HEAVY METALS IN EDIBLE MUSHROOM BROWN BIRCH SCABER STALK *LECCINUM SCABRUM* (Bull. ex. Fr.) S. F. GRAY GROWING IN VARIOUS SITES IN POLAND

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Abstract

To understand pollution picture with heavy metals and to examine usefulness of Brown Birch Scaber Stalk *Leccinum scabrum* (Bull. ex Fr.) S. F. Gray as possible bioindicator the concentrations of ten elements, including toxic cadmium, lead, mercury and silver were determined in the fruiting bodies of that mushroom from a different forest ecosystems in Poland in 2000-2001. There were some variations of elements concentration depending on the sampling site. Heavy metals were determined by ICP-OES after wet digestion of the dried samples with concentrated nitric acid in closed TFM® vessels using microwave oven. Almost for all quantified elements the concentrations were higher in the caps than in the stalks.

Introduction

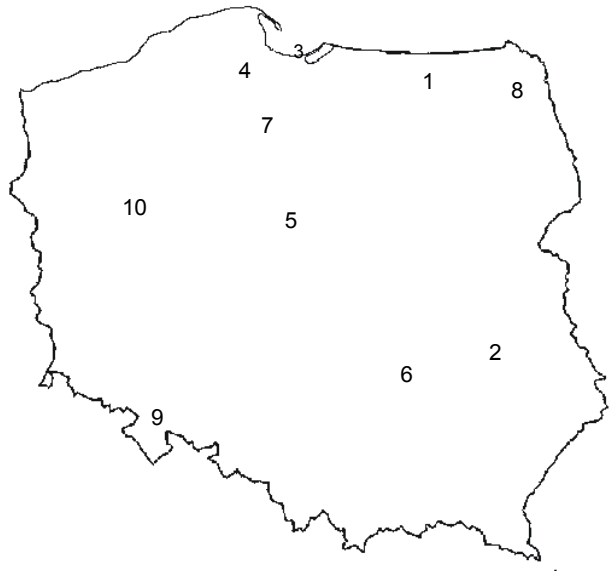
An mass and sometimes highly dramatic and even tragic to human examples of exposure to heavy metals released into the environment from the anthropogenic sources, which take place in the XX-th century, has resulted in various national and international regulations and bans on use, processing and emission of this toxic elements. Some heavy metals when released into the ambient air are transported very effectively through the atmosphere and further deposited at sites far away from the sources of pollution.

A wild growing mushrooms play important role in the decomposition of organic matter in soil or mycorrhizal process. Some species of higher mushrooms are known also due to their ability of efficient uptake and accumulation in the fruiting bodies of metallic and metalloid elements and including highly toxic mercury, cadmium, silver, lead or arsenic (1-5). The content of mercury, cadmium and lead in many wild edible mushroom species collected from background (unpolluted) sites is frequently much higher than in those found in green plant (6-8). In the case of wild edible mushroom species collected from sites close to sources of pollution with various metallic elements, concentrations of toxic metals and metalloid are usually elevated, thus the mushrooms are unfit for human consumption. Also, if grown in contaminated substrate, cultivated mushrooms can effectively take up and bioaccumulate toxic metals at great concentrations in their fruiting bodies.

Materials and methods

The concentrations of 10 elements such as Ag, Al, Cd, Co, Cu, Fe, Hg, Ni, Pb and Zn were determined in fruiting bodies of Common Scaber Stalk or Brown Birch Scaber Stalk *Leccinum scabrum* (Bull. ex Fr.) S. F. Gray collected in summer and autumn 2000-2001 from different sites in Poland (Figure 1). Fresh mushrooms after cleanup from plants and soil were dried for several days in room temperature and further dried in electrical oven at 40ºC for 24 hours. The samples (0.2-0.5 g) of dried and powdered pooled samples of mushrooms (separately caps and stalks) were wet digested with 6 ml of concentrated nitric acid (Suprapur®, Merck) under pressure in closed TFM® vessels in a microwave oven (CEM, Mars 5). With every set of 12 samples digested a blank sample was run. The PerkinElmer Optma 2000™ DV ICP-OES instrument was used for the analysis of mushrooms samples. In the case of mercury CV-AAS technique was used. The method was validated by analysing certified reference materials: CTA-OTL-1 (Oriental Tobacco Leaves, Institute of Nuclear Chemistry and Technology) and IAEA-359 (Cabbage Leaves, International Atomic Energy Agency). For blank samples no major interferences were found. Discrepancies between certified values and concentration quantified were below 10 %, and the coefficient of variation for single measurements was below 5 %.

Figure 1: Location of the sampling sites (see also Tables 1 and 2)



Results and discussion

Mean concentrations of Ag, Al, Cd, Co, Cu, Fe, Hg, Ni, Pb and Zn in the fruiting bodies of Brown Birch Scaber Stalk *Leccinum scabrum* (Bull. ex Fr.) S. F. Gray are presented in tables 1 and 2, respectively, where samples numbers (n), standard deviations and ranges of concentrations are also indicated.

Zinc was the most abundant amongst the elements quantified and the range of the mean values in the caps and in the stalks was between 158±41 and 265±52, and 77±26 and 126±27 mg/kg dry weight respectively. The smallest values were obtained for elements with some toxic abilities such silver, cobalt, mercury and nickel There were some variations of elements concentration depending on the sampling site. The caps usually contained higher concentration of Ag, Cd, Cu, Fe, Hg, Pb and

Table 1: Total concentrations of some elements (Ag, Al, Cd, Co and Cu) in the caps and stalks of *Leccinum scabrum* (mean±SD and range in mg/kg dry weight)

Site and year	n		Ag	Al	Cd	Co	Cu
County of Ketrzyn, 2000 (1*)	16	C	0.82±0.26 (0.38-1.5)	141±71 (45-300)	2.7±1.0 (1.6-4.7)	0.27±0.11 (0.11-0.46)	22.9±4.4 (12.5-30.7)
		S	0.32±0.14 (0.15-0.66)	115±52 (40.4-204)	0.9±0.4 (0.4-1.7)	0.26±0.11 (0.11-0.45)	10.4±1.7 (8.1-13.5)
Lubelska Upland, 2000 (2)	22	C	1.6±0.6 (0.60-2.7)	74.6±51.3 (26.5-230)	6.1±4.0 (0.4-14.1)	0.19±0.19 (0.02-0.57)	31.1±7.4 (20.5-45.4)
		S	0.49±0.24 (0.17-1.0)	84.1±44.8 (21.6-190)	2.2±1.6 (0.1-7.0)	0.18±0.14 (0.03-0.53)	15.2±5.4 (5.5-24.8)
Sobieszewska Island, 2000 (3)	13	C	0.57±0.27 (0.34-1.4)	20.6±11.7 (9.1-44.8)	5.9±1.7 (3.4-8.5)	0.045±0.019 (0.026-0.095)	26.5±7.2 (17.6-44.0)
		S	0.18±0.14 (0.10-0.61)	16.5±11.6 (6.3-47.5)	1.7±0.6 (0.8-2.9)	0.032±0.016 (0.014-0.063)	17.2±8.4 (9.4-41)
Wdzydzki Landscape Park, 2000 (4)	13	C	0.91±0.32 (0.18-1.3)	143±71 (38.0-272)	1.5±1.0 (0.3-3.4)	0.33±0.17 (0.10-0.62)	24.0±7.8 (15.7-39.2)
		S	0.21±0.07 (0.12-0.30)	122±47 (40.2-199)	0.4±0.3 (0.1-0.9)	0.30±0.12 (0.10-0.48)	11.6±5.4 (7.4-27.3)
County of Wloclawek, 2001 (5)	15	C	0.49±0.09 (0.34-0.68)	55.5±37.4 (17.8-146)	3.2±1.0 (1.7-5.3)	0.080±0.036 (0.028-0.17)	26.4±7.5 (15.1-44.9)
		S	0.14±0.03 (0.10-0.20)	34.9±21.1 (16.9-74.9)	1.0±0.5 (0.4-2.0)	0.076±0.043 (0.034-0.19)	10.7±3.2 (4.6-17.7)
County of Starachowice, 2001 (6)	14	C	0.72±0.36 (0.28-1.6)	51.8±22.1 (23.8-91.5)	6.6±1.5 (4.1-9.0)	0.081±0.033 (0.043-0.14)	24.3±6.6 (17.5-42.2)
		S	0.26±0.13 (0.11-0.56)	24.3±11.5 (10.7-53.4)	2.0±0.6 (1.4-3.0)	0.13±0.10 (0.04-0.14)	9.9±3.4 (6.0-18.2)
Tucholskie Forest, 2001 (7)	15	C	0.47±0.14 (0.29-0.74)	33.7±16.2 (12.9-63.1)	3.1±1.3 (1.1-6.0)	0.069±0.046 (0.026-0.19)	21.2±4.9 (10.7-28.8)
		S	0.20±0.09 (0.08-0.38)	33.0±34.8 (10.0-126)	0.7±0.3 (0.3-1.2)	0.077±0.081 (0.019-0.32)	9.5±2.8 (6.2-15.9)
Augustowska Forest, 2001 (8)	77	C	0.46±0.14 (0.21-1.0)	27.6±25.2 (1.2-139)	3.6±2.0 (0.9-9.1)	0.036±0.039 (0.006-0.16)	24.1±8.1 (10.8-41.4)
		S	0.10±0.06 (0.03-0.40)	20.8±18.1 (2.1-118)	1.13±0.9 (0.3-4.8)	0.038±0.039 (0.009-0.15)	7.5±2.4 (3.5-14.6)
Klodzka Hollow, 2000 (9)	15	C	0.67±0.20 (0.29-1.0)	123±77 (16.3-244)	4.6±2.2 (1.1-8.8)	0.13±0.14 (0.01-0.48)	22.1±7.2 (13.8-39.5)
		S	0.25±0.05 (0.18-0.34)	46.4±47.8 (10.2-178)	1.8±0.8 (0.6-3.3)	0.089±0.097 (0.010-0.34)	9.6±2.5 (6.0-14.6)
Notecka Forest, 2000 (10)	15	C	0.77±0.37 (0.22-1.4)	42.2±15.4 (18.8-75.0)	3.4±2.7 (0.5-10.5)	0.089±0.051 (0.029-0.17)	27.4±11.1 (10.4-42.6)
		S	0.22±0.10 (0.11-0.45)	24.3±11.5 (10.7-53.4)	1.1±0.8 (0.1-3.2)	0.076±0.035 (0.027-13)	11.8±3.4 (7.2-19.0)

* - for location of the sampling sites see Figure 1;
# - C-caps, S-stalks;
n – number of samples

Table 2: Total concentrations of some elements (Fe, Hg, Ni, Pb and Zn) in the caps and stalks of *Leccinum scabrum* (mean±SD and range in mg/kg dry weight**)**

Site and year	**n**		**Fe**	**Hg**	**Ni**	**Pb**	**Zn**
County of Ketrzyn, 2000 (1*)	16	C#	135±43 (50-190)	0.43±0.16 (0.26-0.77)	0.50±0.17 (0.28-0.88)	1.2±0.7 (0.6-2.7)	189±55 (109-312)
		S	76.5±17.7 (42.7-102)	0.24±0.09 (0.11-0.41)	0.46±0.20 (0.20-1.1)	0.73±0.22 (0.49-1.2)	93±39 (40-178)
Lubelska Upland, 2000 (2)	22	C	75.9±36.1 (32.6-150)	0.58±0.25 (0.29-1.1)	0.58±0.22 (0.19-0.94)	0.82±0.35 (0.34-1.7)	202±48 (136-302)
		S	43.3±13.2 (18.3-67.9)	0.34±0.17 (0.11-0.74)	0.80±0.43 (0.10-1.4)	0.54±0.21 (0.13-0.89)	85±42 (26-176)
Sobieszewska Island, 2000 (3)	13	C	51.6±11.4 (36.7-75.1)	0.54±0.26 (0.23-1.1)	0.65±0.19 (0.31-0.86)	0.64±0.19 (0.36-0.89)	265±52 (179-338)
		S	26.3±8.1 (14.3-45)	0.24±0.13 (0.12-0.62)	0.63±0.27 (0.24-1.2)	0.40±0.10 (0.24-0.59)	119±35 (80-204)
Wdzydzki Landscape Park, 2000 (4)	13	C	114±38 (54.7-178)	0.46±0.21 (0.13-1.00)	0.66±0.10 (0.51-0.89)	0.34±0.11 (0.23-0.62)	169±59 (100-270)
		S	70.7±21.9 (32.2-97.6)	0.17±0.08 (0.03-0.33)	0.62±0.18 (0.47-1.1)	0.24±0.10 (0.12-0.46)	77±29 (37-128)
County of Wloclawek, 2001 (5)	15	C	60.2±25.1 (37.2-129)	1.1±0.4 (0.58-1.7)	0.45±0.07 (0.36-0.64)	1.3±0.5 (0.5-2.4)	227±39 (158-291)
		S	32.6±15.0 (18.9-65.5)	0.52±0.20 (0.21-0.97)	0.43±0.08 (0.28-0.58)	0.56±0.15 (0.28-0.80)	88±14 (66-114)
County of Starachowice, 2001 (6)	14	C	58.2±21.8 (32.6-107)	1.2±0.37 (0.68-2.0)	0.44±0.11 (0.28-0.64)	0.84±0.36 (0.28-1.6)	219±42 (176-304)
		S	25.9±6.5 (14.8-39)	0.72±0.20 (0.44-1.2)	0.36±0.11 (0.14-0.58)	0.48±0.20 (0.08-0.77)	103±22 (73-159)
Tucholskie Forest, 2001 (7)	15	C	46.3±18.3 (19.6-87)	0.59±0.18 (0.21-1.0)	0.45±0.19 (0.27-0.89)	0.79±0.44 (0.45-2.0)	158±41 (114-280)
		S	26.9±18.0 (12.1-77.9)	0.35±0.14 (0.16-0.63)	0.43±0.17 (0.28-0.80)	0.41±0.21 (0.15-0.95)	77±26 (47-161)
Augustowska Forest, 2001 (8)	77	C	38.1±18.4 (21.9-157)	0.64±0.34 (0.12-1.5)	0.33±0.17 (0.10-0.79)	0.69±0.51 (0.11-2.6)	209±54 (85-334)
		S	18.8±10.0 (6.7-58.3)	0.30±0.17 (0.06-0.77)	0.44±0.20 (0.19-1.2)	0.28±0.16 (0.07-0.72)	103±26 (59-169)
Klodzka Hollow, 2000 (9)	15	C	126±56 (23.8-196)	0.380.23 (0.07-0.76)	0.84±0.05 (0.76-0.91)	3.0±2.0 (0.4-7.5)	211±35 (140-256)
		S	64.8±25.6 (12.5-87.0)	0.21±0.08 (0.06-0.33)	0.98±0.19 (0.64-1.3)	1.3±0.6 (0.2-2.2)	98±34 (38-173)
Notecka Forest, 2000 (10)	15	C	50.6±17.2 (28.5-92.9)	0.64±0.25 (0.24-1.1)	0.56±0.12 (0.32-0.75)	0.70±0.27 (0.28-1.2)	244±55 (143-339)
		S	25.3±10.0 (10.2-51.0)	0.25±0.11 (0.08-0.44)	0.39±0.15 (0.27-84)	0.38±0.15 (0.08-0.72)	126±27 (85-178)

* - for location of the sampling sites see Figure 1;
# - C-caps, S-stalks;
n – number of samples

Zn than stalks ($p < 0.05$; T-test for depended samples).
The metallic elements such as lead, cadmium, mercury and zinc are amongst those elements of which the concentrations in many kinds of foodstuffs are limited by law in Poland. The tolerance limit set in Poland for dried mushrooms is 2 mg/kg for lead, 1 mg/kg for cadmium, 0,5 mg/kg for mercury and 150 mg/kg for zinc. The contents of the elements zinc and cadmium in the caps of *L. scabrum* from all examined sites exceeded tolerance limit mentioned above. In the case of lead the caps collected from Klodzka Hollow exceeded tolerance limit set for dried mushrooms. The mercury content of the caps of *L. Scabrum* collected from the Counties of Wloclawek and Starachowice (Table 2) nearly twice exceeded tolerance limit. Both the Counties of Wloclawek and Starachowice are generally known as somewhat polluted regions but no data on soil mercury levels are known till now. Collection and consumption of wild edible mushroom has a long tradition in Poland and even today is extremely popular both among villagers and citizens. The relatively high mercury, lead, cadmium and zinc content of fruiting bodies of some species of wild edible mushrooms, especially when gathered from potentially polluted regions with heavy metals, demand greater attention, especially if consumption rates by local population are high.

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