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The Heavy Metal Content of Wild Edible Mushroom Samples Collected in Canakkale Province, Turkey

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Abstract In this study, concentrations of heavy metals (Cd, Cr, Cu, Pb, and Zn) were determined in three edible mushroom species (*Lactarius deliciosus*, *Russula delica*, and *Rhizopogon roseolus*) collected in five sampling sites in Canakkale province, Turkey. Mean values of Cd, Cr, Cu, Pb, and Zn were 0.72, 0.26, 28.34, 1.53, and 64.62 mg/kg, respectively. The highest concentrations of Cd, Cu, Pb, and Zn were determined in species *R. delica*, while Cr was observed in *L. deliciosus*. In terms of the nutritional aspect, taking into account the concentration of Provisional Tolerable Weekly Intake recommended by FAO/WHO, the maximum concentration of Cd is a restrictive factor for consumption of the collected mushroom species. The concentrations of the other elements have no health risks when consumed at optimal levels.

Keywords Edible wild mushroom · Canakkale · Heavy metals · Turkey

Introduction

After the Industrial Revolution, due to increasing industrial processes such as fossil fuel combustion and mining activity, many pollutants have been emitted into the environment. This has resulted in an increase in the level of pollutants in the environment. As a result, many mediums such as water, air, soil, and food have been contaminated. Among those pollutants, trace elements, especially heavy metals, are very important in relation to the toxicological and nutritional aspects. In recent years, heavy metal pollution has gained increasing attention due to its possible toxic effects. Many elements, for example arsenic, cadmium, mercury, etc., are toxic to living organisms at trace levels. On the other hand, high concentrations of essential elements are also toxic.

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Many studies related to concentrations of trace elements in mushroom species have been performed. In these studies, mushrooms have been used as bioindicators for determination of toxic element levels such as cadmium, lead, mercury, arsenic, and radionuclides [1–5]. In addition, numerous studies have been carried out using mushrooms in different provinces of Turkey [6–12]. Mushrooms are able to absorb and retain nutrients and minerals directly from the substrate. The accumulative ability of mushrooms can be affected by environmental factors such as pH, metal content of the soil, the amount of organic material, and fungal factors such as species, development stage, and mycelium age [13]. According to Kalac and Svoboda [4], concentrations of elements in fruiting bodies are generally species specific. They also indicated that the content of the substrate is an important factor for the heavy metal content in mushrooms. Because of their higher accumulative capability, they can be used as crucial mineral sources.

Canakkale is located in the western part of Turkey. It is not a large province, but it has various pollutant sources in the near vicinity due to mining and agricultural activities. Because of using of non-approved heating materials in houses, there is intense air pollution especially during the winter season. There is a coal-burning power plant near to Canakkale being in operation since 2005 and using the low-calorie lignite coal. The plant burns 1.82 million tons of lignite and produces about 5,000 tons ash per year [14]. One cement plant is also located in the sampling area, which may possibly contribute to pollution levels in Canakkale. In addition, many active mining areas, with as a basis zinc, lead, copper, silver and iron from polymetallic ores, are available (Fig. 1). Dominant wind directions in the study area are northeast and southwest. The climate of Canakkale province is Continental–Mediterranean. Annual precipitation is approximately 600 mm yearly. The spring, winter, and part of autumn are suitable for fungal growth in Canakkale and its vicinity. People living in Canakkale commonly consume the edible parts of wild mushrooms. Therefore, many people collect and sell them in open-air markets. The species *Lactarius deliciosus* is the most consumed mushroom species due to its delicacy. However, we have no scientific data from the literature about the heavy metal content of mushrooms growing in Canakkale province. Thus, the aim of this study was to obtain the first data about the heavy metal concentrations in mushroom samples which were collected in Canakkale province and to evaluate the obtained results from the point of view of their nutritional aspects.

Materials and Methods

Mushroom samples were collected in five sampling sites in Canakkale province in October 2006 (Fig. 1). In this study, three mushroom species, *L. deliciosus*, *Russula delica*, and *Rhizopogon roseolus*, were evaluated. Four hundred to 500 g samples were collected at each sampling site for each mushroom species. Samples were stored in plastic bags during field and laboratory studies and were cleaned of residual and other waste matter, washed with deionized water (18.2 MΩ cm^{-1}), and then dried in an oven at 105°C until they were dry. The cleaned and dried samples were ground and homogenized using a plastic mill. Mineralization of samples was carried out by using a microwave digestion system (CEM Mars X-press). The closed-vessel microwave digestion system has frequently been used in many works for samples having complex matrices in recent years [10, 15, 16]. The digestion conditions for the microwave digestion system were 15 and 20 min for ramp and hold times at 1,200 W, respectively. For the digestion, dried 0.5 g mushroom tissue was put into a Teflon vessel, 10 ml of concentrated nitric acid (Merck-65%, Darmstadt, Germany) was added, and the mixture was digested. After cooling, the digest was filtered and diluted

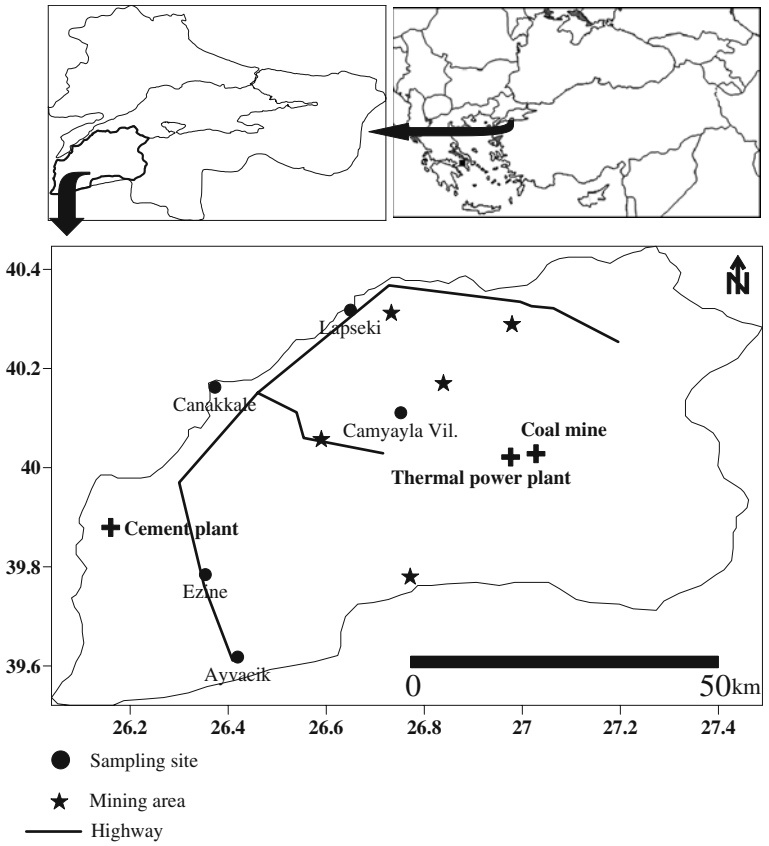

Fig. 1 Sampling sites and possible pollution sources in Canakkale province

with deionized water up to 25 ml. The concentrations of Cd, Cr, Cu, Pb, and Zn were determined by using inductively coupled plasma atomic emission spectroscopy, and the detection limits of those elements were 0.2, 0.3, 0.5, 2, and 0.2 μg/kg, respectively. Concentrations of heavy metals in each sample were measured in triplicate, and all the relative standard deviations for replicates were less than 5%. Standard reference material, M3, which was prepared for European moss survey, was used for accuracy check [17]. SPSS 10.0 for Windows was used for the data analysis.

Results and Discussion

Moisture content of the evaluated species in this study was measured as 88–92%. For the accuracy check, the measured, certified, and recovery values of M3 are presented in Table 1. The difference between the certified and obtained values was insignificant and at a reasonable level. Descriptive statistics of the results obtained were expressed as milligrams per kilogram in dry weight and are given in Table 2. The highest concentrations of Cd, Cu, Pb, and Zn were determined in species *R. delica*, while Cr was observed in *L. deliciosus.* Three samples of *L. deliciosus* from Canakkale center where analyzed, showing high variability. Samples taken from different parts of the city center may be the cause of this

Table 1 Measured and Certified Results of Cd, Cr, Cu, Pb, and Zn in M3 (mg/kg in dry weight)

Element	Measured values	Certified values	Recoveries (%)
Cd	0.12±0[a]	0.11	109
Cr	0.80±0.04	0.82	98
Cu	3.51±0.08	3.64	96
Pb	2.80±0.14	2.94	95
Zn	25.9±0.699	25.9	100

[a] Standard deviation

variability. The intake of metals by taking into account of the mean and maximum concentrations obtained for each species was calculated on a daily basis (Tables 3 and 4). These calculations were done for 60 kg of body weight, EU Scientific Committee for Food Adult Weight parameter.

Long-term exposure to high levels of Cd may lead to considerable accumulation in the liver and kidneys, particularly the renal cortex, resulting in kidney damage [18]. Cd content can vary drastically among different food products, from less than 0.001 to 100 mg/kg [19]. In this study, the minimum and maximum concentrations of Cd in samples were 0.18 and 4.23 mg/kg. The lowest value was found in *R. roseolus*, whereas in *R. delica*, it was the highest, possibly arising from mining areas close to sampling site (Fig. 1).

Cr is one of the essential trace metal nutrients of humans and animals. It is used for helping to maintain normal glucose tolerance in the body [20]. The minimum and maximum Cr concentrations in samples were found to be in range of 0.10–0.80 mg/kg in this study. These values were determined in *R. roseolus* and *L. deliciosus*, respectively.

Table 2 Element Concentrations in Different Samples of Mushrooms (mg/kg dry weight)

Mushrooms	Sampling sites	Cd	Cr	Cu	Pb	Zn
Lactarius deliciosus	Ayvacik	0.26±0.01[a]	0.12±0	6.15±0.08	0.73±0.03	76.77±0.54
Lactarius deliciosus	Camyayla Village	0.89±0.04	0.15±0.01	6.68±0.05	1.32±0.06	74.92±0.150
Lactarius deliciosus	Ezine	0.49±0.02	0.18±0.01	6.61±0.06	1.70±0.06	77.10±0.308
Lactarius deliciosus	Lapseki	0.42±0.02	0.31±0.01	6.79±0.05	0.69±0.03	93.22±0.466
Lactarius deliciosus	Çanakkale center	0.30±0.01	0.21±0.01	6.28±0.04	0.99±0.05	76.50±0.612
Lactarius deliciosus	Çanakkale center	0.42±0.01	0.29±0.01	5.57±0.05	1.35±0.05	81.72±0.899
Lactarius deliciosus	Çanakkale center	0.66±0.03	0.80±0.04	6.82±0.18	1.41±0.05	77.40±0.310
Rhizopogon roseolus	Ayvacık	0.18±0	0.10±0	21.2±0.38	2.01±0.09	36.20±0.326
Rhizopogon roseolus	Lapseki	0.36±0	0.23±0.01	12.4±0.06	2.51±0.12	24.90±0.473
Rhizopogon roseolus	Camyayla Village	0.21±0	0.15±0	7.56±0.11	2.71±0.13	21.94±0.197
Russula delica	Camyayla Village	0.42±0.02	0.27±0.01	52.01±0.884	1.56±0.05	72.28±0.651
Russula delica	Ezine	0.40±0.02	0.32±0.01	57.46±0.632	0.77±0.02	58.08±0.581
Russula delica	Lapseki	4.23±0.03	0.38±0.02	164.2±2.956	3.05±0.12	100.17±0.801
Russula delica	Çanakkale center	0.90±0.03	0.12±0.01	37.07±0.063	0.59±0.03	33.45±0.468
	Mean	0.72	0.26	28.34	1.53	64.62
	Minimum	0.18	0.10	5.57	0.59	21.94
	Maximum	4.23	0.80	164.2	3.05	100.17

[a] Standard deviation

Table 3 Mean Concentrations and Daily Metal Intake by a Normal (60 kg) Person (mg/serving)

Mushroom species	Mean Cd	Daily Cd	Mean Cr	Daily Cr	Mean Cu	Daily Cu	Mean Pb	Daily Pb	Mean Zn	Daily Zn
Lactarius deliciosus	0.49	0.015	0.29	0.009	6.41	0.19	1.17	0.035	79.66	2.390
Rhizopogon roseolus	0.25	0.008	0.16	0.005	13.72	0.41	2.41	0.072	27.68	0.830
Russula delica	1.49	0.045	0.27	0.008	77.69	2.33	1.49	0.045	66.00	1.980

Cu is an essential element. Enzymes containing copper are important for the body to transport and use iron [21]. In 1996, a joint FAO/International Atomic Energy Agency/WHO official report set an upper limit for the safe range of population mean exposures for adults of 0.2 mg/kg bw per day [21]. In the present work, the minimum concentration of Cu was 5.57 mg/kg in *L. deliciosus*, and maximum concentration was 164 mg/kg in *R. delica*.

Pb is used for a number of industrial, domestic, and rural purposes—for example, in lead batteries and in leaded petrol [22]. A significant source of exposure to lead is via the diet [22, 23]. Lead is a cumulative toxin that can primarily affect the blood, nervous system, and kidneys. In the blood at high concentrations, lead inhibits red blood cell formation and eventually results in anemia [22]. In this study, the lowest and highest concentrations of Pb were 0.59 and 3.05 mg/kg in *R. delica* collected at different sampling sites. There are differences within individual species on account of capability of metal accumulation. According to Tyler [24], fungal species differences were the most important with respect to accumulation of metals. The substrate such as soil and tree trunks may also contribute to metal concentrations in mushrooms. In this study, for example, both minimum and maximum concentrations of Pb were found in *R. delica*. This can be explained by the different metal compositions of substrates and/or local pollution sources such as thermal power plant, coal mine, and cement plant. In addition, five active mining areas near the sampling sites also contribute to high levels of metals in the study area.

Zn is an essential nutrient that has an important role in biological systems. Zinc is necessary for the functioning of various enzymes and plays an essential role in DNA, RNA, and protein synthesis. The major symptoms of zinc deficiency are delayed growth and slow maturation [21]. The lowest Zn content was observed in *R. roseolus* as 21.94 mg/kg, whereas the highest Zn value was measured in *R. delica* as 100.17 mg/kg.

The reported mean concentrations and ranges of Cd, Cr, Cu, Pb, and Zn in previous studies and the present work using different species are presented in Table 5. Comparison of mean and range Cd shows that, apart from high levels reported by Tuzen [10], Cd results obtained in this study are similar to those obtained in other studies. Among the studies considered, the mean, minimum, and maximum Cr levels in this study are the lowest. However, the obtained Cr values are similar with those obtained by Soylak et al. [8] and

Table 4 Maximum Concentrations and Daily Metals Intakes by a Normal (60 kg) Person (mg/Serving)

Mushroom species	Maximum Cd	Daily Cd	Maximum Cr	Daily Cr	Maximum Cu	Daily Cu	Maximum Pb	Daily Pb	Maximum Zn	Daily Zn
Lactarius deliciosus	0.89	0.0267	0.8	0.024	6.82	0.2046	1.7	0.051	93.22	2.7966
Rhizopogon roseolus	0.36	0.0108	0.23	0.0069	21.2	0.636	2.71	0,08	36.2	1.086
Russula delica	4.23	0.1269	0.38	0.0114	164.2	4.926	3.05	0.0915	100.17	3.0051

Table 5 Comparison of Present and Previous Studies (mg/kg)

	Cd		Cr		Cu		Pb		Zn	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Tuzen et al. [25]	1.79	0.9–2.5	–	–	32.85	18.9–64.8	–	–	93.53	44.7–198
Sesli et al. [26]	–	–	–	–	39.3	15.5–73.8	1.8	0.9–2.6	109.6	43.5–205
Ouzouni et al. [20]	0.23	0.08–0.41	5.09	0.41–13.1	17.11	3.8–32.6	0.81	0.05–1.37	74.98	35.9–96.9
Soylak et al. [8]	0.66	0.14–0.95	0.69	0.34–1.1	23.21	13.4–50.6	1.28	0.75–1.99	54.54	33.5–89.5
Yamac et al. [11]	0.99	0.26–3.24	13.44	0.54–73.8	51.02	10.6–144.2	2.39	0.3–11.72	132.72	45.70–173.8
Isıldak et al. [7]	1.33	0.3–3	10.34	1.3–24.3	46.92	8.5–107	2.57	2.1–3.5	48.72	23.7–70.3
Tüzen [10]	4.23	1.08–7.5	1.48	0.87–2.66	51.20	24.7–96.2	2.53	1.43–4.17	107.60	45–188
Present Study	0.72	0.18–4.23	0.26	0.1–0.8	28.34	5.57–164.2	1.53	0.59–3.05	64.62	21.94–100.17

Tuzen [10]. Cu mean and range values in this study are in good agreement with those reported by other authors. Mean and range values of Pb are similar with other mentioned studies. But maximum value of Pb obtained by Yamac et al. [11] is three times higher than found in present study. Apart from results published by Tuzen [10], Yamac et al. [11], Tuzen et al. [25], and Sesli et al. [26], the Zn concentration is similar to those of previous studies

When we consider the metal concentration of the mushroom species analyzed in this study from the point of view of the health risk, for intake calculation, the Provisional Tolerable Weekly Intake (PTWI) values for Pb and Cd for adults (of 60 kg) are 1.50 and 0.42 mg, respectively [27]. These values are equivalent to 0.21 and 0.06 mg of Pb and Cd on a daily basis. When the most contaminated mushrooms from the present study (*R. delica*, maximum concentration=4.23 mg/kg) were added to intake, the required amount to exceed the PTWI of Cd would be about 14.2 g dried mushroom or about 140 g fresh mushroom daily. The same calculations were done for maximum concentration of Cd in *L. deliciosus* and *R. roseolus*, and the required amounts for daily consumption were 67.4 and 166.6 g dried mushroom, respectively. For Pb, the required daily amounts to reach the PTWI would be about 68.8, 87.1, and 123.5 g dried mushroom for *R. delica*, *R. roseolus*, and *L. deliciosus*.

In 1996, a joint FAO/International Atomic Energy Agency/WHO report indicated that an upper limit for the safe range of population mean exposures of Cu for adults was 0.2 mg/kg bw per day [21]. This value corresponds to 12 mg for a person with a bodyweight of 60 kg on a daily basis. When eating 73.2 g dried *R. delica* with maximum concentration (164 mg/kg), a person takes sufficient Cu on a daily basis. According to the WHO Expert Consultation Committee on Trace Elements, the adult population mean intake of Zn should not exceed 45 mg/day [21]. The required amount to reach 45 mg/day would be about 450 g dried *R. delica.*

A person with a bodyweight of 60 kg reaches a tolerable daily intake by consumption of a 300-g portion of fresh (approximately 30 g dry weight) mushrooms [20]. In this context, we calculated the daily metal intake considering the mean and maximum concentrations of the mentioned mushroom species collected in Canakkale province (Tables 3 and 4). In general, it can be seen that toxic metals such as Cd and Pb have low levels in the mushroom species. In addition, these species may be suitable sources for Cu and Zn for daily human demand. When considering the maximum concentrations, Cd levels in *R. delica* exceeded the PTWI value given by the Council of Europe [23].

According to US Dietary Reference Intakes, the Recommended Dietary Allowance (RDA) for Cu is 0.9 mg/day for adult men and women [28]. When taking into account mean values of each species, 140.4, 65.59, and 11.58 g dry *L. deliciosus*, *R. roseolus*, and *R. delica*, respectively, are sufficient for RDA values of Cu. Similarly, reported RDA of Zn for adults is 8 mg/day for women and 11 mg/day for men [28]. For Zn, taking into account mean values of dry *L. deliciosus*, *R. roseolus*, and *R. delica*, the required amounts to reach the RDA would be about 100.43, 289.01, and 121.21 g for women and 138.08, 397.40, and 166.67 g for men.

Conclusion

Cd, Cu, Pb, and Zn in *R. delica* from Lapseki are particularly higher with respect to the other sites. This may be an indication of contamination arising from pollutant sources. Collected edible mushroom species can be used as important mineral sources. Apart from the Cd level in *R. delica* at the Lapseki site, toxic metals in other species and at other sites have no health risks for the consumer. When evaluated species are consumed in optimal amounts, they are good sources of functional elements.

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