

Mercury Content of Wild Edible Mushrooms Collected Near the Town of Augustow

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Abstract

Mercury content has been determined separately in the caps, stalks and whole fruiting bodies of thirteen species of popular wild edible mushrooms of the genus *Boletus*, *Xerocomus*, *Leccinum*, *Suillus*, *Tricholoma*, *Rozites*, *Sarcodon* and *Cantharellus* collected from Augustowska Forest, which is located in an unpolluted region in the northeastern part of Poland. The mushroom samples were collected in the summer and autumn of 1997 and 1998. Mercury measurements were by cold-vapour atomic absorption spectroscopy (CV-AAS) after wet digestion of the samples with concentrated nitric acid in closed PTFE vessels in a microwave oven. For each species 16 pooled samples were examined. Pinewood King Bolete *Boletus pinophilus*, King Bolete *Boletus edulis*, Scaly Tooth *Sarcodon imbricatus*, Gypsy *Rozites caperatus*, and Orange Birch Bolete *Leccinum versipelle* were the most contaminated with mean concentrations of $2,000 \pm 800$; $2,300 \pm 1,100$; $2,300 \pm 500$; $1,200 \pm 300$ and 720 ± 380 in the caps and of 850 ± 390 ; $1,000 \pm 500$; $1,100 \pm 400$; 470 ± 150 and 420 ± 170 ng/g dry matter in the stalks, respectively. For the other mushroom species examined the mean mercury concentration were $< 260 \pm 80$ ng/g in the caps and $< 170 \pm 40$ ng/g in the stalks, while the fruiting bodies of Common Cantharelle *Cantharellus cibarius* were the least contaminated, i.e. the range was between 8.0 and 24 ng/g and the mean 14 ± 4 . These findings suggest that mushrooms from Augustowska Forest indicate background contamination by mercury. Nevertheless, some of the mushroom species may possess a specific health risk when frequently consumed due to elevated mercury concentrations.

Keywords: mercury, mushrooms, food, environmental pollution, Augustowska Forest.

Introduction

The fruiting bodies of wild edible mushrooms are an example of a food resource highly vulnerable to contamination with heavy metals and radionuclides migrating from polluted soil or plant substrate. Both the wild and cultivated *macromycetes* of different genus are known due to their high efficiency of biouptake and accumulation in the growing-up the fruiting bodies of many elements and including some toxic metals such as mercury, lead, cadmium, silver or arsenic as well as radionuclides [1-9]. Nevertheless, there are large differences amongst various mushroom species due to their ability

to bioaccumulate or exclude metallic elements or metalloids [10-12]. Some of the higher mushrooms have a species-specific ability to bioaccumulate or exclude particular elements. A good example is the Fly agaric *Amanita muscaria*, which is known as an accumulator of vanadium [13]. Amongst the 23 species of the genus *Amanita* investigated, the Fly agaric is the only one showing a highly elevated, and even increasing vanadium concentration with the age of the fruiting body [13]. Vanadium is present in Fly agaric as an organometallic compound named amavadine [6].

A degree of environmental pollution with mercury has

a high influence on mercury content of the developing fruiting body. In a study by Kalae *et al.* [14] the wild edible mushrooms such as Parasol Mushroom *Macrolepiota procera*, King Bolete *Boletus edulis* and Wood Blewit *Lepista nuda* collected in the vicinity of the copper smelter Krompachy in Slovakia contained mercury in concentrations up to 94,000; 63,000 and 110,000 ng/g dry matter. Even higher concentrations were found in Parasol Mushrooms collected near the mercury smelter of Rudnany in Slovakia, *i. e.* up to 200,000 ng/g dry matter [14].

The common Cantharelle *Cantharellus cibarius* collected in the vicinity (a distance of up to 1 km) of a large Finnish chlor-alkali plant (mercury electrodes) in Aetsa contained mercury in the fruiting bodies in concentration below 10 ng/g, while the fruiting bodies collected from the background control area contained between 10 and 20 ng/g dry matter. In the same study the King Bolete *B. edulis*, Slippery Jack *Suillus luteus* and Variegated Bolete *Suillus variegatus* from the vicinity of a plant in Aetsa (a distance of up to 3 km) contained mercury in concentrations of 1,500, 590 and 3,000 ng/g dry matter, while in the fruiting bodies collected at the control area it was 410-730, 80 and 70-150 ng/g dry matter, respectively [7].

In a similar study performed earlier in Austria various species of higher mushrooms collected at a distance of up to 1 km to the chlor-alkali plant contained around

ten-fold greater concentration of mercury when compared to specimens grown at the control area [15].

In other studies performed in Europe the concentration of mercury in the fruiting bodies of King Bolete *B. edulis* collected from unpolluted sites were from 410 to 3,900 ng/g in Switzerland; from 1,300 to 8,100 ng/g in Austria; from 730 to 7,700 ng/g in Czech Republic and from 1,000 to 17,000 ng/g dry matter in Germany [1, 14-17].

Mushrooms as a food product have been very important in many world cuisines. They are especially popular because of quality of fragrance and taste, they are used as a special supplement to different dishes, and sometimes have medical applications. In Poland there is a long tradition of wild mushroom picking and a large number of species are collected annually. In Poland people usually pick-up mushrooms in forested areas and from the meadows but quite frequently also in potentially polluted industrial or urban regions. The various species of wild growing edible mushrooms are effective accumulators of heavy metals and risks from consumption of this specific food item contaminated with toxic metals has been little studied in Poland.

The purpose of this study is to evaluate data on mercury pollution of species of wild edible mushrooms collected from forested areas in the vicinity of the town of Augustów, which is considered to be free of known sources of mercury and other heavy metals pollution.

Table 1. Mercury content of edible mushrooms from the area of the town of Augustów (ng/g d. m.).

Species	n**	Caps		Stalks	
		Mean ± SD	Range	Mean ± SD	Range
Scaly Tooth <i>Sarcodon imbricatus</i> (L.: Fr.) P. Karst.	16 (48)	2,300 ± 500	1,700 ± 3,400	1,100 ± 400	590 ± 1,800
Common Chanterelle* <i>Cantharellus cibarius</i> Fr.	16 (240)	14 ± 4	8.0 ± 24		
Slippery Jack <i>Suillus luteus</i> (L.) S. F. Gray	16 (96)	140 ± 30	80 – 180	43 ± 15	19 – 79
Variegated Bolete <i>Suillus variegatus</i> (Sw.: Fr.) O. Kuntze	16 (48)	260 ± 80	120 – 430	84 ± 29	50 – 160
Yellow-cracking Bolete <i>Xerocomus subtomentosus</i> (L.) Quélet	16 (64)	54 ± 24	19 – 120	17 ± 5	8.0 – 28
Bay Bolete <i>Xerocomus badius</i> (Fr.) Kühn. ex. Gilb.	16 (48)	110 ± 50	58 – 220	65 ± 22	32 – 100
Pinewood King Bolete <i>Boletus pinophilus</i> Pil. Et. Dermek	16 (24)	2,000 ± 800	1,200 – 4,100	850 ± 390	460 – 2,000
King Bolete <i>Boletus edulis</i> Bull. Fr.	16 (24)	2,300 ± 1,100	590 – 4,500	1,000 ± 500	340 – 2,300
Orange Birch Bolete <i>Leccinum versipelle</i> (Fr.) Snell	16 (48)	720 ± 380	280 – 1,700	420 ± 170	160 – 890
Brown Birch Scaber Stalk <i>Leccinum scabrum</i> (Bull.: Fr.) S. F.	16 (64)	230 ± 90	120 – 400	120 ± 50	61 – 260
Sandy Knight-cap <i>Tricholoma flavovirens</i> (Per. ex. Fr.) Lund.	16 (80)	240 ± 60	170 – 360	170 ± 40	110 – 230
Gray and Yellow Knight-cap <i>Tricholoma portentosum</i> (Fr.) Quélet	16 (80)	96 ± 30	59 – 160	30 ± 11	15 – 58
Gypsy <i>Rozites caperatus</i> (Pers.: Fr.) Kummer	16 (48)	1,200 ± 300	710 – 1,900	470 ± 150	260 – 830

* - a whole fruiting body

** - number of pooled samples and number of the fruiting bodies (in parentheses)

Table 2. Concentrations of mercury (ng/g dry weight) in the caps and stalks of the mushrooms of the genus *Leccinum* and *Tricholoma* from various parts of Poland.

Species Collecting places	n	Caps		Stalks		Reference
		Mean \pm SD	Range	Mean \pm SD	Range	
Brown Birch Scaber Stalk <i>Leccinum scabrum</i>						
The County of Augustów, 1997/1998	16(64) ^a	230 \pm 90	(120 – 400)	120 \pm 50	(61 – 260)	This work
The Area of Rogóźno, 1984/1985		110 ^b				[20]
The County of Gubin, 1994	16	290 \pm 300	(120 – 1,300)	180 \pm 160	(52 – 640)	[21, 22]
The County of Kościerzyna, 1994	15	370 \pm 330	(93 – 1,200)	220 \pm 160	(50 – 650)	[23, 24]
Mierzeja Wiślana sand – bar, 1994	14	290 \pm 100	(140 – 460)	180 \pm 60	(61 – 290)	[24, 25]
Wieluńska Upland, 1995/1996	15	500 \pm 230	(170 – 930)	320 \pm 130	(140 – 640)	[26]
Trójmiejski Landscape Park, 1995/1996	12	6,700 \pm 2,300	(3,200 – 9,600)	4,700 \pm 1,700	(1,700 – 7,700)	d
Gdynia Orłowo, 1989	4/3 ^c	54 \pm 26	(23 – 92)	44 \pm 11	(31 – 57)	[27]
Gdańsk Otomin, 1989	7/4 ^c	100 \pm 88	(38 – 310)	65 \pm 10	(51 – 77)	[27]
The Communes of Łukta and Morąg, 1997/1998	16(26) ^a	700 \pm 270	(140 – 1,100)	350 \pm 140	(98 – 660)	d
The County of Koszalin, 1997/1998	15	300 \pm 110	(170 – 550)	200 \pm 70	(90 – 300)	d
Zaborski Landscape Park, 1997/1998	15	330 \pm 210 ^b	(130 – 930)			d
Borecka Forest – surroundings, 1998	16(45) ^a	1,200 \pm 740	(300 – 2,800)	1,100 \pm 380	(530 – 1,600)	d
Tarnobrzaska Plain, 1995	15/11 ^c	460 \pm 320	(120 – 1,400)	200 \pm 140	(90 – 540)	d
Orange Birch Bolete <i>Leccinum versipelle</i>						
The County of Augustów, 1997/1998	16(48) ^a	720 \pm 380	(280 – 1,700)	420 \pm 170	(160 – 890)	This work
Tarnobrzaska Plain, 1995	15	460 \pm 380	(80 – 1,600)	250 \pm 220	(52 – 910)	d
Red – capped Scaber Stalk <i>Leccinum rufum</i>						
The Communes of Łukta and Morąg, 1997/1998	16(28) ^a	600 \pm 590	(290 – 2,400)	450 \pm 390	(62 – 1,800)	d
Zaborski Landscape Park, 1997/1998	8	720 \pm 490	(320 – 1,700)	470 \pm 240	(210 – 820)	d
Borecka Forest – surroundings, 1998	16(51) ^a	1,300 \pm 350	(790 – 2,300)	930 \pm 310	(570 – 1,700)	d
Sandy Knight – cap <i>Tricholoma flavovirens</i>						
The County of Augustów, 1997/1998	16(80) ^a	240 \pm 60	(170 – 360)	170 \pm 40	(110 – 230)	This work
Wdzydzki Landscape Park, 1995/1996	14	120 \pm 47	(56 – 250)	68 \pm 29	(12 – 110)	[28]
Lake Wdzydzkie – surroundings, 1996/1997	14/15 ^c	1,700 \pm 860	(320 – 3,200)	1,100 \pm 650	(140 – 2,000)	d
Gray and Yellow Knight – cap <i>Tricholoma portentosum</i>						
The County of Augustów, 1997/1998	16(80) ^a	96 \pm 30	(59 – 160)	30 \pm 11	(15 – 58)	This work
Wdzydzki Landscape Park, 1995/1996	15	190 \pm 70	(83 – 350)	90 \pm 32	(30 – 140)	[28]
Zaborski Landscape Park, 1997/1998	14	180 \pm 100	(51 – 440)	88 \pm 57	(35 – 220)	d
Gray Knight – cap <i>Tricholoma trrreum</i>						
The Communes of Łukta and Morąg, 1997/1998	15(75) ^a	25 \pm 34	(23 – 150)	14 \pm 17	(9.0 – 76)	d
Wieluńska Upland, 1995/1996	15	250 \pm 160	(40 – 640)	120 \pm 43	(26 – 170)	[26]

^a - number of pooled samples and number of the fruiting bodies (in parentheses)^b - a whole fruiting body;^c - caps/stalks; d - unpublished data

This site can be considered a background site and possible reference area for any further studies as well as for the purpose of risk assessment of mercury intake with food.

Materials and Methods

The fruiting bodies of thirteen species of wild edible mushrooms were collected from a supposedly unpolluted Augustowska Forest in summer and autumn 1997 and 1998 (Table 1). The sampling site was located near a country road between the villages of Przewiez and Sucha Rzeczka. Total mercury content was determined separately in the caps and stalks or in whole fruiting bodies of the particular species of examined mushrooms. The fresh mushrooms after clean-up from the plant and soil substrate were air dried for several days in outdoor shadow and breezy conditions of warm summer and further dried in an electric laboratory oven at 40°C for 24 hours. The sub-samples (0.2 ~ 0.3 g) of dried and powdered pooled samples of mushrooms (1 to 15 fruiting bodies per sample) were wet digested with 6 ml of concentrated nitric acid (Suprapoor®, Merck) in closed PTFE vessels in a microwave oven (Automatic Digestion System, MLS 1200). The digest was further diluted to 10 ml using bidistilled water. With every set of 50 mushroom samples digested daily two blank samples were run. The method of mercury measurement was validated for several occasions by participation in international calibration trials like GESM/Food Euro proficiency testing exercise, analysis of certified plant material and within-run reproducibility control. A final determination of total mercury content was by cold - vapor atomic absorption spectroscopy (CV-AAS) using a fully automated mercury monitor (Mercury monitor 3200, Thermo Separation Products, USA).

Results and Discussion

The mean values, standard deviations and ranges of total mercury concentrations in the mushroom species examined are presented in Table 1. Table 2 reviews data on total mercury concentrations of mushrooms species of the genus *Leccinum* and *Tricholoma* collected from various sites in Poland.

As stated in a paper by Seeger [17] the mercury content of higher mushrooms is clearly a species-dependent phenomena. Evidently there are some mushroom species that can be described as usually very rich in mercury, like the Yellow-staining Mushroom *Agaricus xanthoderma* with mercury concentration of up to 22,000 ng/g dry matter, while other species had small (<50 ng/g) concentrations of that element. Nevertheless, even in the case of some species of higher mushrooms known as mercury accumulators and which belong to different families there is nearly nothing known of their common features determining their high capacity to biouptake and accumulate mercury [18]. Only recently Fischer and coworkers [10] indicated high rates of biouptake of methylmercury by *macromycetes* and/or a possibility of

the transformation of inorganic mercury to methylmercury by these biota. On the other side it is known that methylmercury represents only a small portion of total mercury concentration found in many higher mushroom species [10].

In this study Scaly Tooth *Sarcodon imbricatus*, King Bolete *B. edulis*, Pinewood Bolete *Boletus pinophilus* and Gypsy *Rozites caperatus* which were collected from an unpolluted Augustowska Forest showed highest mercury concentration with the range between 710 and 4,500 ng/g dry matter in the caps, and between 260 and 2,300 ng/g dry matter in the stalks (Table 1). As mentioned in the introduction the King Bolete *B. edulis* is well known as an effective accumulator of mercury [14, 17, 19]. There is no data available on mercury content of Pinewood King Bolete *B. pinophilus* from the sites other than Augustowska Forest for comparison purpose.

The mean mercury concentration of the caps of Scaly Tooth *Sarcodon imbricatus* in this study was $2,300 \pm 500$ ng/g which is very close to the value of 2,600 ng/g dry matter (range 1,700 - 6,400 ng/g) noted in this species collected 25 years ago from the background site in Austria [26]. Gypsy *Rozites caperatus* in this study contained mercury in the caps in mean concentrations of $1,200 \pm 300$ ng/g, and in a study by Seeger [17] in a single specimen of the same species collected in Germany was 1,000 ng/g dry matter.

The other mushroom species investigated (Table 1) were less contaminated with mercury (<1,000 ng/g in the caps and <500 ng/g in the stalks, on average). Common Chantharelle *C. cibarius* with the mean of 14 ± 4 ng/g dry matter was the least contaminated with mercury among the species examined. When compared to the value mentioned above more contaminated with mercury were the fruiting bodies of Common Chantharelle collected and examined by Seeger (110 ng/g; range from 50 to 250 ng/g dry matter) [17], or in Austria (40 ng/g; range <10 to 100 ng/g) by Rauter [15].

Mercury and other heavy metals contents of edible and inedible higher mushrooms attracts attention of food chemists and toxicologist as well as of environmental chemists [29-32]. The tolerance limit of total mercury concentration in fresh vegetables, potatoes and processed vegetables is 0.02 mg/kg wet weight *i.e.* 20 ng/g, while in dried (> 50% dry matter) plant food is 0.03 mg/kg *i.e.* 30 ng/g [33]. Apart from the Common Chantharelle with mercury concentration of 8.0 to 24 ng/g dry matter the content of this element in all other species of examined wild edible mushrooms from the Augustowska Forest exceeds an official tolerance limit for dried plant food (Table 1). When considering fresh mushrooms (90% of water) the mercury concentrations quantified in Scaly Tooth *S. imbricatus*, Pinewood King Bolete *B. pinophilus*, King Bolete *B. edulis*, Orange Birch Bolete *L. versipelle* and Gypsy *R. caperatus* exceed official tolerance limits both in the caps and stalks, while in the case of Variegated Bolete *S. variegatus*, Brown Birch Scaber Stalk *L. scaprum* and Sandy Knight-cap *T. flavovirens* these limits are exceeded in the caps (Table 1).

As stated by Vetter and Berta [29], the high mercury content of the fruiting bodies of some species of wild edible mushrooms, even when gathered from regions unpolluted with heavy metals, demands greater attention,

especially if consumption rates by local populations are high.

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