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Full Length Research Paper

Metallic elements profile of Hazel (Hard) Bolete (*Leccinum griseum*) mushroom and associated upper soil horizon

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The aim of this study was to determine profile of 19 elements of caps and stipes of Hazel Bolete (*Leccinum griseum*) and soil substratum collected at the area of the Commune of Gołdap, within Gołdap County in the Warmian-Masurian Voivodeship in Poland compared to the Cd, Pb and Hg levels with current hygienic standards. The elements were determined using validated methods, that is, inductively coupled plasma atomic emission spectroscopy (ICP-AES) and cold vapour atomic absorption spectrometry (CV-AAS). K and Mg were particularly abundant, mean values were 41 and 1.2 mg/g dry weight (dw) in caps of Hazel Bolete, respectively, and they were followed by Na, Rb, Zn and Ca at 560, 350, 210, 110 µg/g dw, respectively. Concentrations of Fe, Cu, Al and Mn were ~ 20 to 50 µg/g dw, while concentrations of other elements were ~ l.0 µg/g dw or less. Pb and Cd content of Hazel Bolete from pristine area did not exceed the maximum levels set by European Union for cultivated mushrooms. In the case of Hg and area surveyed, eating Hazel Bolete did not result in exceeding provisional tolerable weekly intake (PTWI) value.

Key words: Food, fungi, heavy metals, higher fungi, mineral composition, mushrooms, nutrition, wild food.

INTRODUCTION

A pick-upping and culinary use of wild grow mushrooms is traditionally popular in many countries across Asia and Europe, and in Mexico. People appreciate mushrooms mostly for their unique aroma and taste but also certain nutrition value and local/traditional gourmet customs. An annual intake rate of mushrooms could be from negligible to up to 28 kg *per capita* regionally (Zhang et al., 2010).

As any other biota, fungi and including mushrooms also need certain quantities of many minerals for balanced growth and reproduction. Mycelia mobilize and up-takes minerals from substratum (surface layer of soil, wood etc.) and translocate them to fruit-bodies or both to fruit bodies and symbiotic trees as is in the case of mycorrhizal fungi. Fungi play a vital role in up-take of mineral constituents from the soil bedrock and their translocation to biosphere. An example could be silver that is abundant in fruit bodies of macromycetes and that biota play a possibly major role in its biogeochemical cycling (Borovička et al., 2010). As a result of these, fungal fruit bodies (carpophores) can be enriched in many metallic elements and sometimes also in metalloids, even if they have grown-up at the background (uncontaminated) areas (Arce et al., 2008; Borovička et al., 2006; Brzostowski et al., 2011b; Chudzyński and Falandysz, 2008; Falandysz, 2008; Falandysz et al., 2001, 2008, 2011; Řanda and Kučera, 2004). Fruit bodies of edible wild grown mushrooms are not only a valuable delicacy but as food resources which are much more abundant in minerals than staple plant food. There are many abiotic and biotic factors that potentially can impact mineral constituents' content of mushrooms. A fundamental role seem to play these which are of a species-specific nature, that is, amount and quality of binding sites for metal ions as well as production and

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activity of specific enzymes and chelating agents, while on the other side are abundance and availability of minerals in substratum. A problem to some degree are metals in mushrooms - and a few examples are Se, Hg or rare earth elements - as noticed recently by some authors (Borovička et al., 2011; Falandysz, 2008; Jarzyńska and Falandysz, 2011).

Hazel Bolete is mushroom of *Boletaceae* family and genus *Leccinum*, which forms mycorrhiza only with hornbeams (*Aspen*). It usually grows up under the mixed hornbeam-beech forests. The fruiting body of Hazel Bolete consists of cap and stipe. The cap with brown in colour is 4 to 12 cm in diameter. The stipe is brown in colour, up to 5 to 15 cm tall and 1 to 3 cm thick, and covered with black fibrils.

This species has been traditionally eaten by some mushroom fanciers because of its delicious and delicate text (Gumińska and Wojewoda, 1985). However, there is lack in open literature of comprehensive survey on minerals profile of Hazel Bolete. Certainly but fragmentary, information on Ca, Cu, Fe, K, Mg, Mn, Na, Zn, Cd, Co and Pb contents of this mushroom as reported by other authors is reviewed shortly in this article too.

The present study describes metal concentrations in mushrooms collected from northern part of Poland (Commune of Gołdap) and concerns 19 elements found in specimens of Hazel Bolete. The Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Rb, Sr, Zn concentrations were determined by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and cold vapour atomic absorption spectrometry (CV-AAS).

MATERIALS AND METHODS

Samples

15 well developed (mature) specimens of Hazel Bolete *Leccinum griseum* (Quel.) Singer synonymous to *Leccinum pseudoscabrum* (Kallenb.) or *Leccinum carpini* Šutara, and corresponding surface layer (0 to 10 cm) of humifying and mineral soil underneath to mushrooms were collected at the area of the Commune of Gołdap, within Gołdap County in the Warmian-Masurian Voivodeship in Poland at the same day in the late summer 2003.

Fresh mushrooms, after cleanup with a plastic knife from any visible plant vegetation and soil substrate debris, were air-dried for several days. Furthermore, each sample of the fruiting body was separated to two parts - cap and stipe and dried at 65°C to constant weight. Dried mushrooms were pulverized in an agate mortar and kept in brand new sealed polyethylene bags in dry condition.

Soil substrate samples, after removal of any visible organisms, small stones, sticks and leaves were air dried in room temperature for several weeks in clean condition. Next, the soil samples were sieved through a pore size of 2 mm plastic sieve and sealed in brand new polyethylene bags and kept in dry and clean condition.

Reagents

All reagents were of analytical reagent grade unless otherwise stated. Double distilled water (resistivity > 10 MΩ cm) was used for the preparation of solutions. The nitric acid (65% HNO_3) was of suprapur quality (Suprapur®, Merck). During the experiments, all glassware and equipment were carefully cleaned starting with 5% HNO_3 and ending with repeated rinsing double distilled water to prevent contamination. Metal standard solutions used (0.05, 0.1, 0.5, 1.0 or 10 mg/L) were prepared by diluting 1000 mg/L stock multi-element standard solution (CertiPUR®, Merc) immediately before use. Yttrium (20 mg/L $Y(NO_3)_3$ in HNO_3 0.5 mol/L; Merck) was used as an internal standard. Mercury standard solution (1000 µg/mL in HNO_3 2.0 mol/L; Merc) and L-cysteine (98%; Nacalai Tesque) were used. The L-cysteine was utilized as a solvent for the Hg standard solution. A 10 µg/mL Hg standard solution was first attained by diluting 1000 µg/mL Hg standard solution in 0.001% L-cysteine. Next, 1.0 µg/mL Hg standard solution was obtained from 10 µg/mL standard solution. Blank and 100, 150 and 200 µL of 1.0 µg/mL Hg standard solution were injected into the analyzer for the calibration curve.

Digestion procedure

Subsamples of dried and powdered caps and stipes (~ 0.5 g) were digested with 7 mL of concentrated HNO_3, (65%) and cold digested for 24 h in “open” polytetrafuoroethylene (PTFE) vessels. Next the vessels were closed and pressure/temperature digested in an automatic microwave digestion system of type MARS 5 (CEM Corporation, Matthews, NC, USA). A microwave digestion conditions was set as follows: power, 1.2 kW; ramp, 10 min.; pressure, 800 psi; temp., 200°C; hold, 15 min. The digest was further diluted to 10 ml using double deionised water and subjected to instrumental analysis. A blank digest was carried out in the same way.

The soil subsamples (~ 2.5 g) were extracted with concentrated HNO_3 (65%; 7.5 ml) in quartz beakers and left for 24 h. Next, the obtained extracts were diluted to 50 ml with double deionised water and filtered through filter paper (Whatmann No. 42) into polyethylene bottle. A blank digest was carried out in the same way.

Instrumentation

Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Rb, Sr and Zn were determined using ICP-AES; (Optima 2000 DV, Perkin-Elmer, Norwalk, CT, USA). A condition used for ICP-AES was as follows: forward RF power, 1.45 kW; plasma gas (Ar) flow rate, 15 L/min; auxiliary gas (Ar) flow rate, 0.5 L/min; nebuliser gas (Ar) flow rate, 0.75 L/min; plasma observation height, 15 mm; integration time, 3 s; sample flow rate, 1.5 mL/min.

Nebulization was achieved with ultrasonic nebulizer with a desolvation system (U-5000 AT+; CETAC Technologies, Omaha, NE) and condition as follows: healer temperature - 140°C; condenser temperature - 2°C, carrier gas flow rate - 1.0 L/min. analytical wavelengths (nm) were as follows: Ag (328.068); Al (396.153); Ba (455.403); Ca (317.933); Cd (228.802); Co (228.616); Cr (267.716); Cu (324.752); Fe (238.204); K (766.490); Mg (285.213); Mn (257.61); Na (589.592); Ni (231.604); Pb (220.353); Rb (780.023); Sr (421.552) and Zn (213.857) (Brzostowski et al., 2009, 2011a).

Hg was determined by CV-AAS after thermal decomposition of sample matrix and further amalgamation and decomposition of element from gold wool (Mercury analyzer type MA-2000, Nippon Instruments Corporation, Takatsuki, Japan). A condition used for CV-AAS was as follows: heating temperature, 850°C; detection, dual beam AAS; determination, 7 min; wavelength, 253.7 nm.

Quality control/quality assurances

The methods of metallic elements measurement was validated and

controlled by preparation of standard solutions, calibration of instrument and daily run of blank samples and duplicates with each analytical cycle. Evaluation of precision and accuracy of the analytical method was based on the analysis of certified reference materials such as Oriental tobacco leaves (CTA-OTL-1), tea leaves (INTC-TL-1) and Polish Herbal Blend (INCT-MPH-2) by the Institute of Nuclear Chemistry and Technology in Warsaw, Poland (Brzostowski et al., 2011a, b; Report ICHTJ, 2002). Discrepancies between certified values and quantified concentrations were below 10%. In day-by-day runs, in every set of 10 mushroom samples, there was one blank sample which was digested, diluted and analyzed.

Data analysis

To investigate potential risk for human health reference dose (RfD), value of provisionally tolerable weekly intake (PTWI) were applied. To estimate the accumulation degree of metals by mushrooms, bioconcentration factor values (BCF) were enumerated. Student's *t*-test was employed to estimate the significance of values. The Shapiro-Wilk W test was used in testing for normality.

RESULTS AND DISCUSSION

In Table 1, data on the elements concentration of Hazel Bolete and soil, cap to stipe content quotient ($Q_{C/S}$) and bioconcentration factor (BCF) values are summarized. All element contents are expressed on a dry weight basis. In Figure 1, concentration ranges for each element determined and given in logarithmic scale are displayed graphically. For an international overview on Hazel Bolete minerals composition, content of eleven major elements are given in Table 2.

Minerals concentrations

There is a little information in the literature concerning minerals profile of Hazel Bolete. Furthermore, there are no references about the BCF values, data relate to a small number of samples of fruiting bodies and only certain metals: Ca, Cu, Fe, K, Mg, Mn, Na, Zn, Cd, Co, Pb (Table 2).

The Hazel Bolete mushroom is wild food resource relatively rich in K. This chemical element (macroelement) occurred in relatively great concentrations both in caps (between 34 and 43 mg/g dry weight) and stipes (between 15 and 34 mg/g dry weight) of Hazel Bolete in this study (Table 1). When expressed on a wet weight (ww) and assuming that water content of fresh fruit bodies is at 90%, on the average, these data corresponds to between 3.4 and 4.3, and 1.5 and 3.4 mg/g, respectively. In the only report available, the mean value of K content in caps of this species from Żarnowiec was the same as in present study (40 ± 0 mg/g dw) (Table 2). These values of K concentrations determined in Hazel Bolete are close to data reported for Brown Birch Scaber Stalk (*Leccinum scabrum*), which is a closely related species. Brown Birch Scaber Stalk contained mean K concentrations in caps at 40,000 ± 3000 (n=3), 34,000 ± 3000 (*n=15*), 52,000 ± 4000 (n=15) and 36,000±4000 (n=15), and in stipes at 11,000±3000 µg/g dw (*n=15*) (Falandysz et al., 2007).

Apart from K among other macroelements determined in Hazel Bolete, Mg was dominant and occurred at concentrations varying in caps between 1000 and 1200 and in stipes between 420 and 860 µg/g dw, while for Na were 170 to 860 and 220 to 1200 µg/g dw, and for Ca 67 to 220 and 78 to 270 µg/g dw, respectively (Table 1). These values on Mg and Na content were of the same order of magnitude as noted in the only report on Hazel Bolete mushrooms from Żarnowiec and showing in caps 1200 ± 0 µg/g dw and 830 ± 510 µg/g dw, respectively (Table 2). An exception is Ca that was noted at 38±12 µg/g dw (Table 2), and was significantly less when compared to a mean value of 110±36 µg/g caps dw in this study (Table 1).

Rb and Zn in Hazel Bolete were even more abundant than Ca and the caps contained them, on the average, at 320 ± 99 µg/g dw and 240 ± 96 µg/g dw, respectively (Table 1). Zn concentrations were found to be greater than those reported in the literature. The lower and higher Zn contents in Hazel Bolete samples have been reported to be in the range from 51 to 150 µg/g dw.

Copper contents in caps collected from Bavaria in Germany (36.1 ± 8.6 C µg/g dw) and from Kluknava in Slovakia (28.2 µg/g dw) were similar to content shown in this study (29 ± 8.7 µg/g dw). However, the contents of this metal in stipes varied significantly depending on the sampling site in Europe (Bavaria - 52.2 ± 22.3, Kluknava - 1.79, Gołdap - 11 ± 2.9 µg/g dw). Fruiting bodies of Hazel Bolete collected from East Black Sea region (Turkey) contained Cu at concentration 47.9 ± 7.0 µg/g dw and its quantity was far beyond that in caps and stipes in our study.

Iron in Hazel Bolete collected from the sites in Czech Republic and Poland has been reported to be in the range from 30 to 34 µg/g dw. A higher Fe values 240 ± 27 µg/g dw were determined in fruiting bodies of Hazel Bolete from East Black Sea region of Turkey. The Fe contents of Hazel Bolete in this study are in agreement with the lower values reported in the literature. It is difficult to deduce, what was the reason for such great concentrations of Fe in this species in Turkey and including a small number of samples, lack of information concerning the BCF values and the unknown level of environmental pollution. Manganese values found were25.1 ± 2.3 µg/g dw in Hazel Bolete from East Black Sea region in Turkey. Our Mn values (21 ± 7.5 µg/g dw) are in agreement with those reported in the literature. Whereas, significantly lower Mn values found were 7.0 µg/g dw in mushrooms from Żarnowiec site in Poland.

The lower Pb value (0.75 ± 0.08 µg/g dw) was found in Hazel Bolete from East Black Sea region in Turkey, Bavaria and Kluknava areas. In this study, the Pb

Table 1. Minerals constituent content of Hazel Bolete and substratum (µg/g dry weight; mean, SD, range and median values) from the Gołdap Community, their cap to stipe content quotient ($Q_{C/S}$) and bioconcentration factor (BCF) values.

Element	Cap (C)	Stipe (S)	Soil	BCF_C	BCF_S	Qc/s
Ag	0.57 ± 0.15 0.4 - 0.96 0.52	0.19 ± 0.074 0.096 - 0.32 0.17	0.0038 ± 0.0015 0.0022 - 0.0068 0.0031	170 ± 75 74 - 300 170	56 ± 31 19 - 120 54	3.4 ± 1.3 1.9 - 5.5 3.0
Al	33 ± 25 14 - 100 22	21 ± 18 7.2 - 71 13	1200 ± 700 810 - 2700 900	0.028 ± 0.017 0.008 - 0.081 0.022	0.018 ± 0.012 0.0067 - 0.053 0.014	1.8 ± 0.77 0.75 - 3.3 1.6
Ba	0.41 ± 0.21 0.2 - 0.95 0.37	0.45 ± 0.34 0.21 - 1.6 0.33	9.1 ± 1.6 7.9 - 14 8.5	0.045 ± 0.02 0.022 - 0.095 0.038	0.048 ± 0.029 0.025 - 0.14 0.035	1.1 ± 0.6 0.26 - 2.7 0.97
Ca	110 ± 36 67 - 220 110	130 ± 51 78 - 270 110	10000 ± 5200 310 - 14000 12000	0.062 ± 0.12 0.0056 - 0.34 0.0081	0.077 ± 0.15 0.0055 - 0.5 0.0092	0.91 ± 0.3 0.41 - 1.5 1
Cd	3.3 ± 2.1 1 - 8.5 2.9	1.2 ± 0.88 0.28 - 3 0.92	0.043 ± 0.016 0.031 - 0.082 0.037	83 ± 57 26 - 240 64	29 ± 22 5.8 - 86 21	3.1 ± 0.71 2.2 - 4.8 2.9
Co	0.069 ± 0.11 0.0033 - 0.37 0.025	0.13 ± 0.23 0.009 - 0.92 0.052	1.1 ± 0.061 1.1 - 1.3 1.1	0.058 ± 0.095 0.0029 - 0.33 0.022	0.11 ± 0.2 0.0074 - 0.82 0.048	0.65 ± 0.54 0.13 - 2.3 0.49
Cr	0.27±0.049 0.21-0.41 0.26	0.15±0.038 0.1-0.23 0.14	1.6±0.33 1.2-2.2 1.4	0.18±0.041 0.11-0.27 0.18	0.098±0.031 0.06-0.17 0.086	1.9 ± 0.52 1.2 - 3.1 2
Cu	29 ± 8.7 19 - 48 27	11 ± 2.9 6.4 - 16 11	1.2 ± 0.21 0.87 - 1.6 1.3	23±4.7 15-31 23	8.6±2.2 4.9-12 8.7	2.7 ± 0.42 2 - 3.5 2.8
Fe	56 ± 22 34 - 110 48	36 ± 18 18 - 82 28	1500 ± 320 1200 - 2300 1400	0.036 ± 0.011 0.026 - 0.063 0.034	0.023 ± 0.0093 0.014 - 0.039 0.018	1.8 ± 0.74 0.84 - 3.5 1.6
Hg	0.34 ± 0.17 0.12 - 0.65 0.33	0.17 ± 0.11 0.067 - 0.44 0.13	0.014 ± 0.0051 0.011 - 0.025 0.012	24 ± 9.3 10 - 41 23	11 ± 4.2 5 - 18 11	2.2 ± 0.37 1.5 - 2.8 2.2
K	40000 ± 2600 34000 - 43000 41000	24000 ± 4600 15000 - 34000 23000	220 ± 51 100 - 310 240	190 ± 71 140 - 400 170	120 ± 63 61 - 320 94	1.7 ± 0.28 1.2 - 2.5 1.7
Mg	1200 ± 56 1000 - 1200 1200	710 ± 110 420 - 860 740	1500 ± 700 280 - 2300 1700	1.2 ± 1.2 0.5 - 3.8 0.7	0.79 ± 0.83 0.2 - 2.8 0.4	1.7 ± 0.34 1.3 - 2.7 1.7
Mn	21 ± 7.5 13 - 44 20	17 ± 6.2 5.9 - 28 14	150 ± 17 130 - 180 140	0.14 ± 0.055 0.091 - 0.32 0.14	0.11 ± 0.04 0.041 - 0.19 0.11	1.4 ± 0.57 0.64 - 2.5 1.4
Na	520 ± 240 170 - 860 560	740 ± 290 220 - 1200 750	16 ± 9.3 4.5 - 45 15	35 ± 14 8.2 - 61 36	52 ± 22 17 - 97 48	0.7 ± 0.24 0.27 - 1.2 0.68
Ni	0.15 ± 0.1 0.049 - 0.34 0.1	0.13 ± 0.086 0.0073 - 0.33 0.096	1.9 ± 0.36 1.2 - 2.4 2.0	0.085 ± 0.074 0.021 - 0.26 0.054	0.068 ± 0.051 0.0038 - 0.2 0.057	2.2 ± 3.4 0.4 - 14 1.2
Pb	0.53 ± 0.28 0.18 - 1.1 0.42	0.27 ± 0.082 0.11 - 0.4 0.28	4.4 ± 2.1 3.1 - 8.6 3.5	0.13 ± 0.078 0.04 - 0.3 0.1	0.066 ± 0.025 0.035 - 0.11 0.067	2.1 ± 1.2 0.81 - 5.4 1.6
Rb	320 ± 99 100 - 420 350	120 ± 48 37 - 220 120	1.1 ± 1.5 0.14 - 4.2 0.53	920 ± 770 26 - 3000 750	320 ± 280 9.3 - 1100 250	3 ± 0.98 1.8 - 5.9 2.8
Sr	0.19 ± 0.084 0.11 - 0.46 0.18	0.22 ± 0.11 0.12 - 0.57 0.18	11 ± 4.9 0.86 - 14 13	0.049 ± 0.08 0.0083 - 0.25 0.013	0.058 ± 0.1 0.0087 - 0.38 0.016	0.98 ± 0.37 0.32 - 1.6 0.96
Zn	240 ± 96 93 - 420 210	110 ± 52 34 - 230 90	7 ± 0.92 6 - 9.5 6.6	35 ± 14 9.8 - 65 32	15 ± 7.4 3.6 - 29 15	2.4 ± 0.44 1.7 - 3.4 2.3

BCF, Bioconcentration factor values; $Q_{C/S}$, cap to stipe content quotient.

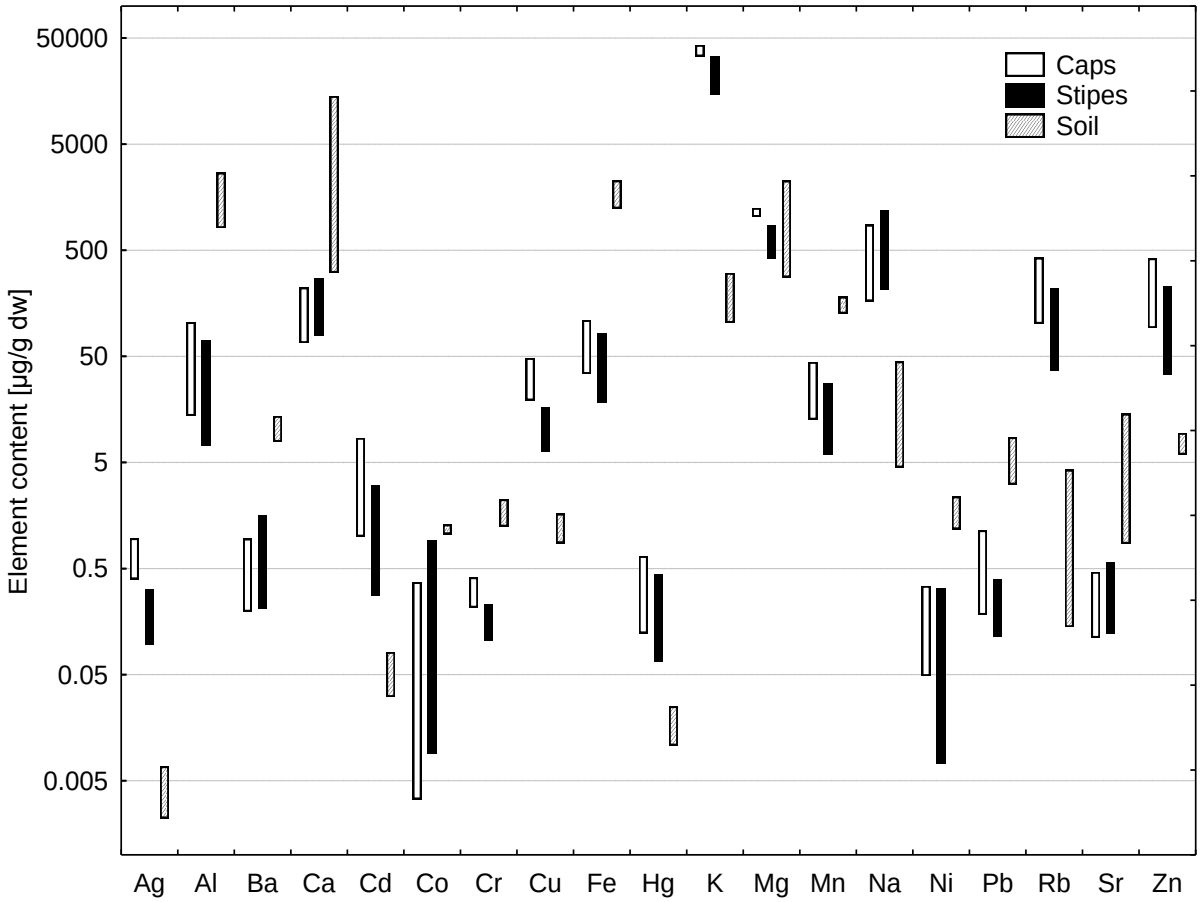

Figure 1. The elements concentrations range for the caps and stipes of Hazel Bolete and for soil substrate.

contents (0.53 ± 0.28 µg/g dw) in caps is in agreement with the lower values reported in the literature.

The lower Cd values in Hazel Bolete samples have been reported to be in the ranges: 1.3 to 5.0 µg/g dw. The Cd contents (3.3±2.1 µg/g dw) in our study are in agreement with the values reported in the literature.

Minimum and maximum values of Hg found were 0.86 ± 0.31 µg/g dw (Borecka Forest; Poland) and 1.92 ± 0.33 µg/g dw (Bavaria, Germany) in the literature, respectively. The Hg contents (0.34 ± 0.17 µg/g dw) in our caps samples of Hazel Bolete are in agreement with the lower values reported in the literature.

Cobalt values in Hazel Bolete mushrooms have been reported to be in the ranges: 0.08 to 0.36 mg/kg (Table 2). In this study the Co levels found in the caps and stipes (0.069 ± 0.11 and 0.13 ± 0.23 µg/g dw, respectively) are in agreement with literature values.

Hazel Bolete contained in its fruiting body metals such as Ag, Ba, Co, Cr, Ni and Sr but at small concentrations, that is close to 0.5 µg/g dw as found for Ag and Ba, or smaller, as noted for the remainders (Table 1).

When based on the median values determined in this study, the caps of Hazel Bolete compared to stipes were more abundant in Ag, Al, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Rb and Zn, while stipes were richer in Ba, Ca, Co, Na and Sr (Figure 1).

Bioconcentration factors

Amongst the metals surveyed, rubidium, potassium and silver were the most bioconcentrated by Hazel Bolete. The median values of these metals concentration of the caps were greater, respectively, in 750-, 170- and 170-fold than that of soil substrate. For the stipes median values of these elements concentration were greater 250-, 94- and 54-fold that of soil substrate. Elements such as Cd, Na, Zn, Hg and Cu were weaker accumulated both in caps and stipes of Hazel Bolete and theirs median BCF values ranged from 11 for Hg in the stipes to 64 for Cd in the caps. Elements bioexcluded by Hazel Bolete are Al, Ba, Ca, Co, Cr, Fe, Mg, Mn, Ni, Pb and Sr (BCF < 1). BCF value of mercury in the literature, have been reported in the ranges of 40 to 76 (Falandysz et al., 2002). Our results (BCF 10-41) closely match the report by other author, who found a similar pattern of Hg pick-up

Table 2. Literature data previously reported for Hazel Bolete.

Element	Site[a]					
	Bavaria Germany	**Borecka Forest Poland**	**Czech Republic**	**Kluknava Slovakia**	**Żarnowiec Poland**	**East Black Sea Turkey**
µg/g dry weight						
Ca	WD[b]	WD	WD	WD	38 ± 12(C) (28-51)	WD
Cd	5.0 ± 3.6(C)[c] 4.4 ± 2.9(S)	WD	WD	1.4(C) 1.5(S)	WD	1.3 ± 0.14(F)[d]
Co	WD	WD	0.08(F)	WD	WD	0.36 ± 0.17(F)
Cu	36 ± 8.6(C) 52 ± 22(S)	WD	WD	28(C) 1.8(S)	WD	48 ± 7.0(F)
Fe	WD	WD	34(F)	WD	30(C) (30-30)	240 ± 27(F)
Hg	1.92 ± .33(C) 2.36 ± 1.53(S)	0.86 ± 0.31(C) 0.82 ± 0.29(S)	WD	WD	WD	WD
Mn	WD	WD	WD	WD	7.0(C)	25 ± 2.0(F)
Pb	1.6 ± 8.6(C) 3.8 ± 1.8(S)	WD	WD	1.4(C) 1.2(S)	WD	0.75 ± 0.08(F)
Zn	WD	WD	97(F)	WD	150 ± 29(C) (130 - 180)	51 ± 3.0(F)
mg/g dry weight						
K	WD	WD	WD	WD	40 ± 0(C) (40 - 40)	WD
Mg	WD	WD	WD	WD	1.2 ± 0(C) (1.2 - 1.2)	WD
Na	WD	WD	WD	WD	0.0.51(C) (0.28 - 1.3)	WD

[a] Ref. Borovička and Řanda (2007); Falandysz et al. (2001, 2002); Sesli and Tüzen (1999); Svoboda et al. (2000). [b]WD, Without data; [c]C, cap; S, stipe; [d]F, fruit body.

by species.

Nutrition and food toxicology aspects

Eating of Hazel Bolete from the site surveyed at amount of 300 g w allows probably the provision with K at 33%, Cu at 31% and Zn at 24% of recommended daily intake, on the average. These figures are smaller for Mn with 14%, Mg with 7%, iron with 7%, Cr with 3%, and Na with 3%. It makes this species potentially good source of nutrients with low Na level. However, more detailed investigation of element availability in indigestion tract is needed.

Lead and cadmium are the only toxic elements for which contents of edible mushrooms are regulated in the European Union. Legal limits for mentioned elements in only fresh three species of cultivated mushrooms are set for 1.0 and 0.3 µg/g ww, respectively (EC, 2008). In the case of Hazel Bolete in this survey, assuming water content of 90%, this value of tolerance limit for Pb was not exceeded for caps and stipes at the Gołdap site. It is worth to mention that Pb is bioexcluded by Hazel Bolete and its BCF is < 0.5. Also in the case of Cd, its content of the caps and stipes of this species is lower when compared to tolerance limit mentioned. Cadmium is well accumulated by Hazel Bolete (BCF>>10).

Risk of toxic element, which consumer could be exposed to, can be calculated in relation to existing reference dose (RfD; 0.0003 mg/kg body weight daily) and provisional tolerable weekly intake (PTWI; 4 µg/kg bw) (JECFA, 2010; US EPA, 1999). Caps of well-grown fruiting body of Hazel Bolete are much bigger by mass than stipes. Hence, Hg contents of caps should be considered for toxicological risk assessment. A meal prepared of 300 g of fresh caps of Hazel Bolete picked-up at the Gołdap area could provide 10.2 µg of Hg. Over two- and fivefold greater Hg intake of 25.8 and 57.6 µg is in the case of specimens collected from the Borecka forest and Bavaria areas, respectively. Thus, consumption of Hazel's Bolete caps from Gołdap area will not result in exceeding mercury RfD limit for 70 kg body weight individual. Nevertheless, depending on region (Table 2), it could constitute 49, 123 and 274% of Hg RfD in the case of mushrooms collected from the Gołdap, Borecka Forest and Bavaria sites, respectively. Depending on a site surveyed, eating of three 300 g fresh the Hazel Bolete meals during a week could provide

0.031 mg Hg (Gołdap), 0.077 mg Hg (Borecka Forest) and 0.172 mg Hg (Bavaria), and this would comprise from 11 to 62% of PTWI of this element.

Cap to stalk element concentration quotients

Ag, Al, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Ni, Pb, Rb and Zn content of the caps of Hazel Bolete prevailed over concentrations in stipes ($p < 0.05$) and arithmetic mean values of the caps to stipes metals concentration quotient ($Q_{C/S}$) for 15 specimens have been reported in the range: from 1.0 for Ca to 3.0 for Ag, respectively (Figure 1 and Table 1). Having surveyed an average Ba, Co, Na and Sr, content of caps do not exceed that of stipes (from 0.49 for Co to 0.97 for Ba). Therefore, there is no a clear relationship between caps and stipes of Hazel Bolete in elements content. However, a tendency to accumulate greater quantities of metals in caps than stipes of Hazel Bolete was observed.

Conclusion

19 metals in caps and stipes of Hazel (Hard) Bolete collected from Poland were determined by ICP-AES and CV-AAS. In the present study, the detected levels of Cd, Co, Cu, Fe, Hg, K, Mg, Mn, Na and Pb were generally in agreement with previously reported, but the Ca and Zn contents were higher than literature values. From the nutritional point of view, Hazel Bolete could be a potential dietary source of Cr, Cu, Fe, K, Mg, Mn and Zn. The total Cd, Hg and Pb dose provided to human body due to consumption of Hazel Bolete does not pose threat to a consumer's health. Nevertheless, data on human bio-availability rates of these elements of surveyed species are needed.

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