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HEAVY METALS IN EDIBLE FRUITS. A CASE STUDY OF BILBERRY *VACCINIUM MYRTILLUS* L.

METALE CIĘŻKIE W OWOCACH JADALNYCH NA PRZYKŁADZIE BORÓWKI CZARNEJ *VACCINIUM MYRTILLUS* L.

Słowa kluczowe: borówka czarna, metale ciężkie, jagody.
Key words: bilberry, heavy metals, berries.

Prezentowane w opracowaniu badania miały na celu określenie zawartości metali ciężkich w owocach jadalnych. Zbadano zawartość Fe, Mn, Cu, Zn, Ni i Pb w owocach borówki czarnej Vaccinium myrtillus L. oraz w glebie. Próby zebrano z dwóch stanowisk znajdujących się pod wpływem zanieczyszczenia pochodzącego z hut (huty miedzi w Głogowie oraz huty aluminium w Koninie) oraz dwóch względnie czystych stanowisk. Gleby z okolic hut zawierały więcej Zn, Mn, Fe, Cu i Ni niż gleby na stanowiskach niezanieczyszczonych. Stężenie Zn, Mn, Cu i Cd było wyższe w owocach zebranych w okolicy hut miedzi i aluminium niż w tych ze stanowisk czystych. Zawartość Zn i Mn w owocach była skorelowana z ich zawartością w glebie.

1. INTRODUCTION

Bilberry *Vaccinium myrtillus* L. (Ericaceae) is a deciduous perennial dwarf shrub, that is commonly found in the herbaceous layer, mainly in pine forests and mixed forests [Szmeja 1993]. Bilberry grows on acidic soils and does not flourish in wet conditions [Reimann et al. 2001]. Fruit is a purple-black, glaucous berry [Ritchie 1995]. Fructification of *Vaccinium myrtillus* lasts from July till September. Fruits are widely collected and consumed by people mainly because of their possible positive health effects [Seneta and Dolatowski 2006]. Therefore the content of heavy metals in consumed fruits seems to be important problem due to the risk of human diseases.

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Since 1968, when the Głogów copper smelter was built, it has been emitting metal-rich dusts into the atmosphere, which is the main source of heavy-metal pollution of the local environment. Dust emission from smelter had notably harmful influence on the natural environment in the early years of its activities. Since the beginning of 1990's, the emissions have been considerably reduced, mainly due to installation of new filters and some changes in process technology [Matkowski 1994, Lis and Pasieczna 2005]. Soils in the vicinity of Głogów copper smelter were found to be contaminated by lead, copper and zinc (rarely cadmium and mercury) [Lis et al. 1999]. Construction of Konin aluminium smelter started in 1960, and finished in 1966. In the first period of its operation the emission of fluorine exceeded 600 tons per year. The technological modernisation resulted in notable reduction of fluorine emission, and in 1993 it was 58 tons per year [Staszewski et al. 1998]. Damage to the vegetation near aluminium smelter is considered to be mainly caused by the emission of gaseous fluoride compounds and sulphur dioxide [Vike 1999].

The purpose of this study was to assess the influence of smelters on concentration of heavy metals in edible berries of *Vaccinium myrtillus*.

2. MATERIAL AND METHODS

2.1. Study area

The study was conducted in two polluted forest sites: about 10–13 km northeast from copper smelter in Głogów (SW Poland) and about 10–11 km northeast from aluminium smelter in Konin (SW Poland). Two relatively clean forest sites were about 10–12 km southwest from Milicz (SW Poland, near Skoroszów) and about 9–10 km northeast from Oława (SW Poland, near Janików).

Ten sampling sites were selected in polluted areas. The same number of sampling sites was selected in relatively non-polluted areas. At each site the bilberry was growing under the canopies of trees. Each sampling site consisted of five 1x1 m squares, from which fruit samples and soil samples (from depth of 0–10 cm) were randomly collected. The sites in the relatively clean areas represented the similar forest type as sampling sites in the vicinity of Cu-smelter and Al-smelter. All samples were collected in July 2008.

2.2. Plant analysis

Fruit samples of bilberry were dried at 50°C to a constant weight and homogenised in a laboratory mill (FexIKA M 20). The heavy metals were extracted using microwave digestion (CEM Mars 5) with HNO_3 (conc.) and HCl (conc.) in Teflon vessels. Total Fe, Mn and Zn levels were measured by flame atomic absorption spectrophotometery (FAAS; GBC Avanta PM), and Cu, Pb, Cd, Ni and Cr levels were measured by electrothermal atomic absorption spectrophotometery (ETAAS; GBC Avanta PM). All metals were measured against standards (BDH Chemicals Ltd, pro analyse quality) and blanks. All the analyses were done in duplicate. The reference material consisted of poplar leaves (GBW 07604).

2.3. Soil analysis

The soil samples were air-dried, sieved to 2 mm and ground to fine powder. Soil total Fe, Mn, Cu, Zn, Pb, Cd, Ni and Cr content was analysed using the same procedures as described for the plant samples. The reference material consisted of a soil (RTH907).

2.4. Statistical analysis

A *t* test was used to determine the significance of the differences between concentration of heavy metals of polluted and undisturbed sites. Pearson's correlations were calculated to examine the relationships between the concentration of the metals in the fruits and the corresponding soils [Sokal and Rohlf 2003]. All calculations were carried out on log-transformed data using STATISTICA (data analysis software system, StatSoft, Inc., ver. 7).

3. RESULTS AND DISCUSSION

The concentration of examined elements in soils and fruits are shown in Table 1.

The research revealed that soils from polluted and undisturbed sites differ significantly with respect to Cu, Fe, Mn, Ni and Zn content. The mean concentration of Cu in soils from polluted sites was as high as 9.94 $mg \cdot kg^{-1}$, whereas in soils from undisturbed sites amounts to 0.98 $mg \cdot kg^{-1}$. Although the difference between these values is rather high, both of them are within the range given by Kabata-Pendias and Pendias [1999] which is 1–25 $mg \cdot kg^{-1}$ (mean concentration in Polish soils is 6.5 $mg \cdot kg^{-1}$).

The content of Fe in soils from polluted areas ranged from 548 to 3429 $mg \cdot kg^{-1}$, while on relatively clean sites from 140 to 1079 $mg \cdot kg^{-1}$. According to Kabata-Pendias and Pendias [1999] the mean concentration of Fe in sandy soils of Poland is about 5700 $mg \cdot kg^{-1}$, therefore both of ranges are below the above-mentioned mean value. However, Lityński and Jurkowska [1982] give the widest range of Fe concentration in soils, which is 20–100 000 $mg \cdot kg^{-1}$.

In general, the soils studied herein, contain small amounts of Mn, which is 2.7 $mg \cdot kg^{-1}$ (unpolluted areas) and 48 $mg \cdot kg^{-1}$ (in vicinity of smelters). According to Markert [1992] the concentration of Mn in soils ranges from 20 to 3000 $mg \cdot kg^{-1}$, whereas Kabata-Pendias and Pendias [1999] report that sandy soils of Poland contain 15–1500 $mg \cdot kg^{-1}$.

The ranges of Ni concentration in relatively clean areas and in affected sites were 0.95–1.92 $mg \cdot kg^{-1}$ and 0.79–3.88 $mg \cdot kg^{-1}$, respectively, and was in the lower part of the range given by Kabata-Pendias and Pendias [1999], which is 1–52 $mg \cdot kg^{-1}$.

Table 1. Minima, maxima, mean values, standard deviations (SD) and *t* test of the concentration (mg·kg^{-1} d.w.) of heavy metals in the soil and in the fruits of *Vaccinium myrtillus* from unpolluted and polluted sites

Tabela 1. Minima, maksima, średnie, odchylenia standardowe (SD) oraz test *t* dla zawartości metali ciężkich w glebie i owocach *Vaccinium myrtillus* ze stanowisk czystych i zanieczyszczonych (mg·kg^{-1} s.m.)

Element		Unpolluted				Polluted				*t* value	p
		mean	max	min	SD	mean	max	min	SD		
Soil	Mn	2.65	3.77	0.69	0.96	48.4	86	26.5	22.52	-14.9	<0.001
	Fe	571	1079	140	303	2109	3429	548	961	-4.91	<0.001
	Zn	4.15	10.5	0.9	2.96	8.32	15.1	5.55	2.86	-3.49	<0.01
	Cd	0.04	0.08	0.01	0.02	0.03	0.08	0.01	0.02	1.58	0.13
	Cu	0.89	1.41	0.56	0.33	10.04	44.72	0.82	13.36	-3.37	<0.01
	Ni	1.4	1.92	0.95	0.36	2.22	3.88	0.79	0.88	-2.81	<0.05
	Pb	11.83	25.21	6.51	6.88	12.04	39.8	2.81	12.27	0.67	0.51
Fruits	Mn	84.1	130	52.1	26.86	374	574	282	90.12	-12.24	<0.001
	Fe	19.5	29.7	14.4	4.72	22.3	28.6	17.5	3.81	-1.58	0.13
	Zn	6.6	9.2	5.45	1.12	10.3	14.4	8.4	1.72	-6.29	<0.001
	Cd	0.02	0.03	0.01	0.01	0.05	0.09	0.02	0.02	-4.91	<0.001
	Cu	4.31	5.11	3.68	0.55	6.87	8.9	4.6	1.17	-6.63	<0.001
	Ni	0.39	1.25	0.05	0.31	0.52	0.97	0.25	0.28	-0.08	0.94
	Pb	0.86	2.65	0.12	0.75	1.34	2.73	0.6	0.66	-1.81	0.09

Although the soils from Głogów and Konin contained significantly higher concentration of Zn (mean 8.32 mg·kg^{-1}) than those from Milicz and Oława (mean 4–15 mg·kg^{-1}), both values are slightly below the range given by Kabata-Pendias and Pendias [1999] (10–200 mg·kg^{-1}).

The *t* test indicated that the relatively clean soils contained significantly lower concetrations of Cu, Fe, Mn, Ni and Zn.

The fruits from studied habitats differ significantly with respect to Cd, Cu, Mn, Zn.

The mean concentration of Cd in fruits from unpolluted sites was as high as 0.02 mg·kg^{-1}, and in vicinity of smelters 0.05 mg·kg^{-1}. The latter value is as high as reported by Barcan et al. [1998].

Although the berries from polluted areas contained significantly higher concentration of Cu (mean 6.87 mg·kg^{-1}) than those from Milicz and Oława (mean 4.31 mg·kg^{-1}), both values are slightly below mean given by Barcan et al. [1998] (9 mg·kg^{-1}) for fruits growing 83 km from smelter.

Mn concentration in berries growing in relatively clean areas ranged from 52 to 130 mg·kg^{-1}, whereas these from Głogów and Konin from 282 to 574 mg·kg^{-1}. According to Kabata-Pendias and Pendias [1999] the concentration of Mn in edible fruits ranges from 1.3 to 15 mg·kg^{-1}.

The level of Zn absorption by berries of *Vacccinium myrtillus* in relatively clean and polluted areas was found to be 5.5–9.2 mg·kg^{-1} and 8.4–14.4 mg·kg^{-1}, respectively. These levels were found to be within the physiological demand range of values given by Kabata-Pendias and Pendias [1999].

The *t* test indicated that the berries from polluted areas contain significantly higher concentrations of Cd, Cu Mn and Zn than berries from control sites. There was no element, which concentration in berries exceeded toxic levels, in respect to values presented by Kabata-Pendias and Pendias [1999].

Correlations between concentration of metals in soil and that in fruits are shown in Table 2. Positive correlations between Mn in soil and in fruits, and Zn in soil and fruits were found. Moreover, some negative correlations were identified as well.

Table 2. Statistically significant relations between concentrations of metals in the fruits and the corresponding soils

Tabela 2. Statystycznie istotne korelacje pomiędzy zawartością pierwiastków w glebie i owocach

No	Relationship	R_{est}	p
1	Mn in the soil and Mn in the fruits	0.89	<0.001
2	Zn in the soil and Zn in the fruits	0.53	<0.05
3	Fe in the soil and Mn in the fruits	0.71	<0.001
4	Cd in the soil and Zn in the fruits	-0.45	<0.05
5	Cd in the soil and Cu in fruits	-0.57	<0.01

4. CONCLUSIONS

1. Although soil from the vicinity of smelters contains significantly higher amounts of Zn, Mn, Fe, Cu and Ni than soil from control sites, concentrations of these elements are found to be within the geochemical background values.
2. Berries of *Vaccinium myrtillus* from areas affected by smelters contain higher concentrations of Zn, Mn, Cu and Cd than berries from control plants. However, these values never reach acute levels.

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