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ORIGINAL ARTICLE

MINERAL CONSTITUENTS OF CONSERVED WHITE BUTTON MUSHROOMS: SIMILARITIES AND DIFFERENCES

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ABSTRACT

Background. Mushrooms are a food that is often considered as an important source of minerals and other nutrients for consumers. There is little data on the minerals in mushrooms processed culinary and on the impact of processing.
Objective. The research was aimed at understanding the similarities and differences in the mineral composition (Hg, Li, Mg, Al, Co, Ni, Cu, As, Se, Rb, Sr, Ag, Cd, Cs, Sb, Tl, Pb, U, Ba, Cr, Zn, Mn and V) of white button mushrooms (*Agaricus bisporus*) processed in industrial conditions.
Material and methods. Fungal materials came from six producers. The elements were determined by ICP-MS DRC and CV-AAS using validated methods and QA/QC protocol. The interdependencies of 18 elements and 10 batches of mushrooms examined were tested with the help of principal component analysis.
Results. Some significant differences were found in the content and composition of minerals in marinated white button mushrooms depending on producer. Conserved white button mushrooms are poorer in major essential elements but also in toxic Hg, As, Ag, Cd, Sb, Tl or Pb which has been reported for unprocessed mushrooms.
Conclusions. The relatively higher levels of Ag in some batches seem to be largely explained by the quality of the substrate used for mushrooms cultivation, while of Li, Rb, Cs, Cr, Al, U, V, As and Mn (in part also of Ba and Sr) largely by the quality of the marinade.

Key words: *white button mushroom*, *pickled mushrooms*, *mineral constituents*, *food*, *nutrition*

STRESZCZENIE

Wprowadzenie. Grzyby jadalne to surowiec spożywczy bogaty w niezbędne pierwiastki metaliczne ale też możliwie źródło narażenia konsumenta na toksyczne metale i metaloidy. Niewiele jest danych na ten temat odnośnie grzybów przetworzonych kulinarnie czy wpływu procesów przetwarzania.
Cel. Badania miały na celu poznanie podobieństw i różnic w składzie mineralnym (Hg, Li, Mg, Al, Co, Ni, Cu, As, Se, Rb, Sr, Ag, Cd, Cs, Sb, Tl, Pb, U, Ba, Cr, Zn, Mn and V) pieczarek (*Agaricus bisporus*) przetworzonych w warunkach przemysłowych.
Materiał i metody. Pieczarki pochodziły z sześciu przetwórni. W analizie zastosowano sprawdzone metodyki analityczne łącznie z bieżącą kontrolą i zapewnieniem jakości wyników analizy. Pomiar wykonano technikami ICP-MS-DRC i CV-AAS. Współzależności pomiędzy 18 pierwiastkami i 10 partiami grzybów badano metodą analizy głównych składowych.
Wyniki. Wykazano duże różnice w zawartości składników mineralnych w pieczarkach z różnych przetwórni. Konserwowe pieczarki są znacznie uboższe w główne pierwiastki niezbędne ale także w pierwiastki toksyczne takie jak Hg, As, Ag, Cd, Sb, Tl czy Pb w porównaniu z opublikowanymi danymi dla grzybów nieprzetworzonych.
Wnioski. Względnie większą zawartość Ag w określonych partiach badanych konserwowych pieczarek wydaje się tłumaczyć jakość podłoża zastosowanego w uprawie grzybów a w przypadku Li, Rb, Cs. Cr, Al, U, V, As i Mn (po części też Ba i Sr) główny wpływ wydaje się mieć jakość użytej zalewy (marynaty).

Słowa kluczowe: *pieczarka dwuzarodnikowa, grzyby marynowane, składniki mineralne, żywność, żywienie*

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INTRODUCTION

Mushrooms, either foraged or cultivated are foodstuffs relatively rich in many essential mineral constituents but in parallel they often accumulate toxic ions both of natural and anthropogenic origin [11, 12, 19, 24, 27]. For cultivated mushrooms, the grower may influence the content of minerals and contaminants accumulated in flesh by selection of a proper substrate and cultivation method [22, 34]. High quality information on the multi-mineral composition and nutritional characteristics of mushrooms is expanding in the recent years thanks to the modern methods of analysis [2, 20, 36-38]. A great biodiversity of mushrooms and their emergence at sites that differ in soil geochemistry or a degree of pollution makes study on the wild mushrooms perceived as organic food challenging. In addition, there is little data available on status of metals, metalloids and other elements in mushrooms processed culinary [6, 40, 42, 45]. The traditional methods of cooking and recipes for mushroom dishes as well as preservation techniques such as freezing and freeze drying are factors contributing variability in the chemical composition and nutritional value of cooked mushrooms [7, 8, 16, 17, 39].

White button mushroom *Agaricus bisporus* [MB#292246] is a popular foodstuff worldwide. This mushroom and other species collected from the wild or cultivated are considered as a good source of proteins, vitamins and mineral constituents (potassium, phosphorus, zinc and copper or selenium) but also of antioxidants and with antibacterial, anti-inflammatory, antitumor, and immunomodulatory properties - see reviews by several authors [4, 14, 32, 33, 37].

A. bisporus has a very short service life, only 1-3 days at ambient temperature [3] or from 5 to 7 days at 0 °C to 2 °C [20], due to its high water content (about 90%) and high enzymatic activity. A common drying or more advanced “traditional” and modern culinary technologies such as pickling, salting, frying, freezing and freeze-drying are used to preserve mushrooms. Apart from a simple household treatment procedures, e.g., salting, blanching/parboiling and pickling in glass [7, 8, 9], deep freezing of fresh mushrooms and canning and industrial pickling become more common. The nutritional properties of mushrooms may be changed by the processing condition [25, 30].

The objective of this study was to understand the similarities and differences in the mineral composition of conserved (pickled) white button mushrooms available in trade in Poland, and estimate their possible loss (Hg, Li, Mg, Al, Co, Ni, Cu, As, Se, Rb, Sr, Ag, Cd, Cs, Sb, Tl, Pb, U, Ba, Cr, Zn, Mn and V) during industrial processing as well as source in conserved product.

MATERIALS AND METHODS

Conserved white button mushrooms (*A. bisporus*) were produced by six manufacturers: the batches of the “marinated and lagoon natural” were by Notre Jardin, Ole, Rolnik, Urbanek and Smak companies, and the batches: “mushrooms marinated – a whole” and “mushrooms marinated – sliced/crushed” were by Bonduelle. In detail they were as: Notre Jardin Champignons de Paris, Pieds Et Morceaux “*Pieczarki marynowane krojone – pickled champignon sliced*”; Notre Jardin Champignons de Paris 1er Choix Entiers “*Pieczarki marynowane całe – pickled a whole champignons*”; Bonduelle “*Pieczarki łagodne marynowane – soft champignons pickled*”; Bonduelle “*Pieczarki marynowane – pickled champignons*”; Rolnik “*Pieczarki marynowane – pickled champignons*”; Urbanek „*Pieczarki marynowane – pickled champignons”*; Smak „*Pieczarki marynowane – pickled champignons*”; Smak „*Pieczarki w zalewie solnej – pickled champignons in a saline juice*”; Ole „*Pieczarki w zalewie naturalnej całe – a whole champignons in a natural marinate*” and Ole “*Pieczarki marynowane z marchewką i cebulą – marinated champignons with a carrot and onion*”. In total 100 unit packages of the processed white button mushrooms were studied. 80 Unit packages (primary samples) of mushrooms were in a glass jars and 20 (Bonduelle) in cans. The original unit packages were sampled randomly from the shops in the city of Gdańsk in 2016.

Mushrooms if not sliced were young fruiting bodies (caps with a piece of a stipe). They were drained from a liquid, placed in a separate polyethylene bags, deep frozen (-30 °C) and next lyophilized to constant mass (model LYOVAC GT2; Steris, Germany), ground to a fine powder using a porcelain mortars and kept sealed in brand new polyethylene bags under clean and dry condition. Any laboratory vessel before use was submerged in solution of 10 % nitric acid for at least 24 hours and next washed with double deionized water and dried at room temperature.

The subsamples of dehydrated and powdered mushrooms subjected for analysis were around 300 to 400 mg. They were flooded with 5 ml solution of concentrated nitric acid (65% HNO_3 - Suprapur®, Merck, Darmstadt, Germany) and cold digested for 24 h in the open polytetrafluoroethylene (PTFE) vessels. The vessels were closed and pressure digested using the MARSXpress microwave oven (Microwave Accelerated Reaction System, CEM Corp., Matthews, NC, USA). The operating conditions for digestion were as follows: power - 1.2 kW; ramp 1-10 min; temp. 1-100 °C; hold 1-10 min, ramp 2-10 min; -800 psi pressure; temp. 2-100 °C; holding time 2-10 min; cooling down time 5 min. The digests were diluted up to 10 ml with double deionized water. The blank digests were carried out in the same way [8, 9].

The elements (except of mercury) were determined using inductively coupled plasma mass spectroscopy (Spectroscope type ELAN DRC II ICP-MS, Perkin Elmer SCIEX, Canada) with dynamic reaction chamber (Table I) [5, 7, 8]. Mercury was determined using a direct fungal matrices thermal decomposition and cold vapor atomic absorption spectroscopy (MA-2000, Nippon Instruments Corporation, Takatsuki, Japan) [11]. All procedures were validated, and the QA/QC protocol routinely followed every set of examined samples [5, 8, 11, 15, 23]. The Polish reference materials used were such as CS-M-2 (dried mushroom powder *Agaricus campestris*) and CS-M-3 (dried mushroom powder *Boletus edulis*) produced by the Institute of Nuclear Chemistry and Technology, Warsaw, Poland [8, 15, 23].

The computer software Statistica version 8.0 (Statsoft, Inc., computer software) was used for statistical analysis and graphical presentation of the results of two dimensional multiple scatter plot relationships between the variables [5, 44]. The interdependencies of 18 elements and 10 batches of mushrooms were tested with the help of PCA (*Principal Component Analysis*). Statistic data have been divided into comparable units with means of 0 and with standard deviation of 1. Correlation matrix reflects the analysis the Kaiser Criterion (factors with eigenvalues greater than 1) and scree test was used. In order to choose the right number of analyzed components, the values have been divided into groups: 0.75 - strong; between 0.75–0.5 - moderate and between 0.5–0.3 - weak. All of them were based on their absolute values. The strongest values of 0.75 have been taken for analyses and interpretation. Varimax normalized rotation was used in order to maximize the variances of normalized factor loadings across variables for each factor.

RESULTS AND DISCUSSION

As, Hg, Cd, Ag, Pb and Se

The definitely toxic elements such as As, Hg, Cd, Ag and Pb occurred in pickled mushrooms respectively (median values) in the range 0.006 to 0.19, 0.028 to 0.065, 0.02 to 0.08, 0.002 to 0.090 and 0.006 to 0.18 mg kg^{-1} dry matter (dm) (Table 2). The overall median value was 0.03 for As, 0.043 for Hg, 0.040 for Cd, 0.020 for Ag and 0.072 mg kg^{-1} dm for Pb. Those elements are common trace contaminants of mushrooms collected from the wild and cultivated, while sometimes at elevated levels [14]. Apart from the cultivated white button mushrooms, the oyster mushroom *Pleurotus ostreatus* can accumulate heavy metals at elevated amount if grew in polluted substrates [1, 13, 36]. The allowed content of Cd and Pb in cultivated *A. bisporus* offered at the European Union markets should not exceed respectively 0.20 mg kg^{-1} and 0.30 mg kg^{-1} (2.0 and 3.0 mg kg^{-1} dm; assuming 90% moisture content) [10].

Exposure to negligible doses of Ag, Hg, Cd and Pb taken with foods is generally considered safe and tolerated by human body due to adaptation mechanisms, e.g., antagonism between certain elements, lack or poor absorption of a particular chemical forms, complexation and excretion. Arsenic is perceived as toxic in every dose because chronic exposure to inorganic As may cause various types of cancers [19, 28].

The toxic mineral constituents and those that are nutritionally essential can substantially leak out of fruiting bodies during the household treatment, e.g. blanching [8, 9] or industrial conserving [42]. Marinated *A. bisporus* in this study was less contaminated with Hg than fresh mushrooms collected by us in 2016, which had 0.069, 0.080 and 0.11 mg kg^{-1} dm (n = 3; pooled samples, each of 1 kg).

In the past, *A. bisporus* collected randomly in Poland in 1984-1985 had Hg at level 0.0059 ± 0.0090 mg kg^{-1} fresh biomass (0.059 ± 0.090 mg kg^{-1} dm; n = 214, pooled samples) on average, and for three other pooled samples mercury results were 0.26, 0.27 and 0.54 mg kg^{-1} fresh biomass (data not included in the overall mean) [31]. In another study *A. bisporus* had 0.039 mg kg^{-1} fresh biomass (0.39 mg kg^{-1} dm; assuming humidity content at 90%) [21].

Regarding As, fresh *A. bisporus* (white strain) available in Poland contained 0.63 ± 0.37 mg kg^{-1} dm (total range 0.15 to 1.4 mg kg^{-1} dm) [37], and what is an order of magnitude higher than in pickled mushrooms in this study. Arsenic was < 0.05 mg kg^{-1} dm in sliced and whole pickled *A. bisporus*, while in the range 0.49 to 3.7 mg kg^{-1} dm (means) in fresh Hungarian mushrooms [42, 43]. Clearly, conserving of mushrooms by blanching or industrial pasteurizing/canning highly decrease content of As. Such tendency has been confirmed for experimentally blanched and pickled caps of *Amanita fulva* (decrease by 89%) [8]. A substantial drop of As from fruiting bodies during boiling can be explained by fact that it occurs in molecular forms such as arsenous acid, arsenic acid, monomethylarsonic acid, dimethylarsinic acid, tetramethylarsonium ion, arsenocholine and arsenobetaine, which are water soluble, dominant and species-specific (different proportion) in total As of mushrooms [19].

Fresh *A. bisporus* from Poland showed Cd, Ag and Pb at levels higher an order of magnitude than has been determined in pickled mushrooms in this study, i.e., 0.36 ± 0.47 mg kg^{-1} dm (total range 0.08 to 1.2) for Cd, 0.19 ± 0.05 mg kg^{-1} dm (0.15 to 0.23) for Ag and 0.54 ± 0.54 mg kg^{-1} dm (range 0.15 to 27) for Pb [37]. Fresh *A. bisporus* produced in Hungary had on the average from 0.12 to 0.22 mg kg^{-1} dm of Cd, and conserved mushrooms imported from Asia had 0.22 ± 0.03 mg kg^{-1} dm (sliced) and 0.22 ± 0.05 mg kg^{-1} dm (whole) [42, 43].

Table 1. Optimized experimental parameters used for elements determination by ICP-DRC-MS

Instrument	PE Sciex ELAN 6100 DRC II
Nebulizer gas flow	(0.88-0.92) L min^{-1}
Auxiliary gas flow	1.2 L min^{-1}
Plasma gas flow	16 L min^{-1}
RF power	1150 W
Lens voltage	(0.75-0.90) V
Lens setting	Autolens calibrated
Dwell time	50
Detector mode	Dual (pulse counting and analogue mode)
Scan mode	Peak hopping
Sweeps/Reading/Replicate	10/ 1/ 3
Measured mass	^{26}Mg, ^{27}Al, ^{51}V, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{82}Se, ^{88}Sr, ^{107}Ag, ^{111}Cd, ^{121}Sb, ^{133}Cs, ^{138}Ba, ^{205}Tl, ^{208}Pb, ^{238}U
DRC gas flow rate	NH_3 0.135 L min^{-1} (^{51}V) NH_3 0.45 L min^{-1} (^{27}Al, ^{52}Cr) NH_3 0.65 L min^{-1} (^{55}Mn, ^{66}Zn) O_2 0.45 L min^{-1} (^{75}As)
Internal standard	^{45}Sc, ^{74}Ge, ^{103}Rh, ^{159}Tb

Due to low concentrations of toxic As, Hg, Cd, Ag and Pb, it can be stated that consuming the conserved white button mushrooms available at Polish market does not show any threat to the consumer.

Similarly to As, Hg, Cd, Ag and Pb, also the Se in the environment is a seeker of sulfur, while is antagonistic to Hg [35]. Selenium at very low doses (ca. 3 µg per kg body mass daily) is essential to human [20, 26]. The medians of Se in pickled mushrooms were in the range 0.19 to 1.6 mg kg^{-1} dm, and the overall median was 0.60 mg kg^{-1} dm (Table 2). In a study, the element Se exceeded 38 times (molar basis) amount of Hg. Nevertheless, the pickled *A. bisporus* clearly can be considered as a weak source of Se. If taken at amount of 100 g can provide about 6 µg of bioavailable Se on average.

Selenium was undetected (< 0.05 mg kg^{-1} dm) in conserved in brine *A. bisporus* sold in Hungary, while in fresh mushrooms was in the range from 1.9 to 3.7 mg kg^{-1} dm (means) [42, 43].

Li, Cs and Rb

Amongst the alkali elements, the Li and Cs with medians respectively in the range 0.01 to 0.40 and 0.004 to 0.02 mg kg^{-1} dm (the overall medians 0.045 and 0.15 mg kg^{-1} dm) were highly minor minerals, and for Rb were in the range 1.1 to 4.1 mg kg^{-1} dm (the overall median was 1.8 mg kg^{-1} dm). In one study lithium was in caps of fresh *A. bisporus* in the range 0.15 ± 0.14 to 0.20 ± 0.13 mg kg^{-1} dm [43], and in a whole fresh individuals (white strain) in range 0.53 to 4.7 mg kg^{-1} dm (mean 2.6 ± 3.0 mg kg^{-1} dm) [36].

Ba and Sr

The medians of Ba were in the range 0.40 to 2.9 mg kg^{-1} dm (the overall median 0.65 mg kg^{-1} dm), while Sr was greater and accounted from 1.6 to 11 mg kg^{-1} dm (the overall median 2.7 mg kg^{-1} dm) (Table 2). Both Ba and Sr are among the lithophile elements. Nothing is known on their compounds in mushrooms. The sulphate of Ba and Sr are hardly or insoluble in water. Blanching and pickling slightly decreased Ba in *A. fulva*, while Sr even multiplied after blanching [8].

In a study in Poland, the mean of Ba in *A. bisporus* (white strain) was 0.76 ± 0.92 mg kg^{-1} dm (0.08 - 2.9 mg kg^{-1} dm), while surprisingly for Sr was 0.36 ± 0.35 mg kg^{-1} dm (range 0.04 to 6.0 mg kg^{-1} dm). As it has been pointed ahead, the Sr overwhelmed Ba in pickled mushrooms (Table 2). Also Vetter *et al*. (42, 43) noted Sr at higher level than Ba in *A. bisporus*: in fresh Sr was in the range 6.7 to 7.5 mg kg^{-1} dm (means), and conserved showed 16 ± 1 mg kg^{-1} dm in sliced and 3 ± 0 mg kg^{-1} dm in whole fruiting bodies. In turn, the Ba in fresh mushrooms was in the range 2.1 to 2.4 mg kg^{-1} dm (mean values), and in conserved from 6.9 ± 0.4 mg kg^{-1} dm (sliced) to 7.8± 0.1 mg kg^{-1} dm (whole) [42, 43].

Mg, Mn, Cu and Zn

The medians for Mg, Mn, Cu and Zn were in the range: 220 to 560 mg kg^{-1} dm (the overall median 330 mg kg^{-1} dm for Mg), 2.4 to 4.8 mg kg^{-1} dm (3.0 mg kg^{-1} dm for Mn), 8.3 to 19 mg kg^{-1} dm (10 mg kg^{-1} dm for Cu) and 13 to 71 mg kg^{-1} dm (26 mg kg^{-1} dm for Zn) (Table 2).

Magnesium occurs in fresh *A. bisporus* at relatively high level: one study reports 1250 ± 219 mg kg^{-1} dm (786 to 1650 mg kg^{-1} dm) [37], and other from 1100 to 1400 mg kg^{-1} dm [42, 43]. Magnesium is essential for mushrooms and its uptake and sequestration is regulated by them. Conserved *A. bisporus* clearly had much less of Mg than uncooked. In a study by Vetter [42] sliced had 390 ± 20 mg kg^{-1} dm, and marinated as a whole had 470± 22 mg kg^{-1} dm [42]. *A. bisporus* marinated or conserved with brine is by 70% depleted from Mg.

Table 2. Macro and trance element content of pickled white bottom mushrooms available from the Polish market (mg kg^{-1} dry mass, mean ± SD, range and median, respectively)

	1*	2	3	4	5	6	7	8	9	10
Li	0.43±0.03	0.16±0.02	0.10±0.02	0.04±0.01	0.07±0.02	0.02±0.01	0.04±0.03	0.03±0.02	0.05±0.03	0.02±0.02
	0.39 - 0.48	0.13 — 0.2	0.07 — 0.16	0.02-0.07	0.05-0.11	0.003-0.04	0.002-0.08	0.003-0.06	0.01-0.12	0.005-0.06
	0.40	0.16	0.10	0.04	0.07	0.01	0.04	0.03	0.05	0.01
Mg	540 ± 41					330±13	230±15	360±32	560±28	310±24
	470-620	WD	WD	WD	WD	310-350	200-250	330-420	510-620	280-360
	540					330	220	340	560	310
Co	0.013 ± 0.015	0.02±0.01	0.03±0.03	0.04±0.05	0.01±0.00	0.02±0.00	0.01±0.00	0.005±0.002	0.007±0.001	0.02±0.00
	0.004-0.04	0.01-0.03	0.01-0.13	0.01-0.22	0.008-0.01	0.01-0.02	0.009-0.01	0,002-0.007	0.004-0.009	0.01-0.02
	0.005	0.02	0.02	0.02	0.01	0.02	0.01	0.004	0.007	0.02
Cu	10 ± 1	20±3	9.5±0.6	11±1	9.9±1.1	13±0.9	11±1	15±1	15±1	8.1±1.6
	8.0-12	17-26	8.0-11	9.0-12	8.7-13	12-15	9.2-12	13-17	13-16	5.6-10
	10	19	9.6	10	9.6	13	10	14	15	8.3
Se	0.38 ± 0.10	0.19±0.05	0.49±0.07	0.66±0.10	0.58±0.11	0.67±0.09	0.60±0.10	1.0±0.2	1.6±0.3	0.51±0.13
	0.20 – 0.54	0.06-0.32	0.32-0.67	0.46-0.97	0.39-0.79	0.49-0.85	0.33-0.79	0.82-1.6	1.2-2.1	0.33-0.75
	0.39	0.19	0.49	0.65	0.59	0.67	0.62	1.1	1.6	0.50
Zn	39±4	54±5	17±9	22±10	10±4	24±2	13±2	29±4	75±14	26±4
	35-49	44-64	1.8-26	4.2-30	2.8-13	21-27	10-15	22-36	62-100	20-35
	38	53	22	27	13	23	13	28	71	25
Mn	2.8±0.8	3.6±0.2	2.5±0.6	4.7±0.5	2.7±0.2	3.9±0.3	2.8±0.6	2.9±0.4	4.7±0.6	3.3±0.3
	1.8-4.2	3.0-4.0	1.5-3.8	3.9-5.6	2.4-3.3	3.5-4.5	2.1-4.0	2.3-3.6	4.1-5.7	2.7-3.9
	2.7	3.6	2.4	4.8	2.7	3.8	2.7	2.8	4.5	3.3
Cs	0.029±0.002	0.019±0.001	0.009±0.001	0.007±0.001	0.004±0.001	0.002±0.001	0.004±0.001	0.001±0.001	0.007±0.001	0.001±0.001
	0.026-0.036	0.017-0.021	0.004-0.011	0.006-0.010	0.003-0.005	< 0.001-0.004	0.001-0.005	< 0.001-0.003	0.004-0.009	< 0.001-0.003
	0.029	0.019	0.009	0.007	0.004	0.002	0.004	0.001	0.006	0.001
Rb	4.1±0.5	3.2±0.4	1.5±0.3	3.4±0.4	1.6±0.1	2.0±0.1	1.1±0.2	1.7±0.2	2.7±0.2	1.2±0.1
	3.6-5.4	2.2-3.8	1.1-2.0	2.7-4.3	1.4-1.8	1.8-2.1	0.8-1.4	1.4-2.0	2.6-3.0	0.9-1.4
	4.1	3.1	1.4	3.4	1.5	2.0	1.1	1.6	2.7	1.3
Al	2.6±0.9	30±11	11±7	8.8±11	4.1±4.9	2.2±0.3	5.5±2.8	3.2±0.5	3.2±1.6	3.0±1.1
	1.4-4.3	12-50	3.6-24	1.5-29	0.8-14	1.7-2.8	2.7-11	2.3-4.2	1.4-6.2	1.3-5.4
	2.6	24	7.7	2.5	1.4	2.2	4.7	3.1	3.0	2.7
Ni	1.1±0.1	1.0±0.1	1.1±0.1	0.20±0.03	0.20±0.03					
	1.0-1.4	0.9-1.2	0.9-1.4	0.10-0.30	0.10-0.20	WD	WD	WD	WD	WD
	1.1	1.0	1.1	0.20	0.10					
Cr	0.08±0.02	0.31±0.03	1.9±3.1	0.76±1.20	0.39±0.59	0.13±0.02	0.20±0.07	0.22±0.01	0.90±0.07	0.32±0.05
	0.05-0.13	0.27-0.39	0.18-12	0.08-5.0	0.02-1.8	0.10-0.17	0.13-0.34	0.20-0.24	0.80-1.0	0.23-0.40
	0.07	0.30	0.32	0.12	0.08	0.13	0.18	0.22	0.88	0.31
V	0.007±0.002	0.063±0.017	0.025±0.008	0.020±0.013	0.026±0.006	0.025±0.002	0.021±0.007	0.015±0.004	0.014±0.003	0.030±0.004

	1*	2	3	4	5	6	7	8	9	10
	0.004-0.011	0.033-0.090	0.011-0.041	0.011-0.054	0.018-0.046	0.021-0.029	0.015-0.036	0.009-0.023	0.008-0.019	0.025-0.040
	0.007	0.059	0.024	0.015	0.023	0.025	0.018	0.014	0.013	0.029
Ba	3.0±0.5	2.0±0.1	0.70±0.01	1.3±0.1	0.70±0.10	0.50±0.20	1.2±0.7	0.60±0.20	1.2±0.1	0.60±0.20
	2.3-4.3	1.8-2.4	0.60-0.90	1.0-1.5	0.60-1.0	0.20-1.0	0.60-2.6	0.30-1.1	0.9-1.4	0.30-0.80
	2.9	2.0	0.70	1.3	0.70	0.40	0.80	0.60	1.2	0.50
Sr	11±1	8.0±1.1	3.1±0.6	3.8±0.6	2.4±0.2	2.1±0.3	1.7±0.3	2.4±0.3	4.0±0.5	2.1±0.4
	9.0-13	6.1-10	2.0-4.3	2.7-4.9	2.1-2.9	1.6-2.6	1.1-2.4	1.7-3.1	3.0-4.7	1.4-2.9
	11	8.0	3.0	3.9	2.3	2.1	1.6	2.4	3.9	2.1
As	0.16±0.02	0.19±0.02	0.03±0.01	0.04±0.01	0.03±0.01	0.01±0.01	0.020±0.019	0.04±0.01	0.03±0.02	0.008±0.008
	0.13-0.19	0.15-0.24	0.02-0.04	0.03-0.06	0.02-0.05	< 0.01-0.03	0.004-0.030	0.02-0.07	< 0.01-0.05	< 0.01-0.02
	0.15	0.19	0.03	0.04	0.03	0.01	0.020	0.040	0.03	0.006
Ag	0.090±0.008	0.070±0.007	0.002±0.001	0.010±0.006	0.030±0.007	0.020±0.004	0.020±0.006	0.020±0.003	0.040±0.020	0.020±0.002
	0.080-0.11	0.050-0.080	< 0.002-0.004	0.003-0.020	0.020-0.050	0.020-0.030	0.009-0.03	0.020-0.030	0.020-0.070	0.010-0.020
	0.090	0.070	0.002	0.010	0.020	0.020	0.010	0.020	0.040	0.020
Cd	0.04±0.01	0.04±0.01	0.02±0.03	0.05±0.01	0.08±0.01	0.03±0.00	0.08±0.02	0.04±0.01	0.04±0.01	0.03±0.00
	0.02-0.05	0.03-0.05	0.01-0.03	0.03-0.06	0.065-0.10	0.02-0.03	0.05-0.11	0.02-0.05	0.02-0.06	0.03-0.04
	0.04	0.04	0.02	0.04	0.08	0.02	0.08	0.03	0.04	0.03
Hg	0.041±0.001	0.047±0.004	0.051±0.003	0.034±0.003	0.061±0.012	0.059±0.007	0.057±0.010	0.028±0.006	0.036±0.005	0.036±0.005
	0.039-0.043	0.042-0.059	0.044-0.056	0.030-0.040	0.042-0.074	0.050-0.073	0.042-0.075	0.020-0.039	0.027-0.041	0.027-0.041
	0.041	0.045	0.052	0.032	0.065	0.058	0.056	0.028	0.038	0.038
Sb	0.008±0.003		0.005±0.002				0.002±0.001	0.003±0.001		0.009±0.003
	0.002-0.012	WD	0.002-0.010	WD	WD	WD	< 0.001-0.004	< 0.001-0.006	WD	0.004-0.012
	0.008		0.005				0.002	0.003		0.009
Tl	0.001±0.000					0.001±0.000	0.001±0.001	0.001±0.001	0.002±0.001	0.001±0.001
	< 0.001-0.002	WD	WD	WD	WD	0.001-0.002	0.001-0.002	< 0.001-0.001	0.001-0.002	< 0.001-0.002
	0.001					0.001	0.001	0.001	0.002	0.001
Pb	0.17±0.01	0.17±0.03	0.14±0.02	0.010±0.020	0.006±0.003			0.020±0.007		
	0.15-0.20	0.13-0.22	0.11-0.18	< 0.001-0.050	0.001-0.020	WD	WD	0.008-0.024	WD	WD
	0.18	0.17	0.13	0.007	0.006			0.014		
U	0.0004±0.0002	0.029±0.004	0.001±0.00	0.002±0.000	0.002±0.001	0.003±0.001	0.001±0.000	0.001±0.000	0.001±0.001	0.001±0.000
	0.0001-0.0006	0.020-0.034	0.001-0.002	0.001-0.003	0.001-0.003	0.002-0.004	0.001-0.002	0.001-0.002	0.001-0.003	0.001-0.002
	0.0004	0.030	0.001	0.002	0.002	0.003	0.001	0.001	0.001	0.001

Notes: *(sample ID) 1. Notre Jardin Champignons de Paris Pieds et morceaux "pieczarki marynowane krojone – pickled champignon sliced"; 2. Notre Jardin Champignons de Paris 1er Choix entiers "pieczarki marynowane całe – pickled a whole champignons"; 3. Bonduelle "Pieczarki łagodne marynowane – soft champignons pickled"; 4. Bonduelle "Pieczarki marynowane – pickled champignons"; 5. Rolnik "Pieczarki marynowane – pickled champignons"; 6. „Pieczarki marynowane – pickled champignons"; 7. Smak „Pieczarki marynowane – pickled champignons "; 8. Smak „Pieczarki w zalewie solnej – pickled champignons in a saline juice"; 9. Ole „Pieczarki w zalewie naturalnej całe – a whole champignons in a natural marinate"; 10. Ole "Pieczarki marynowane z marchewką i cebulą – marinated champignons with a carrot and onion"; WD, without data.

Table 3. Factor loadings (Varimax normalized)

Element	PC1	PC2	PC3	PC4
Li	**0.94**	-0.14	-0.09	-0.25
Al	0.25	0.01	**0.94**	-0.03
Co	-0.30	-0.58	0.32	0.59
Cu	0.19	0.58	0.69	0.11
As	**0.85**	-0.01	0.51	-0.02
Se	-0.30	**0.84**	-0.42	0.12
Rb	**0.85**	0.10	0.01	0.47
Sr	**0.98**	0.00	0.15	0.00
Ag	**0.92**	0.14	0.20	-0.07
Cd	-0.02	-0.07	-0.13	-0.01
Cs	**0.96**	-0.09	0.16	-0.08
U	0.27	0.03	**0.95**	0.12
Ba	**0.98**	0.02	0.11	0.06
Cr	-0.16	**0.83**	0.11	0.09
Zn	0.41	**0.77**	0.28	0.26
Mn	-0.04	0.34	0.05	**0.92**
V	-0.05	-0.15	**0.97**	0.03
Hg	-0.21	-0.35	0.17	-0.28
Eigenvalue	7.491714	3.472054	3.245906	1.610754
Total Variance (%)	41.62063	19.28919	18.03281	8.94864
Cumulative (%)	41.62063	60.90982	78.94263	87.89127

Manganese is also essential for mushrooms. In fresh *A. bisporus* is in the range from 5.7 to 8.3 mg kg^{-1} dm (means) and 6.1 ± 2.0 mg kg^{-1} dm [37, 42, 43]. Conserved has it in the range 6.0± 0.1 (a whole) to 12 ± 0 (sliced) mg kg^{-1} dm [43]. It can be suggested that quality of water used for preparation of marinade or brine can have an impact on content of Mn in processed mushrooms. If marinade is free of Mn, pickling can decrease its content in *A. bisporus* by around 50%. On the other side, a lack of a difference between the fresh mushrooms and those conserved can be because of elevated content of Mn in brine. This is known that sodium can be absorbed by and highly elevated in fruiting bodies conserved with a brine [43].

A. bisporus conserved in brine (two batches) had Cu in the range 15 ± 0 to 15 ± 1 mg kg^{-1} dm [43]. Hence, mushrooms from our study and conserved with brine were > 50% poorer in Cu when relate to fresh mushrooms, which showed 36 ± 14 mg kg^{-1} dm (total range 13 to 75 mg kg^{-1} dm) [37], or from 39 to 65 mg kg^{-1} dm (means) [42, 43]. Marinated mushrooms in this study (Table 2) also had > 50% less of Zn than has been reported for fresh *A. bisporus*: 66 ± 14 mg kg^{-1} dm (range 41 to 95 mg kg^{-1} dm) [37], and 60 to 65 mg kg^{-1} dm (means) [42, 43].

Co and Ni

Both Co and Ni were minor trace elements in marinated *A. bisporus*, while content widely varied between the batches: for Co medians were in the range 0.004 to 0.02 mg kg^{-1} dm (the overall median 0.015 mg kg^{-1} dm), and for Ni in the range 0.10 to 1.1 mg kg^{-1} dm (1.0 mg kg^{-1} dm) (Table 2).

Curiously, Vetter et al. noted cobalt in imported conserved mushrooms at higher level of 0.86 ± 0.07 mg kg^{-1} dm (sliced) and 0.37 ± 0.04 mg kg^{-1} dm (a whole), than in fresh (< 0.002 to 0.09 mg kg^{-1} dm; means) [42, 43]. Nickel in other studies has been found in fresh and conserved mushrooms in roughly similar concentrations, *i.e.* in fresh 1.1 ± 1.4 mg kg^{-1} dm (0.08 to 6.2 mg kg^{-1} dm) [37] and from 0.35 to 2.2 mg kg^{-1} dm (means), and in conserved 1.6 ± 0.2 mg kg^{-1} dm (sliced) and 1.3 ± 0.1 mg kg^{-1} dm (whole) [42, 43].

Al, Cr, V and U

The elements Al, Cr or U are without known role in mushrooms, while V is essential to certain *Amanita* mushrooms and specifically at high level is in some *Amanita* mushrooms, e.g. *Amanita muscaria*, *Amanita regalis* and *Amanita velatipes*. In *A. muscaria* V content was 22 ± 11 to 130 ± 45 mg kg^{-1} dm in caps and 120 ± 29 mg kg^{-1} dm in stems [18, 29].

Processed *A. bisporus* in this study showed Al, Cr, V and U in relatively a wide range of concentrations both for the same element within the product batches and between the elements. They contained respectively Al, Cr, V and U in the range (medians): 1.4 to 24 mg kg^{-1} dm (the overall median 2.8 mg kg^{-1} dm for Al), 0.071 to 0.88 mg kg^{-1} dm (0.20 mg kg^{-1} dm for Cr), 0.007 to 0.059 mg kg^{-1} dm (0.020 mg kg^{-1} dm for V) and 0.0004 to 0.003 mg kg^{-1} dm (0.001 mg kg^{-1} dm for U) (Table 2).

Aluminum in this study was in roughly similar concentration as has been reported in fresh *A. bisporus* in Poland, i.e., 3.0 ± 1.2 mg kg^{-1} dm range (1.7 to 6.5 mg kg^{-1} dm) [37], and what may suggest on a lack of leaching out from mushrooms during industrial marinating. Vetter et al. [42, 43] reports aluminum in fresh *A. bisporus* in the range 19 to 46 mg kg^{-1} dm (means), and for conserved in brine 74 ± 9 mg kg^{-1} dm (sliced) and 54± 3 mg kg^{-1} dm (whole).

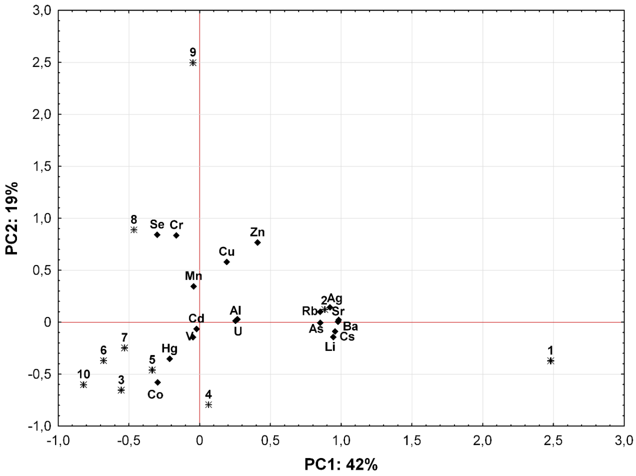

Figure 1. Projection of the elements concentrations in conserved white bottom mushrooms consignments set on the first and second factor-plane

Chromium with the overall median value of 0.20 mg kg^{-1} dm in this study is close to 0.21 ± 0.06 mg kg^{-1} dm (range 0.08 to 0.30 mg kg^{-1} dm) for fresh mushrooms by Rzymski et al. [37], and what may suggest on a lack of decrease during industrial processing. Vetter et al. [42, 43] reported on a somehow higher level of chromium in fresh mushrooms (means in the range 0.73 to 0.83 mg kg^{-1} dm) and mushrooms conserved in brine (1.9 ± 0.4 mg kg^{-1} dm in sliced and 1.6 ± 0.5 mg kg^{-1} dm in a whole).

Vanadium is weakly accumulated by *A. bisporus*. This element in fresh fruiting bodies occurred at level 0.02 ± 0.01 mg kg^{-1} dm (0.01 to 0.04 mg kg^{-1} dm) [37], and from 0.02 to < 0.05 mg kg^{-1} dm [42, 43]. Those values are close to the overall median level of 0.020 mg kg^{-1} dm in marinated mushrooms in this study, and what may imply on lack of a substantial leaking during culinary processing. The white button mushrooms conserved with brine showed vanadium at level higher an order of magnitude than was in mushrooms in this study, *i.e.*, 0.35 ± 0.03 mg kg^{-1} dm (sliced) and 0.25 ± 0.09 mg kg^{-1} dm (whole) [42].

A single result available for uranium in fresh *A. bisprus* (white strain) showed on level < 0.01 mg kg^{-1} dm, while for brown strain it was 0.29 ± 0.14 mg kg^{-1} dm (total range 0.53 - 0.08 mg kg^{-1} dm) [37]. The overall median value of uranium in marinated mushrooms in this study was 0.001 mg kg^{-1} dm.

Principal Component Analysis (PCA)

Major differences in the mineral composition of white button mushrooms between the producers have been observed. Five statistically significant ($p < 0.05$) principal components (PC) were identified, which accounted for 93% of total variability.

The PC1, which accounted for 42% of total variability, was determined by positively correlated Li, As, Rb, Sr, Ag, Cs and Ba (Table 3, Figure 1). Statistically significantly higher content of these elements in mushrooms from the batch marked as ID 1 (Notre Jardin Champignons de Paris Pieds et morceaux "Pieczarki marynowane krojone – pickled champignon sliced" it distinguishes it from the others (Table 2, Fig. 1).

The PC2, which accounted for 19 % of total variability was determined by positively correlated Se, Cr and Zn (Table 3, Fig. 1), which elements at statistically higher level were in a batch of white button mushrooms ID 9 (Ole: „Pieczarki w zalewie naturalnej całe – a whole champignons in a natural marinate") (Table 1, Figure 1). Mushrooms from that batch had also more Cu while less Co (correlations moderately significant) (Tables 2 and 3).

The PC3, which accounted for 18% of total variability was determined by positively correlated Al, U and V (Table 3, Figure 2), which elements at statistically higher level were in a batch of white button mushrooms with ID 2 (Notre Jardin Champignons de Paris 1er Choix entiers "pieczarki marynowane całe – pickled a whole champignons") (Table 2). Also As and Cu were moderately at higher levels in those mushrooms (Table 2, Table 3, Figure 2).

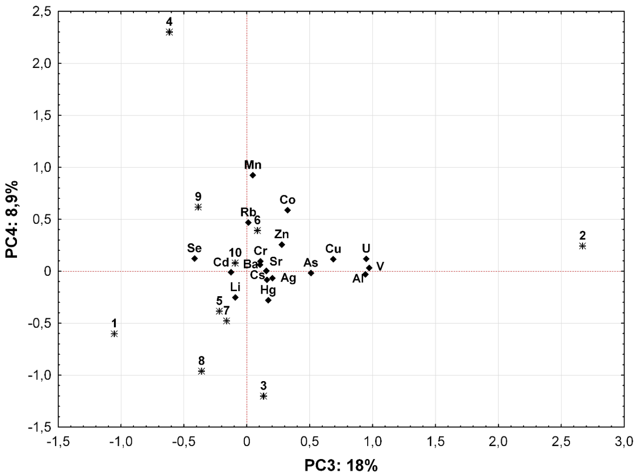

Figure 2. Projection of the elements concentrations in conserved white bottom mushrooms consignments set on the third and fourth factor-plane

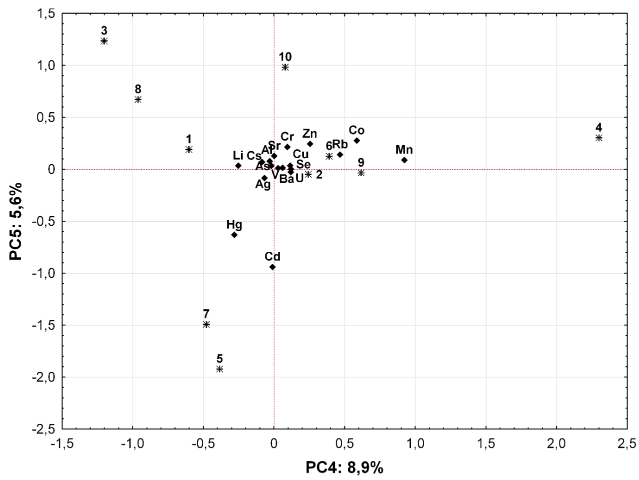

Figure 3. Projection of the elements concentrations in conserved white bottom mushrooms consignments set on the fourth and fifth factor-plane.

The PC4, which accounted for 8.9 % of total variability was determined by Mn, while moderately by Co (Table 3, Figure 2 and Figure 3), and what differentiated mushrooms from the batch with ID 4 (Bonduelle "Pieczarki marynowane – pickled champignons") from others. Manganese at similar level was in mushrooms from the consignments ID 4 and ID 9 (Table 2).

With PC5 were moderately associated the elements such as Cd and Hg (mushrooms from the batches ID 5 and ID 7) (Tables 2 and 3, Fig. 3).

The PC analysis based on total concentration of each chemical element, which could leak out from mushrooms into the marinade at different rate from one side, while some could be absorbed (added in the vinegar or table salt as well as leaked from the vegetables if present) on the other. Hence, it can provide only some piece of information about general tendencies and to feature major differences in technology or quality of marinade and/or containers used by producers. The elements Li, Rb, Sr, Cs and Ba are lithophile and in addition Ba and Sr are seekers for Ca. The elements As and Ag (PC1) and as mentioned already they are seekers for sulphur (Ag also correlated with Cd under PC4) (Figs. 1-3). A difference in a bulk content of those elements in mushrooms depending on the producer was clear for a batch no. 1 (and no. 2) and 9 (Fig. 1; Table 2). White button mushrooms are able to accumulate efficiently Ag [13]. Also As is well accumulated by some *Agaricus* mushrooms [19]. Silver seems to be very hard to remove from mushrooms during blanching and pickling [8]. Arsenic can occur in mushrooms in form of a several compounds while those which usually dominate basically are well water soluble and leak out during blanching and pickling [13, 19]. An external source of contamination (water, table salt, vinegar) cannot be excluded in those cases (samples ID 1 and 2; Table 2).

The components forming PC1, PC2, PC3, PC4 had positive charge values while the PC5 element had a negative one. The differences and similarities in the content of the given elements in the fruiting bodies of the mushrooms from different manufacturers were presented in linear maps. Major differences in the mineral composition of mushrooms from different producers were found. It has been shown that fruit mushrooms from different producers differ in the content of the determinants of PC1, PC2, PC3, PC4 and PC5.

CONCLUSIONS

Some significant differences were found in the content and composition of minerals in marinated white button mushrooms for producers. The relatively higher levels of Ag in some batches seem to be largely explained by the quality of the substrate used for mushrooms cultivation, while of As, Li, Rb, Cs, Cr, Al, U, V and Mn (in part also of Ba and Sr) largely by the quality of the marinade. Conserved white button mushrooms are poorer in major essential elements but also in toxic Hg, As, Ag, Cd, Sb, Tl or Pb than has been reported for unprocessed mushrooms. Due to low concentrations of toxic As, Cd, Hg and Pb, it can be stated that consuming the conserved white button mushrooms available at Polish market does not show any threat to the consumer.

Conflict of interest

The authors declare no conflict of interest.

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