Armillaria mellea*, *Marasmius oreades*, *Morchella vulgaris* and *Agaricus bisporus*.

Keywords: Heavy metals; Wild-grown edible mushroom; Turkey

1. Introduction

Wild-grown edible mushrooms have been a very popular delicacy in many countries and annual consumption may exceed 10 kg for some individuals (Kalac & Svaboda, 2000). Fruit bodies of mushrooms are appreciated, not only for texture and flavour but also for their chemical and nutritional properties (Manzi, Aguzzi, Vivanti, Paci, & Pizzoferrato, 1999). Mushrooms have also been reported to be therapeutic foods, useful in preventing diseases such as hypertension, hypercholesterolemia and cancer. These functional characteristics are mainly due to their chemical composition (Manzi, Aguzzi, & Pizzoferrato, 2001).

Many wild edible mushroom species are known to accumulate high levels of heavy metals and mainly cadmium, mercury and lead (Kalac & Svaboda, 2000). Many investigations have been performed on metal contents of wild edible mushrooms (Gast, Jansen, Bierling, & Haanstra, 1988). The concentrations of heavy metals in the fruiting bodies of edible mushrooms have been measured by atomic absorption spectrometry (Kalac, Burda, & Staskova, 1991). Cd, Cu, Pb and Zn contents were determined in wild-grown mushrooms in polluted and unpolluted regions (Gast et al., 1988). Studies on metals in mushroom have shown a correlation between fungal metal concentrations and point sources of metal pollution, such as smelters and roadsides (McCreight & Schroeder, 1977; Laaksovirta & Alakuijala, 1978; Bargagli & Baldi, 1984). Under natural conditions, heavy metal concentrations of some species of wild-grown edible mushrooms can be high, even if the degree of pollution in soil is low (Falandaysz, Kawano, Swieczkowski, Brzostowski, & Dadej, 2003; Falandysz & Chwir, 1977). The process of heavy metal accumulation of mushrooms is species-specific. Elevated concentrations of heavy metal have been observed in the fruiting bodies of mushrooms collected from the areas adjacent to heavy metal smelters (Isiloglu, Merdivan, & Yilmaz, 2001; Kalac et al., 1991; Kalac, Niznanska, Bevilaqua, & Staskova, 1996).

Concentrations of Hg, Cd, Pb and Cu in 23 variously wild-grown mushroom species, collected in a heavily

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polluted area in eastern Slovakia, were determined by atomic absorption spectrometry (Svoboda, Zimmermanniva, & Kalac, 2000). It has been reported, in previous studies, that the heavy metal contents of edible mushrooms ranged as follows: Cd levels 0.5–50, Cu, 10–70, Pb, 0.5–20; Fe, 30–150, Zn, 30–150, Mn, 5–60, Cr, 0.1–2 and Ni: 0.4–2 μg/g (Andersen, Lykke, Lange, & Bech, 1982; Cibulka et al., 1996; Falandysz, Danisiewicz, & Bona, 1994; Jorhem & Sundström, 1995; Kalac & Svaboda, 2000; Kalac & Staskova, 1991; Sova et al., 1991; Vetter, 1994).

In the Middle Black Sea region of Turkey, the climate is mild and rainy. Therefore, the seasons are normally wet with mild temperatures; especially, spring and autumn are suitable for fungal growth. People who live in this region of Turkey (Tokat) have widely consumed wild edible mushrooms because of their delicacy and abundance.

Many studies have been carried out on the trace element contents of macro fungi in Turkey (Demirbas, 2000; Isiloglu, Yilmaz, & Merdivan, 2001; Tuzen, Ozdemir, & Demirbas, 1998; Turkekul, Elmastas, & Tuzen, 2003; Sesli & Tuzen, 1999; Yildiz, Karakaplan, & Aydin, 1998; Sivrikaya, Bacak, Saracbasi, Toroglu, & Eroglu, 2002). Concentrations of Cu, Cd, Pb, Fe, Mn, Zn, Co, Hg and As of fruiting bodies of two cultivated and 109 wild-grown mushrooms, collected from the East Black Sea Region in Turkey have been determined spectrometrically (Sesli & Tuzen, 1999). In addition, the analysis of heavy metal contents in 16 species of wild-growing macrofungi collected in the Northwestern Part of Turkey has been done by atomic absorption spectrometry (Isiloglu et al., 2001).

However, qualified studies have not been reported on wild-grown edible mushrooms in this area of Turkey. In this study, the contents of heavy metals (Cu, Cd, Pb, Zn, Mn, Fe, Cr and Ni) in the fruiting bodies of some wild-grown edible mushrooms, collected from the Tokat region of Turkey, were determined, using atomic absorption spectrometry.

2. Materials and methods

Mushroom samples were collected in Tokat, in the Middle Black Sea Region of Turkey in spring and autumn 2002 (Fig. 1). They were stored at the Gaziosmanpasa University Faculty of Art and Science Microbiology Herbarium Laboratory (Herbarium number; *Agaricus bisporus*: Uzumoren-Turk., 1201; *Polyporus squamasus*: Basciftlik-Turk., 1360; *Pleurotus ostreatus*: Almus-Turk., 1620; *Armillaria mellea*: Niksar-Turk., 952; *Lepista nuda*: Zile-Turk., 981; *Marasmius oreades*: Tokat-Turk., 1243; *Boletus badius*: Bedirkale-Turk., 1440; *Morchella esculenta*: Tokat-Turk., 1207; *Morchella eleta*: Tokat-Turk., 1341; *Morchella vulgaris*: Tokat-Turk., 1262). Fresh mushrooms, after removal of plant and substrate debris with a plastic knife, were air-dried for several days. They were dried in an oven at 40 °C for 48 h. Dried samples were homogenized, using an agate homogenizer, and stored in pre-cleaned polyethylene bottles until analysis.

One gramme of sample was placed in a porcelain crucible and ashed at 450 °C for 18–20 h; then the ash was dissolved in 1 ml concentrated HNO_3 (suprapur, Merck), evaporated to dryness, heated again at 450 °C

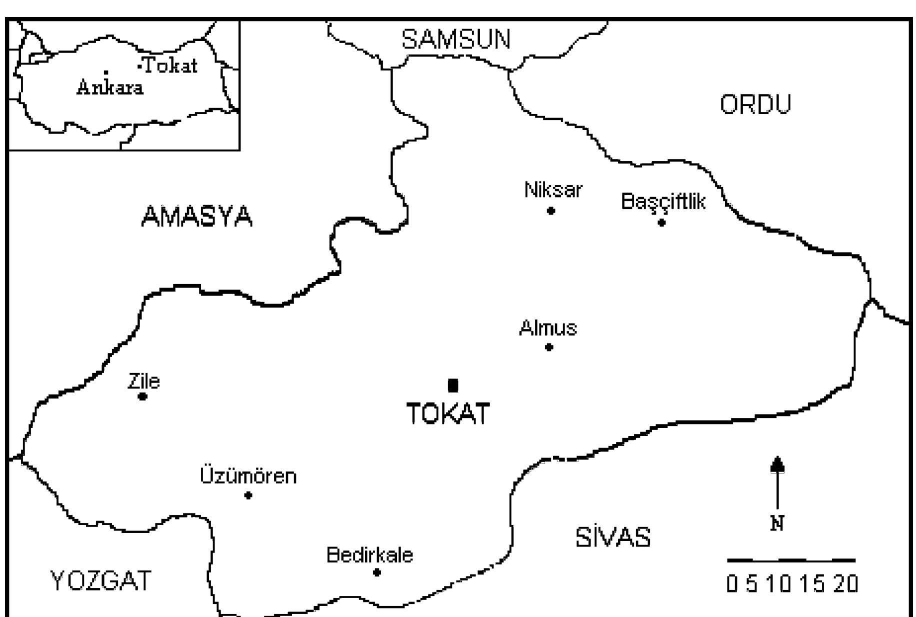

Fig. 1. Map of study area.

for 4 h, treated with 1 ml concentrated H_2SO_4 (suprapur, Merck), 1 ml HNO_3 and 1 ml H_2O_2 (suprapur, Merck), and then diluted with double deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} resistivity) up to a volume of 10 ml. Three blank samples were treated in the same way.

For the element analyses, a Perkin–Elmer Analyst 700 Atomic Absorption Spectrometer (AAS) was used. Pb and Cd levels in the mushroom samples were determined by HGA graphite furnace, using argon as inert gas. Determinations of other heavy metal contents were carried out in an air/acetylene flame.

All the experimental results were means ± SD of three parallel measurements. Data were evaluated by using one way variance analysis (StatMost, 1995).

3. Results and discussion

The habitat, edibility and the families of mushrooms are given in Table 1 (Phillips, 1981). The average heavy metal concentrations of wild-grown edible mushroom species are given in Table 2. The amounts of heavy metal contents are related to species of mushroom, collected site of the sample, age of fruiting bodies and mycelium, and distance from the source of pollution (Kalac et al., 1991). The heavy metal concentrations in the mushroom are hardly affected by pH or organic matter content of the soil (Demirbas, 2002; Sesli & Tuzen, 1999; Gast et al., 1988). The trace element contents of the species depend on the ability of the species to extract elements from the substrate, and on the selective uptake and deposition of elements in tissues (Demirbas, 2001; Sesli & Tuzen, 1999). The uptake of heavy metal ions in mushrooms is higher than in plants. For this reason, the concentration variations of heavy metals could be considered due to mushrooms species and their ecosystems (Seeger, 1982).

Among wild-grown edible mushroom species, the greatest concentrations of Cu were obtained in the *A. bisporus* (107 ± 8.5 μg/g) *L. nuda* (68.4 ± 6.3 μg/g) and *M. oreades* (61.5 ± 4.1 μg/g) (Fig. 2). For the other mushrooms species in this study, Cu concentrations were between 8.5 ± 0.7 and 45.6 ± 3.7 μg/g. Cu value has been reported to be 10–70 μg/g (Andersen et al., 1982; Falandysz et al., 1994; Falandysz & Bona, 1992; Jorhem & Sundström, 1995; Kalac & Staskova, 1991; Kalac, Wittingerova, & Staskova, 1989a; Vetter, 1994).

The levels of Cd in the samples ranged from 0.3 ± 0.01 to 3.0 ± 0.2 μg/g, and the highest Cd levels were obtained for *P. ostreatus* and *L. nuda* (Fig. 3). The Cd levels are in agreement with literature values

Table 1
Families, habitat and edibility of mushroom species

Class, family and species of mushrooms	Habitat	Edibility
Agaricus bisporus (Lange) Pilát	On manure heaps, garden waste and roadsides	Edible
Polyporus squamasus, Huds. Ex Fr.	In parasitic on deciduous trees	Edible
Pleurotus ostreatus (Jacp. Ex Fr.) Kummer	Often in large clusters on stumps and fallen or standing trunks, usually of deciduous trees	Edible
Armillaria mellea (Vahl. Ex Fr.) Kummer	In dense clusters on or around trunks or stumps of deciduous and coniferous trees	Edible
Lepista nuda (Bull. Ex Fr.) Cooke	In woodland, hedgerows and gardens	Edible
Marasmius oreades (Bolt. Ex Fr.) Fr.	Often forming rings in the short grass of pasture or lawns	Edible
Boletus badius Fr.	In mixed woods	Edible
Morchella esculenta (Pers. Ex St.) Amans	In open scrub or woodland or on waste ground	Edible
Morchella eleta Fr.	In conifer woods or on chalk soil	Edible
Morchella vulgaris (Pers.) Boud	In garden and wasteland	Edible

Table 2
Concentrations of Cu, Cd, Pb, Zn, Mn, Fe, Cr and Ni of the mushroom samples analyzed (μg/g, dry weight) (mean ± SD), $n = 5$

Mushroom samples	Cu	Cd	Pb	Zn	Mn	Fe	Cr	Ni
Agaricus bisporus	107 ± 8.5	1.7 ± 0.1	2.1 ± 0.1	57.2 ± 3.9	25.9 ± 2.2	290 ± 20.0	6.5 ± 0.4	7.9 ± 0.7
Polyporus squamasus	14.3 ± 1.2	1.5 ± 0.1	2.1 ± 0.2	23.7 ± 1.5	7.1 ± 0.5	166 ± 10.3	1.9 ± 0.2	1.8 ± 0.1
Pleurotus ostreatus	8.5 ± 0.7	3.0 ± 0.2	*ND	48.8 ± 4.1	20.5 ± 1.4	281 ± 20.5	1.3 ± 0.1	0.4 ± 0.02
Armillaria mellea	45.6 ± 3.7	0.5 ± 0.03	2.1 ± 0.2	70.3 ± 6.0	28.2 ± 2.3	312 ± 22.4	22.7 ± 2.2	15.9 ± 1.5
Lepista nuda	68.4 ± 6.3	2.9 ± 0.2	3.5 ± 0.3	47.6 ± 2.8	49.3 ± 4.2	321 ± 27.6	10.4 ± 0.9	4.2 ± 0.3
Marasmius oreades	61.5 ± 4.1	0.4 ± 0.02	2.1 ± 0.2	47.8 ± 3.5	27.7 ± 1.6	335 ± 26.5	24.3 ± 2.1	13.4 ± 1.1
Boletus badius	26.8 ± 1.6	0.5 ± 0.02	2.1 ± 0.2	51.6 ± 3.2	19.8 ± 1.2	287 ± 18.7	1.9 ± 0.1	ND
Morchella esculenta	ND	1.1 ± 0.1	3.5 ± 0.3	41.4 ± 2.4	20.4 ± 1.4	243 ± 19.9	8.2 ± 0.6	2.5 ± 0.2
Morchella eleta	57.6 ± 4.4	1.4 ± 0.2	3.5 ± 0.3	56.5 ± 4.8	81.3 ± 7.5	299 ± 21.5	22.0 ± 1.6	7.9 ± 0.5
Morchella vulgaris	32.6 ± 2.2	0.3 ± 0.03	2.1 ± 0.2	42.3 ± 3.9	15.2 ± 0.8	174 ± 15.9	4.2 ± 0.3	2.8 ± 0.2

*ND: not determined.

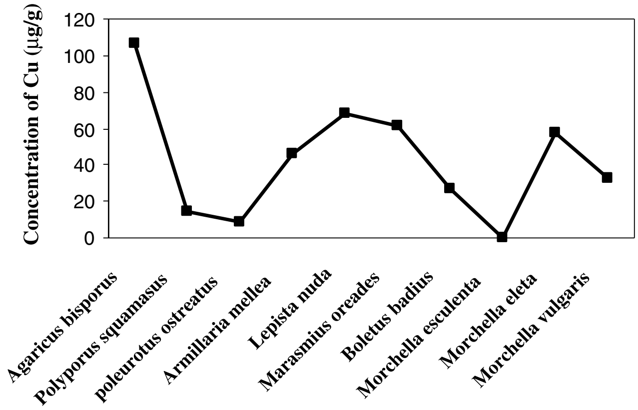

Fig. 2. Distribution of Cu content in mushroom species.

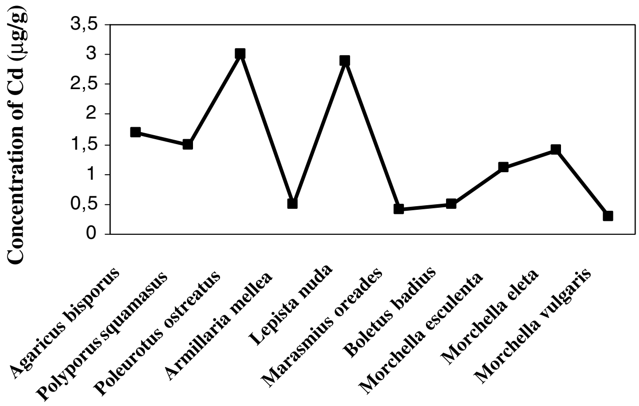

Fig. 3. Distribution of Cd content in mushroom species.

(Cibulka et al., 1996; Falandysz et al., 1994; Kalac, Wittingerova, Staskova, Simak, & Bastl, 1989b; Sova et al., 1991; Vetter, 1994).

The highest Pb content determined was 3.5 ± 0.3 µg/g in *L. nuda*, *M. esculenta* and *M. eleta*. However, the Pb levels in other mushrooms were 2.1 ± 0.2 µg/g. Pb content was not determined in *P. ostreatus.* (Fig. 4). These results conform to the FAO/WHO (1976) standards for Pb and Cd as toxic metals. The Pb concentrations of previous studies were between 0.1 and 40 µg/g (Kalac et al., 1989b; Sesli & Tuzen, 1999).

The highest Zn concentration found was in *A. mellea* (70.3 ± 6.0 µg/g), whereas the lowest Zn concentration was in *P. squamasus* (23.7 ± 1.5 µg/g) (Fig. 5). Zinc is widespread among living organisms, due to its biological significance. Content of zinc in mushrooms ranges from 30–150 µg/g (Kalac & Svaboda, 2000). Hence, zinc content in mushrooms of the present study is in agreement with previous studies (Andersen et al., 1982; Kalac & Svaboda, 2000).

The lowest Mn levels obtained were in *P. squamasus* (7.1 ± 0.5 µg/g) and *M. vulgaris* (15.2 ± 0.8 µg/g). The highest Mn concentration was obtained in *M. elata* (81.3 ± 7.5 µg/g) (Fig. 6). In a previous study, the concentration of Mn in mushrooms was between 5 and 60 µg/g (Falandysz & Bona, 1992; Vetter, 1994). In this study, Mn levels are in agreement with previous studies except in *M. elata*.

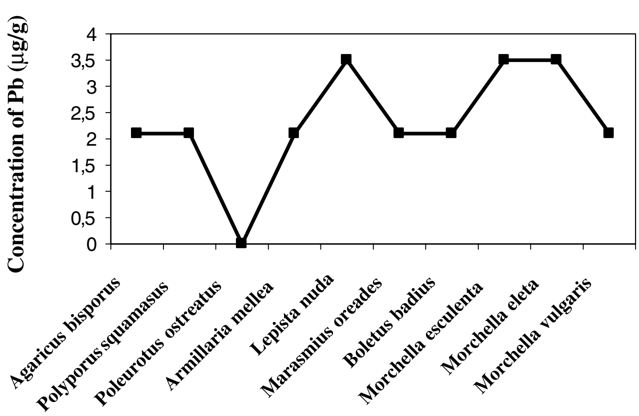

Fig. 4. Distribution of Pb content in mushroom species.

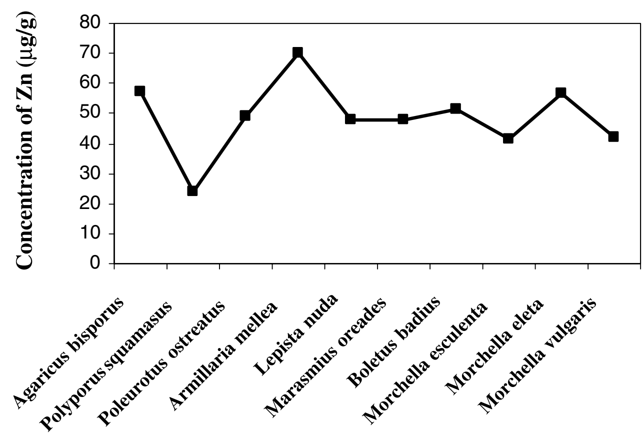

Fig. 5. Distribution of Zn content in mushroom species.

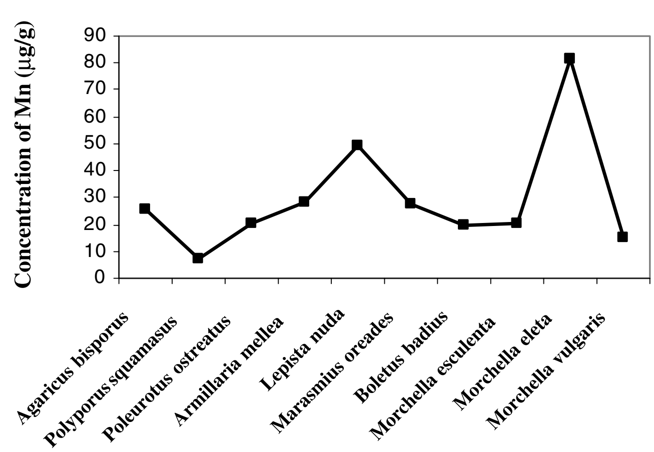

Fig. 6. Distribution of Mn content in mushroom species.

In the mushroom samples, the highest Fe content was 335 ± 26.5 μg/g, in *M. oreades* (Fig. 7). The lowest Fe content found was 166 ± 10.3 μg/g in *P. squamasus* in different species of mushrooms, Fe contents were found to be 100–1216 μg/g by (Latiff, Daran, & Mohamed, 1996). In the present study, Fe contents are in agreement with reports in the literature (Falandysz & Bona, 1992; Falandysz et al., 1994; Kalac et al., 1989a).

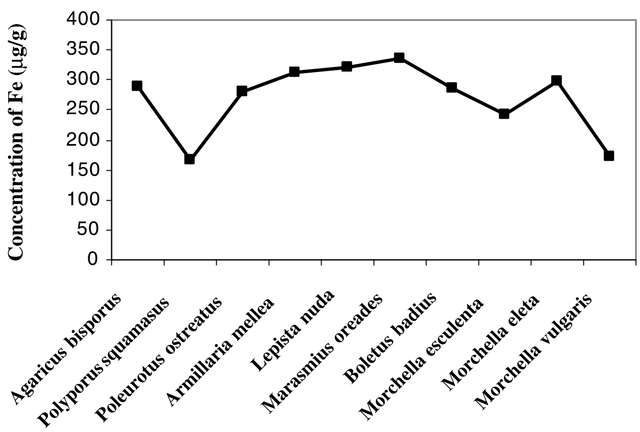

Fig. 7. Distribution of Fe content in mushroom species.

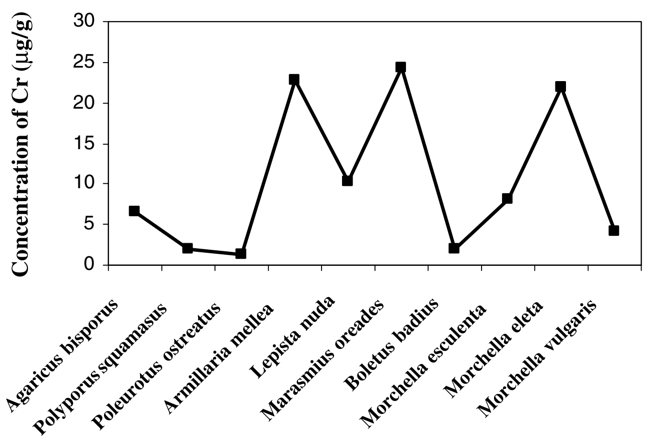

Fig. 8. Distribution of Cr content in mushroom species.

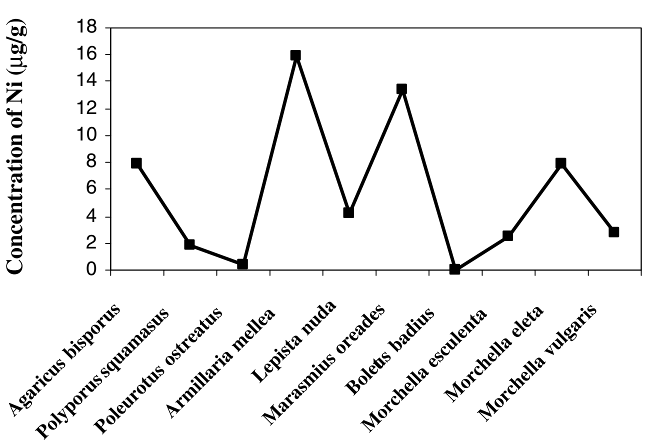

Fig. 9. Distribution of Ni content in mushroom species.

Minimum and maximum values of Cr were obtained for *P. ostreatus* (1.3 ± 0.1 μg/g) and *M. oreades* (24.3 ± 2.2 μg/g) (Fig. 8). Cr results were close to those found in the literature (Sivrikaya et al., 2002; Jorhem & Sundström, 1995; Kalac et al., 1989a; Kalac & Staskova, 1991; Vetter, 1997).

The highest concentration of Ni was found in *A. mellea* (15.9 ± 1.5 μg/g). Ni content was not determined in *B. badius* (Fig. 9). All values of Ni in mushrooms are agreement with previous studies (Sivrikaya et al., 2002; Barcan, Kovnatsky, & Smetannikova, 1998; Jorhem & Sundström, 1995).

4. Conclusion

Heavy metal (Cu, Cd, Pb, Zn, Mn, Fe, Cr and Ni) levels of ten mushrooms (*A. bisporus*, *P. squamasus*, *P. ostreatus*, *A. mellea*, *L. nuda*, *M. oreades*, *B. badius*, *M. esculenta*, *M. eleta*, *M. vulgaris*) collected from Tokat region, Turkey were investigated. Levels of heavy metals are considerably lower in *P. squamasus*, *P. ostreatus*, *B. badius*, *M. esculenta* and *M. vulgaris* than other mushrooms. The highest metal levels are in *A. bisporus*, *A. mellea*, *L. nuda*, *M. oreades* and *M. eleta.*

Further study should be undertaken on of chemical composition, which shows the food quality of the wild-grown edible mushroom.

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