

Article

The Role in the Human Diet of Bioaccumulation of Selenium, Copper, Zinc, Manganese and Iron in Edible Mushrooms in Various Habitat Conditions of NW Poland—A Case Study

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Abstract: The aim of the study was to determine the contents of microelements in *Boletus edulis*, *Imleria badia* and *Leccinum scabrum*, taking into account the soil conditions in selected forest areas of Northwest Poland and the bioaccumulation capacity of these fungi and their role in the human diet. Se, Cu, Zn, Mn and Fe contents were determined in the soil (organic and mineral layers) and mushrooms. The study showed that the soils on which fruiting bodies grew did not differ significantly in the contents of these trace elements. The concentrations of microelements in mushrooms in NW Poland were mostly at the lower range of the contents reported for these species in other regions of Poland and Europe. The uptake of microelements by the studied mushrooms was influenced by soil reaction, organic matter content, and bioavailable and total forms of the elements. *B. edulis* contained significantly more Se than other mushroom species and, together with *I. badia*, was much more abundant in Cu and Zn than *L. scabrum*. Fruiting bodies bioaccumulated Se (most strongly by *B. edulis*; BCF = 120.6), Cu and Zn. The contents of microelements in the tested mushrooms may be supplementary elements in the human diet.

Keywords: fungi; microelements; properties of soil; *Boletus edulis*; *Leccinum scabrum*; *Imleria badia*

1. Introduction

Edible mushrooms are one of the main seasoning ingredients supplementing many world societies' diets. There are particularly long traditions of mushroom preparation in Asia and Eastern Europe. The popularity of various mushroom species is mainly due to their unique taste and, in some cases, their medicinal properties [1–4]. Mushrooms have

historically been considered low-value products in human nutrition. However, they have been shown to contain many ingredients that are important for the proper functioning of the body. In addition to carbohydrates, proteins and fats, they also contain vitamins C and B (niacin and folic acid), small amounts of vitamin D, a number of polyphenols, and macro- and microelements [5–10]. The quantities of microelements in mushrooms are very variable, even within a single species. They are influenced by the different structures of the fruiting bodies and their biochemical compositions, as well as habitat conditions [11–13]. Taken-up microelements are accumulated in the fruiting bodies or exchanged for other chemical compounds with the tree root system [1,14,15].

Selenium is one of the microelements found in mushrooms that is particularly important for the human body. It is a component of two essential amino acids: selenomethionine and selenocysteine, which build many enzymes, including oxidoreductive enzymes [16–18], and it is also a component of selenoproteins [16,19]. Selenium is involved in many metabolic processes of the cell and exhibits high bioactivity, including antioxidant, anti-inflammatory and antiviral properties [20,21]. Recent studies suggest that selenium, in combination with vitamin C and vitamin D, may help strengthen the immune system, preventing the spread of the virus that causes COVID-19 and reducing the disease progressing to severe stages [22].

Other microelements have equally important physiological functions in the human body, including copper, zinc and manganese, which are components of many important enzymes that are effective free radical neutralisers [23]. Copper is involved in the metabolism of iron and the synthesis of haem in the body and the formation of bonds in collagen and elastin, and it is necessary for the proper functioning of the nervous, vascular and bone systems. Zinc, in turn, is involved in the production of proteins, fats and carbohydrates, as well as in energy and hormone metabolism [23,24]. In addition, it plays a key role in the initial stages of germ cell development and spermatogenesis and in sperm development and maturation, as well as in childbirth, in the perinatal and neonatal periods [25]. Manganese, like zinc, is an important element in the formation of proteins and in the synthesis of nucleic and fatty acids and thyroid hormones. Iron is also an essential trace element, as it is involved in tissue respiration, red blood cell formation and DNA synthesis and affects cholesterol metabolism [23].

The body has little need for trace elements, but without them normal development and maintenance of vital functions is impossible. Selenium deficiency can contribute to Keshan and Beck's diseases [20,21], as well as cancer and thyroid disease [26,27]. An insufficient supply of Cu and Fe contributes to reduced resistance to infection and heart disorders; in addition, in the case of Cu, it causes disturbances in glucose and cholesterol metabolism, and insufficient amounts of supplied Fe lead to anaemia. Zinc deficiency in the human diet contributes to stunted growth, hypothyroidism and autism, and in the case of Mn it causes disorders of the nervous system, pancreas, and lipid and carbohydrate metabolism and damage to the skeletal system [23]. Not only a deficiency, but also excessive amounts of trace elements, especially heavy metals, in the human diet can imply disturbances in the functioning of the body and lead to many diseases. Excess Se can cause toxic effects, manifested by gastrointestinal disorders and cardiac symptoms [28]; in extreme cases, with high doses of Se, it can cause selenosis [29,30]. Excess Cu leads to its accumulation in the liver, brain and cornea of the eye, while excessive amounts of Zn can cause a lowering of immune resistance and promote the development of Alzheimer's disease. Increased intake of manganese has a neurotoxic effect [23,31].

Previous studies on the microelement contents of *B. edulis*, *I. badia* and *L. scabrum* have not considered the conditions of trace element accumulation by fruiting bodies of these fungi in Northwest Poland. Soils here are generally characterised by low selenium and copper contents [32,33]. This prompted us to undertake a study in this area which aimed to (a) determine the content of Se as well as those of Cu, Zn, Mn and Fe in fruiting bodies of *B. edulis*, *I. badia* and *L. scabrum* and in soils; (b) determine their bioaccumulation potential,

with consideration of habitat conditions; and (c) estimate their role in covering the human body's need for microelements.

2. Materials and Methods

2.1. Study Area

The studied mushrooms come from three physical–geographical regions of NW Poland: Uznam and Wolin, the Drawsko Plain, and the Ińsko Lakeland [34]. Uznam and Wolin are the islands separating the Szczecin Lagoon from the Pomeranian Bay. The topography of both islands is dominated by low ridges of coastal dunes covered with dry pine forests. The Drawsko Plain is an extensive outwash plain with numerous rivers, lakes, mid-forest pools and peat bogs. Most of the plain is covered with pine forests. The Ińsko Lakeland is an area with a very varied topography, with moraine hills and ravines, numerous lakes and glacial backwaters and vast wetlands. Forests are mainly found in the south, on moraine hills.

In terms of climate, the region of Uznam and Wolin is different from the other two. It has the largest number of sunny, warm and no-rainfall days, as well as a smaller number of days with high cloudiness [35]. The average annual rainfall is 550 mm. The average annual temperature was 8.0 °C, and in autumn it was 9 °C [36]. On the other hand, the Drawsko Plain and the Ińsko Lakeland, which are classified as the same climatic region but different from Uznam and Wolin Islands, have a more severe climate. Atmospheric precipitation is more frequent here [35]. Average annual rainfall totals are in the range of 625–700 mm. Within this range, lower values were noted in the Ińsko Lakeland and higher values in the Drawsko Plain. The average annual air temperature was within the range of 8.0–8.5 °C, and in the autumn it was 7.5–8.5 °C, and then the Drawsko Plain was cooler than the Ińsko Lakeland.

2.2. Characteristics of the Soil

A detailed characterisation of the soil properties on which the studied boletes, boletus and leccinum grew is presented in the first part of the study on the usefulness of mushrooms growing in NW Poland in meeting the elemental requirements of the human diet [10]. Generalizing from this study, it can be seen that the mushrooms grew on sandy soils classified as Arenosols and Podzols, strongly acidic, with varying macroelement contents. These soils were characterised by a well-developed organic horizon. The soils on which the boletus grew had an organic horizon about 5 cm thick, and those of the *I. badia* and *L. scabrum* were 10 cm thick, while below them there was a humus-enriched mineral horizon. The substrate in the organic and mineral horizons was characterised by organic matter contents of 62.05% and 9.7% for *B. edulis*, 71.18% and 21.37% for *I. badia*, and 64.50% and 35.22% for *L. scabrum*, respectively. The pH of the substrate was 3.21 and 3.19 for *B. edulis*, 2.87 and 2.83 for *I. badia*, and 2.89 and 2.86 for *L. scabrum*. The substrate of *B. edulis* was rich in assimilable K, Mg and P, whereas the substrate of *I. badia* and *L. scabrum* was poor in assimilable K and Mg.

2.3. Fungal and Soil Materials

Three species of edible mushrooms were selected for the study: *B. edulis*, *I. badia* and *L. scabrum*. They are among some of the most frequently harvested wild mushrooms in Poland. The sampling sites were located in the forests of Northwest Poland. These sites were most frequently penetrated by mushroom pickers, which gives an idea of the extent to which the mushrooms studied can supplement the inhabitants' diets with essential micronutrients. Therefore, samples were taken in the NE part of Wolin Island—the vicinity of Wiselka and Miedzywodzie; on the Drawskoe Plain—the vicinity of Zatom and Kalisz Pomorski; and in the Ińsko Lakeland—the vicinity of Ciemnik. Sampling followed the generally accepted procedure in this type of research. From each of the three studied regions, 3–7 pooled samples of each species were collected, with each pooled sample consisting of 5 fruiting bodies (15 pooled samples of *B. edulis*, 15 pooled samples of *I. badia* and 11 pooled samples of

L. scabrum were created for the study, for a total of 41 pooled samples of mushrooms). The fruiting bodies of the collected mushrooms were cleaned of litter and sand and dried in the laboratory at 40 °C for 48 h. The dried whole fruiting bodies (without division into caps and stems) were ground in a mortar to powder. The taxonomic identification of mushrooms was made according to Knudsen and Vesterholt [37], using standard methods of studying macrofungi. The fungal nomenclatures were given according to the Index Fungorum database (<http://www.indexfungorum.org/>; accessed on 18 April 2023).

When harvesting fruiting bodies, the soil substrate was also sampled each time from a depth of 0–20 cm for testing. Within the sample, the surface organic level (0–5 (10) cm; decomposed forest litter) and the mineral level below (5–10 (20) cm) were collected.

2.4. Analytical Procedures

2.4.1. Soil

In the soil material, the following determinations were made: contents of available Zn, Cu, Fe and Mn were determined by extracting in 0.5 mol·dm⁻³ HCl; contents of total forms of Zn, Cu, Fe and Mn were determined after mineralisation in HNO₃ and HClO₄ in a ratio of soil 1:1 with flame atomic absorption spectroscopy using the iCE 3000 Series—Thermo Scientific, Waltham, MA, USA. The limits of detection were (mg·kg⁻¹): Cu, 0.005; Zn, 0.003; Fe, 0.004; and Mn, 0.002. Assessments of the accuracy and precision of the analytical methods and procedures used were determined using certified reference material: CRM036–050 Loamy Sand 4 (CRM 036-050 produced by Resource Technology Corporation, Laramie, WY, USA). The effectiveness of the process has been validated with 90–95% efficiency. The results shown are the averages of three measurements; working standards were made from Merck standards with a concentration of 1000 mg/dm³.

Selenium content was determined by the spectrofluorimetric method using 2,3-diaminonaphthalene [38] after prior wet mineralisation in a mixture of concentrated acids: HNO₃ and HClO₄. Soil samples were mineralised according to the method described by Levesque and Vendette [39]. To reduce selenates to selenites, 9% HCl was added to the samples. The selenites were then complexed with 2,3-diaminonaphthalene (Sigma), and the resulting complex was extracted with cyclohexane (Chempur). Fluorescence was measured from the organic layer (cyclohexane) at an emission wavelength of 518 nm and an excitation wavelength of 378 nm.

2.4.2. Mushrooms

After drying the mushrooms at 105 °C, their contents of the following elements were determined: Cu, Zn, Mn and Fe were measured after wet mineralisation in H₂SO₄ and HClO₄ in a ratio of 3:1. The contents of elements were measured with atomic absorption spectroscopy using the iCE 3000 Series. The efficiency of the process was validated with 90–95% success using certified reference materials, namely, tea leaves (INCT-TL-1) and a mixture of Polish herbs (INCT-MPH-2), both produced by the Institute of Nuclear Chemistry and Technology, Warsaw, Poland. All tests were performed in three replications.

The concentration of selenium in mushrooms was determined using Watkinson's spectrofluorometric method [40] modified by Grzebuła and Witkowski [38]. Fungal hyphae were digested in HNO₃ at 230 °C for 180 min and in HClO₄ at 310 °C for 20 min. Then, the samples were hydrolysed with 9% HCl. Selenium was derivatised with 2,3-diaminonaphthalene (Sigma-Aldrich, Burlington, MA, USA), and the complex was extracted into cyclohexane. Se concentration was measured fluorometrically using a RF-5001 PC Shimadzu spectrophotofluorometer (Shimadzu Corporation, Kyoto, Japan). The excitation wavelength was 376 nm, and the fluorescence emission wavelength was 518 nm. The accuracy of the method for herbs was verified based on the BCR-402 White Clover Certified Reference Material. The level of recovery was 89% of the reference value.

The coefficient of bioconcentration of macronutrients was calculated using the equation:

$$BCF = C_m / C_s$$

where BCF is the coefficient of bioconcentration, C_m is the concentration of macronutrient in the mushroom, and C_s is the concentration of macronutrient in the mushroom substrate (soil).

2.5. Statistical Analysis

Statistical analysis of the obtained results of soil chemical properties was performed using Statistica 12.5 (StatSoft Polska, Cracow, Poland). The statistical significance of differences between means was determined by testing the normality of distribution in each group and the homogeneity of variance in all groups, followed by ANOVA with Tukey's post hoc test. The significance was set at $p < 0.05$. The multidimensional analysis was carried out using the analysis of the main components (PCA). The data were scaled during pre-processing automatically. The obtained results were subjected to agglomerative cluster analysis and classified into groups in a hierarchical arrangement by Ward's method.

3. Results and Discussion

3.1. Concentration of Microelements in Soil and Fungi

3.1.1. Selenium

Small Se contents ranging from 0.089 to 0.280 mg/kg Se (Table 1) were found in the substrates taken from beneath *B. edulis*, *I. badia* and *L. scabrum*. Thus, they did not differ from the amounts shown in the soils of NW Poland, ranging from 0.035 to 0.332 mg/kg Se [32]. These soils are some of the poorest in terms of this element not only in Europe [33], but also globally, their contents averaging 0.33 mg/kg but depending on the soil type, e.g., in podzolic soils it is 0.25 mg/kg and in hystosols and rhizosols it is 0.37 mg/kg [41]. The areas of the Drawa National Park (DNP) and its adjacent areas, compared to the other two harvesting regions, were more abundant in Se and at the same time more diverse. However, if we consider the average contents of this microelement in the substrates of the three tested mushroom species, the values did not differ significantly (Table 1).

The concentration of Se in the fruiting bodies of mushrooms ranged from 0.07 to 18.34 mg/kg d.m. and depended largely on the species. The *B. edulis* were the most abundant in this element (11.09–18.34 mg/kg d.m.) and differed significantly from the *L. scabrum* and *I. badia* (0.33–0.79 mg/kg and 0.07–0.24 d.m., respectively). Fruiting bodies from the vicinity of the Drawa National Park (Table 2), where the substrate was richer in Se, contained the highest amount of this microelement among the *B. edulis* studied. The concentration of Se in the mushrooms depended partly on its level in the soil (Figure 1, Tables 3 and 4). In *I. badia* and *L. scabrum* mushrooms, in contrast to *B. edulis*, it was higher in fruiting bodies from the Wolin National Park (WNP), growing on substrate less rich in this trace element (Tables 1 and 2). Temperature and precipitation did not seem to have an effect, as their values were similar or only slightly different in the two study regions. However, it is likely that the surface layers of Se-poor soils in the WNP, compared to DNP-rich soils, may have had a higher content of bioavailable forms of Se, as they contained less organic matter and were more acidic [10]. The Se concentrations in the *B. edulis* we examined, averaging 14.11 mg/kg d.m., were within the ranges typical of this species in Poland, averaging 13.3–20.62 mg Se/kg d.m. [6,8]. However, they sometimes deviated significantly from the values found in some European countries, e.g., Finland (7.5 mg/kg) [42] and the Czech Republic (33.0 mg/kg) [43]. Of the two other species, the more abundant in Se were the *L. scabrum*, with an average of 0.63 mg/kg d.m., which was also within the range characteristic of this species in Poland, with an average of 0.5–1.5 mg/kg d.m. [6,8], and other European countries, with an average of 0.12–0.82 mg/kg d.m. ([6], and references therein), whereas the Se concentration in mushrooms, averaging 0.14 mg/kg d.m., was lower than the values reported so far from Poland (average: 0.21 mg/kg d.m.) but was within the range of averages from other European countries (average: 0.09–0.24 mg/kg d.m.) ([6], and references therein).

Table 1. Contents of available and total forms of micronutrients in soils.

Localisation	Available						Total								
	Cu		Zn		Mn		Cu		Zn		Mn		Fe		Se
mg/kg															
<i>Boletus edulis</i> Soil layer (cm)															
	0–5	5–20	0–5	5–20	0–5	5–20	0–5	5–20	0–5	5–20	0–5	5–20	0–5	5–20	0–10
UW	7.95 a ±0.76	2.40 a ±1.58	42.73 a ±18.96	19.31 a ±25.69	76.37 a ±31.11	11.66 a ±5.56	11.50 a ±1.00	8.24 a ±3.96	46.22 a ±17.99	59.90 a ±95.82	86.14 a ±32.05	32.44 a ±9.14	1858.8 a ±191.6	1806.5 a ±337.6	0.089 a ±0.040
DP	7.21 a ±3.14	2.90 a ±1.74	38.57 a ±22.03	4.18 a ±0.87	672.37 b ±449.9	121.62 b ±61.0	40.74 a ±61.97	6.67 a ±1.03	46.70 a ±23.69	14.01 a ±1.08	782.10 b ±525.0	160.90 b ±64.6	3440.8 a ±1270	3533.4 a ±1271.4	0.164 ab ±0.031
IL	8.31 a ±1.13	2.27 a ±0.54	31.32 a ±13.56	5.79 a ±4.44	109.57 a ±35.93	90.16 ab ±64.29	11.02 a ±1.02	10.02 a ±1.44	46.88 a ±14.91	20.69 a ±6.41	142.16 a ±46.24	144.04 ab ±98.51	3354.0 a ±1468	7494.1 b ±4328.4	0.097 a ±0.029
x	7.76 B	2.52 A	36.88 A	9.76 A	343.65 A	74.48 A	23.86 A	8.31 A	46.66 A	31.53 A	404.41 A	112.46 A	3070.8 B	4278.0 A	0.117 A
<i>Imleria badia</i> Soil layer (cm)															
	0–10	10–20	0–10	10–20	0–10	10–20	0–10	10–20	0–10	10–20	0–10	10–20	0–10	10–20	0–10
UW	5.33 a ±2.62	1.89 a ±0.60	31.45 a ±6.92	10.28 a ±6.63	185.55 a ±65.73	45.02 ab ±26.03	9.10 a ±1.34	6.89 a ±1.22	36.89 a ±7.42	16.24 a ±5.01	204.49 a ±62.47	66.18 ab ±21.34	1804.7 a ±638.3	2423.0 a ±385.5	0.096 a ±0.048
DP	6.10 a ±0.29	2.82 a ±0.29	25.89 a ±5.92	13.48 a ±5.59	136.31 ab ±56.67	59.55 ab ±35.98	11.34 a ±2.07	10.36 a ±0.34	33.34 a ±3.18	19.99 a ±2.79	144.71 ab ±57.51	71.91 ab ±33.04	2005.8 a ±667.1	2226.5 a ±264.4	0.186 ab ±0.014
IL	3.71 a ±2.37	1.86 a ±0.046	24.29 a ±5.09	4.59 a ±2.47	191.65 a ±90.85	44.54 ab ±31.09	14.78 a ±10.30	41.51 a ±70.49	30.13 a ±4.40	23.52 a ±18.34	206.36 a ±92.16	69.79 ab ±40.18	1917.8 a ±936.5	3890.6 ab ±1016.6	0.102 a ±0.023
x	4.83 A	2.06 A	27.47 A	8.64 A	178.14 A	47.73 A	11.82 A	21.43 A	33.48 A	19.90 A	193.23 A	68.77 A	1890.2 A	2970.7 A	0.116 A

Table 1. Cont.

Localisation	Available						Total								
	Cu		Zn		Mn		Cu		Zn		Mn		Fe		Se
mg/kg															
<i>Leccinum scabrum</i> Soil layer (cm)															
	0–10	10–20	0–10	10–20	0–10	10–20	0–10	10–20	0–10	10–20	0–10	10–20	0–10	10–20	0–10
UW	7.40 a ±4.28	3.19 a ±3.57	32.53 a ±16.09	14.25 a ±11.99	111.27 a ±67.01	44.77 ab ±46.14	12.51 a ±8.43	13.04 a ±15.04	39.83 a ±19.98	19.47 a ±13.48	125.44 a ±80.29	63.51 ab ±44.91	1825.2 a 551.3	1874.0 a ±205.2	0.121 a ±0.084
DP	5.18 a ±0.14	3.13 a ±0.53	39.50 a ±16.17	27.41 a ±8.81	70.50 a ±15.13	50.01 ab ±7.86	8.73 a ±1.18	11.39 a ±0.67	45.42 a ±18.12	36.53 a ±18.22	74.67 a ±17.46	65.87 ab ±22.42	1008.8 a ±329.7	1385.0 a ±169.9	0.280 b ±0.079
IL	2.36 a ±1.20	1.51 a ±0.089	39.59 a ±9.22	6.72 a ±2.01	262.30 ab ±156.72	37.82 ab ±18.49	9.29 a ±0.55	7.98 a ±0.86	44.01 a ±12.57	17.30 a ±1.64	284.31 ab ±173.80	62.10 ab ±16.83	1600.2 a ±910.9	4327.9 ab ±100.3	0.118 a ±0.013
x	5.42 AB	2.72 A	36.35 A	15.78 A	141.34 A	44.30 A	10.60 A	11.21 A	42.50 A	23.53 A	154.92 A	63.77 A	1541.2 A	2409.9 A	0.164 A

Abbreviations: UW—Uznam and Wolin, DP—Drawsko Plain, IL—Ińsko Lakeland, x—mean values ± standard deviations, a, b, ab—homogeneous groups, followed by ANOVA with Tukey’s post hoc test, A, B, AB—homogeneous groups for mean values, followed by ANOVA with Tukey’s post hoc test.

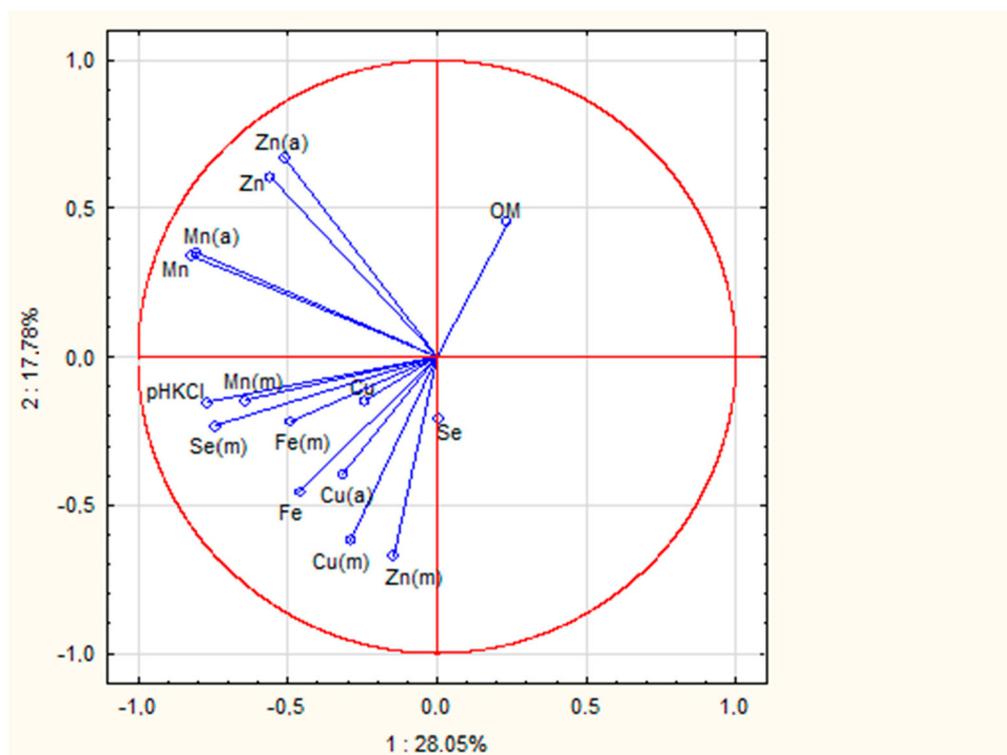


Figure 1. Principal component analysis (PCA) of variable micronutrients in various fungal species, as well as bioavailable and total forms of micronutrients, organic matter and pH in the soil medium. Symbol indications: micronutrients found in fungi, e.g., Cu (m), (m)—mushroom; micronutrients found in soil: total micronutrients, e.g., Cu; bioavailable micronutrients, e.g., Cu (a), (a)—available; OM—organic matter; pH in KCl.

Table 2. The contents of micronutrients in fungi.

Localisation	Se	Cu	Zn	Mn	Fe
	mg/kg				
<i>Boletus edulis</i>					
UW	12.41 b ±2.3	20.36 a ±11.3	126.51 a ±22.8	7.30 a ±3.0	104.27 abc ±35.5
DP	18.34 c ±0.6	22.66 a ±6.42	103.48 a ±11.9	33.62 b ±1.4	237.35 bc ±139.4
IL	11.09 b ±2.5	24.47 a ±7.9	120.17 a ±27.15	12.49 ab ±9.29	48.20 ab ±11.46
x	14.11 B	22.38 B	116.52 A	18.12 A	134.75 A
<i>Imleria badia</i>					
UW	0.24 a ±0.11	22.20 a ±6.10	115.31 a ±24.10	12.70 a ±2.77	287.83 c ±109.24
DP	0.09 a ±0.025	22.06 a ±4.14	128.17 a ±17.77	13.05 ab ±6.96	32.67 abc ±18.49
IL	0.07 a ±0.023	14.86 a ±14.86	107.05 a ±107.05	8.12 a ±8.12	47.23 a ±47.23
x	0.14 A	19.24 AB	114.58 A	10.94 A	140.56 A

Table 2. Cont.

Localisation	Se	Cu	Zn	Mn	Fe
	mg/kg				
<i>Leccinum scabrum</i>					
UW	0.79 a ±0.33	17.76 a ±20.56	114.29 a ±25.54	13.43 ab ±10.06	175.07 abc ±147.16
DP	0.33 a ±0.015	4.90 a ±1.29	82.12 ab ±14.72	6.74 ab ±1.11	32.54 abc ±7.01
IL	0.67 a ±0.016	1.42 a ±0.01	36.45 b ±0.04	2.36 a ±0.010	19.50 ab ±0.010
x	0.63 A	9.80 A	84.29 B	8.59 A	93.77 A

Abbreviations: UW—Uznam and Wolin, DP—Drawsko Plain, IL—Ińsko Lakeland, x—mean values ± standard deviations, a, b, ab, c, abc, bc—homogeneous groups, followed by ANOVA with Tukey's post hoc test, A, B, AB—homogeneous groups for mean values, followed by ANOVA with Tukey's post hoc test.

3.1.2. Copper

In soils, the Cu content ranges from 1 to 140 mg/kg [41]. This element is sorbed in the soil by clay minerals and humus [44,45]. However, solubility and plant uptake mainly depend on the soil pH. The soils on which the *B. edulis*, *I. badia* and *L. scabrum* grew were poor in clay minerals but rich in organic matter in the top layer. They were also characterised by a strongly acid reaction which favours the solubility and availability of Cu. Topsoil organic levels of soils taken from under *B. edulis*, *I. badia* and *L. scabrum* were characterised by a 2–3 times higher content of available Cu than the lower levels (Table 1). The organic layers under *I. badia* were found to be significantly poorer in this element than under *B. edulis* and *L. scabrum* but did not differ in total copper content (Table 1). The lower mineral layers had similar amounts of bioavailable and total Cu. According to the Polish standards for the abundance of bioavailable Cu in soils [46], the soils studied were generally poor in this element. The amounts of total copper in the investigated soils were typical for unpolluted soils [47] and did not exceed the permissible content in soils of forest areas [48].

The Cu content of the substrate of *B. edulis*, *I. badia* and *L. scabrum* was positively related to soil pH, whereas it was negatively related to organic matter content (Figure 1, Tables 3 and 4). The top layer of the substrate consists of poorly decomposed plant remains, which do not have as much sorption capacity as well-humified organic matter. The average Cu content in plants ranges from 5 to 20 mg/kg [41], while in mushrooms it is 10–100 mg/kg [49,50]. The study showed that the studied mushroom species contained an average of 9.80–22.38 mg/kg d.m (Table 2). The boletus were the most abundant in Cu and contained significantly more of this element than the poorest in this element, *L. scabrum*. The average Cu content in *L. scabrum* and *I. badia* was slightly lower than in those found in Europe (for *L. scabrum*, it ranges from 18 to 50 mg/kg d.m. on average; for *I. badia*, it ranges from 22.7 to 100 mg/kg d.m. on average); in contrast, the Cu content in *B. edulis* was within the characteristic range for this species (15 to 85.75 mg/kg d.m. on average) [50–60]. In Japan, the Cu content in various mushroom species ranges from 6.79 to 40.4 mg/kg d.m. [61].

Table 3. Correlation matrix of variables in PCA analysis.

Variable	Variable														
	Se	Cu	Zn	Mn	Fe	Zn (a)	Cu (a)	Mn (a)	pHKCl	OM	Se (m)	Cu (m)	Zn (m)	Mn (m)	Fe (m)
Se	1.000000	0.082182	−0.069493	−0.046534	0.271980	−0.184278	−0.027666	−0.057618	−0.032520	−0.005728	0.138979	−0.044314	0.043395	0.108352	−0.144287
Cu	0.082182	1.000000	0.040028	0.113133	0.299438	0.028682	0.063737	0.096690	0.193418	0.075501	0.298546	0.114400	0.064753	0.028619	−0.013194
Zn	−0.069493	0.040028	1.000000	0.505989	−0.037556	0.920096	0.125103	0.488741	0.290700	0.117241	0.259200	−0.105949	−0.142405	0.186128	0.049862
Mn	−0.046534	0.113133	0.505989	1.000000	0.264900	0.499564	0.045153	0.996619	0.499501	−0.018532	0.494885	0.068756	−0.097055	0.412441	0.205725
Fe	0.271980	0.299438	−0.037556	0.264900	1.000000	−0.201561	0.102066	0.252325	0.290073	−0.330230	0.555407	0.188215	0.160825	0.271893	0.238873
Zn (a)	−0.184278	0.028682	0.920096	0.499564	−0.201561	1.000000	0.113419	0.500324	0.276009	0.201810	0.179189	−0.078998	−0.167734	0.148859	0.047713
Cu (a)	−0.027666	0.063737	0.125103	0.045153	0.102066	0.113419	1.000000	0.040313	0.178141	−0.066058	0.361624	0.570826	0.399150	0.112805	0.066622
Mn (a)	−0.057618	0.096690	0.488741	0.996619	0.252325	0.500324	0.040313	1.000000	0.492279	0.001773	0.468649	0.063954	−0.110045	0.388348	0.206862
pHKCl	−0.032520	0.193418	0.290700	0.499501	0.290073	0.276009	0.178141	0.492279	1.000000	−0.521747	0.496290	0.088086	0.205917	0.434563	0.595848
OM	−0.005728	0.075501	0.117241	−0.018532	−0.330230	0.201810	−0.066058	0.001773	−0.521747	1.000000	−0.174564	−0.092481	−0.210024	−0.041891	−0.285780
Se (m)	0.138979	0.298546	0.259200	0.494885	0.555407	0.179189	0.361624	0.468649	0.496290	−0.174564	1.000000	0.305398	0.118524	0.485819	0.148545
Cu (m)	−0.044314	0.114400	−0.105949	0.068756	0.188215	−0.078998	0.570826	0.063954	0.088086	−0.092481	0.305398	1.000000	0.670788	0.220563	0.156730
Zn (m)	0.043395	0.064753	−0.142405	−0.097055	0.160825	−0.167734	0.399150	−0.110045	0.205917	−0.210024	0.118524	0.670788	1.000000	0.112606	0.044379
Mn (m)	0.108352	0.028619	0.186128	0.412441	0.271893	0.148859	0.112805	0.388348	0.434563	−0.041891	0.485819	0.220563	0.112606	1.000000	0.577788
Fe (m)	−0.144287	−0.013194	0.049862	0.205725	0.238873	0.047713	0.066622	0.206862	0.595848	−0.285780	0.148545	0.156730	0.044379	0.577788	1.000000

Symbol indications: micronutrients found in fungi, e.g., Cu (m), (m)—mushroom; micronutrients found in soil: total micronutrients, e.g., Cu; bioavailable micronutrients, e.g., Cu (a), (a)—available; OM—organic matter; pH in KCl.

Table 4. Correlation of factors and variables in PCA analysis.

Variable	Factor						
	1	2	3	4	5	6	7
Se	0.002951	−0.205177	0.235761	−0.586817	−0.204097	−0.564724	0.290086
Cu	−0.240400	−0.145403	−0.009029	−0.527631	0.286370	0.627371	0.322553
Zn	−0.557810	0.605460	−0.293769	0.004491	0.160971	−0.205486	0.288892
Mn	−0.818969	0.339229	0.050707	−0.112884	−0.048946	0.008960	−0.396418
Fe	−0.461197	−0.454585	0.354049	−0.403455	0.091123	−0.003288	−0.089340
Zn (a)	−0.512067	0.671738	−0.370259	0.094378	0.128312	−0.099349	0.246350
Cu (a)	−0.314388	−0.396654	−0.637538	0.027195	0.055612	−0.120550	0.104320
Mn (a)	−0.802699	0.351863	0.048681	−0.101932	−0.054879	0.016809	−0.414412
pHKCl	−0.767104	−0.153923	0.243697	0.294706	0.271788	−0.007243	0.165737
OM	0.234952	0.452708	−0.385559	−0.347947	−0.545469	0.284759	0.063806
Se (m)	−0.739441	−0.230821	−0.009431	−0.347294	0.023002	−0.021954	−0.014752
Cu (m)	−0.290933	−0.619352	−0.572337	0.044807	−0.158691	0.074581	−0.161906
Zn (m)	−0.145337	−0.669553	−0.450238	0.110132	0.050461	−0.100504	−0.039094
Mn (m)	−0.643156	−0.145148	0.167201	0.119372	−0.597761	0.018068	0.189491
Fe (m)	−0.490297	−0.218819	0.340062	0.549129	−0.266540	0.207179	0.268007

Symbol indications: micronutrients found in fungi, e.g., Cu (m), (m)—mushroom; micronutrients found in soil: total micronutrients, e.g., Cu; bioavailable micronutrients, e.g., Cu (a), (a)—available; OM—organic matter; pH in KCl.

3.1.3. Zinc

In soils, the average Zn content is approximately 40 mg/kg [41]. This element is mainly associated with clay minerals and humus in the soil. Sandy soils are poorer in this element than clay soils. The study showed that the soils on which *B. edulis*, *I. badia* and *L. scabrum* grew did not differ significantly in the contents of bioavailable and total forms of Zn (Table 1). However, the surface organic horizons were more abundant in this element than the mineral ones. According to the Polish standards for the abundance of bioavailable Zn in soils [46], the studied soils were generally moderately abundant in this element. However, the total amounts of Zn found in both layers were typical of unpolluted soils [47] and did not exceed the permissible values in forest areas [48]. It was found that the contents of bioavailable and total zinc in organic levels had no clear relationship with soil pH and organic matter content (Figure 1, Tables 3 and 4). At the same time, the content of bioavailable forms was positively correlated with the total content of this element. It is generally observed in the soil environment that there is an increase in Zn solubility with acidification [45] and increased organic matter [62,63].

Mushrooms take up and accumulate metal ions much more easily than plants [64]. In the case of Zn, 15–30 mg/kg d.m. is sufficient for normal plant growth [41], whereas mushrooms can accumulate up to tens of dozens of milligrams per kilogram of dry matter [50,56,59]. The study showed that the mushroom species tested contained Zn on average between 84.29 and 116.52 mg/kg d.m., with the *B. edulis* and *I. badia* accumulating significantly more Zn than the *L. scabrum* (Table 2). The average Zn contents in the tested mushroom species were within the ranges characteristic of those species occurring in Europe (*L. scabrum* averages 28.6 to 240 mg/kg d.m., while *I. badia* has an average of 121 to 230 mg/kg d.m. and *B. edulis* has an average of 52 to 294 mg/kg d.m.) [50–56,59,60,65,66].

3.1.4. Manganese

In soils, the Mn content ranges from 100 to 1300 mg/kg [41]. This element is bound by clay minerals and carbonates but is bound poorly by organic matter. The soils on which the studied *B. edulis*, *I. badia* and *L. scabrum* grew did not differ significantly in Mn contents (Table 1). However, Mn was more concentrated in the organic than in the mineral levels. A high proportion of the total Mn content was in the available forms of this element, especially in the organic level (>80%). The high percentage of bioavailable forms indicates that this element can be readily taken up by mushrooms. In general, higher amounts of organic

matter in the soil are thought to improve Mn availability [62,63]. Furthermore, its solubility is favoured by a soil pH < 5.5 [67,68]. The study showed that soil Mn content was positively correlated with soil pH, while there was no clear relationship with organic matter content. Furthermore, the content of bioavailable forms of Mn was related to the total content of this element in the soil (Figure 1, Tables 3 and 4).

Most plants contain Mn at a level of 10 to 25 mg/kg, but some plants, e.g., grasses, can take up to about 160 mg/kg [41]. Mushrooms, similarly to plants, take up Mn at up to tens of dozens of milligrams per kilogram of dry matter [56,59,66]. The *B. edulis*, *I. badia* and *L. scabrum* tested took up small amounts of Mn (the least among the analysed elements), (Table 2). The *B. edulis* were the most abundant in this element (average: 18.12 mg/kg d.m.), and the poorest were the *L. scabrum* (average: 8.59 mg/kg d.m.). The average Mn contents of the mushroom species studied were within the characteristic ranges for these mushroom species occurring in Europe (for *L. scabrum*, they range from 5 to 39 mg/kg d.m. on average; for *I. badia*, from 8.0 to 30.0 mg/kg d.m. on average; and for *B. edulis*, from 6.1 to 59 mg/kg d.m. on average) [51–60,65,66]. Barcan et al. [69] suggest the ability of the common mushroom to increase Mn uptake from soils enriched in this element.

3.1.5. Iron

The Fe content in soils ranges widely, from less than one percent to several percent [41]. The solubility of iron in soils increases with increasing acidity [70]. Organic iron combinations are especially mobile and favour plant availability [62]. The soils on which the *B. edulis*, *I. badia* and *L. scabrum* grew contained small amounts of Fe (<0.5%), with the soils from below the *B. edulis* being the most abundant in Fe and the soils from below the *L. scabrum* being the poorest (Table 1). Soil Fe contents were found to be positively correlated with soil pH values and negatively correlated with organic matter (Figure 1, Tables 3 and 4).

Fe in plants occurs in amounts of up to tens of dozens of milligrams per kilogram [41]. Fungi contain comparable amounts of Fe to plants [53,57,66]. The mushrooms tested did not differ significantly in their Fe contents (Table 2). The highest Fe content was found in *I. badia* (140.56 mg/kg d.m. on average) and the lowest in *L. scabrum* (93.77 mg/kg d.m. on average). The Fe contents were within the typical ranges for these mushroom species occurring in Europe (in the case of *L. scabrum* mushrooms, they range from 16.3 to 702.0 mg/kg d.m. on average; in *I. badia*, they range from 34.2 to 183.0 mg/kg d.m. on average; and in *B. edulis*, they range from 33.5 to 287 mg/kg d.m. on average) [51–57,59,65,66].

3.2. The Principal Component Analysis (PCA) for Soil and Mushroom Chemical Composition and Ward's Cluster Analysis for Micronutrient Contents in Soils and Mushrooms

Ward's cluster analysis, taking into account the soil microelements on which fruiting bodies of the studied mushroom species grew, resulted in the separation of two substrate groups differing in chemical composition. The first group was made up of soils from under *B. edulis*, and the second group was made up of soils from under *I. badia* and *L. scabrum* (Figure 2). The same grouping of these soils had already been obtained in earlier studies relating to macronutrient contents [10]. However, when considering the chemical composition of mushrooms in terms of microelements, two groups (cut-off line: 120, Figure 3) were distinguished differently from the soils. The first group consisted of *B. edulis* and *I. badia*, and the second consisted of *L. scabrum*. This separation differed from that obtained for macroelements, where *I. badia* and *L. scabrum* were in the same group and *B. edulis* was in a separate group [10]. These results indicate that the mushroom chemical composition may reflect to varying degrees the concentration and availability of elements in the soil and that it is closely related to mushroom accumulation capacity.

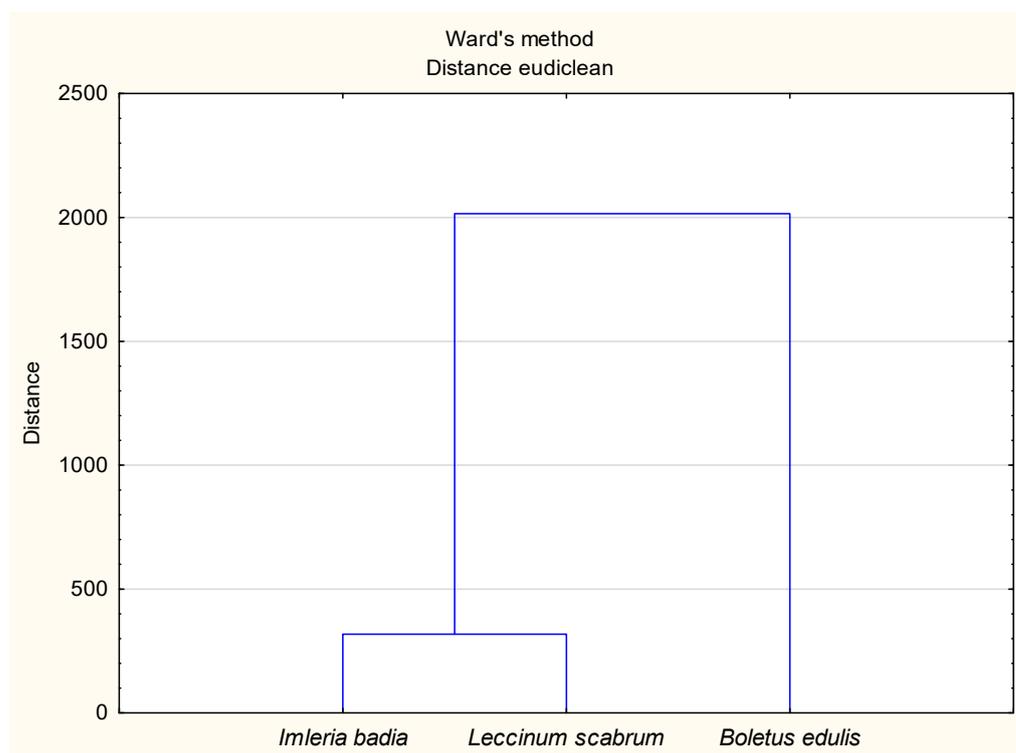


Figure 2. Ward's cluster analysis for the contents of all analysed micronutrients in soils where mushrooms grew (*Leccinum scabrum*, *Imleria badia* and *Boletus edulis*) based on Euclidean distance as the similarity index to determine sub-assemblages. Two clusters were distinguished.

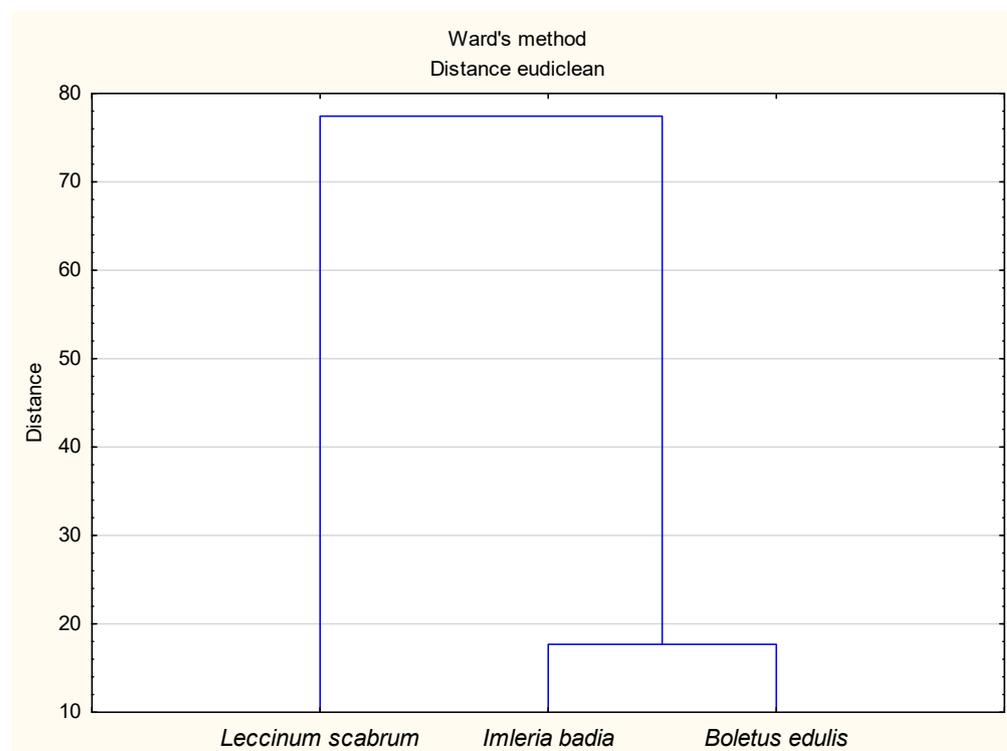


Figure 3. Ward's cluster analysis for the contents of all analysed micronutrients in mushrooms (*Leccinum scabrum*, *Imleria badia* and *Boletus edulis*) based on Euclidean distance as the similarity index to determine clusters. Two clusters were distinguished.

PCA analysis showed that microelement uptake by *B. edulis*, *I. badia* and *L. scabrum* depended positively on pH and the bioavailable and total forms of microelements in the substrate (except Zn) and negatively on organic matter content. In addition, a positive correlation of microelements in mushrooms was found between Zn, Cu, Fe, Se and Mn (Figure 1, Tables 3 and 4). A significant effect of soil pH and organic matter on the uptake of heavy metals (including Zn, Fe, Mn and Cu) by some mushroom species was also found by Gadd [12] and Kokkoris et al. [13]. In contrast, Tyler [71] and Gast et al. [72] showed that soil organic matter and soil pH had only a minor effect on the heavy metal contents of some mushroom species. Kokkoris et al. [13], similarly to this study, found significant correlations between the bioavailable forms of some heavy metals (Mn, Cu and Zn) and their contents in mushrooms, while they did not find this correlation with the total concentrations of these metals. According to Kokkoris et al. [13], Gast et al. [72], Giannaccini et al. [73] and Demirbaş [74], some mushroom species are characterised by an individual preference for heavy metal uptake regardless of substrate content or location. Mushrooms also have the ability to take up elements from dust settled on fruiting bodies [11], which can interfere with the interpretation of correlations with substrate content. This is particularly evident in anthropogenically contaminated areas where large amounts of heavy metals are observed in mushrooms [75,76].

3.3. Accumulation of the Micronutrients in the Studied Fungi

Mushrooms have varying degrees of ability to accumulate some trace elements [7,9,13]. Among the trace elements we studied, selenium was bioconcentrated most strongly by *B. edulis* (BCF = 120.6). The BCF here was several times higher compared to the BCFs of the other trace elements in the fruiting bodies of the three mushroom species studied (Table 5). Se was also accumulated by *I. badia* and *L. scabrum*, but to a much lesser extent, with *L. scabrum* fruiting bodies having a higher BCF. Mushrooms from NW Poland accumulated Se at a similar level to fruiting bodies from the Czech Republic (BCF = 1.03 ± 0.81) [77]. Due to their structure and exposed stipules, mushrooms can accumulate Se and other trace elements [78]. These abilities may also be due to the presence of sulphuric amino acids [79].

Table 5. Bioconcentration factors (BCFs) of micronutrients in fungi.

Mushroom Species	Cu		Zn		Mn		Fe		Se
	Soil layer (cm)								
	0–5	5–20	0–5	5–20	0–5	5–20	0–5	5–20	0–10
<i>Boletus edulis</i>	0.9	2.7	2.5	3.7	0.04	0.16	0.04	0.03	120.6
	Soil layer (cm)								
	0–10	10–20	0–10	10–20	0–10	10–20	0–10	10–20	0–10
<i>Imleria badia</i>	1.6	0.9	3.4	5.8	0.06	0.16	0.07	0.05	1.2
	Soil layer (cm)								
	0–10	10–20	0–10	10–20	0–10	10–20	0–10	10–20	0–10
<i>Leccinum scabrum</i>	0.9	0.9	2.0	3.6	0.06	0.13	0.06	0.04	3.8

Despite the lack of correlation between soil Zn content and uptake of this element by the mushrooms (Figure 1), all the fruiting bodies studied bioaccumulated this element (bioaccumulation coefficient > 1). However, the bioaccumulation coefficient from the soil organic level in all mushrooms was lower (from 2.0 in *L. scabrum* to 3.4 in *I. badia*) than that found in the mineral level (from 3.6 in *L. scabrum* to 5.8 in *I. badia*), (Table 5). This reflected an inverse dependence of Zn concentration in the mushrooms on the organic matter content of the substrate (Figure 1). The highest ability to accumulate Zn, irrespective of the substrate level, was found in *I. badia* fruiting bodies (BCFs = 3.4 and 5.8) and the lowest in *L. scabrum* (BCFs = 2.0 and 3.6), (Table 5). In other regions of Poland, generally higher values of Zn

bioaccumulation factors (BCFs) were found in mushrooms: *B. edulis* ranged from 6.8 (14.4) to 8.1 [55,80]; *I. badia* had an average value of 4.2 (10.6) [80]; and *L. scabrum* ranged from 4.1 to 9.8 on average [52]. Bioaccumulation of *L. scabrum* was observed for Zn also on sites subject to anthropogenic pollution factors [7]. Although mushrooms have a particular ability to take up large amounts of Zn from the substrate [81], comparable amounts of Zn were also found in fruiting bodies and soil [49].

Among the three mushroom species we studied, only *B. edulis* and *I. badia* were bioaccumulators of Cu and not for the whole substrate (Table 5). *B. edulis* showed bioaccumulation only in the mineral layer (BCF = 2.7), and *I. badia* only in the organic layer (BCF = 1.6). Significantly higher BCF values were found in these species in other areas of Poland. In *I. badia*, the BCF was recorded at an average of 8.8 [80], in *L. scabrum* at an average of 1.1 to 7.3 [7,52], and in *B. edulis* at an average of 7.8 to 19 [55,80]. In central and southeastern regions of Poland, *L. scabrum*, in contrast to our findings, was characterised by a bioaccumulation potential of Cu as well as Mn [7].

The mushrooms we studied did not bioaccumulate manganese (BCF < 1), (Table 5). The lack of Mn accumulation capacity of *L. scabrum* is indicated by Mędyk et al. [52] and by *B. edulis* by Frankowska et al. [55]. In contrast, Kalač and Svoboda [49] indicate that the amounts of Mn in mushrooms are similar to those in soil.

Despite the high Fe content in all *B. edulis*, *I. badia* and *L. scabrum* fruiting bodies, its uptake from the substrate was found to be limited. BCF coefficients were in the range of 0.03–0.07 and therefore well below 1, which may indicate the bioexclusion of this element in the fruiting bodies of these fungi (Table 5). The lack of bioaccumulation of iron in *L. scabrum* was found by, among others, Mędyk et al. [52] and Falandysz et al. [7], and in *B. edulis* by Frankowska et al. [55]. Also, Kalač and Svoboda [49] indicate that the amounts of Fe in different mushroom species are lower than in soil. However, there are fungal species that accumulate or have the potential ability to accumulate Fe [82].

3.4. Potential Impact of Mushroom Consumption on Humans

3.4.1. Selenium

Selenium is found in higher amounts in offal, seafood, garlic, mushrooms and legumes. The bioavailability of selenium (selenomethionine) from food is 90%. Mushrooms can convert the intake of inorganic selenium into organic metabolites, such as selenium polysaccharides, selenoamino acids and selenoproteins. These compounds have a higher bioavailability and, at the same time, a lower toxicity compared to the intake of inorganic forms [6,83]. The *L. scabrum* we studied contained more selenium than vegetables (0.017–0.12 mg/kg) and fruit (0.0062–0.089 mg/kg), while the *B. edulis* were also significantly richer in this micronutrient compared to fish and seafood (0.56–2.00 mg/kg) [6].

Selenium intake in European countries ranges from 31.0 to 65.6 µg/day, and in Poland it averages 37.9 to 62.2 µg/day. The average selenium requirement (EAR) in Poland is about 45 µg/day, and the recommended intake (RDA) is 55 µg/day [23]. A consumption of just 3.9 g of dried or 39 g of fresh *B. edulis* from NW Poland covers this requirement in full. The maximum safe daily intake of Se is set at almost 400 µg (0.4 mg) per day [83]. To exceed this in the case of *B. edulis* from NW Poland, 28 g of dried or 280 g of fresh mushrooms would need to be consumed. Regular consumption of Se-rich *B. edulis* can cause toxic effects [28] and lead to the development of type II diabetes [29,30]. However, it should be noted that *B. edulis* should only be consumed in small quantities and relatively infrequently. In addition, there is a loss of Se in mushrooms subjected to thermal cooking [6]. However, *B. edulis*, compared to the fungi *I. badia* and *L. scabrum*, contains 100 and 20 times more selenium, respectively, and can be a very valuable supplement for this micronutrient in the human diet, especially in the case of disease symptoms due to selenium deficiency.

3.4.2. Copper

In the human diet, the main sources of Cu are offal, oatmeal, wheat bran, nuts and sunflower seeds. Human absorption of copper from food products is 35–50%. The average

daily intake of copper varies from 0.9 to 2.2 mg and only occasionally reaches 5 mg [84]. In contrast, it ranges from 1.15 to 2.07 mg/day in European countries, with an average of 1.26 mg/day in Poland [23]. The Institute of Nutrition and Food [23] recommends a daily intake (RDA) of Cu in the range of 0.7–0.9 mg. The tolerable upper intake level (UR) for Cu was set at 10 mg/day [85]. The provisional maximum tolerable daily intake (PMTDI) of Cu is 0.5 mg/kg body weight [86]. The daily Cu requirement is already provided by about 40 g of dried *B. edulis* from NW Poland or 400 g of fresh ones, and the daily tolerable upper intake level (UR) is reached with about 446 g of dried *B. edulis* and 4460 g of fresh ones. Exceeding the PMTDI would require the consumption of approximately 2 kg of dried or 20 kg of fresh *B. edulis*. Although *L. scabrum* contains more than twice as much Cu as *B. edulis* and *I. badia*, taking into account the amounts of mushrooms consumed, it can be concluded that the concentrations of copper contained therein do not pose a threat to the body and that mushrooms can be a good source of this element in human nutrition.

3.4.3. Zinc

Zinc is mainly found in meat, eggs, rennet cheeses and groats. It is absorbed at 20–40% from food. The average daily intake of zinc by humans is in the range of 15–20 mg [87]; in European countries, it ranges from 8.0 to 14.0 mg, and in Poland it is about 10.52 mg [23]. The recommended daily intake (RDA) of Zn should be in the range of 8 to 11 mg per day [23]. The tolerable upper intake level (UR) for Zn is 30 mg/day [85]. The provisional maximum tolerable daily intake (PMTDI) of Zn is between 0.3 and 1.0 mg/kg body weight [86]. Consumption of approximately 94 g of dried or 940 g of fresh *B. edulis* from NW Poland will provide the recommended daily intake of Zn for men. However, above 257 g of dried or 2570 g of fresh *B. edulis* per day may already pose a risk to human health. Exceeding the provisional maximum tolerable daily intake (PMTDI) of Zn for a 70 kg person would require an intake of 180 g to 601 g of dried or 1800 g to 6010 g of fresh *B. edulis*. Similar amounts of Zn to *B. edulis* are contained in *I. badia*, while *L. scabrum* contains 27% less of this element.

Research shows that mushrooms, especially *B. edulis* and *I. badia*, can be a good source of Zn in covering the body's need for this microelement. However, consuming large amounts of mushrooms regularly can be a health risk.

3.4.4. Manganese

Foods providing the highest amounts of Mn include dark bread, legumes, buckwheat groats, nuts and tea. The average daily human intake of Mn is 2–3 mg [85], with a range of 2–6 mg/day in Europe and 4.70 mg/day in Poland. A sufficient daily intake of Mn is 1.6–2.3 mg [23]. As an acceptable range of Mn intake, WHO [87] indicates 2–3 mg/day, while the SCF [85] indicates 1–10 mg/day. No adverse effects of Mn consumed at 8–9 mg/day have been found for humans. A sufficient daily intake for men is provided by 127 g of dried *B. edulis* or 1270 g of fresh *B. edulis*. However, consumption should not exceed 500 g of dried or 5000 g of fresh mushrooms. Almost half as poor in this element are *I. badia* and *L. scabrum*.

3.4.5. Iron

The main sources of Fe are, for example, meat and offal, eggs, parsley and legumes. Fe is absorbed from food at about 10–15%. In Europe, its average daily intake ranges from 9.4 mg/day to 17.9 mg/day, and in Poland it is 12.4 mg/day. The human diet is generally iron deficient according to the SCF [85]. The recommended daily intake (RDA) of Fe is in the range of 10–18 mg [23]. For men, this requirement is provided by approximately 89 g of dried or 890 g of fresh *B. edulis*. The temporary maximum tolerable daily intake (PMTDI) of iron is 0.8 mg/kg body weight/day [86]. The temporary maximum tolerable daily intake will be exceeded after a 70 kg man eats approximately 416 g of dried or 4160 g of fresh *B. edulis*. *I. badia* has a similar iron abundance, while *L. scabrum* is about 30% poorer.

The results obtained indicate that, despite a very low BCF (well below 1), the mushrooms studied can be a source of this element, as approximately 90% of the bioavailable Fe in an edible mushroom is easily absorbed [88].

4. Conclusions

The sandy soils with strongly acidic pH levels and varying organic matter contents on which *B. edulis*, *I. badia* and *L. scabrum* grew in the NW Polish forests showed similar abundance in available and total forms of Cu, Zn, Mn and Fe. The contents of these elements were typical for forest soils, with higher concentrations generally in the surface layer of the subsoil. The bioavailable forms were found to be correlated with their total contents in the soil. Furthermore, it was noted that the contents of Cu, Fe and Mn depended on soil pH and organic matter content (in the case of Cu and Fe).

Concentrations of microelements in the studied *B. edulis*, *I. badia* and *L. scabrum* in NW Poland were generally within the lower limits of the ranges of the contents found in these species in other regions of Poland and Europe. Their uptake by the mushrooms was influenced by soil reaction, organic matter content, and the bioavailable and total forms of the elements in the soil. The most abundant in selenium was *B. edulis*, and in the case of Cu and Zn, *B. edulis* and *I. badia* were. In contrast, the studied species did not differ significantly in Mn and Fe contents. Although the mushrooms contained the most Fe, its bioconcentration was not found in the fruiting bodies. In contrast, they showed the ability to bioaccumulate Cu, Zn and Se, with Se bioaccumulated most strongly by *B. edulis*.

The microelement contents recorded in the studied mushrooms of NW Poland, especially in *B. edulis*, namely, Se, Cu, Zn, Fe and Mn, are at sufficient levels for these mushrooms to constitute an important source of them in the diet of the local population. In the case of *B. edulis*, the elements which may limit their intake are Se, which occurs in the fruiting bodies in very large amounts, and Zn, to a lesser extent.

The results presented here indicate that mushrooms can play a significant role in the sustainable food consumption of local people. Mushroom picking, attractive because of mushrooms' taste and health-promoting qualities, makes this activity preferred by many people over other forms of recreation. It can also have an economic dimension when the harvested mushrooms are sold, as it supplements the budget of the local people.

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