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PROGNOSIS CONTENT OF HEAVY METALS IN SOIL AND HERBACEOUS PLANTS IN SELECTED PINE FORESTS IN THE SŁOWIŃSKI NATIONAL PARK

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Abstract: This paper presents the results of study on heavy metals in soil and in herbaceous plants in selected pine forests in Słowiński National Park. The heavy metals, such as Zn, Cu, Mn and Fe were studied. Concentrations of zinc in tested soil are strongly and very strongly related to manganese and copper content ($r = 0.57$ do $r = 0.98$, $p < 0.05$). Moreover, the soil moistening has vital impact on copper content in the plants of the ground cover. It was also found that moss in comparison to other forest plants captures higher volume of zinc and copper. The content of the above mentioned metals in the plants of dry coniferous forests (Bs), fresh coniferous forests (Bśw) and humid coniferous forests (Bw) of the ground cover constitute the following decreasing series: Mn(438.1) > Fe(98.6) > Zn(35.2) > Cu(3.5).

INTRODUCTION

From among various contaminants, heavy metals have a very negative impact on the environment [10, 19]. Their noxiousness consists in their accumulation in living organisms and their chronic toxicity. Propagation of heavy metals in air and in water environment leads to increase of their concentration in different ecosystems [21, 31]. Premature deaths are both due to $PM_{2.5}$ emissions from Poland and transportation of $PM_{2.5}$ from other European countries, both of them in almost equal parts [30]. At present, there is a substantial increase of concentration of metallic elements in food, soil, and plants, both in industrial areas [12] as well as in the protected ones [5, 7, 14, 18, 22, 24]. Heavy metals migrate in the soil very slowly and belong to the most persistent contaminants. Independent of their source of origin, heavy metals in excessive volume constitute a serious threat to life of plants, animals and the man [15]. Soil humus which has a high absorbing capacity limiting transfer of ions of heavy metals to the root system of plants, plays a very important protective role in soils and plants against contamination by heavy metals [20]. Soil reaction as well as a type and soil characteristic constitute important factors, which have influence on the release of heavy metals from organic connections. The release of most heavy metals to the soil solution increases with the soil acidity [15, 16], which increases the availability of such metals to plants, especially in the case of the acid podzolic soil.

PURPOSE AND RANGE OF RESEARCH

The aim of the research was to evaluate the content of selected heavy metals (Zn, Cu, Mn, Fe) in soil and dominating plant species of the ground cover of the selected pine coniferous forests in Słowiński National Park which differ in the level of the solum moistening.

The aim of the paper was to check the influence of humidity of the forest ecosystem (Bs, Bśw and Bw) on Zn, Cu, Mn and Fe content in the forest vegetation. The research comprised three forest areas of 0.5 ha each. A soil pit was made at each research area and the profile structure was described. The soil taxonomy was described based on the Polish Taxonomy of Soils PTG [29].

STUDY AREA

Three pine coniferous forest systems (the area of 0.5 ha) which differ in the level of the solum moistening at the territory of Słowiński National Park (SNP) in Forest Disticts: 20 and 21 were selected for the purpose of the research. The first one comprises a 110 years' old cup moss coniferous forest (*Empetro nigri-Pinetum cladonietosum,* dry coniferous forests − Bs) covering loose regsol: O, AC, C, situated at the level of about 10 m a.s.l. outside the reach of underground water. A very poor ground cover contains dwarf shrubs of red bilberry (*Vaccinium vitis-idaea*), as well as heather (*Calluna vulgaris*). The moss-grown layer of the examined area is represented by *Pleurozium schreberi* and *Dicranum scoparium* − dicranoid moss. There were also substantial volumes of cup moss (*Cladonia sylvatica*). The second research area comprises a 120 years' old crowberry coniferous forest (*Empetro nigri-Pinetum*, fresh coniferous forest – Bśw) at about 4 m a.s.l. which covers proper podzolic soil gleyed from the bottom (O, A, Eesgg, Bfegg, Cgg). An average depth of location of the water table of ground water is about 60 cm. The layer of the ground cover consisted mainly of dwarf shrubs of bilberry (*Vaccinium myrtillus*), red bilberry (*Vaccinium vitis-idaea)* and common heather (*Calluna vulgaris*). The moss layer was represented by: *Pleurosium schreberi* and *Hylocomium splendens*. A 125 years' old sea coast heath coniferous forest is found over the third research area (*Empetro nigri-Pinetum ericetosum,* wet coniferous forests − Bw), situated at the level of about 2.5 m a.s.l., which covers proper podzolic soil gleyed from the bottom: O, A, Eesgg, Bfegg, Cgg. The soils of the tested forest complexes (Bs, Bśw and Bw) originated from deep dune sands. The average depth of dipping ground water is about 45 cm. The ground cover layer was represented by numerous dwarf shrubs of vacciniaceous plants: bilberry (*Vaccinium myrtillus*), red bilberry (*Vaccinium vitis-idaea)* and bog bilberry (*Vaccinium uliginosum).* Besides, there were frequent instances of black crowberry (*Empetrum nigrum*) as wells as marsh tea (*Ledum palustre*). The moss layer consisted of *Peurosium schreberi* and *Hypnum cupressiforme*.

METHODS OF RESEARCH

Study and Plant Analyses

The plant material was collected for research in September 2010 from several sites of each forest complex, then it was put together with consideration of diversity of species. In the case of the dwarf shrubs of the ground cover – whole sprouts were collected, in the case of moss – stems with leaves, and in the case of lichen − the whole thallus. After its transport to the laboratory, the plant material was cleaned of the mineral parts of the soil and was divided into species. After initial preparation, the plants were dried to the constant mass at the temperature of 65°C, they were was homogenized in a grind. The soil samples were also collected for the purpose of research, in which after initial preparation the following parameters were determined: active acidity (pH in water solution) and exchangeable acidity (pH in 1n KCl) and organic carbon by means of the Tiurin method according to Bednarek *at al*. [1] Selected metals Zn, Cu, Mn, Fe were determined after mineralization in the mixture of concentrated HNO_3 and 30% H_2O_2 by means of the method of atomic absorption spectrometry (AAS) according to Ostrowska *et al*. [28] in plant and soil samples. The tests were carried out following the original standards (Merck KGaA, 1g/1000 ml).

Statistical Analysis

In order to characterize and compare the concentrations of selected heavy metals in the tested plants, mean values, standard deviations, enrichment factors (*EF*) as well as Spearman's correlations were calculated. *Statistica* (7.1) software was used for calculations.

RESULTS AND DISCUSSION

Physicochemical properties of soil

The soils of the tested forest ecosystems (Bs, Bśw and Bw) do not show vital statistic differences as to their granulometric composition (Tab. 1). They are characteristic of similar grain size consisting mainly of medium grained sand (0.5–0.25 mm) and fine grained sand (0.25–0.1 mm). There is a little more medium grained sand in the tested soils, whose content is from 50.1% in the dry coniferous forest to 58.4% in the humid coniferous forest. The fine sand is within the range from 40.1% (Bw) to 49.1% (Bs).

The soils of forest complexes show acidic reaction and strong acidic reaction. The organic (Ofh) and the humus levels (A) represent the highest acidity, with pH between 3.52 and 3.88 (pH_{H2O}). The Ofh sublevels are characterized by the highest acidity in the humid coniferous forest and the lowest acidity in the dry coniferous forest (Tab. 2).

The acidity decreases along with the depth, which is reflected in the increase of pH value to 4.20−4.24 at the bed rock level. The organic matter accumulated mainly at organic and humus levels (Tab. 2). The largest volumes of organic carbon were found at raw sublevels (Ol) of humid coniferous forests (Bw) and dry coniferous forests (Bs). At Ofh sublevels the highest concentration of organic carbon was found at the humid coniferous forest (Bw) profile, and the lowest in dry coniferous forests (Bs). The carbon content decreases deeper into the tested soil profiles, reaching the lowest values at the bed rock level (0.10−0.24%), (Tab. 2). According to Czępińska-Kamińska *et al*. [4] the carbon

Table 1. The soil fractions content

Forest association	Soil genelic horizons	The soil fractions content [%]					
		> 1 [mm]	1-0.5 [mm]	0.5-0.25 [mm]	0.25-0.1 [mm]	0.1-0.05 [mm]	< 0.05 [mm]
Bs	AC	0	2.8	49.0	47.7	0.4	0.1
	C_1	0	1.5	51.0	47.0	0.4	0.1
	C_2	0	0.5	50.0	49.1	0.4	0.0
	C_3	0	0.3	54.9	44.4	0.4	0.0
Bśw	A	0	2.0	55.0	42.6	0.3	0.1
	Eesgg	0	1.4	58.5	39.7	0.3	0.1
	Bfegg	0	0.9	58.0	40.8	0.2	0.1
	Cgg	0	1.2	56.8	42.0	0.2	0.1
Bw	A	0	1.4	56.9	40.9	0.5	0.2
	Eesgg	0	1.1	58.4	40.1	0.3	0.1
	Bfegg	0	1.1	56.1	42.5	0.2	0.1
	Cgg	0	3.2	51.3	44.6	0.3	0.2

Table 2. Physicochemical properties of research soil in SNP

Forest association	Soil genelic horizons	Depth [cm]	pH		C [%]
			H_2O	KCl	
Bs	Ol	5-3	4.22±0.35	3.90±0.19	54.00±1.20
	Ofh	3-0	3.81±0.40	2.90±0.20	32.40±1.00
	AC	0-12	4.10±0.30	3.52±0.20	0.32±0.05
	C_1	12-30	4.20±0.22	3.92±0.15	0.24±0.02
	C_2	30-50	4.43±0.20	4.14±0.15	0.23±0.01
	C3	50-100	4.24±0.20	4.32±0.10	0.12±0.01
Bśw	Ol	7-5	4.88±0.43	4.39±0.22	50.40±1.20
	Ofh	5-0	3.80±0.50	2.87±0.21	37.20±1.10
	A	0-2	3.88±0.31	3.25±0.16	1.40±0.06
	Eesgg	2-13	3.93±0.23	3.37±0.15	0.38±0.05
	Bfegg	13-25	4.13±0.12	4.14±0.15	0.12±0.01
	Cgg	25-100	4.24±0.10	4.34±0.10	0.10±0.01
Bw	Ol	9-1	4.21±0.40	3.78±0.20	55.20±1.30
	Ofh	1-0	3.52±0.26	2.65±0.18	43.00±1.10
	A	0-3	3.88±0.25	3.58±0.14	0.42±0.05
	Eesgg	3-11	3.81±0.20	3.78±0.13	0.17±0.01
	Bfegg	11-20	4.11±0.10	4.10±0.10	0.12±0.01
	Cgg	20-100	4.21±0.10	4.14±0.10	0.10±0.01

Note: (±) standard deviation

content at organic levels of the forest soils is mostly within the limits of: 25.9−36.0%, and 0.75−2.11% at humus levels. Consequently, the carbon content in the tested soils of Słowiński National Park is typical of podzolic soils.

Contents of heavy metals in soil

The zinc content in the tested soils remained within the range from 9.8 to 70.6 mg·kg^{-1}, while the largest concentration of that element was found at organic levels (37.7−70.6 mg·kg^{-1}). The zinc content decreased along with the depth of the profiles in dry coniferous forests (Bs) and humid coniferous forests (Bw) and slightly increased at the erosion level (Bfegg) of fresh coniferous forests (Bśw) (Tab. 3).

The zinc content substantially depends on the organic carbon content, which is highly confirmed by vital statistic Spearman's correlation coefficients both in dry coniferous forests (Bs), fresh coniferous forests (Bśw) soils and in humid coniferous forests (Bw) (respectively r = 0.95, r = 0.71 and r = 0.95, $p < 0.05$). Correlation between the zinc content and reaction was found only in the case of the fresh coniferous forests (r = 0.82, pH(H_2O) and r = 0.74, pH(KCl), $p < 0.05$), which results from substantially higher zinc content at respective mineral levels of dry coniferous forests (Bs) and humid coniferous

Table 3. The content of heavy metals in the soil under Bs, Bśw and Bw in SNP

Forest association	Soil genelic horizons	Zn	Cu	Mn	Fe
		mg·kg-1 d.m.			
Bs	Ol	65.6(±0.03)	4.3(±0.001)	486.0(±0.09)	2040(±0.01)
	Ofh	32.0(±0.01)	4.5(±0.001)	101.0(±0.03)	6960(±0.01)
	AC	21.6(±0.01)	0.67(±0.001)	10.8(±0.01)	740(±0,19)
	C1	14.0(±0.01)	0.55(±0.000)	6.3(±0.02)	659(±0.14)
	C2	15.2(±0.02)	0.53(±0.000)	6.1(±0.03)	655(±0.02)
	C3	15.6(±0.02)	0.53(±0.001)	6.0(±0.03)	654(±0.02)
Bśw	Ol	70.6(±0.02)	4.9(±0.001)	471.2(± 0.07)	105(±0.01)
	Ofh	37.7(±0.03)	5.5(±0.002)	29.5(±0.01)	1450(±0.02)
	A	12.1(±0.01)	1.1(±0.002)	4.7(±0.01)	401(±0.07)
	Eesgg	12.9(±0.01)	0.6(±0.001)	5.6(±0.01)	523(±0.12)
	Bfegg	49.7(±0.02)	0.6(±0.001)	5.8(±0.01)	525(±0.12)
	Cgg	45.6(±0.02)	0.61(±0.002)	5.9(±0.02)	524(±0.15)
Bw	Ol	52.0(±0.05)	5.6(±0.002)	182.3(±0.013)	137(±0.01)
	Ofh	36.7(±0.02)	6.1(±0.002)	52.6(±0.02)	2403(±0.04)
	A	12.5(±0.02)	0.7(±0.00)	7.2(±.02)	205.4(±0.08)
	Eesgg	9.8(±0.01)	0.6(±0.002)	5.2(±0.01)	303(±0.01)
	Bfegg	15.4(±0.01)	0.6(±0.002)	5.6(±0.01)	363(±0.11)
	Cgg	14.4(±0.02)	0.5(±0.002)	5.5(±0.02)	360(±0.08)

Note: (±) standard deviation

forests (Bw). Zinc concentrations in tested soils are additionally very strongly correlated with the manganese and copper content (Tab. 4).

Zinc found in acid soils is easily accessible for plants. In Poland, the lowest zinc volume is found in potzolic soil. The average zinc volume in sandy soils of Poland varies from 7 to 150 mg·kg^{-1} [15]. In the soils of Białowieża Primeval Forest the zinc content was at the level 65–86 mg·kg^{-1} [6], in the soils of Roztocze National Park about 54 mg·kg^{-1} [3], in the soils of coniferous forest complexes of Central Poland: 12–70 mg·kg^{-1} [11], w in the Sudety soils – on average 260.5 mg·kg^{-1} [32], and in potsolic soil of Kampinos Primeval Forest from 20.5 to 62 mg·kg^{-1} [14]. The zinc content in the soil of Słowiński National Park is relatively low and does not constitute any hazard to the plants.

The copper content in the soils of Słowiński National Park was a the level from 0.53 to 6.1 mg·kg^{-1}. The highest volume of Cu was found at organic levels and the lowest at the bed rock level (C), (Tab. 3). The total copper content in uncontaminated soils is at the

Table 4. Spearman's correlation coefficients ($p < 0.05$) betwenn of heavy metals concentrations in soils ($n = 18$, $p < 0.05$, $r_{crit.} = 0.399$)[a]

Forest association		Zn	Cu	Mn	Fe	pH (H_2O)	pH (KCl)
Bs	Zn	-					
	Cu	**0.98**	-				
	Mn	**0.97**	**0.93**	-			
	Fe	0.27	**0.45**	0.09	-		
	pH (H_2O)	-0.14	-0.27	0.06	**-0.84**	-	
	pH (KCl)	-0.07	-0.20	0.15	**-0.87**	**0.98**	-
	C org.	**0.95**	**0.99**	**0.89**	**0.53**	-0.33	-0.27
Bśw	Zn	-					
	Cu	**0.57**	-				
	Mn	**0.77**	**0.58**	-			
	Fe	-0.20	**0.39**	**-0.51**	-		
	pH (H_2O)	**0.82**	0.36	**0.95**	**-0.66**	-	
	pH (KCl)	**0.74**	-0.06	**0.67**	**-0.75**	**0.86**	-
	C org.	**0.71**	**0.96**	**0.79**	0.13	**0.60**	0.19
Bw	Zn	-					
	Cu	**0.91**	-				
	Mn	**0.90**	**0.76**	-			
	Fe	0.30	**0.61**	-0.05	-		
	pH (H_2O)	0.20	-0.19	**0.43**	**-0.81**	-	
	pH (KCl)	-0.17	**-0.65**	-0.05	**-0.92**	**0.85**	-
	C org.	**0.95**	**0.98**	**0.88**	**0.42**	0.01	0.01

Note: [a] – critical values of Spearman's correlations reffered to Wołek [33].

level from 1 to 140 mg·kg^{-1}, and in podzolic soils from 1 to 70 mg·kg^{-1} [15]. In the soils of coniferous forest complexes of Central Poland the content of Cu was determined at the level 2–70 mg·kg^{-1} [11], in the soils of Kampinos Primeval Forest from 4.9 to 45.5 mg·kg^{-1} [14], and in the soils of the Sudety from 30 to 178 mg·kg^{-1} [32]. Low concentration of cooper in the soils of Słowiński National Park indicates that there is no hazard as to that element. It was also discovered that the copper content in the tested soil was substantially connected with zinc, manganese, iron and organic carbon content which can be evidenced by correlation coefficient (Tab. 4). In the case of the soil under the humid coniferous forest (Bw) an additional negative correlation with pH (KCl) was found. Most probably the high level of ground water (~ 45 cm) and high acidity of the soil (Tab. 2) have vital impact on the increase of solubility and availability of copper ions for plants in this forest ecosystem.

The content of manganese in the soils of Słowiński National Park was quite variable. The highest volume of that element was found in substrata (Ol): from 182.3 mg·kg^{-1} (wet coniferous forests Bw) to 486.0 mg·kg^{-1} (dry coniferous forests Bs) and (Ofh): from 29.5 mg·kg^{-1} (fresh coniferous forest – Bśw) to 101.0 mg·kg^{-1} (dry coniferous forest – Bs) (Tab. 3). The concentrations of manganese decrease along with the depth to the volume of 5.5–6.0 mg·kg^{-1} at the bed rock level (C). The appearance of manganese in the soil depends on its content in the bedrock as well as on the soil building processes which is decisive as to the profile distribution. The Mn content in podzolic soil can appear in a wide range from 7 to 2000 mg·kg^{-1} [15]. As to other metals, manganese is bound by organic matter (Tab. 4), which decides about its small mobility at organic levels. Only in the case of the soils of fresh coniferous forest, strong, positive correlations of manganese with the soil reaction and vital negative correlation with iron was found ($r = -0.51$, $p < 0.05$).

Iron concentration in the soils of Słowiński National Park remained at the level from 137 to 6960 mg·kg^{-1} at organic levels and from 205 to 740 mg·kg^{-1} at mineral levels (Tab. 3). According to research done by Gworek and Degórski [11] the iron content in the soils of forest habitat of Central Poland is from 63 to 3100 mg·kg^{-1}. Iron is an element which undergoes bio-accumulation. Solubility of iron elements increases along with the level of soil acidity. At wet, acid level there is a fast activation of iron due to its reduction [15]. Increased Fe content at organic levels of a dry coniferous forest can be an effect of a stronger retention of this element due to a slightly lower acidity of that level in comparison to fresh coniferous forests (Bśw) and humid coniferous forests (Bw) as well as much lower moisture due to the lack of the access to ground water (Tab. 2).

The soils of the tested pine woods, due to the location of Słowiński National Park far away from the sources of contamination, do not show the body burden of heavy metals determined and the relations between them are the following:

Fe (1294.2) > Mn (102.4) > Zn (29.1) > Cu (2.6). In brackets average volumes of element contents in tested podzolic soils are provided.

Contents of heavy metals in plants

On the basis of analyses held, diversification of heavy metals content in the ground level plants of the tested woods was found (Tab. 5, Fig. 1).

Zinc content in plant sprouts was at the level from 17.5 to 76.2 mg·kg^{-1}, while the species of the humid coniferous forest showed the highest average as well as highest

Table 5. The content of heavy metals in selected herbaceous plants in Bs, Bśw and Bw in SNP

Forest association	Species	Zn	Cu	Mn	Fe
		mg·kg^{-1} d.m.			
Bs	*Vaccinium vitis-idaea*	34.4(±0.01)	2.3(±0.02)	110.8(±0.05)	53(±0.02)
	Calluna vulgaris	25.3(±0.01)	3.2(±0.02)	541.9(±0.12)	70(±0.02)
	Pleurozium schreberi	41.5(±0.02)	2.6(±0.01)	272.9(±0.04)	175(±0.04)
	Dicranum scoparium	34.3(±0.01)	2.7(±0.01)	212.5(±0.02)	150(±0.05)
	Cladonia sylvatica	30.5(±0.02)	2.0(±0.01)	76.3(±0.01)	91(±0.03)
Bśw	*Vaccinium vitis-idaea*	30.5(±0.01)	3.0(±0.01)	922.0(±0.18)	55.0(0.01)
	Vaccinium myrtillus	35.9(±0.02)	3.1(±0.01)	1849.0(±0.12)	63.0(±0.03)
	Calluna vulgaris	27.2(±0.02)	3.5(±0.03)	756.2(±0.17)	132.0(±0.02)
	Pleurozium schreberi	38.7(±0.02)	3.4(±0.01)	351.5(±0.05)	140.0(±0.03)
	Hylocomium splendens	32.9(±0.01)	3.5(±0.01)	300.3(±0.05)	75.0(±0.01)
Bw	*Vaccinium vitis-idaea*	28.7(±0.02)	3.8(±0.01)	609(±0.12)	58(117(±0.01)
	Vaccinium myrtillus	41.8(±0.05)	4.1(±0.01)	1096(±0.25)	66(±0.01)
	Vaccinium uliginosum	76.2(±0.02)	4.3(±0.01)	214(±0.02)	84(±0.01)
	Empetrum nigrum	17.5(±0,01)	4.0(±0.01)	183(±0.02)	57(±0.01)
	Ledum palustre	34.5(±0.01)	4.5(±0.05)	460(± 0.01)	153(±0.01
	Pleurozium schreberi	39.5(±0.01)	5.3(±0.02)	117(±0.04)	126(±0.03)
	Hypnum cupressiforme	28.4(±0.02)	4.3(±0.02)	75.0(±0.04)	129(±0.02)

Note: (±) standard deviation

diversity (Fig. 1). However, no vital statistic differences in zinc content of the tested forests were found. The Zn content in moss *Pleurozium schreberi* and *Hylocomium splendens* of the tested forests is comparable to that found by Gałuszka [5]: 33−54 mg·kg^{-1} in research held at the area of Wigry National Park, Kozanecka *et al.*, [18]: 33−43 mg·kg^{-1} at the area of Biała Primeval Forest and Malzahn [23] at the area of Białowieża Primeval Forest: the average of 46 mg·kg^{-1}. Plants absorb Zn in proportion to its content in soil. Average zinc content in over-ground parts of the plants non-affected by contamination, is about

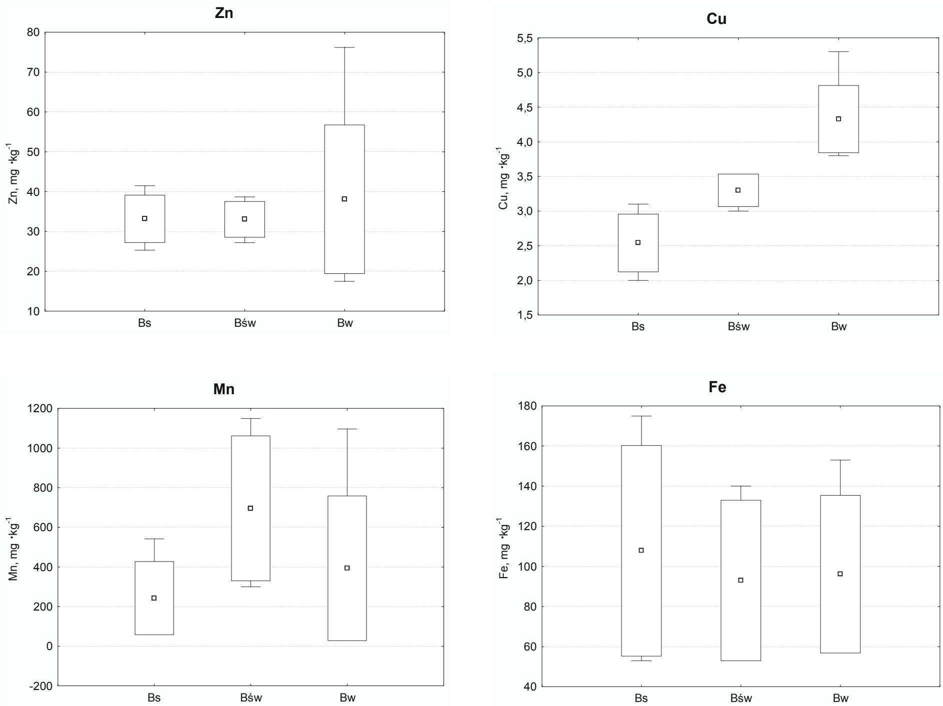

Fig. 1. Comparison of the heavy metals in herbaceous plants in Bs, Bśw and Bw. Point (mean), rectangle (standard deviation), whiskers (minimum-maximum)

10–70 mg·kg^{-1}. Kozanecka *at al.*, [18] found the zinc content in the plants of the ground cover of Biała Primeval Forest at the level from 14 to 105 mg·kg^{-1}. Concentration in the leaves within the range of 15–30 mg·kg^{-1} [15] is sufficient to fulfill physiological needs of majority of plants. Low concentration of Zn in tested plants reflects a low content of that element in podzolic soils of Słowiński National Park produced from deficient dune sands and relatively clean air [2].

The copper content in the plants of the coniferous forests of Słowiński National Park was kept at the level from 2.0 to 5.3 mg·kg^{-1}, while the highest volume of copper was found in the species of humid coniferous forest (Bw), and the lowest in the species of dry coniferous forest (Bs), (Tab. 5, Fig. 1). A statistically vital difference in the content of Cu between the plants of humid coniferous forests (Bs) as well as fresh coniferous forests (Bśw) and the species of humid coniferous forests (Bw) was discovered. On a basis of the obtained results, we can say that the moisture of the soil has a vital effect on the copper content in plants of the ground cover. It was also found that moss absorbs more zinc and especially copper in comparison to other forest plants (Tab. 5). A similar correlation was discovered during research in Kampinos Primeval Forest by Janowska [13].

Copper in plants is an element of low mobility. A small content of Cu about > 2 mg·kg^{-1} is sufficient to cover physiological needs of most plants. The copper content in plants usually remains at the level below 4–5 mg·kg^{-1} and is quite diverse depending on the part of a plant, its developmental stage, variation and species. Its average content in over ground parts of the plants is from 5–20 mg·kg^{-1} [15]. In the species of the ground cover of Biała Primeval Forest, Cu appeared at the level from 2.5 to 13 mg·kg^{-1} [18] and in *Pleurozium schreberii* SNP – 7 mg·kg^{-1} [7, 8]. A low content of Cu in dominating species of plants of dry coniferous forest (Bs), fresh coniferous forest (Bśw) and humid coniferous forest (Bw) does not constitute any hazard to them, and on the contrary, it is sufficient only to cover their physiological needs.

In the case of manganese, a big diversity of the content of that element was discovered depending on the species of the plant of the ground cover of pine coniferous forest. Its average content was at the level from 75 to 1849 mg·kg^{-1}, while the highest average Mn content was in the species of fresh coniferous forests (Bśw) (Tab. 5, Fig. 1). The highest accumulation was discovered in the sprouts of bilberry: 1096.0 mg·kg^{-1} (humid coniferous forests – Bw) and 1849.0 mg·kg^{-1} (fresh coniferous forests – Bśw). According to Kabata-Pendias and Pendias [15], the plants' demand for manganese is diverse. In most cases 10–25 mg·kg^{-1} is sufficient. A concentration of about 500 mg·kg^{-1} can be toxic for most plants. Much higher manganese content in the sprouts of *Vaccinium myrtillus* than those in Słowiński National Park was found by Mróz and Demczuk [25]: 1471–3996 mg·kg^{-1} in south western Poland. According to various authors, Mn concentration in plants within the areas outside the influence of contamination is mostly: 340–1339 mg·kg^{-1} [23], 1540–3952 mg·kg^{-1} [18], 122–837 mg·kg^{-1} [5] and 180–300 mg·kg^{-1} [7, 8].

The iron content in dominating plant species of the ground cover was of little diversity and was kept at a similar level in dry coniferous forests (Bs), fresh coniferous forests (Bśw) and humid coniferous forests (Bw), (Tab. 5, Fig. 1). Similar volumes of iron were found in the sprouts of bilberry: (120–217 mg·kg^{-1}) as well as in moss *Pleurozium schreberi*: (194–795 mg·kg^{-1}, WNP) – Gałuszka [5] and from 326 to 650 mg·kg^{-1} [18] by Mróz and Demczuk [25].

The relationship between determined heavy metals in plants make up the following decreasing series: Mn (438.1) > Fe (98.6) > Zn (35.2) > Cu (3.5).

Low content of metals determined in the soils and plant of ground cover of dry coniferous forests (Bs), fresh coniferous forests (Bśw) and humid coniferous forests (Bw) can be transferred onto low values of enrichment factors (*EF*), Fig. 2. The lowest enrichment factors were found in the case of iron ($EF < 0.1$), cooper ($EF < 0.87$) and zinc ($EF < 2.1$).

These values indicate the soil as the source of these elements. Higher values of enrichment factors *EF* were found only in the case of manganese: ($EF < 5$ in Bs and Bśw oraz $EF < 21$ in Bw). According to Kłos [17] the values of enrichment factors $EF > 10$ indicate the alluvial form of contamination with manganese, e.g. along with dry and wet atmospheric precipitation. However, the volume of heavy metals absorbed in this way is minimal. It was confirmed by the results of the tests of the suspended particulate matter PM_{10} (a potential source of heavy metals) preformed in 2010 within the area of Słowiński National Park SNP (17 µg·m^{-3}), [2]. In 1995 (529 t), emission of suspended particulate matter substantially decreased in comparison to the year 1990 (1165 t), [26, 27]. The area of Słowiński National Park SNP has been considered by many researchers to be one of the cleanest park areas in Poland [7, 8, 9], however, with further development of industry and location of new industrial establishments in the north of Poland, even this park can be under the pressure of pollution. The obtained values of enrichment factors *EF* should be treated only for orientation purposes since they were determined on a basis of total

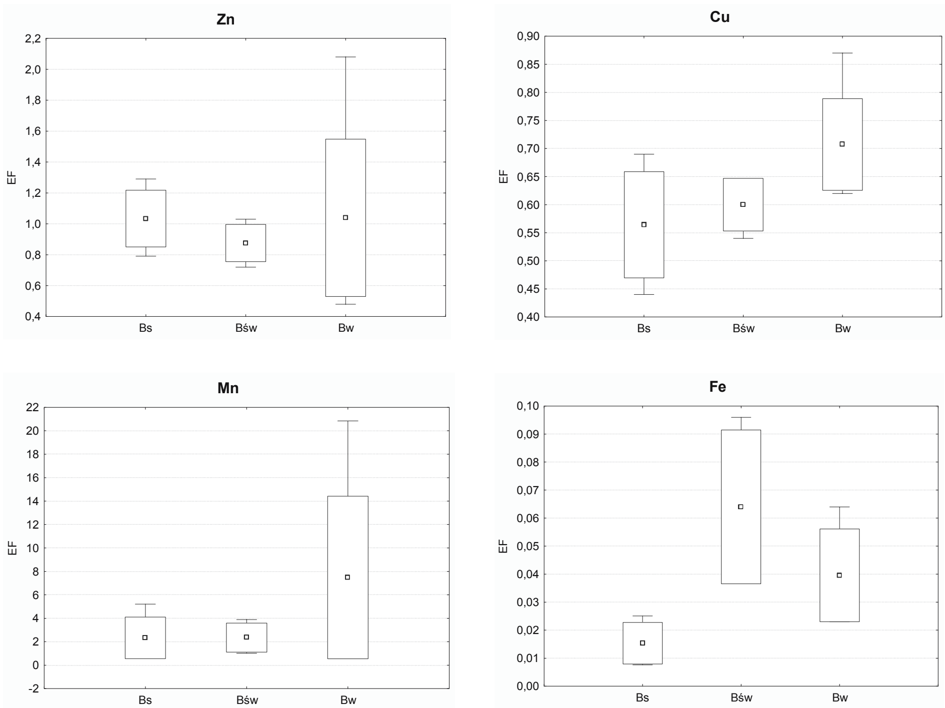

Fig. 2. Enrichment factors EF calculated for the mean concentrations of heavy metals of herbaceous plants and organic horizons (Ofh) of soil. Point (mean), rectangle (standard deviation), whiskers (minimum-maximum)

Table 6. Spearman's correlation coefficients ($p < 0.05$) betwenn of heavy metals concentrations in plants ($n = 21$, $p < 0.05$, $R_{crit.} = 0.368$)[a]

Forest association	Heavy metals	Zn	Cu	Mn	Fe
Bs	Zn	-			
	Cu	-0.24	-		
	Mn	**-0.42**	**0.92**	-	
	Fe	**0.72**	0.14	-0.01	-
Bśw	Zn	-			
	Cu	-0.11	-		
	Mn	-0.23	**-0.76**	-	
	Fe	0.07	**0.70**	**-0.50**	-
Bw	Zn	-			
	Cu	-0.09	-		
	Mn	0.01	-0.12	-	
	Fe	0.01	**0.56**	**-0.38**	-

Note: [a] – critical values of Spearman's correlations reffered to Wołek [33].

concentrations of metals in the soil, where the plants accumulate only bio-available form of such contamination.

CONCLUSIONS

The increased Fe and Mn content at Ol Ofh Bs levels in relation to respective Bśw and Bw levels is probably the result of the decreased soil humidity caused by the lack of access to underground water. The heavy metals content in the samples of plants of the ground cover of selected pine coniferous forests in Słowiński National Park belonging to the group of elements of high potential threat for the environment was low, at the level close to the natural. According to Kabata-Pendias and Pendias [15], only the species of bilberries (*Vaccinium vitis-idaea* and *Vaccinium myrtillus*) and the sprouts of common heather (*Calluna vulgaris*) showed values exceeding the toxicity level Mn in the fresh coniferous forests (Bśw) and humid coniferous forests (Bw). The contents of other metals (Zn, Cu i Fe) were within the scope of normal values, not exceeding the values recognized as toxic at any area in spite of a relatively big variation of particular metals. The contents of the above mentioned metals in the plants of the ground cover of dry coniferous forests, fresh coniferous forests and humid coniferous forests (Bs, Bśw and Bw) constitute the following decreasing series: Mn(438.1) > Fe(98.6) > Zn(35.2) > Cu(3.5).

The increased manganese content in the species of bilberries and in sprouts of common heather reflects the alluvial character of contamination which is confirmed by the value of enrichment factors (*EF* > 10).

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