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Metals bioaccumulation by bay bolete, *Xerocomus badius*, from selected sites in Poland

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Abstract

The concentrations of 14 elements (Pb, Cd, Ag, Cu, Mn, Cr, Co, Ni, Fe, Zn, Na, K, Ca, Mg) were determined in fruiting bodies of bay bolete, *Xerocomus badius*, and the underlying soil substratum collected from northern and north-eastern Poland. The total metals content was determined by flame atomic absorption spectrometry (AAS), using deuterium-background correction. The caps of the mushroom examined showed greater concentrations of some metals than the stalks, and the values of the cap to stalk ratio were similar despite different sampling sites. In order to estimate the degree of accumulation of each element by mushrooms, bioconcentration factor values (BCFs) were calculated. Significant correlation coefficients ($P < 0.001$, $P < 0.01$ and $P < 0.05$) were found between concentrations of metals in the caps, stalks of *Xerocomus badius* and the associated soil as a substratum. Cluster analysis (CA) and discriminant function analysis (DFA) were applied to the concentration data obtained. Some spatial differences in metal concentrations, especially concerning Pb were identified.

Keywords: Metals; Bioconcentration; *Xerocomus badius*; AAS; DFA; CA

1. Introduction

According to international data (Işiloglu, Ylmaz, & Merdivan, 2001; Kalač, Nižnamská, Bevilaqua, & Stašková, 1996; Kalač & Svoboda 2000; Kuusi, Laaksovirta, Liukkonen-Lilja, Lodenius, & Piepponen, 1981; Svoboda, Zimmermannová, & Kalač, 2000) many species of wild growing mushrooms possess ability to effective takeup and accumulate (in their fruiting bodies) several metals, such as cadmium, lead, arsenic, copper, nickel, silver, chromium and mercury, especially growing in the vicinity of sites with high traffic density or other pollution sources. Apart from anthropogenic factors, some natural factors determine the ability of mycelium to takeup several elements. Density and depth of the mycelium living in the soil for several months, or even years, influence metal content in fruiting bodies. In addition, soil properties, such as pH, redox potential, organic matter content, clay mineralogy, cation exchange capacity of the solid phase, competition with other metal ions and composition of the soil solution concentrations influence metal exchange with the substratum (Mejstřik & Lepšová, 1993; Schmitt & Sticher, 1991; Wondratschek & Röder, 1993). Because macrofungi are an integral part of forest ecosystems, sometimes the soil-to-mycelium transfer of metals depends on relationships between mycelium and symbiotic plant species affecting element absorption and translocation (Yoshida & Muramatsu, 1997). Hymenophore usually contains a greater concentration of heavy metals than flesh (Melgar, Alonso, Perez-Lopez, & Garcia, 1998).

The aim of the present investigations was to analyse and compare concentrations of heavy metals and their accumulation, with respect to the substratum, in *Xerocomus badius*, a very popular edible wild mushroom species in Poland. Distribution of 14 elements in the fruiting body and specific accumulation of some elements are considered.

2. Materials and methods

The mushroom samples (166) were collected during the years 1993–1998 from forests in northern and north-eastern Poland (Fig. 1). Mushrooms were cleaned from

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residues of plants and substratum, dried and powdered in an agate mortar. Caps and stalks were analysed separately. Soil samples (31), after removal of leaves, stones and living organisms were dried, sieved through a 1-mm plastic sieve and powdered in an agate mortar. Digestions of mushroom and soil samples were performed in an automatic microwave digestion system (MLS 1200) using concentrated HNO_3 (Suprapur® Merck). The concentrations of elements were determined in an air-acetylene flame by the AAS method, using a deuterium-background correction. In the case of Na and K determinations, Cs was added to samples as an ionisation buffer at a concentration of 0.2% w/v, and in the case of Ca and Mg measurements, La was used as a releasing agent at a concentration of 0.1% w/v.

The reliability of the method was tested with certified standard reference materials of fish tissue (MAB-3-1 IAEA) and sea lettuce (BCR-279 IRMM *Ulva lactuca*). The agreement between the analytical results for the reference materials and their certified values was satisfactory, the recovery and the standard deviation were >82 and $<10\%$, respectively.

Linear regression analysis and cluster analysis (CA) of the obtained data were performed using STATISTICA software. Discriminant function analysis (DFA) of the concentration data was done using Sigma Plot 2000. The 14 metals determined were considered as chemical descriptors of each sample.

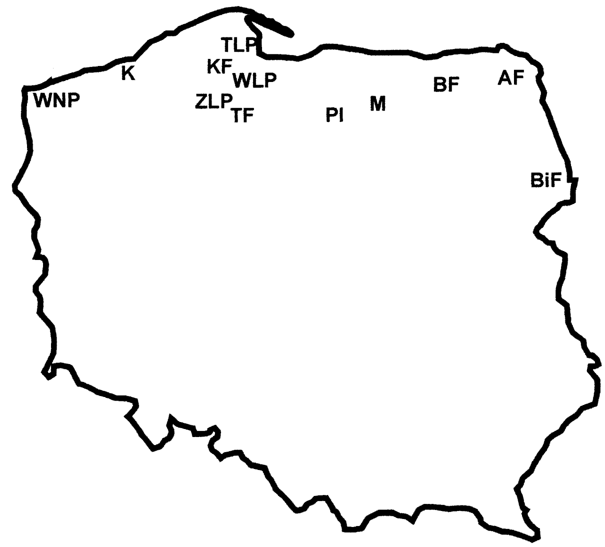

Fig. 1. Location of sampling spots (WNP—Wolinski National Park, K—Adjacent area of Kolobrzeg, KF—Kaszubskie Forest, TLP—Trojmiejski Landscape Park, WLP—Wdzydzki Landscape Park, ZLP—Zaborski Landscape Park, TF—Tucholskie Forest, PI—Ilawskie Lake district, M—Adjacent area of Morag, BF—Borecka Forest, AF—Augustowska Forest, BiF – Bialowieska Forest.

3. Results

3.1. Metals concentrations in mushrooms

Data of the analysed elements are listed in Tables 1–6. The metal concentrations in the samples are characterised by arithmetical mean value, the corresponding standard deviations (S.D.) and ranges on a dry weight basis.

The highest concentration of Pb was found in samples from Trojmiejski Landscape Park, i.e., 8.15 mg kg^{-1} in caps and 7.92 mg kg^{-1} in stalks. Mushrooms collected in the adjacent area of Kolobrzeg were characterised by significantly lower Pb concentrations, namely 0.42 in caps and 0.89 mg kg^{-1} in stalks. The highest Cd level was found in mushrooms collected in Wolinski National Park. The average concentrations of Cd in caps were 2.10 mg kg^{-1} and in stalks 1.53 mg kg^{-1}. Lower levels of Cd were determined in samples collected from Augustowska Forest, 0.38 mg kg^{-1} in caps and 0.13 mg kg^{-1} in stalks. Comparable results were observed by Melgar et al. (1998). The Cd levels also increased with increasing Cd concentration in the soil samples. The highest Ag concentration in mushrooms from Bialowieska Forest were found in caps and stalks, amounting to 1.43 and 0.68 mg kg^{-1}, respectively. Similar to these data are those reported by Falandysz, Bona, and Danisiewicz (1994). Lower levels of Ag were determined in fruiting bodies collected in Augustowska Forest, 0.36 mg kg^{-1} in caps and 0.12 mg kg^{-1}, in stalks. Copper levels in the caps ranged from 27.0 to 65.1 mg kg^{-1} with a higher mean value in caps from Zaborski Landscape Park. In the stalks, Cu levels ranged from 10.9 to 32.9 mg kg^{-1} with a higher mean value in stalks from Kaszubskie Forest. The results are comparable with findings of Lasota and Florczak (1979), Barcan, Kovnatsky, and Smetannikova (1998) or Kalač and Svoboda (1998). The concentration of Cu in fruiting body is generally high and depends on its content in soil and anthropogenic influences (Kalač, Burda, & Stašková, 1991). The highest concentrations of Mn obtained in the present study were 21.5 mg kg^{-1} in the caps from Ilawskie Lake district and 52.7 mg kg^{-1} in stalks from Trojmiejski Landscape Park. Similar results were reported by Lasota and Florczak (1979). The concentrations of Cr were the highest in the caps from Wdzydzki Landscape Park and stalks from Trojmiejski Landscape Park, amounting to 0.75 and 0.71 mg kg^{-1}, respectively. Vetter's (1997) reports of levels of Cr in mushrooms belonging to the genus *Xerocomus* are very similar to those described in this study. The concentrations of Co in the caps and stalks were the highest in samples collected from the adjacent area of Kolobrzeg, amounting to 0.76 and 0.55 mg kg^{-1}, respectively, while fruiting bodies from Borecka Forest had lowest levels of Co—in caps (0.28 mg kg^{-1}) and in stalks (0.19 mg kg^{-1}). The values obtained here are similar to those reported by Barcan et al. (1998) for the genus *Xerocomus*. The con-

Table 1
Trace metal concentrations (mg kg^{-1} dry wt.) in the fruiting bodies (C—cap, S—stalk) of bay bolete, *Xerocomus badius* (Fr.) Kühn. ex Gilb., and in the underlying substratum (So) from selected forest areas of Poland (*N*—number of samples)

Sample location	*N*		±S.D. (range)									
			Pb	Cd	Ag	Cu	Mn	Cr	Co	Ni	Fe	Zn
Augustowska Forest	16	C	0.96±0.41 (0.24–1.58)	0.38±0.19 (0.04–0.93)	0.36±0.20 (0.10–0.65)	42.4±16.9 (22.4–78.5)	14.0±4.56 (7.56–23.1)	0.33±0.09 (0.20–0.48)	0.36±0.28 (0.12–0.79)	0.33±0.24 (0.08–0.76)	34.2±15.1 (36.2–85.3)	190±49.1 (126–272)
	16	S	1.32±0.59 (0.33±2.38)	0.13±0.06 (0.02–0.24)	0.12±0.07 (0.03–0.29)	16.3±6.03 (7.19–31.9)	21.1±6.49 (11.9–31.9)	0.32±0.07 (0.13–0.51)	0.19±0.16 (0.03–0.56)	0.23±0.20 (0.02–0.74)	32.1±11.1 (21.1–51.8)	119±24.1 (89.9–176)
	4	So	17.5±2.40 (14.4–20.0)	0.12±0.01 (0.12–0.15)	0.31±0.10 (0.24–0.45)	1.80±0.30 (1.46–2.08)	158±26.2 (119–180)	4.01±0.70 (3.45–4.93)	0.54±0.03 (0.51–0.57)	1.29±0.30 (1.08–1.58)	4385±680 (3977–5401)	16.9±2.71 (14.0–20.2)
Bialowieska Forest	11	C	0.66±0.37 (0.22–1.34)	0.55±0.26 (0.23–1.07)	1.43±0.80 (0.41–2.66)	47.2±23.1 (13.4–84.0)	19.8±8.49 (7.37–38.6)	0.37±0.24 (0.21–0.98)	0.48±0.25 (0.18–1.06)	0.97±0.49 (0.37–2.08)	98.6±71.6 (38.2–259)	145±34.4 (93.4–192)
	11	S	1.67±1.03 (0.43–3.32)	0.26±0.13 (0.07–0.54)	0.68±0.47 (0.32–1.94)	22.3±12.5 (5.85–46.4)	34.1±13.5 (10.6–55.0)	0.52±0.24 (0.24–0.85)	0.31±0.16 (0.08–0.60)	0.54±0.34 (0.20–1.10)	131±56.0 (42.3–241)	106±28.1 (74.2–151)
	5	So	10.6±0.60 (9.90–11.5)	0.31±0.02 (0.29–0.33)	0.27±0.04 (0.22–0.32)	3.51±0.50 (2.60–3.84)	136±23.2 (122–178)	6.84±0.80 (6.03–7.91)	0.89±0.20 (0.67–1.08)	2.07±0.30 (1.70–2.47)	6000±811 (5118–7214)	29.7±5.62 (21.8–36.5)
Borecka Forest	15	C	1.11±0.45 (0.34–2.06)	0.62±0.19 (0.42–0.90)	0.36±0.14 (0.12–0.70)	33.0±8.67 (20.3–47.6)	10.8±4.06 (4.36–36.1)	0.22±0.08 (0.08–0.46)	0.28±0.10 (0.10–0.44)	0.73±0.28 (0.20–1.38)	103±35.5 (47.0–171)	130±14.5 (82.2–155)
	15	S	1.42±0.43 (0.76–2.24)	0.44±0.18 (0.18–0.70)	0.31±0.12 (0.14–0.54)	10.9±2.06 (7.02–13.8)	26.8±9.00 (10.4–44.2)	0.20±0.03 (0.14–0.26)	0.19±0.09 (0.06–0.34)	0.51±0.29 (0.22–1.02)	122±58.4 (55.0–287)	95.0±9.78 (75.6–133)
	7	So	9.46±2.70 (5.95–12.6)	0.33±0.10 (0.24–0.42)	0.37±0.10 (0.26–0.54)	1.58±0.20 (1.15–1.87)	62.1±12.1 (46.4–80.1)	4.68±0.70 (3.44–5.70)	0.71±0.20 (0.48–0.91)	1.76±0.20 (1.33–1.92)	4366±755 (3368–5275)	25.9±6.03 (18.0–32.9)

Table 2
Trace metal concentrations (mg kg^{-1} dry wt.) in the fruiting bodies (C—cap, S—stalk) of bay bolete, *Xerocomus badius* (Fr.) Kühn. ex Gilb., and in the underlying substratum (So) from selected forest areas of Poland (*N*—number of samples)

Sample location	*N*		±S.D. (range)									
			Pb	Cd	Ag	Cu	Mn	Cr	Co	Ni	Fe	Zn
Adjacent area of Morag	16	C	3.70±1.02 (2.04–5.78)	1.03±0.88 (0.35–4.02)	0.59±0.30 (0.22–1.30)	35.2±12.8 (9.46–60.9)	15.4±5.56 (7.86–29.3)	0.58±0.19 (0.37–1.03)	0.54±0.32 (0.10–1.00)	1.01±0.34 (0.26–1.81)	142±65.0 (62.9–293)	184±48.2 (112–260)
	16	S	4.82±1.81 (2.75–15.6)	0.60±0.42 (0.16–1.58)	0.23±0.16 (0.04–0.57)	16.8±5.04 (5.27–23.7)	20.3±7.44 (12.2–36.7)	0.53±0.25 (0.24–1.07)	0.60±0.51 (0.07–1.74)	0.76±0.42 (0.07–1.82)	62.9±20.4 (35.1–146)	126±26.4 (84.6–195)
	4	So	12.3±2.00 (10.4–14.1)	0.34±0.01 (0.34–0.35)	0.37±0.04 (0.33–0.44)	1.84±0.32 (1.46–2.04)	39.2±38.2 (10.4–94.1)	4.06±0.30 (3.80–4.29)	0.33±0.10 (0.23–0.43)	0.64±0.20 (0.35–0.93)	2720±298 (2326–3006)	10.7±3.72 (7.90–16.3)
Ilawskie Lake District	10	C	0.50±0.44 (0.14–1.43)	0.64±0.35 (0.22–1.14)	0.72±0.22 (0.45–1.05)	48.2±12.5 (31.6–62.9)	21.5±5.13 (14.7–30.7)	0.33±0.11 (0.22–0.53)	0.74±0.13 (0.51–0.92)	1.56±0.34 (1.18–2.11)	207±57.5 (119–290)	210±48.3 (119–260)
	10	S	1.22±0.74 (0.60–2.66)	0.30±0.19 (0.12–0.66)	0.31±0.16 (0.12–0.55)	19.1±7.00 (11.0–30.9)	32.2±10.9 (20.2–50.5)	0.54±0.25 (0.23–0.87)	0.53±0.11 (0.39–0.72)	1.61±0.70 (0.62–2.69)	150±65.9 (72.0–264)	155±50.5 (79.1–215)
	4	So	18.4±2.41 (16.3–22.7)	0.23±0.01 (0.21–0.25)	0.41±0.20 (0.17–0.51)	2.13±0.25 (1.53–2.36)	34.7±18.2 (21.3–49.8)	4.86±0.64 (3.90–5.12)	0.38±0.20 (0.20–0.54)	1.24±0.17 (0.86–1.37)	2963±319 (2563–3120)	13.7±4.80 (8.56–24.3)
Wdzydzki Landscape Park	15	C	1.56±0.78 (0.17–3.04)	1.34±0.58 (0.64–2.56)	0.57±0.35 (0.21–1.52)	39.6±12.9 (7.69–66.3)	9.86±3.17 (6.12–19.2)	0.75±0.32 (0.21–1.32)	0.64±0.24 (0.07–1.09)	0.69±0.42 (0.24–1.64)	80.3±30.0 (36.8–137)	152±22.0 (116–194)
	15	S	1.95±1.04 (0.82–3.76)	0.93±0.39 (0.36–1.74)	0.32±0.25 (0.06–1.02)	17.4±6.50 (3.60–34.3)	10.1±3.54 (5.68–19.2)	0.62±0.33 (0.12–1.06)	0.37±0.18 (0.03–0.67)	0.40±0.35 (0.06–1.17)	34.0±13.0 (14.5–73)	109±18.1 (85.6–147)
	3	So	7.14±0.40 (6.76–7.57)	0.42±0.02 (0.37–0.45)	0.35±0.10 (0.24–0.45)	1.15±0.10 (1.04–1.32)	70.3±12.5 (61.0–84.6)	3.54±0.20 (3.30–3.74)	0.63±0.20 (0.51–0.80)	1.61±0.20 (1.49–1.83)	3858±20.5 (3835–3875)	13.0±2.37 (11.4–15.9)

Table 3
Trace metal concentrations (mg kg^{-1} dry wt.) in the fruiting bodies (C—cap, S—stalk) of bay bolete, *Xerocomus badius* (Fr.) Kühn. ex Gilb. from selected forest areas of Poland (*N*—number of samples)

Sample location	*N*		±S.D. (range)									
			Pb	Cd	Ag	Cu	Mn	Cr	Co	Ni	Fe	Zn
Tucholskie Forest	15	C	1.69±1.21	0.81±0.40	1.41±0.74	44.0±25.0	17.2±4.40	0.60±0.31	0.49±0.24	1.09±0.52	79.0±36.9	230±55.0
			(0.53–3.12)	(0.54–1.60)	(0.63–3.70)	(21.9–68.0)	(9.50–24.5)	(0.24–1.12)	(0.18–0.88)	(0.60–2.54)	(28.4–140)	(140–310)
	15	S	2.80±1.52	0.54±0.03	0.67±0.45	24.1±12.1	20.0±5.20	0.43±0.25	0.31±0.16	0.57±0.29	67.4±34.0	180±62.4
			(1.03–5.12)	(0.51–0.57)	(0.24–2.10)	(2.50–74.0)	(13.0–32.9)	(0.07–0.88)	(0.09–0.63)	(0.22–1.08)	(17.8–122)	(86.9–300)
Kaszubskie Forest	15	C	0.50±0.06	1.40±0.60	0.92±0.76	27.0±17.1	9.80±3.20	0.58±0.34	0.44±0.26	0.52±0.26	40.6±19.3	130±64.0
			(0.43–0.56)	(0.65–2.60)	(0.17–3.10)	(6.50–53.0)	(6.50–14.0)	(0.05–1.12)	(0.04–0.86)	(0.15–1.26)	(10.4–84.2)	(17.9–200)
	15	S	2.20±0.74	1.00±0.50	0.66±0.57	32.9±19.0	15.4±3.21	0.49±0.33	0.29±0.20	0.33±0.19	36.8±16.8	230±82.3
			(0.57–4.50)	(0.36–2.00)	(0.09–2.05)	(5.50–69.0)	(13.0–20.4)	(0.02–1.02)	(0.07–0.68)	(0.11–0.86)	(8.56–56.3)	(78.0–480)
Zaborski Landscape Park	10	C	1.56±0.94	0.81±0.49	1.20±0.58	65.1±11.2	13.3±5.60	0.43±0.09	0.39±0.16	1.17±0.63	97.2±45.9	225±123
			(0.68–2.31)	(0.31–1.96)	(0.29–2.07)	(45.6–76.5)	(7.92–22.7)	(0.20–0.56)	(0.15–0.77)	(0.50–2.46)	(51.4–163)	(115–450)
	10	S	1.39±0.68	0.40±0.29	0.45±0.20	30.3±6.70	15.1±5.64	0.44±0.18	0.38±0.22	0.92±0.75	97.4±63.1	207±50.0
			(0.18–2.44)	(0.11–1.05)	(0.23–0.89)	(19.9–44.4)	(6.82–23.1)	(0.18–0.73)	(0.09–0.79)	(0.25–2.75)	(27.2–196)	(132–287)
Trojmiejski Landscape Park	15	C	8.15±2.80	1.67±0.27	1.16±0.84	44.4±18.0	18.4±15.8	0.56±0.36	0.57±0.37	1.01±0.55	183±112	188±54.5
			(3.45–14.4)	(1.31–2.21)	(0.29–3.42)	(13.6–78.4)	(8.60–71.6)	(0.03–1.22)	(0.06–1.26)	(0.46–2.36)	(46.7–450)	(114–305)
	15	S	7.92±1.92	1.53±0.47	0.64±0.58	29.5±18.4	52.7±51.9	0.71±0.36	0.46±0.24	0.81±0.34	205±153	125±45.3
			(4.41–10.3)	(0.89–2.42)	(0.23–2.44)	(8.40–74.0)	(11.4–191)	(0.22–1.68)	(0.03–0.94)	(0.33–1.44)	(72.2–610)	(65.6–228)

Table 4
Trace metal concentrations (mg kg^{-1} dry wt.) in the fruiting bodies (C—cap, S—stalk) of bay bolete, *Xerocomus badius* (Fr.) Kühn. ex Gilb., and in the underlying substratum (So) from selected forest areas of Poland (*N*—number of samples)

Sample location	*N*		±S.D. (range)									
			Pb	Cd	Ag	Cu	Mn	Cr	Co	Ni	Fe	Zn
Adjacent area of Kolobrzeg	7	C	0.42±0.18 (0.13–0.69)	1.03±0.27 (0.75–1.34)	1.02±0.46 (0.62–1.91)	44.4±8.03 (32.4–53.9)	13.4±3.08 (10.2–18.7)	0.41±0.27 (0.21–1.01)	0.76±0.12 (0.55–0.92)	0.54±0.28 (0.25–0.94)	97.3±34.2 (63.4–166)	184±15.6 (156–197)
	7	S	0.89±0.47 (0.31–1.51)	0.47±0.19 (0.30–0.85)	0.28±0.21 (0.10–0.73)	20.4±4.29 (12.9–26.0)	25.8±6.64 (15.5–33.9)	0.55±0.20 (0.30–0.92)	0.55±0.09 (0.47–0.69)	0.52±0.30 (0.20–1.02)	118±24.1 (90.5–164)	132±11.8 (119–148)
	4	So	8.99±0.70 (8.05–9.50)	0.33±0.03 (0.31–0.37)	0.23±0.02 (0.18–0.27)	1.38±0.20 (1.20–1.64)	28.4±3.40 (25.1–32.5)	4.23±0.80 (3.35–4.90)	0.82±0.04 (0.79–0.90)	1.61±0.90 (0.63–2.73)	3498±574 (2854–4226)	26.1±6.70 (18.7–32.4)
Wolinski National Park	21	S	0.54±0.38 (0.10–1.54)	2.10±1.65 (0.21–5.30)	1.37±0.47 (0.44–2.19)	50.6±14.3 (18.7–78.6)	8.81±2.76 (2.18–13.9)	0.16±0.07 (0.05–0.28)	0.52±0.29 (0.08–1.06)	0.53±0.30 (0.07–1.23)	61.1±36.7 (28.0–160)	182±42.7 (106–298)
	21	C	1.57±0.93 (0.66–3.90)	0.96±0.88 (0.03–3.15)	0.53±0.50 (0.03–2.18)	22.7±6.06 (5.88–32.4)	19.5±9.84 (4.87–39.8)	0.31±0.20 (0.11–0.82)	0.31±0.21 (0.03–0.90)	0.76±0.45 (0.08–1.55)	79.2±30.3 (37.8–135)	121±24.3 (82.1–163)

centrations of Ni were the highest in caps and stalks from Ilawskie Lake district, 1.56 and 1.61 mg kg^{-1}, respectively. However, the lowest levels of Ni were determined in caps (0.33 mg kg^{-1}) and stalks (0.23 mg kg^{-1}) from Augustowska Forest. The results presented in this paper are generally lower than those obtained by Vetter (1997) and are comparable with data published by Kalač and Svoboda (1998). For instance, the estimated high values of Fe in caps (207 mg kg^{-1}) from Ilawskie Lake district and in stalks (205 mg kg^{-1}) from Trojmiejski Landscape Park are similar to the values measured by Kalač and Svoboda (1998). The highest concentration of Zn, amounting to 230 mg kg^{-1} in caps from Tucholskie Forest and stalks from Kaszubskie Forest, accords well with the data reported by Statkiewicz and Gayny (1994) for wild growing mushrooms from several areas of Poland. The concentration of Na was the highest in caps collected in Bialowieska Forest and in stalks from Borecka Forest, i.e., 509 and 1083 mg kg^{-1}, respectively. The lowest values of Na were obtained in the fruiting bodies from Kaszubskie Forest, i.e., 269 mg kg^{-1} in caps and 419 mg kg^{-1} in stalks. Potassium was the metal showing higher levels in fruiting bodies of bay bolete, with values ranging from 22.5 to 35.1 g kg^{-1} in caps and from 14.4 to 32.1 g kg^{-1} in stalks. The highest concentrations were found in samples from Wolinski National Park and the adjacent area of Morag, while the lowest are from Borecka Forest and Wdzydzki Landscape Park. The levels of Ca were the highest in caps from Wdzydzki Landscape Park and in stalks from Bialowieska Forest, amounting 153 and 216 mg kg^{-1}, respectively. The lowest amounts of Ca were observed in caps from Augustowska Forest—33.6 mg kg^{-1} and in stalks from Borecka Forest—95.9 mg kg^{-1}. The concentrations of Mg in caps and stalks ranged from 162 to 648 and 84.6 to 356 mg kg^{-1}, respectively. The lowest concentrations were obtained in caps and stalks from Borecka Forest while the highest levels were in caps collected in the adjacent area of Morag and in stalks from Bialowieska Forest. As for concentrations of macroelements in the fruiting bodies of *X. badius*; these data are similar to those published by Lasota and Florczak (1984). Also this is in agreement with results reported by Vetter (1994) for the family *Boletaceae*, although Michelot, Siobud, Dore, Viel, and Poirier (1998) obtained higher levels of Mg than those found in this study.

3.2. Metal concentrations in soil

The contents of 14 metals in soil samples examined are given in Tables 1, 2 and 4–6. The highest level of Pb found was 18.4 mg kg^{-1} in soil samples from Ilawskie Lake district. Pollution with Pb is observed in industrial areas where Pb is released into the atmosphere due to human activities. Natural amounts of Pb in soil range

Table 5
Trace metal concentrations (mg kg^{-1}, *g kg^{-1} dry wt.) in the fruiting bodies (C—cap, S—stalk) of bay bolete, *Xerocomus badius* (Fr.) Kühn. ex Gilb., and in the underlying substratum (So) from selected forest areas of Poland (*N*—number of samples)

Sample location	*N*		±S.D. (range)			
			Na	*K	Ca	Mg
Augustowska Forest	16	C	493±88.0 (351–740)	30.5±3.90 (22.2–38.5)	33.6±20.6 (13.5–63.3)	608±65.0 (256–742)
	16	S	859±384 (376–1716)	27.4±5.90 (19.2–40.8)	113±49.6 (26.2–168)	295±29.0 (254–344)
	4	So	469±11.2 (460–484)	0.68±0.10 (0.59–0.83)	144±29.0 (117–172)	248±42.6 (209–301)
Bialowieska Forest	11	C	509±266 (123–773)	30.2±8.30 (20.0–51.8)	142±62.0 (70.4–304)	574±132 (325–746)
	11	S	843±313 (274–1130)	23.9±3.00 (19.9–28.0)	216±57.0 (122–329)	356±86.0 (222–532)
	5	So	317±52.8 (245–386)	1.10±0.11 (0.99–1.24)	202±34.8 (175–261)	356±47.7 (275–400)
Borecka Forest	15	C	599±162 (376–1004)	22.5±5.30 (14.1–35.2)	46.8±17.0 (27.0–95.0)	162±23.0 (103–193)
	15	S	1083±329 (596–1432)	21.8±6.40 (12.9–37.5)	95.9±26.0 (60.0–159)	84.6±11.0 (58.0–108)
	7	So	369±41.8 (315–448)	0.70±0.10 (0.58–0.89)	106±21.5 (78.8–137)	302±57.3 (227–354)
Adjacent area of Morag	16	C	585±252 (311–1069)	32.2±3.40 (20.3–40.7)	116±65.0 (25.1–263)	648±59.0 (534–756)
	16	S	2516±1396 (528–4480)	32.1±9.90 (13.4–49.9)	201±112 (49.9–443)	272±56.0 (144–346)
	4	So	630±48.4 (579–694)	0.69±0.32 (0.65–0.73)	124±44.1 (65.4–159)	210±35.1 (169–254)
Ilawskie Lake district	10	C	391±108 (254–553)	30.2±2.30 (23.4–33.2)	79.8±22.0 (39.4–112)	587±23.0 (560–617)
	10	S	807±271 (369–1098)	28.7±2.90 (20.7–33.4)	215±62.0 (131–306)	291±35.0 (252–342)
	4	So	596±24.3 (529–664)	0.72±0.22 (0.66–0.73)	148±32.1 (131–160)	238±42.6 (184–260)

from 20 to 25 mg kg^{-1} (Kabata-Pendias & Pendias, 1999). The average concentrations of Cd in the soil studied ranged from 0.12 mg kg^{-1} in Augustowska Forest to 0.42 mg kg^{-1} in Wdzydzki Landscape Park. The highest concentrations of Cd were measured by Kot (1999). A significant effect on Cd concentration in soil is caused by its level in the bed rock. Intake of pollutants from anthropogenic sources, especially from the phosphatic fertiliser industry or sewage disposal, can locally increase concentration of Cd in soil. The content of Ag ranged from 0.23 mg kg^{-1} in soil from the adjacent area of Kolobrzeg to 0.40 mg kg^{-1} in soil from Ilawskie Lake district. Silver is known to be accumulated in the surface soil layer because of its low mobility (Kabata-Pendias & Pendias, 1999).

Copper, Cr, Ni, Co, Fe and Zn exhibited high levels in soil samples from Bialowieska Forest, amounting to 3.50, 6.84, 2.07, 0.89, 6000 and 29.7 mg kg^{-1}, respectively. The average concentrations of Mn in soil samples ranged from 28.4 mg kg^{-1} in the adjacent area of Kolobrzeg to 158 mg kg^{-1} in Augustowska Forest. The highest concentrations of K and Mg, namely 1104 and 356 mg kg^{-1}, respectively, were determined in soil from Bialowieska Forest. The average concentration of Na in the soil studied was 466 mg kg^{-1} while the highest value of 630 mg kg^{-1} was measured in soil from the adjacent area of Morag. Concentrations of Ca in the soils from all the studied areas were very similar and ranged from 106 mg kg^{-1} in Borecka Forest to 222 mg kg^{-1} in the adjacent area of Kolobrzeg. Based on literature data it is concluded that a significant portion of Pb, Cd or Zn in the soil is derived from atmospheric deposition. Other elements, namely Cu, Cr, Ni, Fe, Zn or Mn, may be mainly supplied from the bed rock or the original material of the soil (Yoshida & Muramatsu, 1997). It is assumed that the concentration data in soil samples presented in this study are mainly attributable to natural origin, except for Pb in substratum from Trojmiejski Landscape Park.

3.3. Metals cap to stalk quotients

In order to indicate differences in the accumulative abilities of elements in particular morphological parts of fruiting body, cap metal to stalk metal ratios were estimated and are presented in Table 7. The cap to stalk ratios for metals such as Cd, Ag, Cu, Cr, Co, Ni, Fe, Zn, K and Mg were greater than unity. The ratios for Pb, Mn, Na and Ca were close to or below 1. These results indicate that caps have higher metal levels as compared to stalks of *X. badius*.

3.4. Bioconcentration factors (BCF)

In order to estimate the accumulation of each element by the fruiting body of bay bolete, *Xerocomus badius*, BCF were calculated according to the formula:

$$BCF = \frac{M_{C,S}}{M_{SO}}$$

where $M_{C,S}$ is the mean concentration of metal in cap (c) or stalk (s) and M_{so} is the mean concentration of the metal in the soil (so) on a dry weight basis. The calculated BCFs for 14 elements are summarised in Table 7. The BCFs of Pb, Mn, Cr, Co, Ni, Fe and Ca in caps were less than 1 (from 0.02 to 0.95). The BCFs of Cd, Ag, Cu, Zn, Na, K and Mg in caps were greater than 1.

Table 6
Macroelement concentrations [mg kg^{-1}, *g kg^{-1} dry wt.] in the fruiting bodies (C—cap, S—stalk) of bay bolete, *Xerocomus badius* (Fr.) Kühn. ex Gilb., and in the underlying substratum (So) from selected forest areas of Poland (*N*—number of samples)

Sample location	*N*		±SD (range)			
			Na	*K	Ca	Mg
Wdzydzki Landscape Park	15	C	387±101 (273–684)	25.2±7.00 (15.1–39.5)	153±32.0 (98.8–200)	328±52.0 (254–466)
	15	S	523±149 (314–786)	14.4±4.20 (9.63–24.2)	150±25.0 (112–186)	165±30.0 (130–226)
	3	So	480±12.0 (470–493)	0.42±0.08 (0.41–0.43)	179±15.6 (162–193)	231±14.0 (217–245)
Tucholskie Forest	15	C	392±54.0 (278–463)	28.4±5.10 (20.8–39.7)	77.5±16.0 (50.4–101)	261±60.0 (179–406)
	15	S	531±70.0 (380–626)	19.8±2.70 (13.4–22.4)	124±17.0 (97.2–149)	150±36.0 (89.0–215)
Kaszubskie Forest	15	C	269±60.0 (189–413)	29.4±5.80 (18.9–39.6)	90.9±21.0 (52.3–122)	368±89.0 (227–512)
	15	S	419±102 (238–692)	22.1±6.00 (13.6–33.1)	122±30.0 (64.5–165)	222±66.0 (145–369)
Zaborski Landscape Park	10	C	305±133 (117–591)	25.6±6.90 (18.1–31.7)	115±48.0 (22.9–166)	233±65.0 (97.6–321)
	10	S	432±196 (290–466)	14.0±4.80 (6.64–26.4)	173±115 (35.2–351)	154±62.0 (72.0–293)
Trojmiejski Landscape Park	15	C	280±42.0 (200–367)	23.5±4.40 (15.8–31.0)	89.6±18.0 (65.5–116)	498±122 (381–686)
	15	S	431±96.0 (318–636)	15.9±2.90 (10.6–18.7)	111±17.0 (84.4–134)	284±87.0 (159–436)
Adjacent area of Kolobrzeg	7	C	495±157 (353–716)	26.3±1.20 (25.0–28.0)	78.6±28.0 (46.4–121)	560±44.0 (501–638)
	7	S	853±219 (579–1108)	22.3±2.00 (18.7–25.2)	128±24.0 (88.5–148)	310±31.0 (278–363)
	4	So	532±46.9 (468–576)	0.66±0.49 (0.61–0.71)	222±15.3 (199–232)	222±53.6 (168–296)
Wolinski National Park	21	C	356±116 (198–675)	35.1±3.80 (33.3–40.0)	51.8±25.0 (18.2–109)	496±45.0 (393–581)
	21	S	692±388 (307–1350)	30.5±5.70 (19.2–38.5)	96.4±47.0 (26.9–168)	311±59.0 (179–409)

Accumulation of Cd, Ag, Na and Mg in caps was lower than those of K (41.9), Cu (23.9) and Zn (9.45).

3.5. Statistical evaluation of the data

Statistically significant correlations ($P<0.001$, $P<0.01$ and $P<0.05$) between concentrations of the metals studied in the caps and stalks of bay bolete, *Xerocomus badius*, and underlying soil substratum are listed in Table 8. Significant positive correlations ($P<0.001$) were observed between the concentrations of Cd and Ca in caps and the associated soil as a substratum. No significant relationships were noted between concentrations of Pb, Ag, Mn, Co, Ni, Zn, Na and Mg in caps and the underlying soil. Significant negative correlations ($P<0.001$) were found for the concentrations of Fe in caps and soil. Significant positive correlations ($P<0.001$) were observed between the concentrations of Cd, Na, K and Ca in stalks and those in the surrounding soil. The data obtained after processing metal concentrations by discriminant function analysis for caps, stalks and soil are illustrated in Figs. 2–4. In the caps, the functions F_1, F_2 and F_3 explained 75.8% of the total variance. The lowest values of function F_1 (Fig. 2) describe samples from Trojmiejski Landscape Park and the adjacent area of Morag with the highest levels of Pb and Mg. In stalks, the functions F_1, F_2 and F_3 explained 67.9% of the total variance. Data from Zaborski Landscape Park, discriminated by the high value of F_1 (Fig. 3), are clearly separated from other data by high levels of Zn. The high value of F_2 discriminate samples from Trojmiejski Landscape Park by high levels of Pb. Discriminant analysis of soil sample data (Fig. 4) shows that the functions F_1, F_2 and F_3 explained 91.3% of the total variance. The function F_1 discriminated data attributable to the adjacent area of Morag and Ilawskie Lake district by high levels of Na. The highest and lowest values of F_2 identify objects from Augustowska Forest and Ilawskie Lake district (with the greatest concen-

Table 7
Cap-stalk ratio (C/S) and bioconcentration factor (BCF) values for caps and stalks in bay bolete, *Xerocomus badius* (Fr.) Kühn. ex Gilb

Metal	C/S		BCF^C		BCF^S	
		(range)		(range)		(range)
Pb	0.72	(0.20–2.00)	0.13	(0.01–0.47)	0.19	(0.02–1.27)
Cd	2.18	(0.54–8.55)	2.70	(0.25–11.8)	1.43	(0.17–4.65)
Ag	2.75	(0.43–8.90)	2.41	(0.31–9.84)	1.07	(0.05–7.19)
Cu	2.54	(1.00–5.40)	23.9	(3.82–57.7)	10.2	(1.67–29.7)
Mn	0.69	(0.20–1.59)	0.23	(0.05–0.75)	0.39	(0.07–1.19)
Cr	1.07	(0.23–2.99)	0.10	(0.02–0.36)	0.10	(0.02–0.30)
Co	1.80	(0.44–4.35)	0.95	(0.06–5.26)	0.70	(0.05–5.26)
Ni	1.89	(0.48–6.48)	0.54	(0.01–2.80)	0.38	(0.001–2.83)
Fe	1.54	(0.30–5.26)	0.02	(0.01–0.11)	0.01	(0.004–0.07)
Zn	1.44	(0.97–2.58)	9.45	(3.15–24.2)	6.54	(2.50–18.0)
Na	0.59	(0.11–1.40)	1.15	(0.39–3.13)	2.34	(0.64–7.10)
K	1.28	(0.42–2.61)	41.9	(18.2–93.8)	34.7	(18.1–73.4)
Ca	0.62	(0.13–1.18)	0.58	(0.10–2.12)	1.03	(0.17–7.01)
Mg	2.00	(0.50–4.54)	1.93	(0.33–3.60)	0.97	(0.18–1.65)

Table 8
Significant correlations between metal concentrations in the caps, stalks of bay bolete, *Xerocomus badius* (Fr.) Kühn. ex Gilb. and its concentrations in soil

Cap to soil		Stalk to soil	
Pb	Cd(+)**, Mn(−)**, Ag(+)*, Cr(−)**, Co(−)***, Ni(−)***, Fe(−)***, Zn(−)***, Hg(+)***, Na(+)***, K(−)*, Ca(−)***, Mg(−)***	Pb	Cd(+)*, Mn(−)*, Co(−)***, Ni(−)***, Fe(−)***, Zn(−)**, Hg(+)***, Na(+)***, Mg(−)*
Cd	Cd(+)***, Pb(−)***, Mn(−)***, Cu(−)**, Cr(−)**, Fe(−)**, Zn(−)*, K(−)**, Na(+)*, Mg(−)**	Cd	Pb(−)***, Cd(+)***, Cu(−)***, Mn(−)***, Cr(−)***56, Fe(−)**, Zn(−)*, Hg(+)**, K(−)***, Mg(−)**
Ag	Cu(+)***,Cr(+)***, Co(+)**, Ni(+)*, Fe(+)*, Zn(+)***, K(+)***, Ca(+)***, Mg(+)***	Ag	Pb(−)*, Cu(+)***, Cr(+)***, Co(+)**, Ni(+)**, Fe(+)**, Zn(+)***, K(+)***, Na(−)**, Ca(+)***, Mg(+)***
Cu	Cu(+)*, Ca(+)*	Cu	Ag(−)*, Cu(+)**, Hg(+)*, K(+)*, Ca(+)***, Mg(+)*
Mn	Pb(+)*, Cu(+)***, Cr(+)***, K(+)***, Ca(+)*	Mn	Pb(+)**, Cu(+)***, Cr(+)***, Ni(+)*, Fe(+)*, Zn(+)***, Hg(+)**, K(+)***, Mg(+)***
Cr	Pb(−)***, Cd(+)***, Cr(−)**, Ni(−)**, Zn(−)***, K(−)***, Na(+)*, Ca(+)*, Mg(−)**	Cr	Cd(+)**, Zn(−)*, Na(+)*, Ca(+)***
Co	Cd(+)**, Mn(−)***, Fe(−)**, Hg(+)*, Na(+)***, Ca(+)**, Mg(−)*	Co	Cd(+)*, Mn(−)***, Fe(−)***, Zn(−)**, Na(+)***, Mg(−)**
Ni	Cd(+)*, Ag(+)**, Cu(+)**, Mn(−)***, Cr(+)*, Co(−)**, Fe(−)*, Hg(+)**, Na(+)*	Ni	Pb(+)***, Ag(+)**, Mn(−)***, Co(−)**, Fe(−)**, Na(+)***
Fe	Pb(+)*, Ag(+)**, Mn(−)***, Co(−)**, Ni(−)*, Fe(−)***, Hg(+)***, Na(+)**	Fe	Cu(+)***, Mn(−)*, Cr(+)***, Co(+)**, Ni(+)***, Fe(+)**, Zn(+)***, Hg(+)***, K(+)***, Mg(+)***
Zn	Pb(+)***, Cd(−)**, Co(−)***, Ni(−)***, Fe(−)**, Na(+)***, Mg(−)***	Zn	Pb(+)**, Co(−)***, Ni(−)**, Fe(−)***, Na(+)***, Mg(−)**
Hg	Pb(−)**, Cd(+)**, Cu(−)**, Hg(+)***, Cr(−)**, Ni(+)*, K(−)**, Ca(+)**	Hg	Pb(−)**, Cd(+)**, Cu(−)**, Cr(−)**, Co(+)**, Ni(+)**, Hg(+)***, K(−)***, Ca(+)***
Na		Na	Mn(−)*, Co(−)***, Ni(−)***, Fe(−)***, Zn(−)**, Na(+)***, Ca(−)*
K	Pb(+)*, Cd(−)*, Cu(+)**, Co(−)*, Ni(−)**, Hg(−)**, K(+)*	K	Pb(+)***, Cd(−)**, Ag(+)*, Cu(+)*, Co(−)***, Ni(−)***, Fe(−)*, Hg(−)**, K(+)***, Na(+)***, Ca(−)**
Ca	Pb(−)***, Cd(+)***, Ca(+)***	Ca	Cr(+)**, Cu(+)***, K(+)*, Na(+)**, Ca(+)***
Mg	Pb(+)***, Cd(−)***, Cu(+)***, Co(−)***, Ni(−)***, Fe(−)*, Zn(−)**, Na(+)***, K(+)**, Ca(+)**	Mg	Pb(+)***, Cd(−)***, Ag(−)***, Cu(+)***, Mn(+)**, Cr(+)**, K(+)***, Ca(+)***, Mg(+)*

(+) = positive correlation (−) = negative correlation.
* $P<0.05$; ** $P<0.01$; *** $P<0.001$.

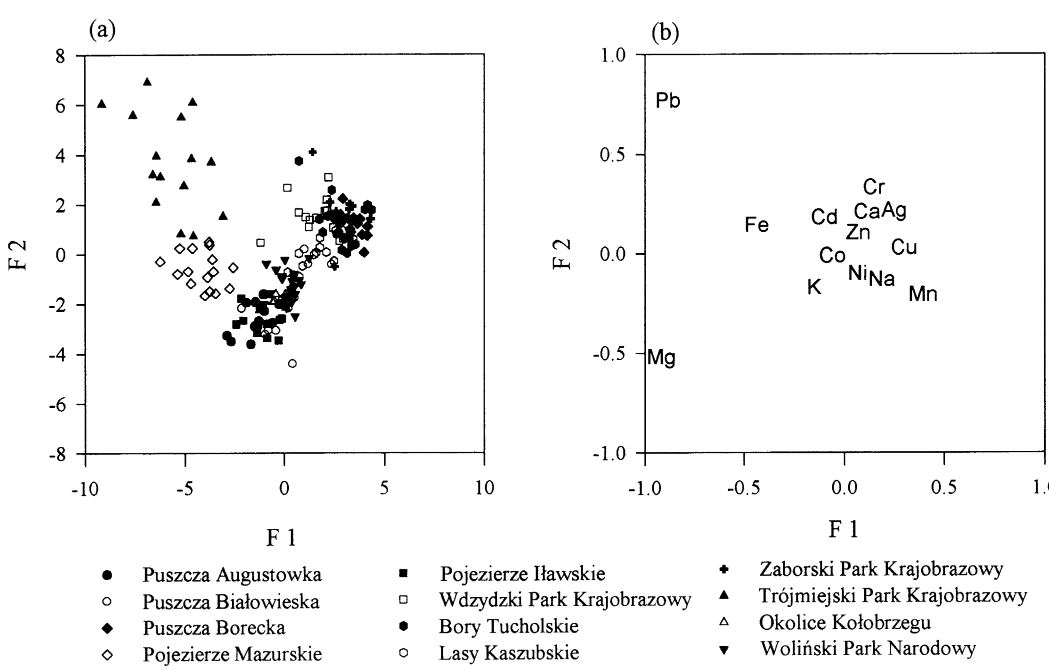

Fig. 2. (a) Scatterplot of object scores of the two first discriminant functions of 166 samples of caps; (b) location loadings for 14 metals in the caps.

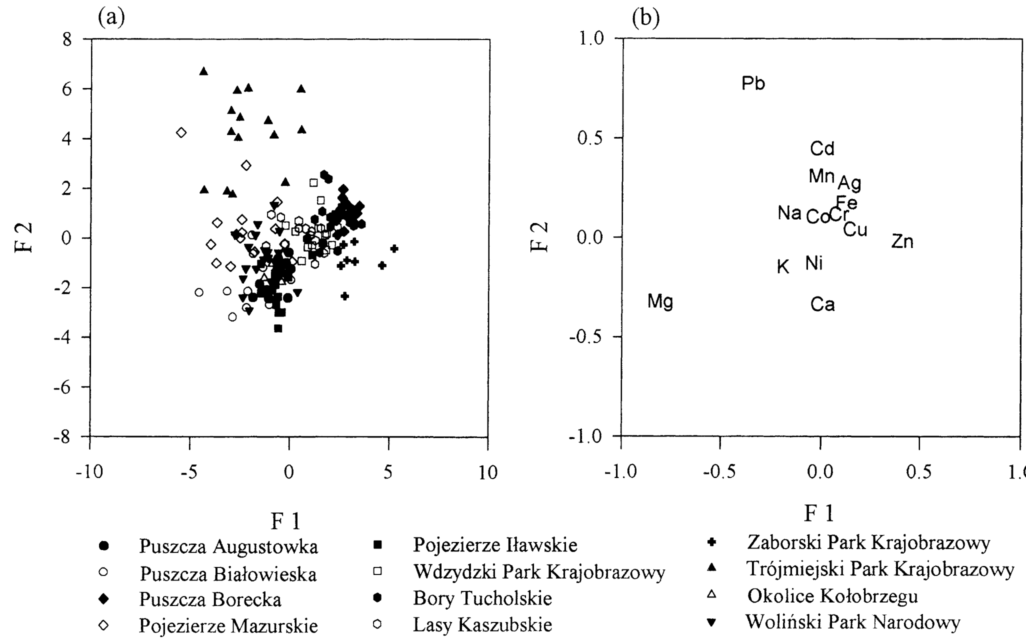

Fig. 3. (a) Scatterplot of object scores of the two first discriminant functions of 166 samples of stalks; (b) location loadings for 14 metals in the stalks.

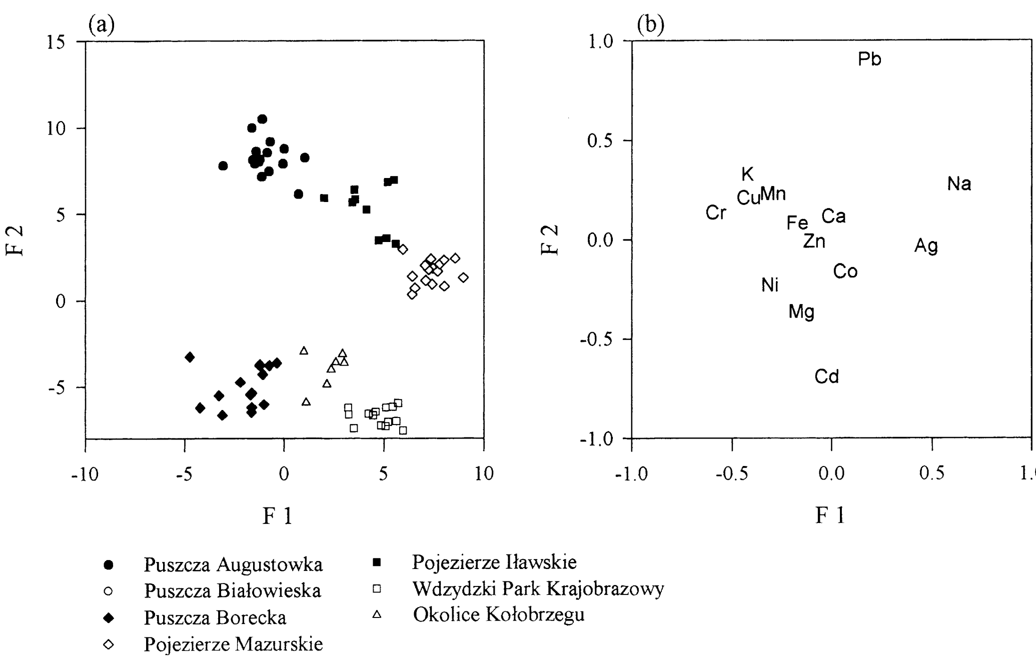

Fig. 4. (a) Scatterplot of object scores of the two first discriminant functions of 90 samples of soil; (b) location loadings for 14 metals in soil.

tration of Pb) and objects from Borecka Forest, Wdzydzki Landscape Park and the adjacent area of Kolobrzeg (with greatest concentration of Cd).

The cluster analysis results (hierarchical clustering, Ward's method) for the sampling sites as objects are shown in Fig. 5. The dendrogram is built up of two main clusters.

The first one contains two subclusters with the objects from Ilawskie Lake district (C59–C68) and the adjacent area of Morag (C43–C58), the most similar regions by environmental conditions. A second cluster contains five subclusters with the objects from Augustowska Forest (C1–C16), Bialowieska Forest (C17–C27), Borecka Forest (C28–C42), Wdzydzki Landscape Park (C69–C83) and the adjacent area of Kolobrzeg (C139–C145). The most similar regions were separated. Augustowska and Bialowieska Forests are protected areas, deprived of industrial or urban influences.

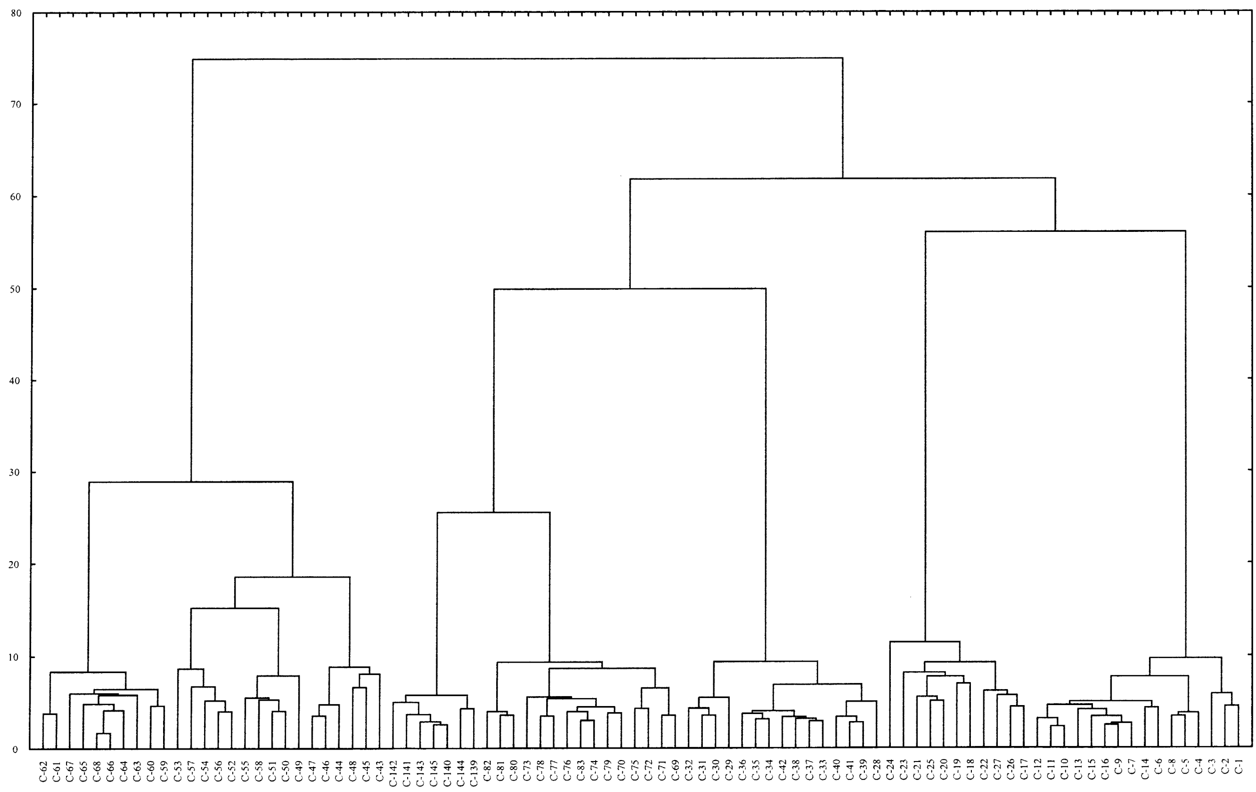

Fig. 5. Hierarchical dendrogram for 90 sampling sites as objects (1–16 Augustowska Forest, 17–27 Bialowieska Forest, 28–42 Borecka Forest, 43–58 Adjacent area of Morag, 59–68 Ilawskie Lake district, 69–83 Wdzydzki Landscape Park, 139–145 Adjacent area of Kolobrzeg).

4. Discussion

Concentrations of some metals in *X. badius* were locally elevated and seem to be hardly influenced by soil metal content. The levels of elements such as Cd, Ag, Cu, Co, Ni, Fe, Zn, K and Mg in caps were generally higher than those in stalks. The fruiting bodies of *Xerocomus badius* tended to accumulate Cd, Ag, Cu, Zn, Na, K and Mg; the BCFs estimated in this study are greater than unity. No bioconcentration of Pb, Mn, Cr, Co, Ni, Fe and Ca relative to the adjacent soil was observed in *X. badius*—the BCFs values were less than 1.

Most of the examined metals in the caps and stalks showed significant correlation with concentrations in soil. The studied fruiting bodies of *X. badius* were to, different degrees, polluted by Pb and Cd. The data warranted making a base of objects in which detained analysis showed separate features, identifying sources of material to be taken for the study. Discriminant function analysis was useful for identifying elements typical for the objects (samples) representative for selected forest areas. For example, an identifier of samples collected in Trojmiejski Landscape Park is Pb, anthropogenic in origin. Lead is emitted in significant amounts into the air as a result of burning car petrol containing tetraethyl lead.

Cluster analysis made it possible to separate the most similar forest areas in relation to chemical composition of both the underlying soil substratum and biomass overgrown with *X. badius* in the studied areas.

The results obtained imply that *X. badius* could be used as a sensitive bioindicator for environmental monitoring of heavy metal pollution, especially Pb.

The principal factor governing the accumulation of heavy metals in macrofungi is contamination by atmospheric deposition. Apart from anthropogenic factor, the natural effects, such as mineral composition of bed rock, pH and granulometric character of soil, genetic potential of fungi, ectomycorrhizal occurrence and the kind of undergrowth (mosses, lichens, ferns) have a real influence on some metal contents of mushrooms.

4.1. Toxicological risks

In Poland, there is a recommendation about the concentration of some heavy metals in fresh and dried mushrooms. The tolerance limits set for Pb, Cd and Zn in dried mushrooms are 2.0, 1.0 and 150 mg kg^{-1}, respectively (Dziennik Ustaw No. 9, poz. 72, 2001). In accordance with recommendation of FAO/WHO (Raport, 1996) a provisional tolerable weekly intake (PTWI) for Pb is 25 μg kg^{-1} of body weight for an adult, i.e., 1.5 mg weekly for a 60 kg person. The results obtained in this study showed that mushrooms collected from Trojmiejski Landscape Park and the adjacent area of Morag, containing the greatest lead concentrations, considerably exceed the tolerance limit for edible higher mushrooms. A provisional tolerable weekly intake for Cd is 7 μg kg^{-1} of body weight for an adult, i.e. 420 μg weekly. A portion of 300 g fresh mushrooms, containing 1.4 mg Cd for kg, provides all the weekly tolerable intake of Cd. According to the present knowledge, Cd and Pb are not necessary for metabolic processes in the human organism and their toxicity depends on the dose and capacity for accumulation in some organs. On the other hand, Zn is an essential microelement in the human diet and the recommended doses per day for an adult vary from 13 to 16 mg (Panczenko-Kresowska, 2001). Based on Zn concentration in the studied mushrooms, 10 g of dried mushrooms provides 14.1–33.2% of the recommended daily intake of Zn for an adult person.

Mushrooms are very popular and are often used for garnishing of dishes to alter the aroma and taste. They are collected in the rural areas, especially by villagers where the consumption of mushrooms can be periodically increased. Also, some species of wild growing mushrooms are available in markets during all seasons, as dried, frozen or pickled products. Mushrooms from the polluted areas should not be collected and consumed at all. It is necessary to control the concentrations of essential elements as well as toxic metals in natural food products, to evaluate exposure of some populations and to protect human health.

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